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İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF MALEIMIDE COPOLYMERS

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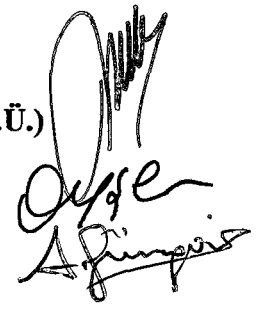

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LIST OF ABBREVIATIONS

ATRP : Atom Transfer Radical Polymerization

FRP : Conventional Free Radical Polymerization

CTC : Charge Transfer Complex

CRP : Controlled / Living Free Radical Polymerization

THF : Tetrahydrofuran

TEA : Triethylamine

Bpy : 2,2'-Dipyridyl (Bypyridine)

MAh : Maleic Anhydride

St : Styrene

PSt : Polystyrene

MMA : Methyl Methacrylate

PMMA : Polymethylmethacrylate

UV : Ultra-Violet

AIBN : 2,2'- azobisisobutyronitrile

MI : Maleimide

MBr : (2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate

DSC : Differential Scaning Calorimetry

NMR : Nuclear Magnetic Resonance

GPC : Gel Permeation Chromatography

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymer
M_w	: Weight average molecular weight of polymer
MWD	: Molecular weight distribution of polymer
MW	: Molecular weight of monomer
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
K_{eq}, k_p	: Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively
k_{tc}, k_{td}	: Rate constant of termination by combination and rate constant of termination by disproportionation
I, M	: Initiator and monomer respectively
Tg	: The Glass Transition Temperature
Mw/Mn	: The Moleular Weight Distribution

SYNTHESIS OF MALEIMIDE COPOLYMERS

SUMMARY

Maleimide and its *N*-substituted derivatives are 1,2-disubstituted ethylenes. Their radical polymerization and copolymerization behaviours and thermal properties of the polymers have been extensively studied by many workers. It is well known that an alternating copolymer can easily be obtained by copolymerization of an electron-rich monomer and an electron-deficient monomer through the formation of charge transfer complexes. Extensively studied systems of this type are maleic anhydride (MAh)/ styrene or maleimide(MI)/styrene. Polymerization can be initiated by radical initiators such as 2,2'-azobisisobutyronitrile (AIBN) or by UV irradiation, but the polymerization process is uncontrollable.

Alternating copolymers of maleimide and styrene which are synthesized by free radical copolymerization show excellent thermal stability. The well defined alternating copolymers (such as styrene-alt-maleic anhydride (St-alt-MAh), St-alt-maleimide, etc.) exhibit unique properties such as superior thermal stabilities, fire resistances, photo-, X-ray and E-beam sensitivities, catalytic and chiroptical activities, and extremely low band gap materials.

It is well known that poly(maleimide) is a potential heat and chemical resistant material, so MI is widely used as a comonomer for modified polymeric systems. The bulkiness of *N*-substituents in functional maleimide prevents molecular motion of the main chain and can raise the glass transition temperatures (T_g).

In this study, *N*-substituted maleimide having ATRP functional bromine moiety was copolymerized with styrene giving an alternating copolymer (as a macroinitiator) and grafted with MMA to obtain heat resistant graft copolymers.

In the first step *N*-methylolmaleimide was synthesized according to the literature as Tawney synthesized in 1960. Then in the second step, (2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)methyl 2-bromopropionate(MBr) was synthesized by the esterification of *N*-methylolmaleimide with 2-Bromopropionylbromide. In the third step, MBr was

copolymerized with styrene monomer by the thermal decomposition of AIBN at 70^0C via conventional free radical polymerization. Consequently, poly(MBr)-alt-poly(Styrene) copolymer was obtained to use as a macroinitiator in ATRP with a grafting site at each repeat unit to make well defined graft copolymers. In the last step, MMA was grafted from poly(MBr)-alt-poly(styrene) copolymer in the presence of a catalytic system of CuBr/Bpy via ATRP at 110 ^{0}C. GPC (Gel Permeation Chromatography) measurements showed that the polydispersity of the obtained graft copolymers decreased so, well-defined high T_g graft copolymers were obtained.

