INFLUENCE OF TYPE OF INITIATION ON THIOL-ENE "CLICK" CHEMISTRY

M. Sc. Thesis by
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TİYOL-EN CLICK KİMYASINA BAŞLATICI TİPLERİNİN ETKİSİ

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ABBREVIATIONS

IR	**:** Infrared Spectrophotometer
^{1}H-NMR	**:** Nuclear Magnetic Resonance Spectroscopy
FT–IR	**:** Fourier Transform Infrared Resonance
GPC	**:** Gel Permeation Chromatography
CRP	**:** Controlled Radical Polymerization
ATRP	**:** Atom Transfer Radical Polymerization
RAFT	**:** Reversible Addition Fragmentation Chain Transfer
NMRP	**:** Nitroxide Mediated Radical Polymerization
PMDETA	**:** *N, N, N',N'', N''-Pentamethyldiethylenetriamine*
Me$_6$-TREN	**:** Tris[2-(dimethylamino) ethyl]amine
THF	**:** Tetrahydrofuran
St	**:** Styrene
MMA	**:** Methyl methacrylate
MA	**:** Methyl acrylate
PSt	**:** Polystyrene
DMPA	**:** 2,2-Dimethoxy-2-phenylacetophenone
BP	**:** Benzophenone
TX	**:** Thioxanthone
CQ	**:** Camphorquinone
TMDPO	**:** (2,4,6 Trimethylbenzoyl) diphenylphosphine oxide
AIBN	**:** 2,2'-Azobis-(isobutyronitrile)
MPA	**:** 3-Mercaptopropionic acid
PI	**:** Photoinitiator

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LIST OF SYMBOLS

PI   **:** Photoinitiator
M   **:** Monomer
λ   **:** Wavelength
hv   **:** Radiation
R$^{\cdot}$ **:** Radical
l   **:** Light path length
C   **:** Concentration
A   **:** Absorbance
ε   **:** Molar extinction coefficient
M_n   **:** The number average molecular weight
(*c*)   **:** Conversion
T   **:** Time

INFLUENCE OF TYPE OF INITIATION ON THIOL-ENE "CLICK CHEMISTRY"

SUMMARY

Thermally and photochemically initiated thiol-ene "click" reactions using thiol- and allyl- end functionalized linear polystyrenes with various enes (allyl bromide, methyl acrylate and methyl methacrylate) and thiol (3-mercaptopropionic acid) have been investigated.

Allyl- and thiol- end-capped polystyrenes with controlled molecular weight and low polydispersity were prepared by atom transfer radical polymerization (ATRP) of styrene using functional initiator and end group modification approaches, respectively. Thiol-ene reactions can be initiated by both cleavage type photoinitiators such as 2, 4, 6-trimethylbenzoyl diphenylphosphine oxide (TMDPO) and 2, 2-dimethoxy-2-phenyl acetophenone (DMPA) and H-abstraction type photoinitiators such as benzophenone (B), thioxanthone (TX), camphorquinone (CQ), and classical thermal initiator, 2,2′-azobis(isobutyronitrile) (AIBN) at 80°C. The kinetics of the reactions were monitored online with a real time ATR-FTIR monitoring system and the conversions were determined by ^{1}H-NMR spectroscopy. A comparison of "click" efficiencies of the studied initiator systems was performed. Compare to the thermal initiators and H-abstraction type photoinitiators, cleavage type photoinitiators were found to induce thiol-ene "click" reactions with higher efficiency.

TİYOL-EN "CLICK" KİMYASINA BAŞLATICI TİPLERİNİN ETKİSİ

ÖZET

"Tiyol" ve "en" fonksiyonlu polistirenler ile karşılık gelen "en" (allil bromür, metil akrilat and metil metakrilat) ve "tiyol" (3-merkaptopropiyonik asit) moleküller kullanılarak termal ve fotokimyasal başlatılmış tiyol-en "click" reaksiyonları incelendi.

Sırasıyla, fonksiyonel başlatıcı ve uç grup modifikasyonu yaklaşımları kullanılarak tiyol ve en fonksiyonlu iyi tanımlanmış lineer polistirenler atom transfer radikal polimerizasyonuyla sentezlendi. Tiyol-en reaksiyonları hem 2, 4, 6-trimetoksibenzoil difenilfosfin oksit (TMDPO) ve 2,2-dimetoksi-2-fenil asetofenon (DMPA) gibi kırılma tipi fotobaşlatıcıların yanında benzofenon (B), tiyoksanton (TX), kamforkinon (CQ) gibi H-koparma tipi fotobaşlatıcılarla hem de 2,2′-azobis(izobutironitril) (AIBN) gibi klasik termal başlatıcılarla 80°C'de başlatılabilir. Reaksiyonların kinetiği ATR-FTIR izleme sistemiyle online olarak izlendi ve dönüşümler ^{1}H-NMR spektroskopisiyle belirlendi. Çalışılan başlatıcı sistemlerinin "click" kimyası etkinliklerinin karşılaştırılmaları gerçekleştirildi. Kırılma tipi fotobaşlatıcıların, termal başlatıcılara ve H-koparma tipi fotobaşlatıcılara kıyasla, thiol-en "click" reaksiyonlarını yüksek etkinlikle başlattığı bulundu.

1. INTRODUCTION

Over the last decade, growing interest has been devoted to the use of rapid reactions that meet the three main criteria of an ideal synthesis: efficiency, versatility, and selectivity. To date, the most popular reactions that have been adapted to fulfill these criteria are known as ''click'' reactions. These reactions have been classified in four categories: (i) cycloaddition reactions (most commonly Huisgen 1,3-dipolar cycloaddition, but also Diels-Alder reaction), (ii) nucleophilic ring-opening reactions of strained heterocyclic electrophiles (epoxides, aziridines and aziridinium ions), (iii) non-aldol carbonyl chemistry (ureas, oximes and hydrazones) and (iv) additions to carbon-carbon multiple bonds (especially oxidative addition, such as epoxidation, dihydroxylation and aziridination but also Michael additions) [1-3]. Among them, particularly Cu (I) catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes to form triazole rings, is the most widely used. "click" reactions have been subsequently expanded in macromolecular engineering as a versatile method for synthesis of functional monomers and polymers [4-21], bioconjugated polymers [22-24], block [25-30], graft [24, 31-36], star [37-41] and brush copolymers [31, 42].

Despite many potential applications, the existing "click" reactions have several disadvantages. For example, the removal of toxic heavy metal impurities from the polymer products and the explosive nature of the azide groups are the major concerns in the 1,3-dipolar cycloaddition reactions. Moreover, Diels-Alder "click" reaction is limited by the reactivities of the reagents and the potential retro reactions at elevated temperatures [43]. Although, oxime bond formation does not require any catalyst and is proved to be a reaction with very high conversion, the unprotected amine and aldehyde/ketone functional groups are unlikely to be compatible. More recently, thiol-ene chemistry has been introduced as a new "click" reaction [44] and successfully used for bioconjugated polymers [45, 46], modification of polymers [47-52] and surfaces [53-55], synthesis of star polymers [56], dendrimers [57] and disaccharides [58]. Thiol-ene reactions can be induced photochemically or thermally

at ambient temperature in the presence of oxygen without undesirable side reactions such as sulfenyl radical coupling [59-62]. Importantly, these reactions can be considered as environmentally-friendly processes since they precede in the absence of solvent under benign reaction conditions without the use of any potentially toxic metal. Recently, Hawker and co-workers investigated and compared the efficiency and orthogonality of thermally and photochemically initiated thiol-ene "click" coupling reactions. Although only single photoinitiator was tested, the photochemical coupling was found to proceed with higher efficiency and required shorter reaction time for complete conversion compared to the thermal counterpart [49].

In this thesis, a comparative study of the thiol-ene "click" reactions between a library of several ene groups such as allyl bromide, methyl acrylate and methyl methacrylate with thiol-end functional polystyrene using both cleavage (*Type I*) and H-abstraction type (*Type II*) initiators, and classical thermal radical initiator is reported. "click" reaction was also performed using opposite end functional (ene functional) polymer and 3-mercaptopropionic acid. The kinetics of the reactions was followed by a real time ATR-FTIR monitoring system and the functionalized polymers were analyzed by ^{1}H-NMR.

2. THEORETICAL PART

2.1 "Click" Chemistry

The term ''click chemistry'' introduced in 2001 by Sharpless and coworkers[1], as a class of efficient and selective reactions that could be used to join molecules together rapidly and in high yield. The "click"reactions commonly include the formation of a carbon-heteroatom bond and can be ranked in four categories:

• Cycloadditions of unsaturated species (most commonly Huisgen 1,3-dipolar cycloaddition, but also Diels-Alder reaction)

• Nucleophilic ring-opening reactions of strained heterocyclic electrophiles (such as epoxides, aziridines, aziridinium ions and episulfonium ions)

• Carbonyl chemistry of the "non-aldol" type (ureas, oximes, and hydrazones),

• Additions to carbon-carbon multiple bonds, (especially oxidative addition, such as epoxidation, dihydroxylation, aziridination, and sulfenyl halide addition but also Michael additions)

2.1.1 Copper-catalyzed azide-alkyne cycloadditions

An extensively studied reaction is copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) reaction between azides and terminal alkynes, which is the most prominent example of "click chemistry", discovered by the groups of Sharpless [2] and Meldal [63] (see reaction 2.1). While traditional uncatalyzed cycloadditions of azides and alkynes require long reaction times, high temperatures and produce a mixture of the 1,4- and 1,5-triazole products, Cu(I) catalyzed variation of this reaction allows very fast and regioselective formation of only the 1,4-triazoles at mild reaction conditions. Since its extraordinary success under different reaction conditions, with highly diverse building blocks, in high yields and with no (or conveniently separated) by-products, the "click" reaction has been applied widely in organic chemistry [63-65], supramolecular chemistry [66, 67], drug discovery [1], bioconjugation [23, 68] and materials science [69-74].

(2.1)
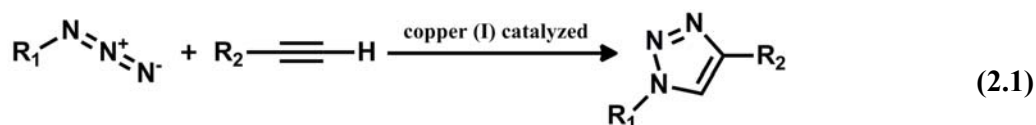
2.1.2 Diels-Alder reaction

Since reported in 1928 [75], Diels-Alder reaction has been employed in organic chemistry for many years. However, this reaction gained increased attention in the field of materials science with the discovery of "click chemistry" concept. These reactions possess characteristics of "click" reactions in terms of being specific, atom-economical, and highly efficient. Furthermore, these reactions advantageously performed in the absence of a metal catalyst, whereas the majority of "click" reactions require metal catalyst. The Diels-Alder reaction involves the [4+2] cycloaddition of an electron-rich conjugated diene to an electron-deficient dienophile and results with the formation of a partially hydrogenated six-membered ring. On the contrary to the majority of "click" reactions, Diels-Alder "click" reactions not only create new carbon-heteroatom bonds, but also create carbon-carbon bonds. This feature increases the value of this reaction as a synthetic tool. A simple and efficient DA cycloaddition reaction can be used in the syntheysis of linear thermoplastic[76] and thermosetting polymers[77] such as, polyimides[78-87], polyphenylenes[88-91], ladder polymers etc [92, 93] (see reaction 2.2).

(2.2)
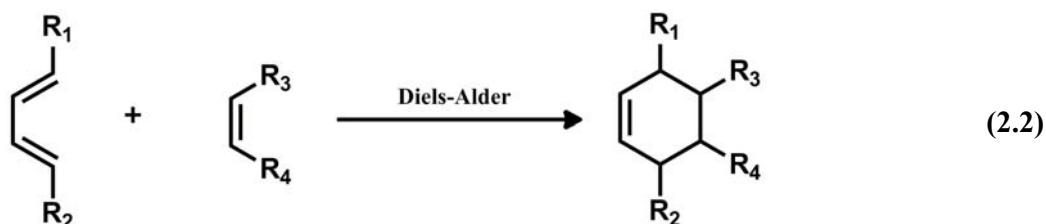
2.1.3 Thiol-ene reaction

The thiol-ene reaction is, simply, the radical addition of thiols to carbon-carbon double bonds, discovered in the early 1900s by Posner [94]. The generally accepted mechanism of the thiol-ene free radical addition reaction, first proposed by Kharasch and coworkers in 1938 [95]. There have been several efforts since the discovery of this reaction to review the use of thiol–ene photopolymerization in material scince. Among them two excellent reviews were written by Jacobine [96] and Woods [97].

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More recently, thiol–ene chemistry has been introduced as a new "click" reaction and successfully used for bioconjugated polymers [45,46], modification of polymers [47–52] and surfaces [53–55], synthesis of star polymers [56], dendrimers [57], and disaccharides [58] (see reaction 2.3.).

$$R_1 \diagup\diagup \quad + \quad SH^{-R_2} \quad \xrightarrow{\text{thiol-ene}} \quad R_1 \diagdown \overset{S^{-R_2}}{\underset{H}{\diagup}} \qquad \textbf{(2.3)}$$
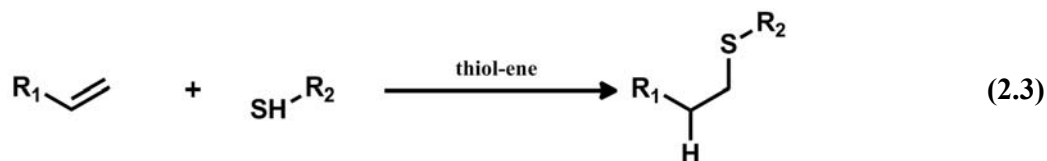
Thiols are known transfer agents and their reaction with alkenes can be induced photochemically or thermally at ambient temperature in the presence of oxygen without undesirable side reactions such as sulfenyl radical coupling. Importantly, these reactions can be considered as environmentally friendly processes since they preceed in the absence of solvent under benign reaction conditions without the use of any potentially toxic metal. In order to ensure completion of reaction without byproduct formation, a large excess of one of the reagents should be used.