MALEİMİD KOPOLİMERLERİNİN SENTEZİ

ÖZET

Maleimid ve onun *N*-sübstitie türevleri 1,2-disübstitie etilenlerdir. Onların radikal polimerizasyonları, kopolimerizasyon davranışları ve polimerlerinin termal özellikleri geniş bir şekilde bir çok bilim adamı tarafından incelenmiştir. Çok iyi bilinmektedir ki, bir ardışık kopolimer ; elektronca zengin ve elektronca fakir iki monomerin kopolimerizasyonundan yük transfer kompleksinin oluşması ile kolayca elde edilebilir. Bu mekanizmanın geniş bir şekilde çalışılan sistemleri maleik anhidrit (MA)/stiren veya maleimid(MI)/stiren sistemleridir. Polimerizasyon, AIBN ya da UV ışığı gibi radikal başlatıcılar tarafından başlatılabilir, fakat polimerizasyon kontrol edilemez. Maleimid ve stirenin serbest radikal kopolimerizasyonu ile elde edilen ardışık kopolimerleri mükemmel bir termal kararlılık gösterirler. İyi tanımlanmış ardışık kopolimerler (St-alt-MAh, St-alt-MI v.b) üstün termal kararlılık, ısıya dayanıklılık, ışığa, X-ışınlarına ve elektron demetlerine hassasiyet, katalitik ve kiroptikal aktivite ve çok geniş düşük bant aralığında bulunma gibi emsalsiz özellikler gösterirler.

Çok iyi bilinmektedir ki, poli(maleimid) ısıya ve kimyasallara dayanma potansiyeli olan bir malzemedir. Bu yüzden maleimid değiştirilen polimerik sistemler için geniş bir şekilde komonomer olarak kullanılır. Fonksiyonel maleimiddeki, *N*-sübstitientlerin kalabalıklılığı esas zincirin moleküler hareketini engeller ve camsı geçiş sıcaklığını yükseltebilir.

Bu çalışmada ATRP fonksiyonel brom uç gruplu *N*-sübstitie maleimid monomerinin stiren ile ardışık kopolimer (makrobaşlatıcı) veren kopolimerizasyonu gerçekleştirildi ve bu kopolimerin metilmetakrilat (MMA) ile ısıya dayanıklı graft kopolimerleri sentezlendi.

Birinci adımda 1961 de Tawney'in sentezlediği gibi literatüre uygun olarak *N*-metilolmaleimid sentezlendi. İkinci adımda *N*-metilolmaleimid ile 2-bromopropiyonilbromürün esterifikasyon reaksiyonu ile (2,5-diokso-2,5-dihidro-1*H*-

pirol-1-yl)metil 2-bromopropiyonat (MBr) sentezlendi. Üçüncü adımda 70^0 C de AIBN nin termal olarak parçalanması ile serbest radikal polimerizasyon mekanizması üzerinden MBr ile stiren monomerinin kopolimerizasyonu yapıldı. Sonuç olarak iyi tanımlanmış graft kopolimer elde edebilmek için her bir tekrar eden biriminde graft olma bölgesi bulunan ve ATRP de makrobaşlatıcı olarak kullanılmak üzere MBr-alt-St kopolimeri elde edildi. Son adımda, 110 ^{0}C de ATRP üzerinden CuBr/Bpy katalizör sistemi varlığında MBr-alt-St kopolimerinden MMA nın graft kopolimeri sentezlendi.GPC (jel geçirgenlik kromotografisi) ölçümleri elde edilen graft kopolimerlerin polidispersitelerinin düştüğünü gösterdi, böylece iyi tanımlanmış yüksek camsı geçiş sıcaklığına sahip graft kopolimerler elde edildi.

1. INTRODUCTION

The synthesis of polymers with well defined compositions, architectures, and functionalities has become an important topic of contemporary polymer science. Living radical polymerizations such as nitroxide-mediated polymerization, atom transfer radical polymerization (ATRP), reverse ATRP, and reversible addition-fragmentation chain transfer (RAFT) polymerization have witnessed impressive growth in the past few years.

Copper mediated atom transfer radical polymerization (ATRP) has been one of the most efficient controlled/living polymerization methods since its introduction by Wang and Matyjaszewski [1]. As a novel precision polymerization, ATRP has received rapidly increased interest recently, since it furnishes control over the resulting polymers, which possess narrower molecular weight distributions .The merit of the ATRP system is that it can be performed by an ordinary radical polymerization procedure. A general ATRP catalyst is composed of a simple alkyl halide as an initiator and a copper(I)-bipyridine complex as a catalyst. The mechanism of ATRP is shown to be a reversible homolytic cleavage of a carbon-halogen bond catalyzed by a transition metal in the form of a complex. Many vinyl monomers were successfully demonstrated by ATRP to be usable for the preparation of traditional homopolymers, random copolymers, block/graft copolymers, and gradient copolymers. The controlled chain growth and living nature of ATRP make it very useful for the preparation of well-defined block and graft copolymers [2,3]. In addition, ATRP alo shows its potential in the synthesis of a new well-defined macromolecular architectures such as comb, star, and dendritic macromolecules. Another advantage of this method over common initiation methods is that only negligible homopolymer formation is observed when it is employed in graft copolymerizations [4,5].