Typically, the thiol-ene reaction is conducted through generation of radical centers, the most common method photochemically induced. The reaction proceeds through a typical chain process which contains initiation, propagation and termination steps, in reaction 2.4. Initiation includes the interaction of a thiol with photoinitiator, upon light exposure, resulting in the formation of a thiyl radical, RS˙. Propagation involves the direct addition of the thiyl radical to the C=C bond and hydrogen abstraction of a thiol group by a carbon-centered radical resulting the synchronous generation of a new thiyl radical, respectively. Termination takes place via typical radical–radical coupling processes.

$$R{-}SH + \text{photoinitiator (PI)} \xrightarrow{h\upsilon} R{-}S\cdot \qquad (2.4)$$
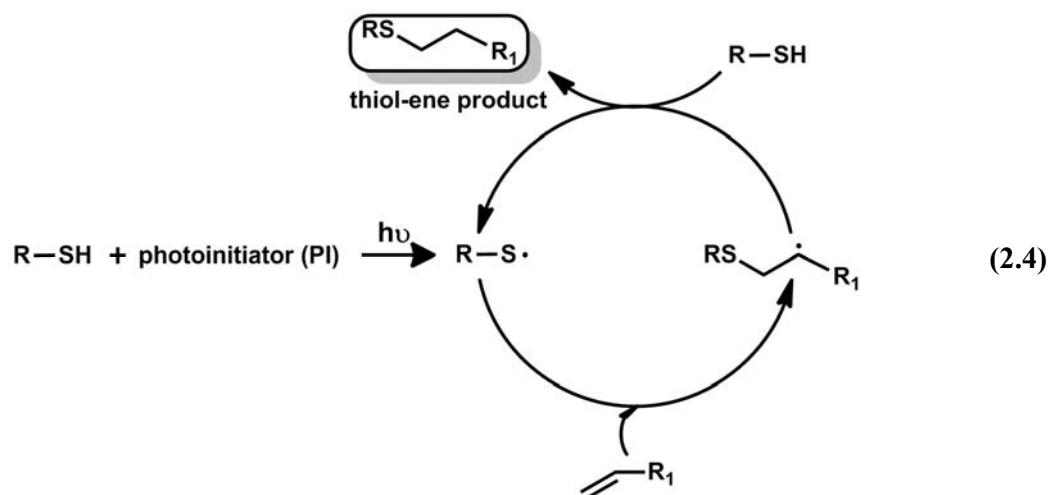
2.2 Controlled Radical Polymerization Methods

Nowadays, radical polymerization is a very useful commercial process for the preparation of high molecular weight polymers since it can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions, requiring an oxygen free medium, but tolerant to water, and can be conducted over a large temperature range (-80 to $250^{o}C$) [98]. Furthermore, a wide range of monomers can easily be copolymerized through a radical route, and this leads to an infinite number of copolymers with properties dependent on the proportion of the incorporated comonomers. Besides, rigorous process conditions are not needed for the polymerization. On the other hand, some important elements of the polymerization process that would lead to the well-defined polymers with controlled molecular weight, polydispersity, composition, structural architecture, and functionality are poorly controlled.

Advanced structures can be synthesized via living polymerization techniques. Moreover, living polymerization techniques allow preparation of macromonomers, macro initiators, functional polymers, block, graft copolymers, and star polymers. Well known example of these techniques is anionic polymerization [99], which is known to allow the synthesis of low PDI materials as well as block copolymers. The main disadvantages of anionic polymerization are the limited choice of monomers, and the extremely demanding reaction conditions.

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In order to overcome the disadvantages of RP without sacrificing the above-mentioned advantages, it was recognized that a living character had to be realized in conjunction with the free-radical mechanism. At present three main mechanisms exist that ensure this living character by establishing an equilibrium between active (radical) and dormant chains. These are atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMRP) or stable free radical polymerization (SFRP) and reversible addition-fragmentation chain transfer polymerization (RAFT). In either of these controlled radical polymerization methods (CRP), all chains are started early in the reaction, and are allowed to grow throughout the reaction. In general, the result of a successful CRP will be a polymer with low polydispersities, and predetermined (number-average) molar mass.

2.2.1 Atom transfer radical polymerization (ATRP)

Metal-catalyzed controlled radical polymerization, mediated by Cu, Ru, Ni, and Fe metal complexes, is one of the most efficient methods to produce polymers in the field of CRP [100]. Among aforementioned systems, copper-catalyzed ATRP in conjunction with organic halide initiator and amine ligand received more interest. The name ATRP comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [101]. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [102, 103].

$$P_n\text{-}X + M_t^n\text{-}Y/\text{Ligand} \quad \underset{k_{\text{deact}}}{\overset{k_{\text{act}}}{\rightleftharpoons}} \quad P_n^* + X\text{-}M_t^{n+1}\text{-}Y/\text{Ligand} \qquad (2.5)$$
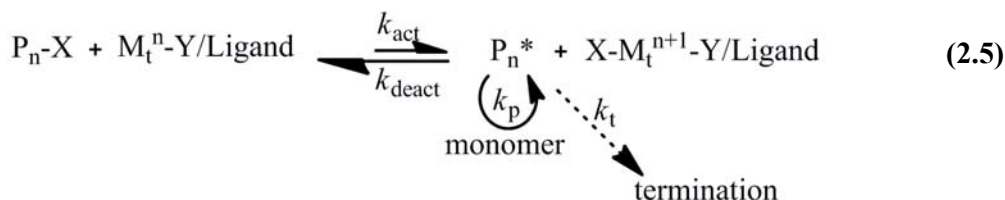
A general mechanism for ATRP is represented by (2.5). The radicals, i.e., the propagating species P_n^*, are generated through a reversible redox process catalyzed by a transition metal complex (activator, M_t^n –Y / ligand, where Y may be another

ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, P_n–X. Radicals react reversibly with the oxidized metal complexes, X–M_t^{n+1} / ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a, and deactivation k_{da}, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below (2.6a-e) [104].

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [105]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

Initiation

$$\text{R-X} \ + \ M_t^n\text{-Y/Ligand} \ \underset{k_{deact}^o}{\overset{k_{act}^o}{\rightleftarrows}} \ \text{R} \ + \ \text{X-}M_t^{n+1}\text{-Y/Ligand} \tag{2.6a}$$

$$\text{R} \ + \ \text{M} \ \xrightarrow{k_i} \ P_1 \tag{2.6b}$$

Propagation

$$P_n\text{-X} \ + \ M_t^n\text{-Y/Ligand} \ \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} \ P_n^* \ + \ \text{X-}M_t^{n+1}\text{-Y/Ligand} \tag{2.6c}$$

$$P_n \ + \ \text{M} \ \xrightarrow{k_p} \ P_{n+1} \tag{2.6d}$$

Termination

$$P_n \ + \ P_m \ \xrightarrow{k_t} \ P_{n+m} \quad \text{or} \quad P_n^= \ + \ P_m^H \tag{2.6e}$$

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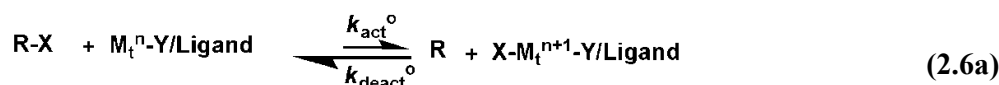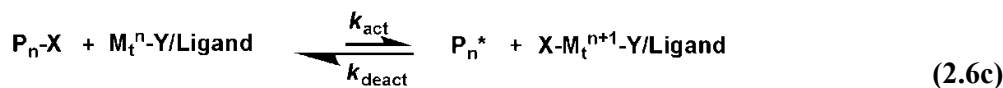
As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. Basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents are discussed as follows:

Monomers

A variety of monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [102]. In fact, all vinyl monomers are susceptible to ATRP except for a few excep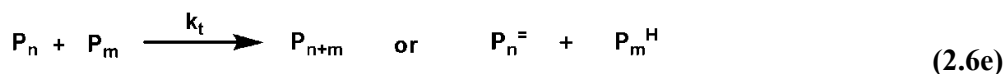tions. Notable exceptions are unprotected acids (eg (meth)acrylic acid). Some other monomers may be difficult to polymerize since they exhibit side reactions, which may be affected by the choice of reaction conditions, nature of the catalyst, etc. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [106]. Nevertheless, successful polymerization of 4-VP has been reported.

The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides.

Initiators

The main role of the initiator is to determine the number of growing polymer chains. The initiation in ATRP may occur in one of two different ways. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of styrene in ruthenium and ruthenium-based ATRP.

The alternative way to initiate ATRP is via a conventional free-radical initiator, which is used in conjunction with a transition-metal complex in its higher oxidation state. Typically one would use AIBN in conjunction with a Cu(II) complex. Upon

formation of the primary radicals and/or their adducts with a monomer unit, the Cu(II) complex very efficiently transfers a halogen to this newly formed chain. In doing so the copper complex is reduced, and the active chain is deactivated. This alternative way of initiation was termed "reverse ATRP" [107].

Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

1. The metal center must have at least two readily accessible oxidation states separated by one electron.

2. The metal center should have reasonable affinity toward a halogen.

3. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo) halogen.

4. The ligand should complex the metal relatively strongly.

5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [108].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [109], Ni [110], Ru [111], etc have been used to some extent.

Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as *N,N,N',N'',N''* -pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me$_6$-TREN). Examples of ligands used in copper-mediated ATRP are illustrated below [101, 112].
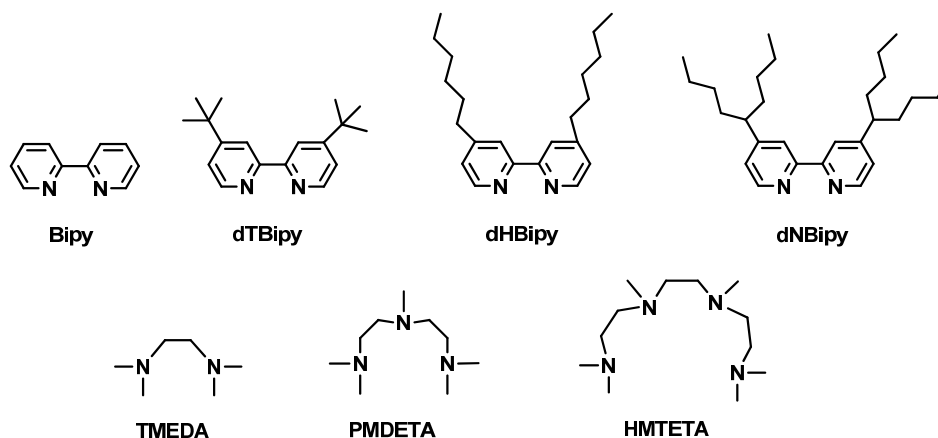
Figure 2.1 : Examples of ligands used in copper-mediated ATRP

In addition to those commercial products, it has been demonstrated that hexamethyltriethylene tetramine (HMTETA) provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [113]. Since copper complexes of this new ligand are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspensions [114].

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion.

2.2.2   Nitroxide-mediated radical polymerization (NMRP)

Nitroxide-mediated radical polymerization (NMRP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species (P_n·) reacts with a stable radical (X·) as seen in reaction 2.5 [115]. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6- tetramethylpiperidine-N-oxyl (TEMPO). The resulting dormant species (P_n-X) can then reversibly cleave to regenerate the free radicals once again. Once P_n· forms it can then react with a monomer, M, and propagate further.

$$\text{wwww } P_n-O-N \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} \text{wwww } P_n^{\bullet} + {}^{\bullet}O-N \qquad (2.5)$$

$$k_p \bigg) \quad k_t \cdots \text{wwww } P_n^{\bullet}$$

$$+ \text{ Monomer} \qquad \text{wwww } P_{n+m}$$
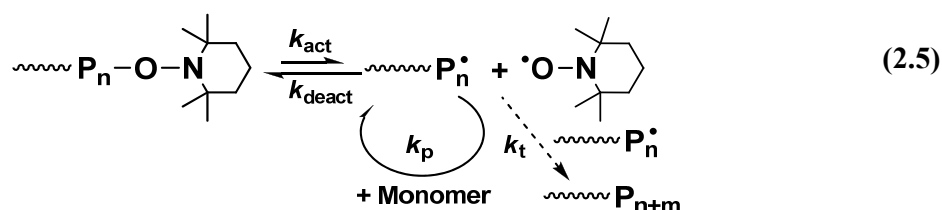
Two initiation systems have been generally employed in the NMRP. First is a bimolecular system consisting of conventional radical initiator such as BPO or azoisobutyronitrile (AIBN), and a nitroxide (i.e., TEMPO). The conventional radical initiator is decomposed at an appropriate temperature to initiate free-radical polymerization. The initiator-monomer adduct is trapped by the nitroxide leading to formation of the alkoxyamine *in situ*. Second is the unimolecular system using the alkoxyamine that is decomposed into a nitroxide and an initiating radical. This radical subsequently initiates the free-radical polymerization (2.5). By using the unimolecular initiator, the molecular weight can be properly controlled, because the number of initiating sites per polymeric chain is defined. In addition, functionalized unimolecular initiators can afford the fully functional groups at the ends of the polymer chain.

Unfortunately, TEMPO can only be used for the polymerization of styrene-based monomers at relatively high temperatures (>120ºC). With most other monomers, the bond formed is too stable and TEMPO acts as an inhibitor in the polymerization, preventing chain growth. Numerous advances have been made in both the synthesis of unimolecular initiators (alkoxyamines) that can be used not only for the polymerization of St-based monomers, but other monomers as well [116-120]. Most recently, the use of more reactive alkoxyamines and less reactive nitroxides has expanded the range of polymerizable monomers to acrylates, dienes, and acrylamides

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[121-123]. Several nitroxides that have been employed as mediators in stable free-radical polymerizations [124].

2.2.3 The reversible addition–fragmentation chain transfer process (RAFT)

Reversible addition-fragmentation chain transfer polymerization is one of the most efficient methods in controlled/living radical polymerization. An important advantage of this method over ATRP and NMRP is its tolerance to a wide range of functionalities, namely -OH, -COOH, $CONR_2$, NR_2, SO_3Na, etc., in monomer and solvent. This provides the possibility of performing the polymerization under a wide range of reaction conditions and polymerizing or copolymerizing a wide range of monomers in a controlled manner. In contrast to the previously described NMRP and ATRP, this system relies on chain transfer for the exchange between active and dormant chains. The chain end of a dormant chain carries a thiocarbonylthio moiety, which is chain-transfer-active. Upon chain transfer, the thiocarbonylthio moiety is transferred to the previously active chain, which now becomes dormant, and the previously dormant chain carries the radical activity and is able to propagate.

There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: (1) dithioesters (Z = aryl or alkyl), (2) trithiocarbonates (Z = substituted sulfur), (3) dithiocarbonates (xanthates) (Z = substituted oxygen), and (4) dithiocarbamates (Z = substituted nitrogen.