Graft copolymers exhibit good phase separation and are used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers. Moreover they generally have lower melt

viscosities because of their branched structure, which is advantageous for processing. To make graft copolymers with specific properties, the structures must be controlled. For this reason, grafting from method is one of the most useful ways to design and get well-defined graft copolymersby ATRP.

Since Tawney and co-worker [6] successfully synthesized maleimide (MI) in 1960, there have been many reports on the copolymerization of MI (and its *N*-substituted derivatives) with various substituted ethylenes such as methyl methacrylate, vinylidene vinyl acetate, and styrene [7-14], and in all cases MI and its comonomers readily underwent thermal, free radical, anionic, UV light, or γ-ray-induced polymerization. Because the maleimide functional group is particularly versatile, many unsaturated polymeric systems have been modified with it to obtain improved heat resistance, coatings, adhesives, laminations, and fibers [15-18].

N-substituted maleimides are 1,2-disubstituted ethylene-type monomers having cyclic structures with two carbonyl groups, which polymerize and copolymerize easily by a free radical mechanism [19-21].Many works on *N*-substituted maleimide radical polymerization and copolymerization have been performed so far because of the superiority of their polymers or copolymers in thermal stability [22,23]. It is well known that high dipole moment of the maleimide unit at right angle to the backbone and its cyclic structure (rigid imide ring) impart great stiffness to the polymer chain, thus resulting in high T_g. Alternating copolymerization is an example of chain copolymerization where each of the monomers adds preferentially to the other, which results in an alternating monomer sequence distribution along the backbone.Monomers that are difficult to homopolymerize are often found to be capable of alternating copolymerization. For example, if a strong electron acceptor is added together with a strong electron donor, regular alternating copolymers may result from either spontaneous initiation or a free radical source. The most widely studied comonomers for producing alternating copolymers is maleic anhydride or N-substituted maleimides.

In the present work, to get heat resistant polymers with well-defined architectures, controlled molecular weights and narrow polydispersities the graft copolymerization of MMA monomer with poly(maleimide)-alt-poly(styrene) copolymer having bromine moiety was performed.

2. THEORETICAL PART

2.1. Free Radical Polymerization (FRP)

Free-radical reactions are of importance in a wide variety of commercial applications. Polymers prepared by free-radical means are used in the manufacture of numerous products, such as fabrics, surface coatings and paints, plastics, packaging, spectacle and contact lenses and surgical devices. Free radical polymerization has distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers.

2.1.1. Steps of the Polymerization Process

A typical free-radical polymerization comprises four elementary steps [24-25]:

1. initiation,
2. propagation,
3. chain transfer,
4. termination.

The first step, *initiation* is decomposition of the initiator molecule into primary radicals R$^{\cdot}$. The actual initiation occurs when free radical react with a monomer (2.1a). The *propagation* or growth reaction consists of the (rapid) addition of monomer molecules to the radical species. In this step reaction is repeated many times (2.1b). Usually, it occurs in head-to-tail fashion, because the free radical formed is more stable. However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents.

Initiation

$$I \longrightarrow 2\,R^{\bullet}$$

$$R^{\bullet} + M \longrightarrow M_1^{\bullet} \text{ (growing chain)} \qquad (2.1a)$$

Propagation

$$M_1^{\bullet} + M \longrightarrow M_2^{\bullet}$$

$$M_n^{\bullet} + M \longrightarrow M_{n+1}^{\bullet} \qquad (2.1b)$$

Chain transfer to monomer or solvent

$$M_n^{\bullet} + M'' \longrightarrow M_n + M''^{\bullet}$$

$$M_n^{\bullet} + S \longrightarrow M_n + S^{\bullet} \qquad (2.1c)$$

Reinitiation by transfer radicals

$$M''^{\bullet} + M \longrightarrow M''\text{—}M^{\bullet}$$

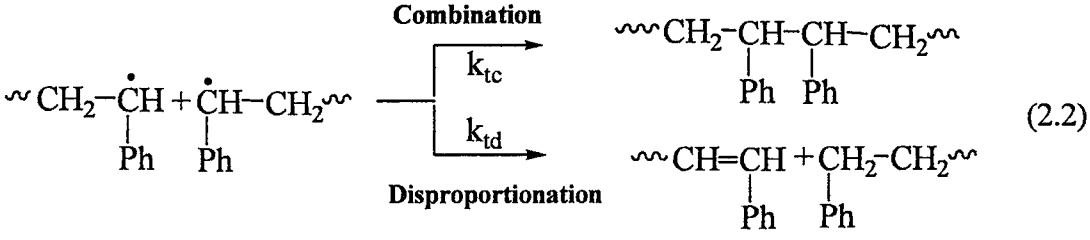
$$S^{\bullet} + M \longrightarrow S + M^{\bullet} \qquad (2.1d)$$

Termination

$$M_m^{\bullet} + M_n^{\bullet} \longrightarrow M_{m+n}$$

$$M_m^{\bullet} + M_n^{\bullet} \longrightarrow M_m + M_n \qquad (2.1e)$$

In *termination*, growth of polymer chains is brought to an end by the destruction of propagating radicals (2.1e). Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals. These processes, analogous to those taking place with simple alkyl radicals, consist of radical combination or disproportionation (2.2).



(2.2)

Disproportionation leads to two polymer molecules, one saturated and one containing a terminal double bond. Many monomers show both types of termination: thus in methyl methacrylate, disproportionation is approximately twice as rapid as combination at room temperature and increases in importance as the temperature is raised. On the other hand, styrene and acrylonitrile radicals terminate preponderantly by combination (Table 2.1).

Table 2.1. Termination ratios of monomers

Monomer	k_{td} / k_{tc}	Temparature
Styrene	0.07	20
Styrene	0.10	118
MMA	0.62	90

It is possible to make some generalizations:

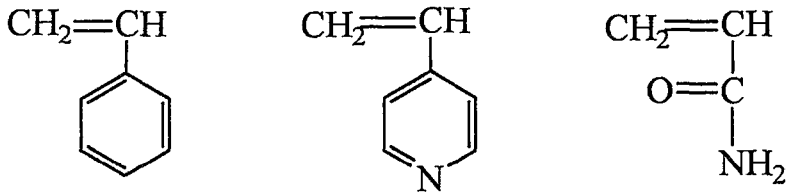
- Termination of polymerizations involving vinyl monomers involves predominantly combination.
- On the other hand, termination of polymerizations involving α – methylvinyl monomers always includes a measurable proportion of disproportionation.
- During disproportionation of radicals bearing an α – methyl substituent (for example, those derived from MMA), there is a strong preference for transfer of a hydrogen from the α – methyl group rather than the methylene group.
- Within a series of vinyl or α – methylvinyl monomers, k_{td} / k_{tc} appears to decrease according to the ability of the substituent to stabilize a radical center in the series Ph > CN >> CO_2R.

Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free-radical polymerization. It leads to the *chain-transfer* process, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate (2.1c and d). A great variety of species can participate in chain transfer, act as transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent or other additive and is well established for polymers and some initiators. Atoms other than hydrogen, notably halogens (except fluorine), may be transferred. Transfer to carbon tetrachloride is illustrated in 2.3.

$$R_n^{\bullet} + CCl_4 \longrightarrow R_n{-}Cl + {}^{\bullet}CCl_3 \qquad (2.3)$$

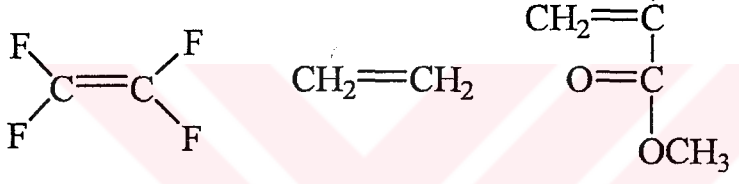
2.1.2. Monomers

Most of vinyl and diene monomers (2.4) can undergo free radical polymerization.



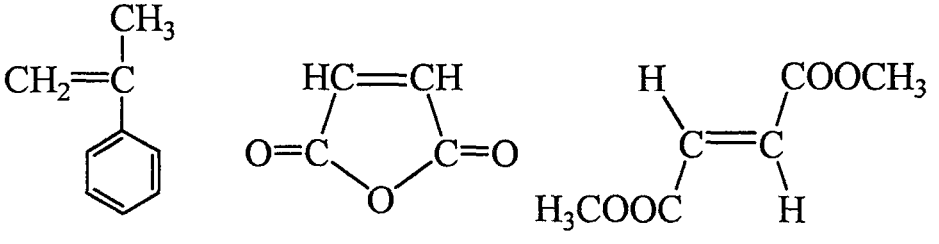
Styrene 4-vinyl pyridiene Acrylamide

Acrylonitrile Vinyl chloride (2.4)



Tetrafluoro ethylene Ethylene Methyl methacrylate

Some potential monomers do not form polymers under usual free radical polymerization conditions. Such as α-methyl styrene is involved in polymerization-depolymerization equilibrium above a ceiling temperature. Maleic anhydride and dimetyl fumarate (2.5) are symmetrically substituted ethylenes therefore, they can not be hopolymerize easily by free radical polymerization.