The RAFT system basically consists of a small amount of RAFT agent and monomer and a free-radical initiator. Radicals stemming from the initiator are used at the very beginning of the polymerization to trigger the degenerative chain transfer reactions that dominate the polymerization. Free radicals affect both the molecular weight distribution of the polymer as the dead polymer chains of uncontrolled molecular weight are formed and the rate of polymerization. Therefore, the concentration of free radicals introduced in the system needs to be carefully balanced. In RAFT polymerization radicals may be generated in three different ways: (1) by decomposition of organic initiators, (2) by the use of an external source (UV–vis or γ-ray), and (3) by thermal initiation. Polymerization temperature is usually in the range of 60–80 ^{o}C, which corresponds to the optimum decomposition temperature interval of the well-known initiator AIBN. However, even room temperature and high-temperature conditionscan also be applied [125, 126]. Generally, a RAFT

agent/free-radical ratio of 1:1 to 10:1 yields polymers with narrow molecular weight distributions.
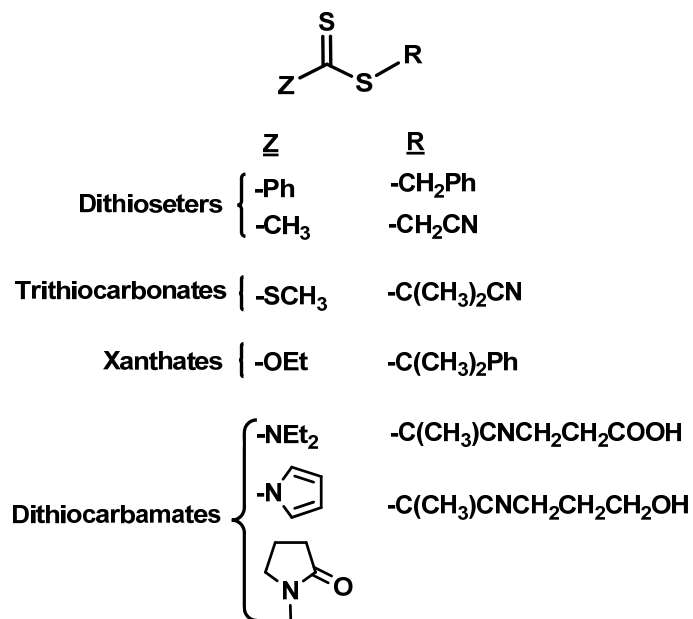

	Z	R
Dithioseters	-Ph	-CH₂Ph
	-CH₃	-CH₂CN
Trithiocarbonates	-SCH₃	-C(CH₃)₂CN
Xanthates	-OEt	-C(CH₃)₂Ph
Dithiocarbamates	-NEt₂	-C(CH₃)CNCH₂CH₂COOH
	-N (pyrrole)	-C(CH₃)CNCH₂CH₂CH₂OH
	(pyrrolidinone)	

Figure 2.2 : Examples of the different classes of thiocarbonylthio RAFT agents.

The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below (reaction 2.6 a-e). As for conventional free-radical polymerization, initiation by decomposition of an initiator leads to formation of propagating chains. In the early stages, addition of a propagating radical (P$_n$·) to the RAFT agent [S=C(Z)SR] followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical (R·). The radical R· reinitiates polymerization by reaction with monomer to form a new propagating radical (P$_m$·). In the presence of monomer, the equilibrium between the active propagating species (P$_n$· and P$_m$·) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow. This feature of the RAFT process leads to the production of narrow polydispersity polymers. When the polymerization is complete, the great majority of the chains contain the thiocarbonylthio moiety as the end group (reaction 2.6e) which has been identified by ^{1}H-NMR and UV–vis spectroscopy [127]. Additional evidence for the proposed mechanism was provided by the identification of the intermediate thioketal radical ((A) and/or (B), reaction 2.6b,d) by ESR spectroscopy [128, 129].

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Initiation and propagation

initiator + monomer $\longrightarrow$ $P_n^{\bullet}$ **(2.6a)**

Addition to RAFT agent   **(2.6b)**

$P_n^{\bullet} \quad S=C-S-R \rightleftharpoons P_n-S-C-S-R \rightleftharpoons P_n-S-C=S + R^{\bullet}$
$\qquad\quad \overset{|}{Z} \qquad\qquad\qquad \overset{|}{Z} \qquad\qquad\qquad \overset{|}{Z}$

(A)

Reinitiation   **(2.6c)**

$R^{\bullet}$ + monomer $\longrightarrow$ $P_m^{\bullet}$

    (2.6d)

Chain equilibration by reversible addition fragmentation

$P_m^{\bullet} \quad S=C-S-P_n \rightleftharpoons P_m-S-C-S-P_n \rightleftharpoons P_m-S-C=S \quad P_n^{\bullet}$
$(M) \quad \overset{|}{Z} \qquad\qquad\qquad \overset{|}{Z} \qquad\qquad\qquad \overset{|}{Z} \quad (M)$

(B)

    (2.6e)

Overall

initiator + monomer + $S=C-S-R \longrightarrow R-P_m-S-C=S$
$\qquad\qquad\qquad\qquad\quad \overset{|}{Z} \qquad\qquad\qquad\qquad \overset{|}{Z}$
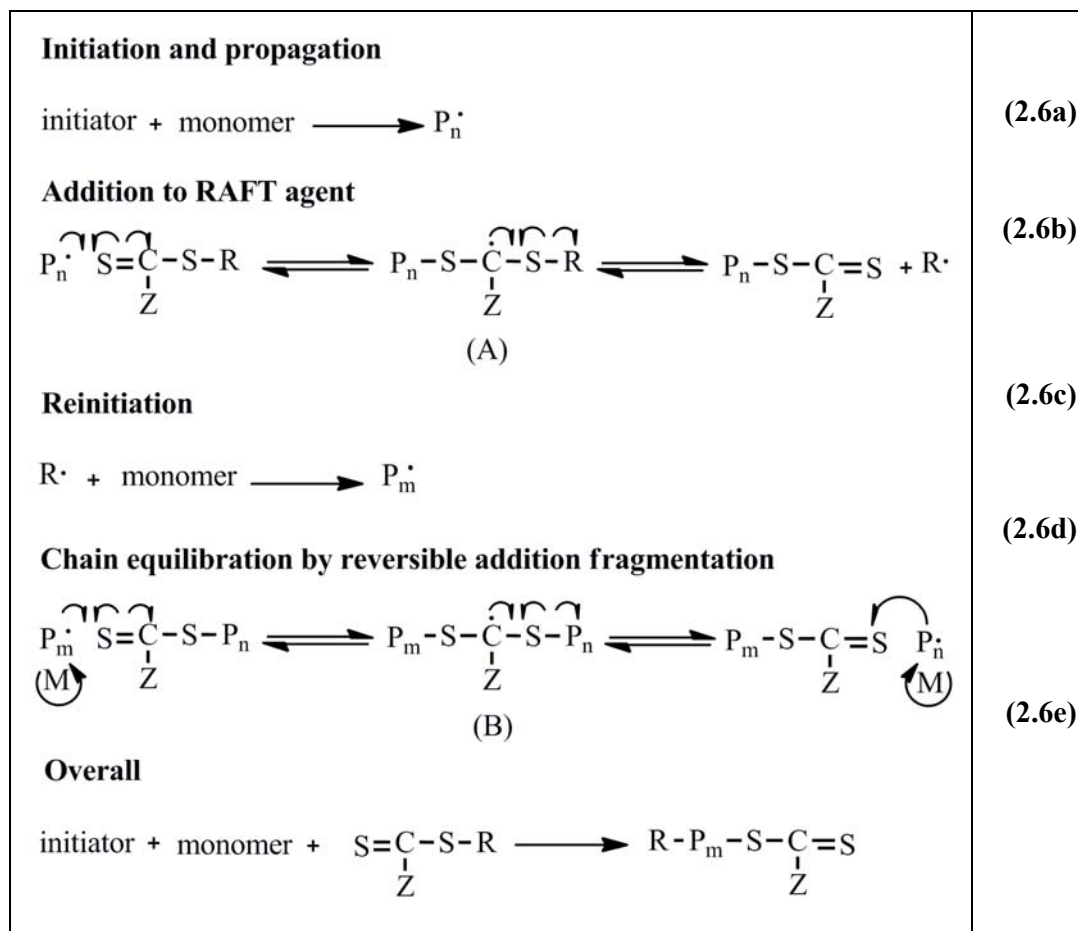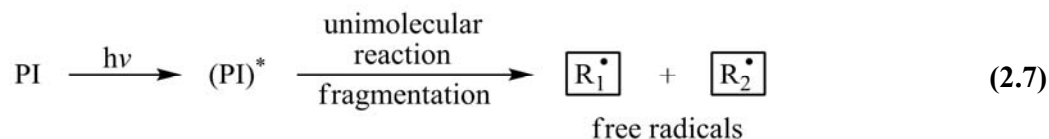
2.3 Photoinitiating Systems

Photochemistry is concerned with chemical reactions induced by optical radiation [130-132]. The radiation is most often ultraviolet (200–400 nm) or visible (400–800 nm) light but is sometimes infrared (800–2500 nm) light.

The chemical moiety, like phenyl rings or carbonyl groups, responsible for the absorption of light and defined to as chromophoric groups. Typical chromophores contain unsaturated functional groups such as C=C, C=O, NO2, or N=N [133-136].

Absorption of a photon of light by any compound causes electronic excitation. The energy causing excitation, E, is described by $E=hc/\lambda$ where h is Planck's constant, c is the speed of light, and , is the wavelength of the exciting light. Light absorption is described by $A= \varepsilon Cl$, where ε is the molar absorptivity (extinction coefficient), C is the concentration of the species, and l is the light path length.

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A photoinitiator is a compound that, under absorption of light, undergoes a photoreaction, producing free radicals. These species are capable of initiating the polymerization of suitable monomers. Photoinitiators are generally divided into two classes according to the process by which initiating radicals are formed.

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in reaction 2.7 are termed as *Type I* photoinitiators [137].

$$PI \xrightarrow{h\nu} (PI)^* \xrightarrow[\text{fragmentation}]{\substack{\text{unimolecular} \\ \text{reaction}}} \boxed{R_1^{\bullet}} + \boxed{R_2^{\bullet}} \qquad (2.7)$$

free radicals

If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in reaction 2.8, the initiating system is termed as "*Type II* Photoinitiator" [137].

$$PI \xrightarrow{h\nu} (PI)^* + COI \xrightarrow[\substack{\text{hydrogen} \\ \text{abstraction}}]{\substack{\text{bimolecular} \\ \text{reaction}}} R_1^{\bullet} + \boxed{R_2^{\bullet}} \qquad (2.8)$$

free radicals
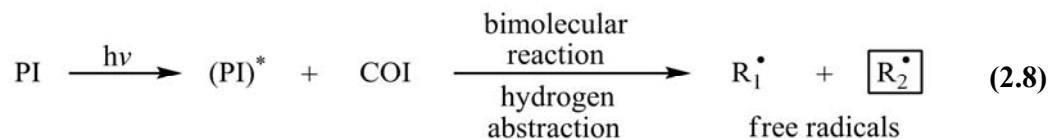
Efficient photoinitiators of both classes are known and find everyday usage. *Type I* photoinitiators are highly reactive UV photoinitiators, but are less frequently used in visible light curing systems. *Type II* photoinitiators are versatile initiators for UV curing systems and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

2.3.1 *Type I* photoinitiators (Unimolecular photoinitiator systems)

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 (reaction 2.9).
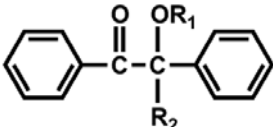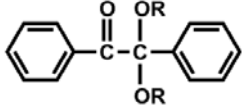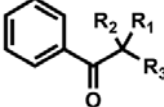
$$PI \xrightarrow{h\nu} PI^* \xrightarrow{k} R_1^{\bullet} + R_2^{\bullet} \qquad (2.9)$$

(2.10)

(2.11)
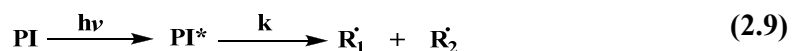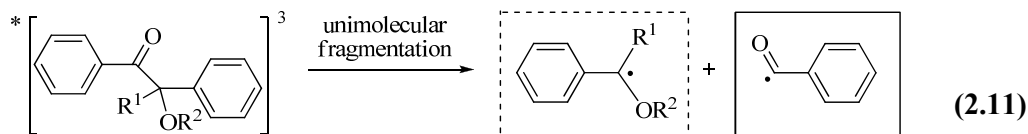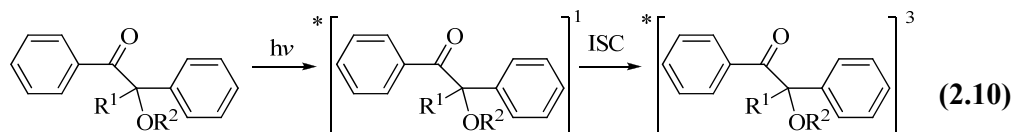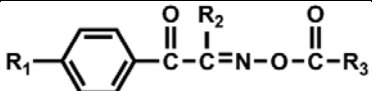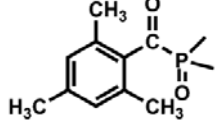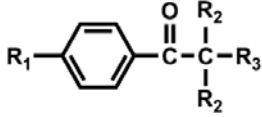
R^1 = H, Alkyl, substituted Alkyl, R^2 = H, Alkyl, substituted Alkyl

Type I photoinitiators which undergo a direct photofragmentation process (α or less common β cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerization. As illustrated in reaction 2.10, the photoinitiator is excited by absorption of ultraviolet light and rapid intersystem crossing to the triplet state. In the triplet state, the bond to the carbonyl group is cleaved, producing an active benzoyl radical fragment and another fragment. The benzoyl radical is the major initiating species, while, in some cases, the other fragment may also contribute to the initiation. The most efficient *Type I* initiators are benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides (Table 2.1) [138-141].

Table 2.1 :   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		335
	$R_1 = H, SC_6H_5$ $R_2 = CH_3, C_6H_{13}$ $R_3 = C_6H_5, OC_2H_5$	
Acylphosphine oxides		380
	$R = C_6H_5$ or OCH_3	
Aminoalkyl phenones		320
	$R_1 = SCH_3$, morpholine $R_2 = CH_3, CH_2Ph$ or C_2H_5 $R_3 = N(CH_3)_3$, morpholine	

2.3.2 *Type II* photoinitiators (Bimolecular photoinitiator systems)

Bimolecular photoinitiators are so-called because two molecular species are needed to form the propagating radical: a photoinitiator that absorbs the light and a co-initiator that serves as a hydrogen or electron donor. These photoinitiators 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 co-initiator to produce initiating radicals (reactions 2.12). In this case, radical generation follows 2nd order kinetics.

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

In these systems, photons are absorbed in the near UV and visible wavelengths. Free radical active centers are generated by hydrogen abstraction or photo-induced electron transfer process aforementioned.

Hydrogen abstraction
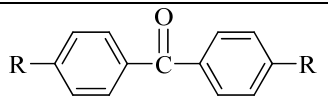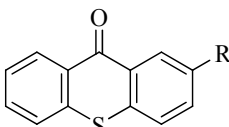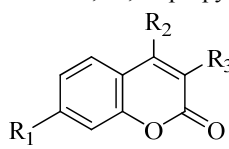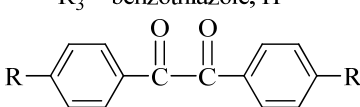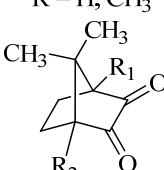
Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (reaction 2.13). When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and

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typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.

$$R = amines, alcohols, ethers, thiols$$

(2.13)
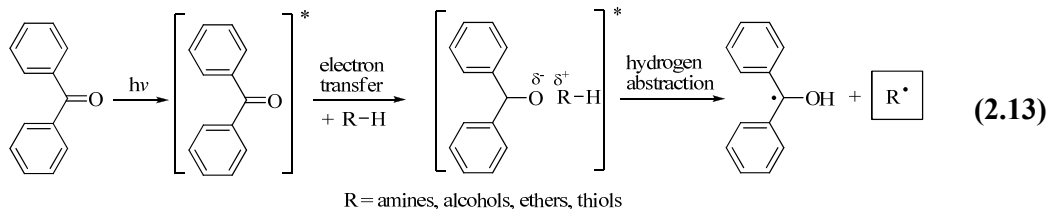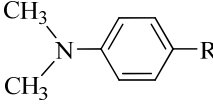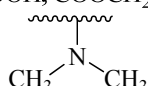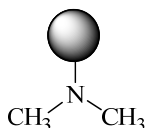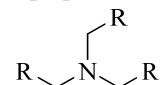
Photosensitizers of *Type II* system including benzophenones, thioxanthones, camphorquinones, benzyls, and ketocoumarins are listed in Table 2.2.

Table 2.2 : Structures of typical *Type II* photosensitizers

Photosensitizers	Structure	λmax (nm)
Benzophenones	$R = H, OH, N(C_2H_5)_2, C_6H_5$	335
Thioxanthones	$R = H, Cl, isopropyl$	390
Coumarins	$R_1 = N(C_2H_5)_2, N(CH_3)_2$ $R_2 = CH_3, cyclopentane$ $R_3 = benzothiazole, H$	370
Benzils	$R = H, CH_3$	340
Camphorquinones	$R_1 = CH_3, H$ $R_2 = H, CH_3$	470

The co-initiators such as an amine, ether, thiol or alcohol with an abstractable α-hydrogen are also classified in Table 2.3.

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Table 2.3 :   Structures of typical *Type II* hydrogen donors

Hydrogen Donors	Structure
Aliphatic Amines	$R_2-\overset{\overset{\textstyle R_1}{\mid}}{N}-R_3$ $R_1 = C_2H_5, CH_3, CH(CH_3)_2$ $R_2 = C_2H_5, C_2H_4OH, CH(CH_3)_2$ $R_3 = C_2H_5, C_2H_4OH, CH(CH_3)_2$
Aromatic Amines	CH_3–N(CH_3)–C$_6$H$_4$–R $R = H, COOH, COOCH_2CH_3, COOC_8H_{17}$
Polymeric Amines	CH_3–N(CH_3) polymer = poly(methyl methacrylate)s, polyacrylates or polyurethanes
Dendrimeric Amines	CH_3–N(CH_3) core = polyglycerols or poly(propylene imine)s
Acrylated Amines	$R-N(R)-R$ R = acrylates or methacrylates
Alcohols	$R-OH$ R = isopropyl, hydroxyethyl methacrylate
Ethers	$R-O-R$ R = tetrahydrofuran, benzodioxole poly(ethylene oxide), poly(propylene oxide), poly(tetrahydrofuran)
Thiols	$R-SH$ R = benzimidazole, benoxazole, benzthiazole, thioxanthone

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

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electron transfer can generally undergo fragmentation to yield initiating radicals (reaction 2.14).

$$PS \xrightarrow{h\nu} PS*$$

$$PS* \; + \; A \longrightarrow PS^{\cdot+} \; + \; A^{\cdot-} \longrightarrow R_1^{\cdot} \; + \; R_2^{\cdot} \qquad \textbf{(2.14)}$$

$$PS* \; + \; D \longrightarrow PS^{\cdot-} \; + \; D^{\cdot+} \longrightarrow R_1^{\cdot} \; + \; R_2^{\cdot}$$
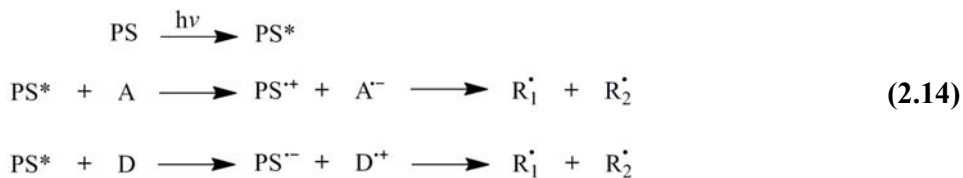
2.4 Telechelic Polymers

Telechelic polymers are macromolecules that contain reactive end groups that have the capacity to enter into further polymerization or other reactions. The range of monomers and functional groups employed in the preparation of telechelic polymers has been expanded in recent years owing to developments in the controlled radical polymerization routes as well as metathesis polymerization. A lot of new catalysts, used in metathesis polymerization, have been developed and applied to the preparation of advanced materials [142, 143].
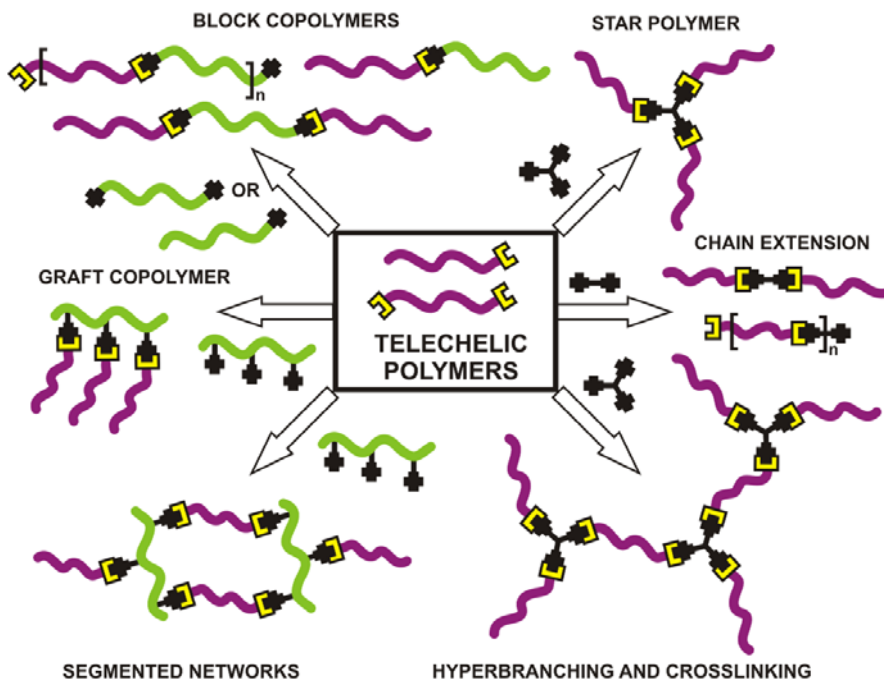
Figure 2.1 : Various architectures obtained by the reactions of telechelics.

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A telechelic contains end groups that react selectively to give a bond with another molecule. Depending on the functionality, which must be distinguished from the functionality of the end group itself, telechelics can be classified as mono-, di-, tri-, and multi-functional telechelics (polytelechelics).

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Furthermore, star and hyper-branched or dendritic polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents (Figure 2.1).

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Reagents for synthesis of ene-monomer

Styrene (St; 99%, Aldrich) : Styrene was passed through a basic alumina column to remove the inhibitor.used as received.

Methyl methacrylate (MMA, 99%, Aldrich): Methyl methacrylate was passed through a basic alumina column to remove the inhibitor.

Methyl acrylate (MA, 99%, Aldrich): Methyl acrylate was passed through a basic alumina column to remove the inhibitor.

3-Mercaptopropionic acid (MPA, >98%, Fluka)

3-Mercaptopropionic acid was used as received.

Trimethylolpropane tris(2-mercaptoacetate) (technical grade, Aldrich) : Trimethylolpropane tris(2-mercaptoacetate) was used as received.

3.1.2 Solvents

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

Toluene (Aldrich 99%) : Toluene was dried with calcium chloride and distilled over sodium wire.

Tetrahydrofuran (THF) (99.8%, J.T.Baker) : Tetrahydrofuran was used as received.

Dichloromethane (99.8%, J.T.Baker): Dichloromethane was dried with P_2O_5.

3.1.3 Other chemicals and reagents

2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba) : It was used as received.

Benzophenone (BP, 99%, Acros) : It was used as received.

Thioxanthone (TX, Aldrich) : It was used as received.

Camphorquinone (CQ, 98%, Fluka) : It was used as received.

(2,4,6 trimethylbenzoyl) diphenylphosphine oxide (TMDPO, Ciba) : It was used as received.

2,2'-azobis(isobutyronitrile) (AIBN, 98%, Aldrich) : It was used as received.

Ethyl-2-bromopropionate (>99%, Aldrich) : It was used as received.

N, N, N', N'', N'' -Pentamethyldiethylene triamine (PMDETA, Aldrich) : PMDETA was used as a ligand, was distilled before used.

Copper bromide (CuBr, 98%, Acros) : It was used as received.

3.2 Equipments

3.2.1 Photoreactor

Photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350 nm was used for photopolymerization of formulations containing DMPA which absorbs around 350 nm.

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

^{1}H-NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.3 Infrared spectrophotometer (IR)

FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One spectrometer via attenuated total reflectance (ATR) technique with 4 scans for each sample.

3.2.4 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H$_{HR}$, G3000H$_{HR}$ and G4000H$_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were

456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PSt standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation Methods

3.3.1 General procedure for atom transfer radical polymerization

To a Schlenk tube equipped with a magnetic stirring bar, the degassed monomer (St, 44 mmol), ligand (PMDETA, 0.44 mmol), catalyst (CuBr, 0.44 mmol), initiator (ethyl-2-bromopropionate, 0.44 mmol for PSt-Br (monomer/initiator/ CuBr/PMDETA: 100/1/1/1, 90 ^{o}C, 50 min) or allyl bromide, 0.22 mmol for PSt-allyl (monomer/initiator/CuBr/PMDETA: 200/1/1/1, 110 ^{o}C, 180 min)) and deoxygenated solvent toluene were added respectively. The tube was degassed by three freeze-pump-thaw cycles, left under vacuum, and placed in a thermostated oil bath. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. The polystyrene was dissolved in THF, precipitated in 10-fold excess methanol. The polymers were dried in vacuum at RT. Molecular weights and molecular weight distributions of polymers (M_n= 2500 g/mol, PDI= 1.18 for PSt-Br and M_n= 3900 g/mol, PDI= 1.09 for PSt-allyl were determined by GPC. The thiol end-functional polystyrene (M_n= 2600 g/mol, PDI= 1.15 for PSt-SH) was synthesized from PSt-Br by organic substitution reaction following the literature [144].

3.3.2 General procedures for thiol-ene "click" reactions

A solution of PSt-SH (1 equiv, 10^{-2} mmol) ene (10 equiv, 10^{-1} mmol) and a photoinitiator (1 equiv, 10^{-2} mmol) in 1 mL of CH$_2$Cl$_2$ were introduced in a Pyrex tube and irradiated at 350 nm at room temperature for 4 h. Light intensity was 1.04 mW cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. After this time, polymers were first precipitated in methanol then reprecipitated in acetonitrile for the removal of homopolymer formation of (meth)acrylates. Thermally initiated reactions

were conducted in the presence of AIBN (1 equiv, 10^{-2} mmol) at 80 °C for 4 h. Conditions and results are summarized in Table 4.1.

3.3.3 Real-time infrared spectroscopy

The real time FT-IR experiments were performed using a Perkin-Elmer FTIR Spectrum One B spectrometer in attenuated total reflection (ATR) mode. A sample drop was deposited and spread out over the ATR diamond crystal by means of a quartz plate. A polyethylene film was introduced between this filter and the solution drop. UV light (320–500 nm) was applied by a light guide (OmniCure Series 2000) with a light intensity of 18.40 mW·cm^{-2} at the level of the surface of the cured samples. Series scans were recorded, with spectra taken at the rate of approximately 4 scans/s. All reactions were performed under ambient conditions. Conversion rates of each bond were calculated according to the disappearance of IR absorption bands: 2570 cm^{-1} for the thiol of trimethylolpropane tris(2-mercaptoacetate), 1640 cm^{-1} for the methyl acrylate or methyl methacrylate and 1636 cm^{-1} for the allyl of allyl bromide. At a subsequent time t, the area of the peak was integrated and the conversion at that time was determined as follows: where x(t) is the conversion at time t, A_0 is the initial absorbance, and A_t is the absorbance of these bonds at time t.

x(t) = (A_0- A_t)/ A_0

4. RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of Allyl- and Thiol- End Functionalized Linear Polystyrenes

Appropriate allyl- and thiol- end functionalized linear polystyrenes were synthesized by ATRP according to the procedures reported by Matyjaszewski and co-workers [145] and Hilborn and co-workers [144], respectively. For the thiol-end functionalized polystyrene (PSt-SH), ethyl-2-bromopropionate was used as an initiator in the ATRP of styrene. The resulting halide end functional polystyrene was then converted to thiol group by organic substitution reaction (Reaction 4.1). The polymer (PSt-SH) was characterized by GPC (Mn= 2600 g/mol, PDI= 1.15 for PSt-SH) and ^{1}H-NMR analyses. The methine proton close to the halide chain end has a chemical shift at 4.30–4.42 ppm in Figure 4.1, which shifts quantitatively to 3.80 ppm, as a result of efficient nucleophilic substitution of the halogen atom at a polymer chain end by a thiol.
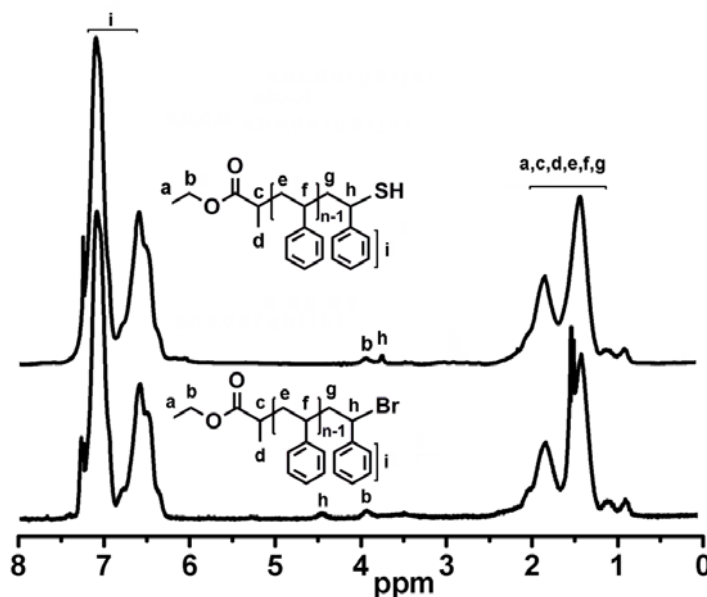
Figure 4.1 : ^{1}H-NMR spectra of PSt-Br (bottom) and the PSt-SH after the nucleophilic substitution (top).

(4.1)
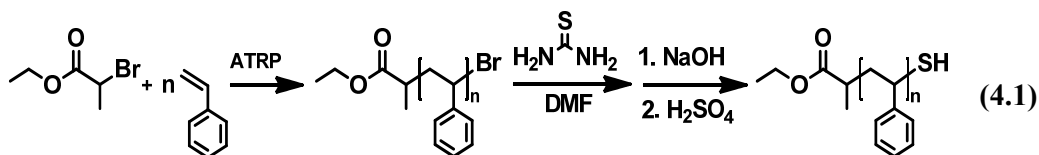
4.2 Thiol-ene "Click" Reactions

Thiol-ene "click" reactions have been carried out under a variety of initiating systems. We started performing the photoinitiating reactions at room temperature by irradiation with a UV- lamp (emitting nominally at 350 nm, light intensity= 1.04 mW.cm^{-2}) in the presence of the *Type I* photoinitiators, 2, 4, 6 trimethylbenzoyl diphenylphosphine oxide (TMDPO) and 2, 2-dimethoxy-2-phenyl acetophenone (DMPA) or *Type II* photoinitiators, benzophenone (BP), thioxanthone (TX), and camphorquinone (CQ)[146]. For comparison, thermally initiating system in the presence of thermal radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN) was also carried out at 80 $^{\circ}$C [147]. Summary of the reaction conditions and conversion yields for the individual initiating systems are collected in Table 4.1.