α-methyl styrene maleic anhydride dimetyl fumarate (2.5)

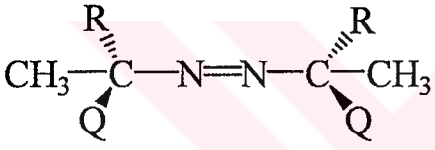
2.1.3. Initiator

Polymerization of a reactive vinyl monomer is initiated by free radicals having sufficiently high activity. These may be generated from initiators in diverse ways, among which thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the commenest, but other processes such as use of γ-radiation or electron beams find applications.

2.1.3.1. Thermal Initiators

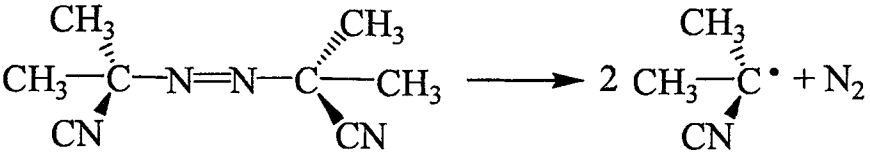
Azo Initiators

Most of the compounds are represented by the formula where R is an alkyl and Q is a simple carboxylic acid residue or a derivative (nitrile, ester) (2.6).



(2.6)

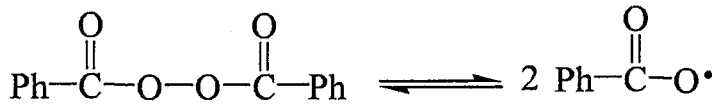
Azobisisobutyronitrile (AIBN) is very widely used initiator. Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to the following reaction 2.7.



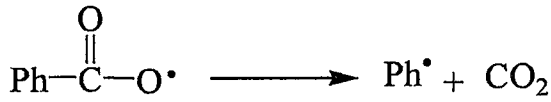
(2.7)

Peroxy Compounds

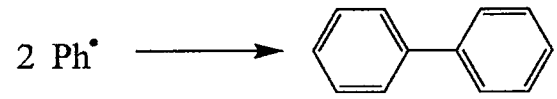
Benzoyl peroxide is a well-established initiator of polymerization. Like other peroxides, the primary step in the thermal decomposition is scission of the — O — O — bond to give two acyloxy radicals (2.8a). A number of secondary processes may follow; in addition to reacting with monomer, benzoyloxy radicals may recombine or undergo β-scission to phenyl radicals and carbon dioxide (2.8b). Further, recombination reactions giving biphenyl and phenyl benzoate may then occur (2.8c and d).



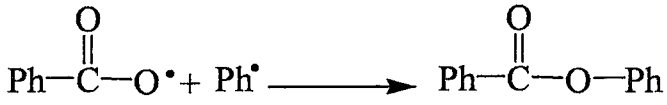
(2.8a)



(2.8b)



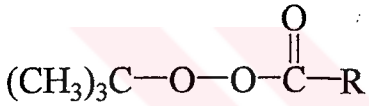
(2.8c)



(2.8d)

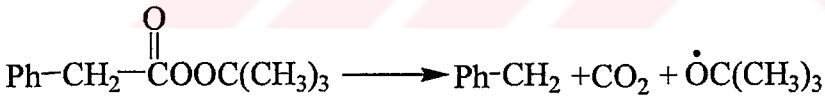
Peresters

The thermolysis of *t*-butyl peresters has received detailed attention [26-28].



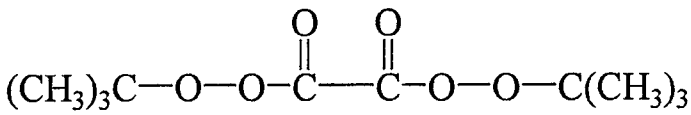
(2.9)

Evidence was adducted for the occurrence of concerted rupture of C — C and O — O bonds on thermolysis , for example with *t*-butyl phenylperacetate (2.10) [29].