In the case of *Type I* photoinitiators, TMDPO and DMPA, upon the absorption of a photon of light two radicals are formed by a unimolecular cleavage reaction [148]. Either or both radicals may add into a carbon-carbon double bond directly or abstract hydrogen from a thiol group to initiate the thiol-ene coupling reactions (Reaction 4.2) (Table 1, Run 1, 2, 7, 8, 13, 14, 19, and 20).

(4.2)
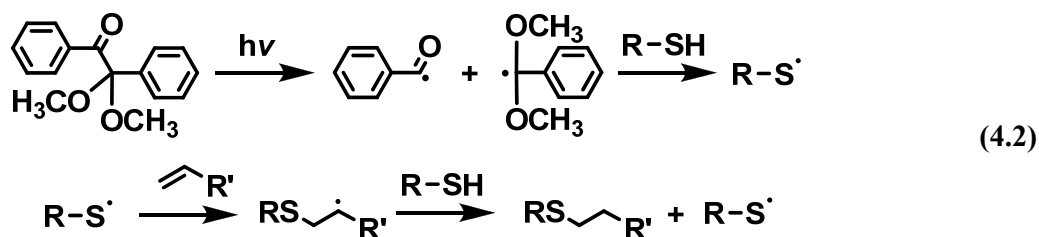
Thiol-ene "click" reaction can also be initiated by the reaction of the excited state of *Type II* photoinitiator with a thiol. In this case, reactive sulfenyl radicals and nonreactive ketyl radicals are concomitantly formed by a hydrogen abstraction reaction (Reaction 4.3) (Table 1, Run 3, 4, 5, 9, 10, 11, 15, 16, 17, 21, 22, and 23). Only, the sulfenyl radicals initiate the coupling reaction by inserting into the carbon-

carbon double bond of the enes. The ketyl radicals are usually not reactive toward double bond due to the steric hindrance and the delocalization of unpaired electron.

Table 4.1 :   Summary of the reaction conditions and product conversions of the thiol-ene "click" reactions.

| Run[a]	Thiol	Ene	Initiation type[b]	Initiator	Conversion (%)[c]
1	PSt-SH	MA	*Photo, Type I*	DMPA	**98**
2	PSt-SH	MA	*Photo, Type I*	TMDPO	**96**
3	PSt-SH	MA	*Photo, Type II*	BP	**91**
4	PSt-SH	MA	*Photo, Type II*	TX	**92**
5	PSt-SH	MA	*Photo, Type II*	CQ	**93**
6	PSt-SH	MA	*Thermal*	AIBN	**86**
7	PSt-SH	MMA	*Photo, Type I*	DMPA	**96**
8	PSt-SH	MMA	*Photo, Type I*	TMDPO	**95**
9	PSt-SH	MMA	*Photo, Type II*	BP	**94**
10	PSt-SH	MMA	*Photo, Type II*	TX	**89**
11	PSt-SH	MMA	*Photo, Type II*	CQ	**93**
12	PSt-SH	MMA	*Thermal*	AIBN	**89**
13	PSt-SH	AllylBr	*Photo, Type I*	DMPA	**100**
14	PSt-SH	AllylBr	*Photo, Type I*	TMDPO	**97**
15	PSt-SH	AllylBr	*Photo, Type II*	BP	**95**
16	PSt-SH	AllylBr	*Photo, Type II*	TX	**94**
17	PSt-SH	AllylBr	*Photo, Type II*	CQ	**96**
18	PSt-SH	AllylBr	*Thermal*	AIBN	**88**
19	MPA	PSt-Allyl	*Photo, Type I*	DMPA	**95**
20	MPA	PSt-Allyl	*Photo, Type I*	TMDPO	**95**
21	MPA	PSt-Allyl	*Photo, Type II*	BP	**89**
22	MPA	PSt-Allyl	*Photo, Type II*	TX	**89**
23	MPA	PSt-Allyl	*Photo, Type II*	CQ	**90**
24	MPA	PSt-Allyl	*Thermal*	AIBN	**87**

[a]Reactions were carried out in CH_2Cl_2 for 4 h with [PSt-SH]/[ene]: 1/10 mol ratio; [b]Photochemical reaction which included a photoinitiator was irradiated under 350 nm at room temperature, and the thermal reaction which included AIBN was heated to 80 °C. Light intensity is 1.04 mW cm^{-2}; [c]Percent conversion was obtained from the disappearance of the alkene peaks by ^{1}H-NMR and the appearance of peaks corresponding to the product. MA: methyl acrylate, MMA: methyl methacrylate, AllylBr: allyl bromide, MPA: 3-mercaptopropionic acid, DMPA: 2, 2-dimethoxy-2-phenyl acetophenone, TMDPO: (2, 4, 6 trimethylbenzoyl) diphenylphosphine oxide, BP: benzophenone, TX: thioxanthone, CQ: camphorquinone, AIBN: 2,2′-azobis(isobutyronitrile).

$$(4.3)$$
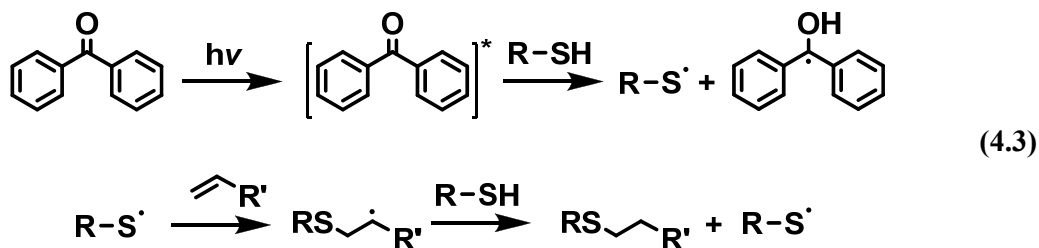
Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals which can abstract a hydrogen atom from thiol group, forming a sulfenyl radical, which reacts in the usual manner (Table 1, Run 6, 12, 18, and 24). A more advanced way of investigating the thiol-ene "click" reaction is real time FTIR analysis, which allows monitoring the reaction without the need of solvent. This system consists of trimethylolpropane tris(2-mercaptoacetate) (TRIS) which is known to work efficiently in thiol-ene photopolymerization with as methyl acrylate (MA), methyl methacrylate (MMA) and allyl bromide (AllylBr) in the presence of *Type I* or *Type II* photoinitiator without solvent. As the thiol signal is a clearly distinguishable in the region of 2500-2600 cm^{-1}, the decrease in absorbance of this signal has been monitored as a function of time. Data presented in Table 1 and Figures 4.2-4 show that the initiation with the *Type I* photoinitiators is more efficient than the one with *Type II* photoinitiators for thiol-ene "click" reactions [149, 150].
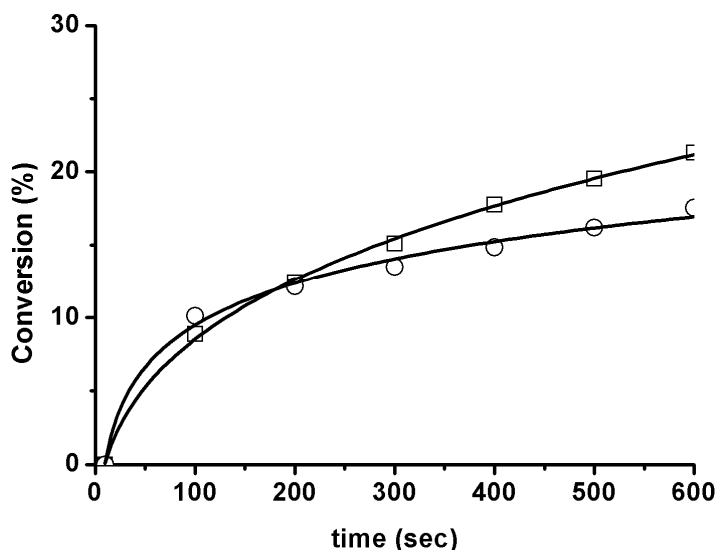
Figure 4.2 : Conversion of thiol–ene [trimethylolpropane tris(2-mercaptoacetate) and MA] system with the simultaneous FTIR monitoring of the thiol (S–H, 2570cm^{-1}) peak: (□) TMDPO, (○) CQ.

This behavior is due to the fact that, in the latter case, reactive radicals are produced by a bimolecular reaction with a lower quantum yield. When using *Type I* photoinitiators, the transient excited states (singlet and triplet) have very short lifetimes, thus preventing any quenching by the thiol [151]. Interestingly, the photochemical thiol coupling between TRIS and MA gave the lowest conversion efficiency, possibly due to the poor miscibility of the photoinitiators in the systems (Figure 2) [49]. Notably, thermally initiated thiol-ene "click" reaction reaches the lowest conversion of all the ene systems since the side reactions are more favored at relatively high temperatures.
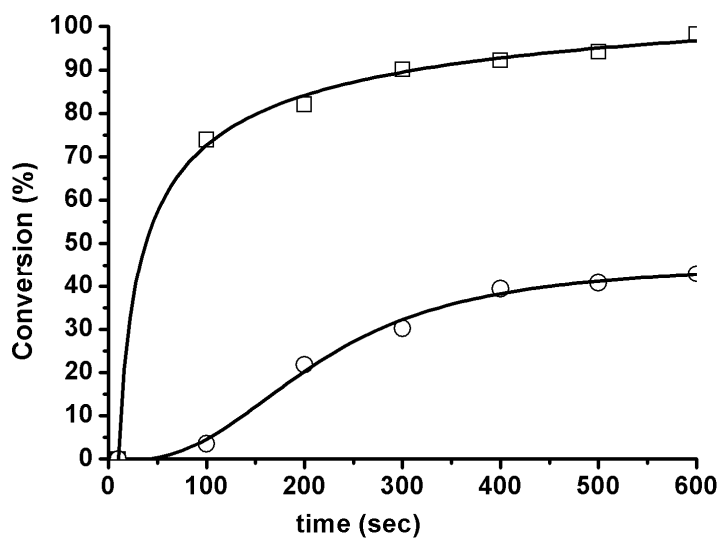
Figure 4.3 :   Conversion of thiol–ene [trimethylolpropane tris(2-mercaptoacetate) and MMA] system with the simultaneous FTIR monitoring of the thiol (S–H, 2570cm^{-1}) peak: (□) TMDPO, (○) CQ.
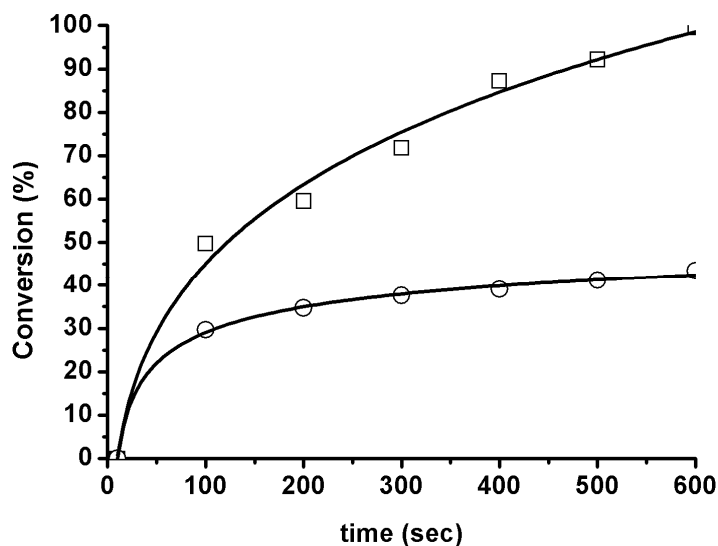
Figure 4.4 : Conversion of thiol–ene [trimethylolpropane tris(2-mercaptoacetate) and AllylBr] system with the simultaneous FT-IR monitoring of the thiol (S–H, 2570cm^{-1}) peak: (□) TMDPO, (○) CQ.

Efficiencies of thiol-ene "click" reactions of three different types of ene structures such as methyl acrylate, methyl methacrylate and allyl bromide, with thiol end-functional polystyrene (Reaction 4.4) have been studied for a molar ratio of 1:10 (thiol:ene).

(4.4)
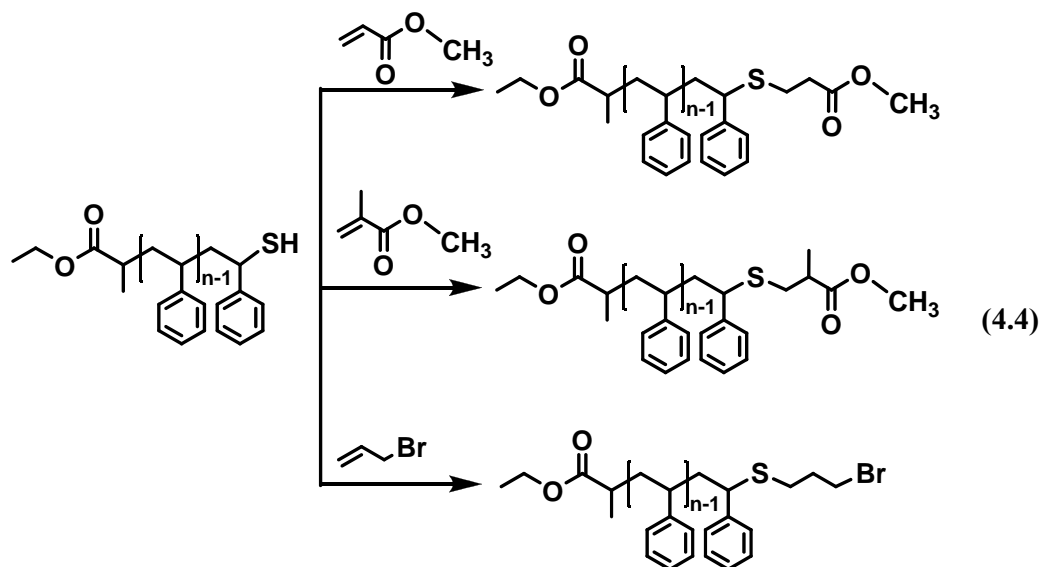
As shown in Figures 4.5 and 4.6, the signal of the methine proton next to thiol at 3.80 ppm shifted to 3.40 ppm during the course of the reaction, indicating the conversion of the thiol units. Simultaneously, new shifts from the (meth)acrylate protons appeared at 3.70 and 2.30 ppm.
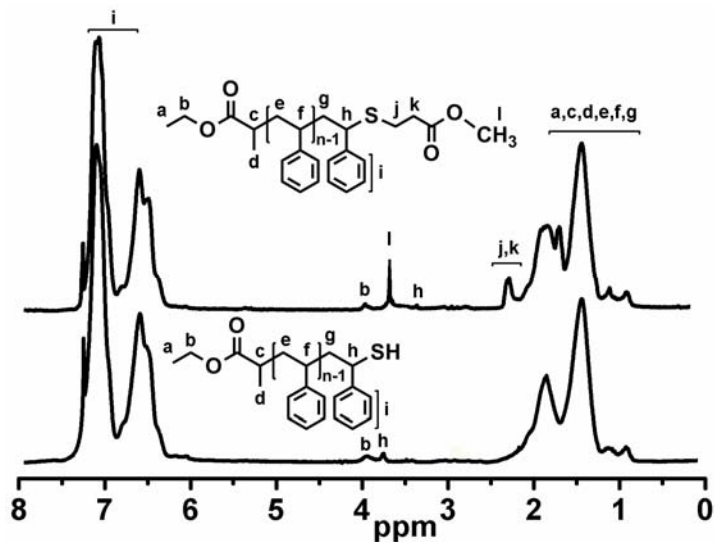
Figure 4.5 : ¹H-NMR spectra of PSt-SH (bottom) and the product after the thiol-ene "click" coupling with methyl acrylate (top).

Examination of the ¹H-NMR spectrum of the coupling product between PSt-SH and AllylBr (Figure 4.7) clearly shows that the signal of the methine proton of the polymer next to thiol at 3.80 ppm is shifted to 3.40 ppm. In addition, the new peaks corresponding to methylene atoms of AllylBr (3.05 and 2.30 ppm) were also clearly visible in the final product. In the case of the thiol-ene coupling reaction using acrylate or methacrylate group, homo poly(methyl acrylate) and poly(methyl methacrylate) formations are inevitable. The process frequently proceeds largely through the homopolymerization at early stages of the reaction followed by a more like thiol-ene coupling reaction at the end. For the removal of homopolymers, a second precipitation in acetonitrile was done before the ¹H-NMR measurements. After purification, in all cases, almost quantitative functionalizations of PSt-SH (85-100%) were attained by both photochemical and thermal initiation.
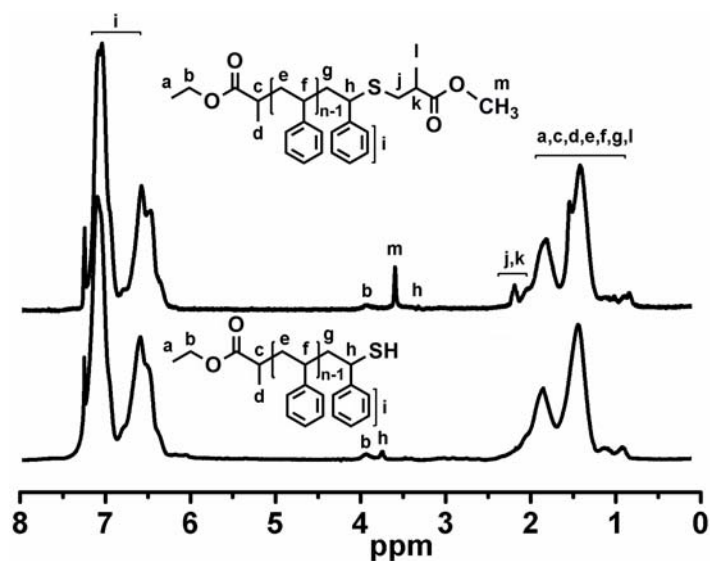
Figure 4.6 : ^{1}H-NMR spectra of PSt-SH (bottom) and the product after the thiol-ene "click" coupling with methyl methacrylate (top).
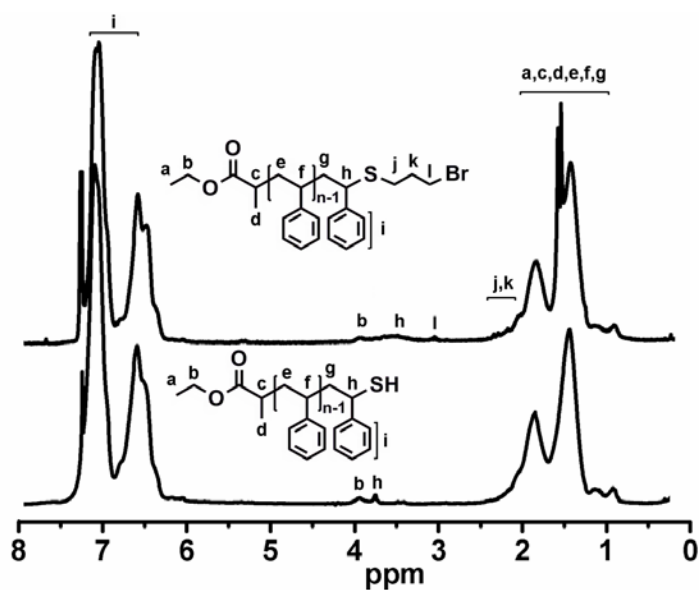
Figure 4.7 : ^{1}H-NMR spectra of PSt-SH (bottom) and the product after the thiol-ene "click" coupling with allyl bromide (top).

The other antagonist functional group, alkene was introduced to the polymer chains directly by using allyl bromide as an initiator in ATRP of St (Reaction 4.5). The molecular weight characteristics and structure of the resulting alkene-end functionalized polystyrene (PSt-Allyl) were confirmed by GPC (Mn= 3900 g/mol,

PDI= 1.09) and ^{1}H-NMR measurement, respectively. As can be seen from Figure 4.8, the resonance of the methylene protons adjacent to the bromine could be found at 4.30-4.42 ppm, while that of the allyl protons appeared at 5.56-5.74 and 4.84-4.94 ppm.

(4.5)
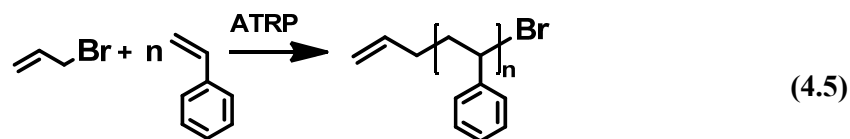
Experiments following the opposite strategy, which consists of the reaction of PSt-Allyl with 3-mercaptopropionic acid, were also performed under similar photochemical and thermal conditions (Reaction 4.6). From the ^{1}H-NMR spectrum of the thiol-ene coupling product shown in Figure 2, the resonance of the methine protons close to the bromine could be found at 4.30-4.42 ppm, while that of the allyl protons at 5.56-5.74 and 4.84-4.94 ppm disappeared completely. Moreover, the allyl-end groups of the PSt have been switched to terminal carboxylic acid telechelic polymer quantitatively by thiol-ene reaction "click" reaction.

(4.6)
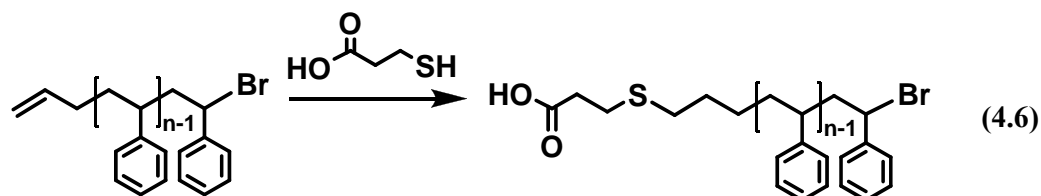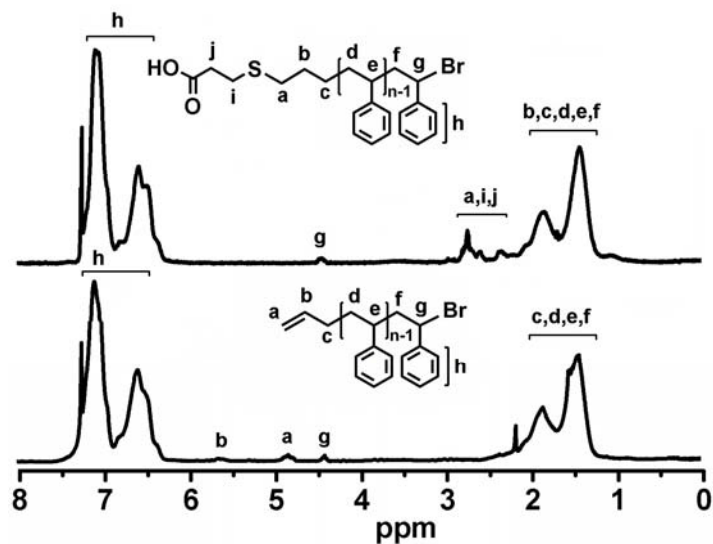
Figure 4.8 : ^{1}H-NMR spectra of PSt-Allyl (bottom) and the product after the thiol-ene "click" coupling with mercaptopropionic acid (top).

In conclusion, in order to evaluate the influence of the type of the initiation on polymer functionalization by thiol-ene chemistry, we reported the synthesis of the polymeric components, i.e., well defined and narrow molecular weight distributed allyl- and thiol- end functionalized polystyrenes by atom transfer radical polymerization and organic substitution reactions. The subsequent thiol-ene coupling reaction was found to have the characteristics of a "click"reaction. The reactions can be initiated using photochemical and thermal radical initiators where the use of a *Type I* photoinitiators led to highest efficiencies.

REFERENCES

[1] **Kolb, H.C., Finn, M.G., and Sharpless, K.B.**, 2001, Click chemistry: Diverse chemical function from a few good reactions, *Angewandte Chemie-International Edition*, 40, 2004-2021.

[2] **Rostovtsev, V.V., Green, L.G., Fokin, V.V., and Sharpless, K.B.**, 2002, A stepwise huisgen cycloaddition process: Copper(i)-catalyzed regioselective "ligation" of azides and terminal alkynes, *Angewandte Chemie-International Edition*, 41, 2596-2599.

[3] **Tornoe, C.W., Christensen, C., and Meldal, M.**, 2002, Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(i)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides, *Journal of Organic Chemistry*, 67, 3057-3064.

[4] **Binder, W.H. and Kluger, C.**, 2004, Combining ring-opening metathesis polymerization (romp) with sharpless-type "click" reactions: An easy method for the preparation of side chain functionalized poly(oxynorbornenes), *Macromolecules*, 37, 9321-9330.

[5] **Tsarevsky, N.V., Bernaerts, K.V., Dufour, B., Du Prez, F.E., and Matyjaszewski, K.**, 2004, Well-defined (co)polymers with 5-vinyltetrazole units via combination of atom transfer radical (co)polymerization of acrylonitrile and "click chemistry"-type postpolymerization modification, *Macromolecules*, 37, 9308-9313.

[6] **Sumerlin, B.S., Tsarevsky, N.V., Louche, G., Lee, R.Y., and Matyjaszewski, K.**, 2005, Highly efficient "click" functionalization of poly(3-azidopropyl methacrylate) prepared by atrp, *Macromolecules*, 38, 7540-7545.

[7] **Mantovani, G., Ladmiral, V., Tao, L., and Haddleton, D.M.**, 2005, One-pot tandem living radical polymerisation-huisgens cycloaddition process ("click") catalysed by n-alkyl-2-pyridylmethanimine/cu(i)br complexes, *Chemical Communications*, 2089-2091.

[8] **Gao, H.F., Louche, G., Sumerlin, B.S., Jahed, N., Golas, P., and Matyjaszewski, K.**, 2005, Gradient polymer elution chromatographic analysis of alpha,omega-dihydroxypolystyrene synthesized via atrp and click chemistry, *Macromolecules*, 38, 8979-8982.

[9] **Englert, B.C., Bakbak, S., and Bunz, U.H.F.**, 2005, Click chemistry as a powerful tool for the construction of functional poly(p-phenyleneethynylene)s: Comparison of pre- and postfunctionalization schemes, *Macromolecules*, 38, 5868-5877.

[10] **Malkoch, M., Thibault, R.J., Drockenmuller, E., Messerschmidt, M., Voit, B., Russell, T.P., and Hawker, C.J.**, 2005, Orthogonal approaches to the simultaneous and cascade functionalization of macromolecules using click chemistry, *Journal of the American Chemical Society*, 127, 14942-14949.

[11] **Tsarevsky, N.V., Sumerlin, B.S., and Matyjaszewski, K.**, 2005, Step-growth "click" coupling of telechelic polymers prepared by atom transfer radical polymerization, *Macromolecules*, 38, 3558-3561.

[12] **Lutz, J.F., Borner, H.G., and Weichenhan, K.**, 2005, Combining atom transfer radical polymerization and click chemistry: A versatile method for the preparation of end-functional polymers, *Macromolecular Rapid Communications*, 26, 514-518.

[13] **Vogt, A.P. and Sumerlin, B.S.**, 2006, An efficient route to macromonomers via atrp and click chemistry, *Macromolecules*, 39, 5286-5292.

[14] **Oral, A., Tasdelen, M.A., Demirel, A.L., and Yagci, Y.**, 2009, Poly(methyl methacrylate)/clay nanocomposites by photoinitiated free radical polymerization using intercalated monomer, *Polymer*, 50, 3905-3910.

[15] **Ergin, M., Kiskan, B., Gacal, B., and Yagci, Y.**, 2007, Thermally curable polystyrene via click chemistry, *Macromolecules*, 40, 4724-4727.

[16] **Kiskan, B., Demiray, G., and Yagci, Y.**, 2008, Thermally curable polyvinyl chloride via click chemistry, *Journal of Polymer Science Part a-Polymer Chemistry*, 46, 3512-3518.

[17] **Kukut, M., Kiskan, B., and Yagci, Y.**, 2009, Self-curable benzoxazine functional polybutadienes synthesized by click chemistry, *Designed Monomers and Polymers*, 12, 167-176.

[18] **Gacal, B.N., Koz, B., Gacal, B., Kiskan, B., Erdogan, M., and Yagci, Y.**, 2009, Pyrene functional poly(vinyl alcohol) by "click" chemistry, *Journal of Polymer Science Part a-Polymer Chemistry*, 47, 1317-1326.

[19] **Ak, M., Gacal, B., Kiskan, B., Yagci, Y., and Toppare, L.**, 2008, Enhancing electrochromic properties of polypyrrole by silsesquioxane nanocages, *Polymer*, 49, 2202-2210.

[20] **Tasdelen, M.A., Van Camp, W., Goethals, E., Dubois, P., Du Prez, F., and Yagci, Y.**, 2008, Polytetrahydrofuran/clay nanocomposites by in situ polymerization and "click" chemistry processes, *Macromolecules*, 41, 6035-6040.

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

[22] **Ladmiral, V., Mantovani, G., Clarkson, G.J., Cauet, S., Irwin, J.L., and Haddleton, D.M.**, 2006, Synthesis of neoglycopolymers by a combination of "click chemistry" and living radical polymerization, *Journal of the American Chemical Society*, 128, 4823-4830.

[23] **Lutz, J.F., Borner, H.G., and Weichenhan, K.**, 2006, Combining atrp and "click" chemistry: A promising platform toward functional biocompatible polymers and polymer bioconjugates, *Macromolecules*, 39, 6376-6383.

[24] **Parrish, B., Breitenkamp, R.B., and Emrick, T.**, 2005, Peg- and peptide-grafted aliphatic polyesters by click chemistry, *Journal of the American Chemical Society*, 127, 7404-7410.

[25] **Opsteen, J.A. and van Hest, J.C.M.**, 2005, Modular synthesis of block copolymers via cycloaddition of terminal azide and alkyne functionalized polymers, *Chemical Communications*, 57-59.