(2.10)

Many of these peresters function as low-temperature initiators of free-radical polymerization. Although some of the stabilized radicals may not be effective initiators, the *t*-butoxy radical and its β-scission product, methyl, initiate readily (2.11). Di-*t*-butyl peroxyoxalate initiates well at 25°C. Di-isopropyl peroxydicarbonate is a familiar perester which initiates well at moderate temperatures [30].



(2.11)

2.1.3.2. Redox Initiators

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. This type of initiation is referred as *redox initiation, redox catalysis,* or r*edox activation.* A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50°C and even lower. This allows a greater freedom of choice of the polymerization temperature that is possible with the thermal homolysis of initiators [31].

Types of Redox Initiators

1- Peroxides in combination with a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion (2.12).

$$HO{-}OH + Fe^{2+} \longrightarrow HO^{\bullet} + {}^{-}OH + Fe^{3+} \qquad (2.12)$$

Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides (2.13).

$$ROOR \xrightarrow{Fe^{2+}} 2\ RO^{\bullet} \qquad (2.13a)$$

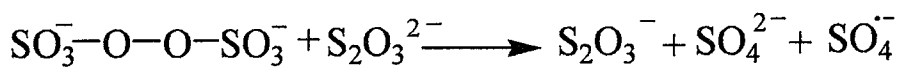
$$ROOH \xrightarrow{Fe^{2+}} RO^{\bullet} + {}^{\bullet}OH \qquad (2.13b)$$

$$ROOCR'' \xrightarrow{Fe^{2+}} RO^{\bullet} + {}^{\bullet}OCR'' \qquad (2.13c)$$

Other reductants such as Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+}, and Cu^{+} can be employed in place of ferrous ion in many instances.

2- The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example,

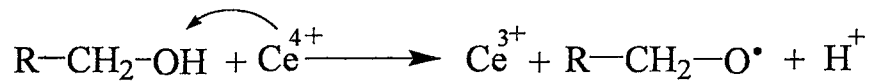
(2.14a)



(2.14b)

Other redox systems include reductants such as HSO_3^-, SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_5^{2-}$ in combination with oxidants such as Ag^+, Cu^{2+}, Fe^{3+}, ClO_3^-, and H_2O_2.

3- Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+}or by V^{5+}, Cr^{6+}, Mn^{3+} (2.15a and b).



(2.15a)

(2.15b)

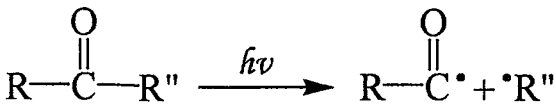
4- There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and N, N-dimethylaniline plus methyl methacrylate.

2.1.3.3. Photoinitiators

Photoinitiators for free-radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals.

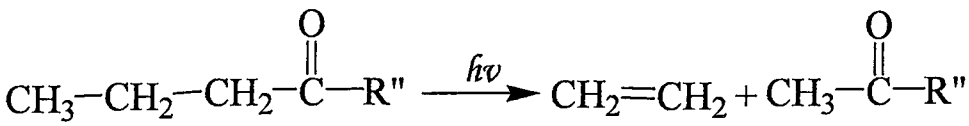
Photoinitiation by Intramolecular Bond Cleavage

Most peroxy initiators yield radicals on photolysis and benzoyl peroxide has frequently been used as a photoinitiator [32,33]. They require shorter wavelengths than azo compounds (<300nm), a disadvantage since many monomers absorb in this region. The same remark applies to many simple ketones which photodissociate according to the Norrish type I mechanism (2.16) [34].



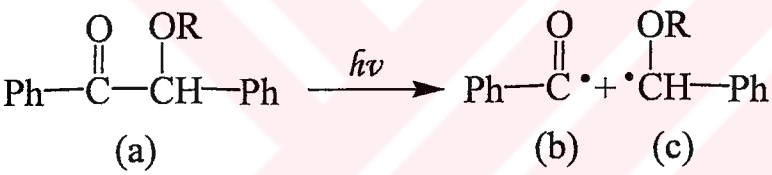
(2.16)

Ketones carrying alkyl chains three or more carbon atoms long may undergo the essentially nonradical Norrish type II fission (2.17):



(2.17)

Benzoin is a well-known photoinitiator [35,36]. Benzoin ethers (a) which are much used in photocuring process undergo a type I photodissociation into two different radicals. It has been reported that both types of radicals can initiate the polymerization (2.18).