[26] **Quemener, D., Davis, T.P., Barner-Kowollik, C., and Stenzel, M.H.**, 2006, Raft and click chemistry: A versatile approach to well-defined block copolymers, *Chemical Communications*, 5051-5053.

[27] **Durmaz, H., Dag, A., Altintas, O., Erdogan, T., Hizal, G., and Tunca, U.**, 2007, One-pot synthesis of abc type triblock copolymers via in situ click [3+2] and diels-alder [4+2] reactions, *Macromolecules*, 40, 191-198.

[28] **Opsteen, J.A. and Van Hest, J.C.M.**, 2007, Modular synthesis of abc type block copolymers by "click" chemistry, *Journal of Polymer Science Part a-Polymer Chemistry*, 45, 2913-2924.

[29] **Agut, W., Taton, D., and Lecommandoux, S.**, 2007, A versatile synthetic approach to polypeptide based rod-coil block copolymers by click chemistry, *Macromolecules*, 40, 5653-5661.

[30] **Hasneen, A., Kim, S.J., and Paik, H.J.**, 2007, Synthesis and characterization of low molecular weight poly(methyl acrylate)-b-polystyrene by a combination of atrp and click coupling method, *Macromolecular Research*, 15, 541-546.

[31] **Gao, H.F. and Matyjaszewski, K.**, 2007, Synthesis of molecular brushes by "grafting onto" method: Combination of atrp and click reactions, *Journal of the American Chemical Society*, 129, 6633-6639.

[32] **Gacal, B., Akat, H., Balta, D.K., Arsu, N., and Yagci, Y.**, 2008, Synthesis and characterization of polymeric thioxanthone photoinitatiors via double click reactions, *Macromolecules*, 41, 2401-2405.

[33] **Riva, R., Schmeits, S., Jerome, C., Jerome, R., and Lecomte, P.**, 2007, Combination of ring-opening polymerization and "click chemistry": Toward functionalization and grafting of poly(epsilon-caprolactone), *Macromolecules*, 40, 796-803.

[34] **Li, H.Y., Riva, R., Jerome, R., and Lecomte, P.**, 2007, Combination of ring-opening polymerization and "click" chemistry for the synthesis of an amphiphilic tadpole-shaped poly(epsilon-caprolactone) grafted by peo, *Macromolecules*, 40, 824-831.

[35] **Tsarevsky, N.V., Bencherif, S.A., and Matyjaszewski, K.**, 2007, Graft copolymers by a combination of atrp and two different consecutive click reactions, *Macromolecules*, 40, 4439-4445.

[36] **Dag, A., Durmaz, H., Demir, E., Hizal, G., and Tunca, U.**, 2008, Heterograft copolymers via double click reactions using one-pot technique, *Journal of Polymer Science Part a-Polymer Chemistry*, 46, 6969-6977.

[37] **Gao, H.F. and Matyjaszewski, K.**, 2006, Synthesis of star polymers by a combination of atrp and the "click" coupling method, *Macromolecules*, 39, 4960-4965.

[38] **Whittaker, M.R., Urbani, C.N., and Monteiro, M.J.**, 2006, Synthesis of 3-miktoarm stars and 1st generation mikto dendritic copolymers by "living" radical polymerization and "click" chemistry, *Journal of the American Chemical Society*, 128, 11360-11361.

[39] **Durmaz, H., Dag, A., Hizal, A., Hizal, G., and Tunca, U.**, 2008, One-pot synthesis of star-block copolymers using double click reactions, *Journal of Polymer Science Part a-Polymer Chemistry*, 46, 7091-7100.

[40] **Altintas, O., Hizal, G., and Tunca, U.**, 2006, Abc-type hetero-arm star terpolymers through "click" chemistry, *Journal of Polymer Science Part a-Polymer Chemistry*, 44, 5699-5707.

[41] **Altintas, O., Yankul, B., Hizal, G., and Tunca, U.**, 2006, A(3)-type star polymers via click chemistry, *Journal of Polymer Science Part a-Polymer Chemistry*, 44, 6458-6465.

[42] **Yin, J., Ge, Z.S., Liu, H., and Liu, S.Y.**, 2009, Synthesis of amphiphilic copolymer brushes possessing alternating poly(methyl methacrylate) and poly(n-isopropylacrylamide) grafts via a combination of atrp and click chemistry, *Journal of Polymer Science Part a-Polymer Chemistry*, 47, 2608-2619.

[43] **Pool, B.R. and White, J.M.**, 2000, Structural manifestations of the retro diels-alder reaction, *Organic Letters*, 2, 3505-3507.

[44] **Dondoni, A.**, 2008, The emergence of thiol-ene coupling as a click process for materials and bioorganic chemistry, *Angewandte Chemie-International Edition*, 47, 8995-8997.

[45] **van der Ende, A., Croce, T., Hamilton, S., Sathiyakumar, V., and Harth, E.**, 2009, Tailored polyester nanoparticles: Post-modification with dendritic transporter and targeting units via reductive amination and thiol-ene chemistry, *Soft Matter*, 5, 1417-1425.

[46] **Chen, G.J., Amajjahe, S., and Stenzel, M.H.**, 2009, Synthesis of thiol-linked neoglycopolymers and thermo-responsive glycomicelles as potential drug carrier, *Chemical Communications*, 1198-1200.

[47] **ten Brummelhuis, N., Diehl, C., and Schlaad, H.**, 2008, Thiol-ene modification of 1,2-polybutadiene using uv light or sunlight, *Macromolecules*, 41, 9946-9947.

[48] **Nurmi, L., Lindqvist, J., Randev, R., Syrett, J., and Haddleton, D.M.**, 2009, Glycopolymers via catalytic chain transfer polymerisation (cctp), huisgens cycloaddition and thiol-ene double click reactions, *Chemical Communications*, 2727-2729.

[49] **Campos, L.M., Killops, K.L., Sakai, R., Paulusse, J.M.J., Damiron, D., Drockenmuller, E., Messmore, B.W., and Hawker, C.J.**, 2008, Development of thermal and photochemical strategies for thiol-ene click polymer functionalization, *Macromolecules*, 41, 7063-7070.

[50] **Gress, A., Volkel, A., and Schlaad, H.**, 2007, Thio-click modification of poly[2-(3-butenyl)-2-oxazoline], *Macromolecules*, 40, 7928-7933.

[51] **Pounder, R.J., Stanford, M.J., Brooks, P., Richards, S.P., and Dove, A.P.**, 2008, Metal free thiol-maleimide 'click' reaction as a mild functionalisation strategy for degradable polymers, *Chemical Communications*, 5158-5160.

[52] **Boyer, C., Granville, A., Davis, T.P., and Bulmus, V.**, 2009, Modification of raft-polymers via thiol-ene reactions: A general route to functional polymers and new architectures, *Journal of Polymer Science Part a-Polymer Chemistry*, 47, 3773-3794.

[53] **Connal, L.A., Kinnane, C.R., Zelikin, A.N., and Caruso, F.**, 2009, Stabilization and functionalization of polymer multilayers and capsules via thiol-ene click chemistry, *Chemistry of Materials*, 21, 576-578.

[54] **Campos, L.M., Meinel, I., Guino, R.G., Schierhorn, M., Gupta, N., Stucky, G.D., and Hawker, C.J.**, 2008, Highly versatile and robust

materials for soft imprint lithography based on thiol-ene click chemistry, *Advanced Materials*, 20, 3728-+.

[55] **Goldmann, A.S., Walther, A., Nebhani, L., Joso, R., Ernst, D., Loos, K., Barner-Kowollik, C., Barner, L., and Muller, A.H.E.**, 2009, Surface modification of poly(divinylbenzene) microspheres via thiol-ene chemistry and alkyne-azide click reactions, *Macromolecules*, 42, 3707-3714.

[56] **Chan, J.W., Yu, B., Hoyle, C.E., and Lowe, A.B.**, 2008, Convergent synthesis of 3-arm star polymers from raft-prepared poly(n,n-diethylacrylamide) via a thiol-ene click reaction, *Chemical Communications*, 4959-4961.

[57] **Killops, K.L., Campos, L.M., and Hawker, C.J.**, 2008, Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene "click" chemistry, *Journal of the American Chemical Society*, 130, 5062-+.

[58] **Fiore, M., Marra, A., and Dondoni, A.**, 2009, Photoinduced thiol-ene coupling as a click ligation tool for thiodisaccharide synthesis, *The Journal of Organic Chemistry*, 74, 4422-4425.

[59] **Sangermano, M., Bongiovanni, R., Malucelli, G., Priola, A., Harden, A., and Rehnberg, N.**, 2002, Synthesis of new fluorinated allyl ethers for the surface modification of thiol-ene ultraviolet-curable formulations, *Journal of Polymer Science Part a-Polymer Chemistry*, 40, 2583-2590.

[60] **Sangermano, M., Gross, S., Priola, A., Rizza, G., and Sada, C.**, 2007, Thiol-ene hybrid organic/inorganic nanostructured coatings based an thiol-functionalized zirconium oxoclusters, *Macromolecular Chemistry and Physics*, 208, 2560-2568.

[61] **Eisele, G., Fouassier, J.P., and Reeb, R.**, 1997, Kinetics of photocrosslinking reactions of a dcpa/ea matrix in the presence of thiols and acrylates, *Journal of Polymer Science Part a-Polymer Chemistry*, 35, 2333-2345.

[62] **Morgan, C.R., Magnotta, F., and Ketley, A.D.**, 1977, Thiol-ene photo-curable polymers, *Journal of Polymer Science Part a-Polymer Chemistry*, 15, 627-645.

[63] **Tornoe, C.W., Christensen, C., and Meldal, M.**, 2002, Peptidotriazoles on solid phase: 1,2,3 -triazoles by regiospecific copper(i)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides, *Journal of Organic Chemistry*, 67, 3057-3064.

[64] **Kamata, K., Nakagawa, Y., Yamaguchi, K., and Mizuno, N.**, 2008, 1,3-dipolar cycloaddition of organic azides to alkynes by a dicopper-substituted silicotungstate, *Journal of the American Chemical Society*, 130, 15304-15310.

[65] **Yamaguchi, K., Oishi, T., Katayama, T., and Mizuno, N.**, 2009, A supported copper hydroxide on titanium oxide as an efficient reusable heterogeneous catalyst for 1,3-dipolar cycloaddition of organic azides to terminal alkynes, *Chemistry-a European Journal*, 15, 10464-10472.

[66] **Kolb, H.C. and Sharpless, K.B.**, 2003, The growing impact of click chemistry on drug discovery, *Drug Discovery Today*, 8, 1128-1137.

[67] **White, M.A., Johnson, J.A., Koberstein, J.T., and Turro, N.J.**, 2006, Toward the syntheses of universal ligands for metal oxide surfaces:

Controlling surface functionality through click chemistry, *Journal of the American Chemical Society*, 128, 11356-11357.

[68] **Wu, P., Feldman, A.K., Nugent, A.K., Hawker, C.J., Scheel, A., Voit, B., Pyun, J., Frechet, J.M.J., Sharpless, K.B., and Fokin, V.V.**, 2004, Efficiency and fidelity in a click-chemistry route to triazole dendrimers by the copper(i)-catalyzed ligation of azides and alkynes, *Angewandte Chemie-International Edition*, 43, 3928-3932.

[69] **Lutz, J.F.**, 2007, 1,3-dipolar cycloadditions of azides and alkynes: A universal ligation tool in polymer and materials science, *Angewandte Chemie-International Edition*, 46, 1018-1025.

[70] **Iha, R.K., Wooley, K.L., Nystrom, A.M., Burke, D.J., Kade, M.J., and Hawker, C.J.**, 2009, Applications of orthogonal "click" chemistries in the synthesis of functional soft materials, *Chemical Reviews*, 109, 5620-5686.

[71] **Hawker, C.J. and Wooley, K.L.**, 2005, The convergence of synthetic organic and polymer chemistries, *Science*, 309, 1200-1205.

[72] **Johnson, J.A., Finn, M.G., Koberstein, J.T., and Turro, N.J.**, 2008, Construction of linear polymers, dendrimers, networks, and other polymeric architectures by copper-catalyzed azide-alkyne cycloaddition "click" chemistry, *Macromolecular Rapid Communications*, 29, 1052-1072.

[73] **Michinobu, T.**, 2008, Click-type reaction of aromatic polyamines for improvement of thermal and optoelectronic properties, *Journal of the American Chemical Society*, 130, 14074-14075.

[74] **Li, Y.R., Tsuboi, K., and Michinobu, T.**, 2010, Double click synthesis and second-order nonlinearities of polystyrenes bearing donor-acceptor chromophores, *Macromolecules*, 43, 5277-5286.

[75] **Diels, O. and Alder, K.**, 1928, Synthesen in der hydroaromatischen reihe, *Justus Liebig's Annalen der Chemie*, 460, 98-122.

[76] **Kennedy, J.P. and Carlson, G.M.**, 1983, Synthesis, characterization, and diels–alder extension of cyclopentadiene telechelic polyisobutylene. Iv. A,ω-di(3-cyclopentadienylpropyldimethylsilyl)polyisobutylene, *Journal of Polymer Science: Polymer Chemistry Edition*, 21, 3551-3561.

[77] **Goodall, G.W. and Hayes, W.**, 2006, Advances in cycloaddition polymerizations, *Chemical Society Reviews*, 35, 280-312.

[78] **Diakoumakos, C.D. and Mikroyannidis, J.A.**, 1992, Polyimides derived from diels-alder polymerization of furfuryl-substituted maleamic acids or from the reaction of bismaleamic with bisfurfurylpyromellitamic acids, *Journal of Polymer Science Part a-Polymer Chemistry*, 30, 2559-2567.

[79] **Mikroyannidis, J.A.**, 1992, Synthesis and diels-alder polymerization of furfurylidene and furfuryl-substituted maleamic acids, *Journal of Polymer Science Part a-Polymer Chemistry*, 30, 125-132.

[80] **Gousse, C. and Gandini, A.**, 1999, Diels-alder polymerization of difurans with bismaleimides, *Polymer International*, 48, 723-731.

[81] **Kamahori, K., Tada, S., Ito, K., and Itsuno, S.**, 1999, Optically active polymer synthesis by diels-alder polymerization with chirally modified lewis acid catalyst, *Macromolecules*, 32, 541-547.

[82] **Mallakpour, S.E., Hajipour, A.R., Mahdavian, A.R., and Khoee, S.**, 2000, Synthesis and characterization of novel optically active and flame-retardant heterocyclic polyimides, *Journal of Applied Polymer Science*, 76, 240-248.

[83] **Mikroyannidis, J.A.**, 1992, Furyl-maleimide insitu generated ab-monomers - synthesis, characterization, and diels-alder polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, 30, 2017-2024.

[84] **Alhakimi, G., Gorls, H., and Klemm, E.**, 1994, Polyimides by diels-alder polyaddition of alpha-pyrones, *Macromolecular Chemistry and Physics*, 195, 1569-1576.

[85] **Kumar, U. and Neenan, T.X.**, 1995, Hybrid polyimide-polyphenylenes by the diels-alder polymerization between biscyclopentadienones and ethynyl-terminated imides, *Acs Symposium Series*, 614, 518-526.

[86] **Ben Romdhane, H., Baklouti, M., Chaabouni, M.R., Grenier-Loustalot, M.F., Delolme, F., and Sillion, B.**, 2002, Polypentamethylnadimides obtained by diels-alder reaction, *Polymer*, 43, 255-268.

[87] **Alhakimi, G., Klemm, E., and Görls, H.**, 1995, Synthesis of new polyimides by diels–alder reaction of bis(2-pyrone)s with bismaleimides, *Journal of Polymer Science Part A: Polymer Chemistry*, 33, 1133-1142.

[88] **Stille, J.K. and Noren, G.K.**, 1972, Catenation and kinetics of the diels-alder step-growth reaction in the synthesis of phenylated polyphenylenes, *Macromolecules*, 5, 49-55.

[89] **Schilling, C.L., Reed, J.A., and Stille, J.K.**, 1969, Diels-alder polymerization. Vi. Phenylated polyphenylenes from bis-2-pyrones and p-diethynylbenzene, *Macromolecules*, 2, 85-88.

[90] **Stille, J.K., Rakutis, R.O., Mukamal, H., and Harris, F.W.**, 1968, Diels-alder polymerizations. Iv. Polymers containing short phenylene blocks connected by alkylene units, *Macromolecules*, 1, 431-436.

[91] **Mukamal, H., Harris, F.W., and Stille, J.K.**, 1967, Diels-alder polymers. Iii. Polymers containing phenylated phenylene units, *Journal of Polymer Science Part A-1: Polymer Chemistry*, 5, 2721-2729.

[92] **Schluter, A.D.**, 1991, Ladder polymers - the new generation, *Advanced Materials*, 3, 282-291.

[93] **Scherf, U. and Mullen, K.**, 1995, The synthesis of ladder polymers, *Advances in Polymer Science*, 123, 1-40.

[94] **Posner, T.**, 1905, Information on unsaturated compounds ii the addition of mercaptan to unsaturated hydrocarbon, *Berichte Der Deutschen Chemischen Gesellschaft*, 38, 646-657.

[95] **Kharasch, M.S., Read, J., and Mayo, F.R.**, 1938, The peroxide effect in the addition of reagents to unsaturated compounds. Xvi. The addition of thio-glycolic acid to styrene and isobutylene., *Chemistry & Industry*, 752-773.

[96] **Jacobine, A.F.**, *Thiol-ene photopolymers, in radiation curing*, in *Polymer science and technology*, J.P. Fouassier and J. Rabek, Editors. 1993, Plenum Press: New York. p. 219.

[97] **Woods, J.G.**, *Radiation curable adhesives*, in *Radiation curing: Science and technology*, S.P. Pappas, Editor. 1992, Plenum Press: New York. p. 333.

[98] **Matyjaszewski, K. and Gaynor, S.G.**, *In applied polymer science, ,* ed. C.D. Craver and C.E. Carraher. 2000, Oxford: Pergamon Press. 929.

[99] **Swarc, M.**, 1960, Termination of anionic polymerization*, Advances in Polymer Science*, 2, 275-306.

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

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

[102] **Patten, T.E. and Matyjaszewski, K.**, 1998, Atom transfer radical polymerization and the synthesis of polymeric materials*, Advanced Materials*, 10, 901.

[103] **Patten, T.E. and Matyjaszewski, K.**, 1999, Copper(i)-catalyzed atom transfer radical polymerization*, Accounts of Chemical Research*, 32, 895-903.

[104] **Matyjaszewski, K. and Xia, J.**, *Fundamentals of atom transfer radical polymerization*, in *Handbook of radical polymerization*, K. Matyjaszewski and T.P. Davis, Editors. 2002, John Wiley and Sons, Inc.: New York.

[105] **Fischer, H.**, 1999, The persistent radical effect in controlled radical polymerizations*, Journal of Polymer Science Part a-Polymer Chemistry*, 37, 1885-1901.

[106] **Sonmez, H.B. and Bicak, N.**, 2002, Quaternization of poly(4-vinyl pyridine) beads with 2-chloroacetamide for selective mercury extraction*, Reactive & Functional Polymers*, 51, 55-60.

[107] **Xia, J.H. and Matyjaszewski, K.**, 1997, Controlled/"living" radical polymerization. Homogeneous reverse atom transfer radical polymerization using aibn as the initiator*, Macromolecules*, 30, 7692-7696.

[108] **Klumperman, B.**, *Living radical polymerization*, in *Encyclopedia of polymer science and technology*. 2004, John Wiley & Sons, Inc.: New York.

[109] **Teodorescu, M., Gaynor, S.G., and Matyjaszewski, K.**, 2000, Halide anions as ligands in iron-mediated atom transfer radical polymerization*, Macromolecules*, 33, 2335-2339.

[110] **Moineau, G., Minet, M., Teyssie, P., and Jerome, R.**, 2000, Synthesis of fully acrylic thermoplastic elastomers by atom transfer radical polymerization (atrp), 2 - effect of the catalyst on the molecular control and the rheological properties of the triblock copolymers*, Macromolecular Chemistry and Physics*, 201, 1108-1114.

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

[112] **Haddleton, D.M., Jasieczek, C.B., Hannon, M.J., and Shooter, A.J.**, 1997, Atom transfer radical polymerization of methyl methacrylate

initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper(i) complexes, *Macromolecules*, 30, 2190-2193.

[113] **Acar, M.H. and Bicak, N.**, 2003, Synthesis of hexylated triethylenetetramine: New ligand for homogeneous atom transfer radical polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, 41, 1677-1680.

[114] **Bicak, N., Gazi, M., Tunca, U., and Kucukkaya, I.**, 2004, Utility of atom transfer radical polymerization for the preparation of poly(methyl methacrylate) beads in an aqueous suspension, *Journal of Polymer Science Part a-Polymer Chemistry*, 42, 1362-1366.

[115] **Catala, J.M., Bubel, F., and Hammouch, S.O.**, 1995, Living radical polymerization - kinetic results, *Macromolecules*, 28, 8441-8443.

[116] **Wang, D. and Wu, Z.**, 1998, Facile synthesis of new unimolecular initiators for living radical polymerizations, *Macromolecules*, 31, 6727-6729.

[117] **Miura, Y., Hirota, K., Moto, H., and Yamada, B.**, 1998, High-yield synthesis of alkoxyamine initiators carrying a functional group by reaction of ethylbenzenes with di-tert-butyl diperoxalate in the presence of nitroxides, *Macromolecules*, 31, 4659-4661.

[118] **Zink, M.O., Kramer, A., and Nesvadba, P.**, 2000, New alkoxyamines from the addition of free radicals to nitrones or nitroso compounds as initiators for living free radical polymerization, *Macromolecules*, 33, 8106-8108.

[119] **Benoit, D., Chaplinski, V., Braslau, R., and Hawker, C.J.**, 1999, Development of a universal alkoxyamine for "living" free radical polymerizations, *Journal of the American Chemical Society*, 121, 3904-3920.

[120] **Grimaldi, S., Finet, J.P., Le Moigne, F., Zeghdaoui, A., Tordo, P., Benoit, D., Fontanille, M., and Gnanou, Y.**, 2000, Acyclic beta-phosphonylated nitroxides: A new series of counter-radicals for "living"/controlled free radical polymerization, *Macromolecules*, 33, 1141-1147.

[121] **Benoit, D., Grimaldi, S., Robin, S., Finet, J.P., Tordo, P., and Gnanou, Y.**, 2000, Kinetics and mechanism of controlled free-radical polymerization of styrene and n-butyl acrylate in the presence of an acyclic beta-phosphonylated nitroxide, *Journal of the American Chemical Society*, 122, 5929-5939.

[122] **Baldovi, M.V., Mohtat, N., and Scaiano, J.C.**, 1996, Influence of acids on reaction rates of free radical scavenging by tempo. Relevance to "living" free radical polymerizations, *Macromolecules*, 29, 5497-5499.

[123] **Skene, W.G., Belt, S.T., Connolly, T.J., Hahn, P., and Scaiano, J.C.**, 1998, Decomposition kinetics, arrhenius parameters, and bond dissociation energies for alkoxyamines of relevance in "living" free radical polymerization, *Macromolecules*, 31, 9103-9105.

[124] **Tunca, U., Hizal, G., Acar, M.H., Tasdelen, M.A., Yagci, Y., and Mishra, M.K.**, *Controlled/living radical polymerization*, in *Handbook of vinyl polymers*, Y. Yagci and M.K. Mishra, Editors. 2009, CRC Press Taylor & Francis Group,: New York. p. 256-281.

[125] **Convertine, A.J., Ayres, N., Scales, C.W., Lowe, A.B., and McCormick, C.L.**, 2004, Facile, controlled, room-temperature raft polymerization of n-isopropylacrylamide, *Biomacromolecules*, 5, 1177-1180.

[126] **Quinn, J.F., Rizzardo, E., and Davis, T.P.**, 2001, Ambient temperature reversible addition-fragmentation chain transfer polymerisation, *Chemical Communications*, 1044-1045.

[127] **Chiefari, J. and Rizzardo, E.**, *Control of free radical polymerization by chain transfer methods*, in *Handbook of radical polymerization*, K. Matyjaszewski and T.P. Davis, Editors. 2002, John Wiley and Sons, Inc.: New York.

[128] **Degee, P., Dubois, P., and Jerome, R.**, 1997, Bulk polymerization of lactides initiated by aluminium isopropoxide .3. Thermal stability and viscoelastic properties, *Macromolecular Chemistry and Physics*, 198, 1985-1995.

[129] **Johns, D., Lenz, R.W., and Luecke, A.**, *Lactones, *, in *Ring-opening polymerization*, I. K.J. and T. Saegusa, Editors. 1984, Elsevier: London. p. 464.

[130] **Rabek, J.F.**, 1987, Mechanisms of photophysical and photochemical reactions in polymer: Theory and practical applications, wiley, new york.

[131] **Wayne, R.P.**, 1988, Principles and applications of photochemistry, oxford univ. Press, oxford, uk.

[132] **Calvert, J.G. and Pitts, J.N.**, 1966, Photochemistry, wiley & sons, new york.

[133] **Rabek, J.F.**, *Mechanisms of photophysical and photochemical reactions*, in *Polymer: Theory and practical applications*. 1987, Wiley: New York.

[134] **Wayne, R.P.**, *Principles and applications of photochemistry*. 1988, Oxford Univ. Press: Oxford UK.

[135] **Calvert, J.G. and Pitts, J.N.**, *Photochemistry,*. 1966, Wiley & Sons, : New York.

[136] **Silverstein, R.v., Bassler, G.C., and Morrill, T.C.**, *Spectrometric identification of organic compounds*. 1991, Wiley & Sons. 5th ed.: New York.

[137] **Arsu, N., Reetz, I., Yagci, Y., and Mishra, M.K.**, *Photoinitiated radical vinyl polymerization* in *Handbook of vinyl polymers: Radical polymerization & technology*, Y. Yagci and M.K. Mishra, Editors. 2008, Taylor & Francis, Inc. p. 141-204.

[138] **Hageman, H.J.**, 1985, Photoinitiators for free-radical polymerization, *Progress in Organic Coatings*, 13, 123-150.

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

[140] **Davidson, R.S.**, 1993, The chemistry of photoinitiators - some recent developments, *Journal of Photochemistry and Photobiology a-Chemistry*, 73, 81-96.

[141] **Gruber, H.F.**, 1992, Photoinitiators for free-radical polymerization, *Progress in Polymer Science*, 17, 953-1044.

[142] **Frenzel, U. and Nuyken, O.**, 2002, Ruthenium-based metathesis initiators: Development and use in ring-opening metathesis polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, 40, 2895-2916.

[143] **Novak, B.M., Risse, W., and Grubbs, R.H.**, 1992, The development of well-defined catalysts for ring-opening olefin metathesis polymerizations (romp)*, Advances in Polymer Science*, 102, 47-72.

[144] **Garamszegi, L., Donzel, C., Carrot, G., Nguyen, T.Q., and Hilborn, J.**, 2003, Synthesis of thiol end-functional polystyrene via atom transfer radical polymerization*, Reactive & Functional Polymers*, 55, 179-183.

[145] **Jakubowski, W., Tsarevsky, N.V., Higashihara, T., Faust, R., and Matyjaszewski, K.**, 2008, Allyl halide (macro)initiators in atrp: Synthesis of block copolymers with polyisobutylene segments*, Macromolecules*, 41, 2318-2323.

[146] **Yagci, Y. and Schnabel, W.**, 1990, Light-induced synthesis of block and graft-copolymers*, Progress in Polymer Science*, 15, 551-601.

[147] **Yagci, Y., Tunca, U., and Bicak, N.**, 1986, A new macroazo-initiator for the synthesis of polymers with crown-ether units*, Journal of Polymer Science Part C-Polymer Letters*, 24, 49-52.

[148] **Yagci, Y. and Onen, A.**, 1991, Bifunctional initiators .3. Photochemical-synthesis of block copolymers of styrene and methyl-methacrylate with the aid of azo-benzoin initiators*, Journal of Macromolecular Science-Chemistry*, A28, 129-141.

[149] **Hoyle, C.E., Lee, T.Y., and Roper, T.**, 2004, Thiol-enes: Chemistry of the past with promise for the future*, Journal of Polymer Science Part a-Polymer Chemistry*, 42, 5301-5338.

[150] **Burget, D., Mallein, C., and Fouassier, J.P.**, 2004, Photopolymerization of thiol-allyl ether and thiol-acrylate coatings with visible light photosensitive systems*, Polymer*, 45, 6561-6567.

[151] **Cramer, N.B. and Bowman, C.N.**, 2001, Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared*, Journal of Polymer Science Part a-Polymer Chemistry*, 39, 3311-3319.

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- Kahveci, M.U., **Uygun, M.**, Tasdelen, M.A., Schnabel, W., Cook, W.D., Yagci, Y., Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides. *Macromolecules*, 2009: 42(13): 4443–4448.

- **Uygun, M.**, Kahveci, M.U., Odaci, D., Timur, S., Yagci, Y., Antibacterial Acrylamide Hydrogels Containing Silver Nanoparticles by Simultaneous Photoinduced Free Radical Polymerization and Electron Transfer Processes. *Macromolecular Chemistry and Physics*, 2009: 210(21): 1867-1875.

- **Uygun, M.**, Tasdelen, M.A., Yagci, Y., Influence of Type of Initiation on Thiol-Ene "Click" Chemistry. *Macromolecular Chemistry and Physics*, 2010: 211(1): 103-110.

- Tasdelen, M.A., **Uygun, M.**, Yagci, Y., Photoinduced Controlled Radical Polymerization in Methanol, *Macromolecular Chemistry and Physics,* 2010, 211, 2271–2275.

- Tasdelen, M.A., **Uygun, M.**, Yagci, Y., Photoinduced Controlled Radical Polymerization, Macromolecular Rapid Communications, 2010, in press.

- Aydogan, B., Durmaz, Y. Y., Kahveci, M. U., **Uygun, M.**, Tasdelen, M. A. and Yagci, Y., 2010: New Photoinitiating Systems for Cationic Polymerization Acting at Near UV and Visible Range, *Macromolecular Symposia*, in press.