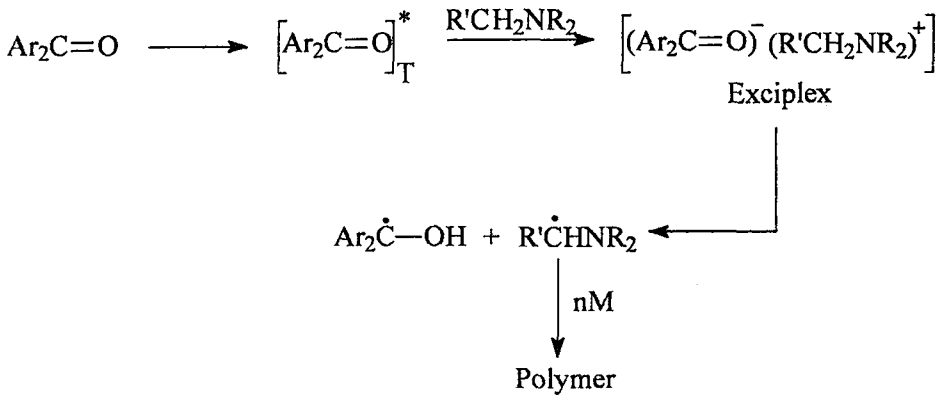


(2.18)

Photoinitiation by Hydrogen Abstraction

Photoinitiators of this type include benzophenone and derivatives such as Michler's ketone (14), thioxanthones, benzyl and quinones. In contrast to cleavage type photoinitiators, which are capable of generating radicals independently, this type of initiators must undergo a bimolecular reaction with hydrogen donors. Tertiary amines with abstractable hydrogen atoms are particularly effective H-donors for UV curing of acrylate monomers [37,38].

The classical example is benzophenone, of which the photochemistry is well-known [39]. The lowest excited singlet (S_1) is of $n \rightarrow \pi^*$ character and yields by intersystem crossing the lowest excited triplet (T_1). In the presence of a hydrogen donor RH the following reaction occurs (2.19).



(2.19a)

(2.19b)

2.2 Free Radical Chain Copolymerization

The demand for new and improved materials often can be achieve as a result of altering the properties of existing polymeric materials. For example, the use of additives can incorporate desirable properties into an existing polymer material that is to be used for specialized applications. Common additives include plasticizers, stabilizers, flame retardants, fillers, colorants, processing aids, and impact modifiers[40]. Another approach is to combine the beneficial properties of different known polymer structures. One known technique to achieve this is to simply blend two individual polymers to give a material whose mechanical properties exceed those of the individual blend components (*i.e.*, synergism). A few advantages of blending include reducing the cost of expensive high performance polymers, improving the processability of a high temperature material, and improving impact resistance of materials. However, because few polymers are miscible, their blends form immiscible phase separated materials. These immiscible blends often have poor physical properties due to inadequate interfacial strength between the phases [41]. A desirable alternative is to copolymerize different monomer structures into a single polymeric material (Figure 2.1) [42]. Prime examples include the important commercial materials produced from vinyl chloride/vinyl acetate and styrene/butadiene copolymers. Careful consideration of such factors as the selection of the comonomers and the copolymerization reaction conditions allows one to precisely tailor the properties of the resulting copolymer and provides a useful method of synthesizing an almost unlimited number of polymeric structures with a wide range of properties and applications.

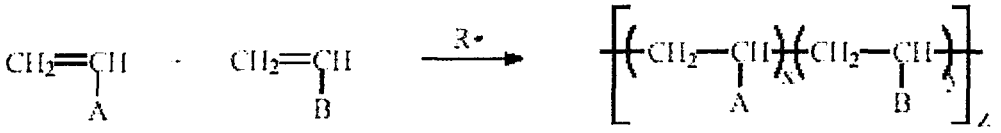


Figure 2.1 Generalized free radical chain copolymerization reaction

Copolymer structures can be described in a variety of ways. Different types of copolymers include statistical, alternating, block, and graft copolymers (Figure 2.2). Statistical copolymers result from a single process where the incorporation of the comonomers follow some statistical law that is due solely to kinetic factors[43].Alternating copolymerization, which will be focused in the preceding sections, is an example of chain copolymerization where each of the monomers adds preferentially to the other and homopropagation is effectively nonexistent [44]. Block and graft copolymers differ in that they contain long sequences of each comonomer either along the backbone or as side chains (grafts) and are often the result of a multi-step process [45].

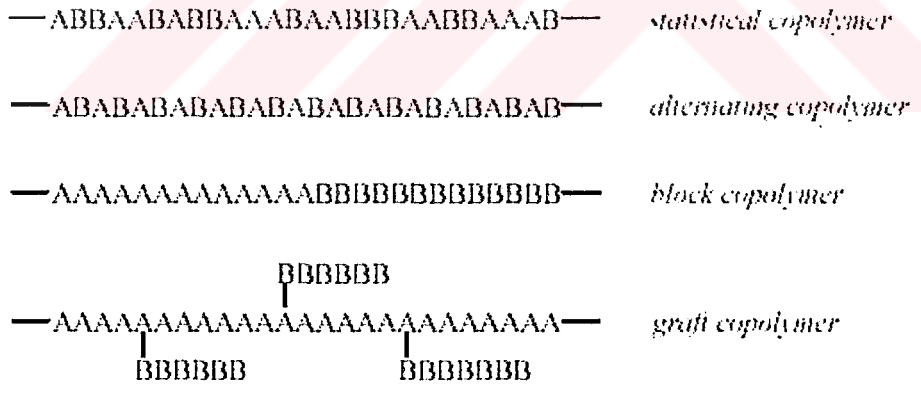


Figure 2.2 Types of copolymer topologies.

The manner in which comonomer repeat units are incorporated into the polymer backbone is determined from the reactivities of the monomers and radicals involved in the reaction. Reaction conditions such as solvent and temperature can also have a marked effect on the monomer reactivities and will contribute to the copolymer composition.

Therefore, in only a few select cases of chain copolymerization will the copolymer composition be directly proportionate to the monomer feed. More typically, both the comonomer feed and instantaneous copolymer composition vary throughout the copolymerization, which results in heterogeneity.

2.2.1. Copolymerization Models

2.2.1.1. Terminal Model

The simplest quantitative statistical treatment for the determination of copolymerization composition, which is generally referred to as the terminal model, was first hypothesized by Dostal [46] in 1936 and later elucidated by others [47]. The terminal model is based upon the assumption that the chemical reactivity of a propagating polymer chain is independent of the size or composition of the chain and is only influenced by the active end group [48]. Though the terminal model is dependent on several assumptions and may not be the most accurate model to describe a copolymer process, it is relatively simple to apply and provides a facile starting point when evaluating copolymerizations of various monomer pairs. When two monomers, M_1 and M_2 are copolymerized by free radical methods, four reactions are feasible according to the terminal model:

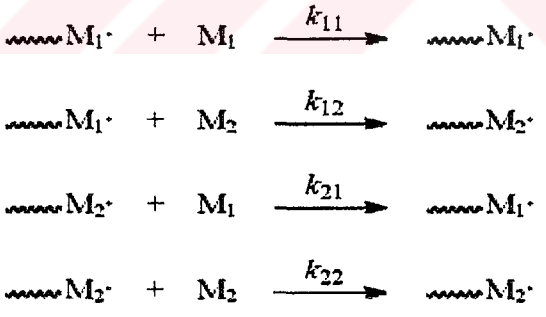


Figure 2.3 Terminal model of copolymerization.

Where k_{11} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_1, k_{12} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_2, and so on. The rate constants can then be expressed in terms of the monomer reactivity ratios, r_1 and r_2, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. Monomer reactivity ratios may either be experimentally [49] determined

or estimated [50] and for free radical polymerizations are generally independent of initiator and solvent with only slight temperature dependence. The different types of copolymerization behaviors can then be described based upon the values of the monomer reactivity ratios. "Random copolymerization" results when $r_1 = r_2 = 1$ due to the equal reactivity of the monomers toward both types of propagating chain ends and the resulting copolymer composition will directly reflect the comonomer feed. When $r_1r_2 = 1$, the two different types of propagating chain ends both add preferentially to one of the monomers, and is described as "ideal copolymerization". The case when r_1 and r_2 are much greater than one results in a tendency to form blocks of both monomers and is appropriately termed "block copolymerization". The copolymerization behavior focused upon in this review, which describes the situation when $r_1 = r_2 = 0$, is referred to as "alternating copolymerization". The mechanism of most typical copolymerizations fall somewhere between the extremes of "ideal copolymerization" and "alternating copolymerization". The mechanism of becomes increasingly "alternating" as the r_1r_2 product decreases from one toward zero. For polymerizations where the r_1r_2 product lies somewhere between zero and one, the composition of the copolymer can be controlled to some extent by variation of the monomer feed ratio. However, as r_1r_2 approaches very close to zero, the "alternating" behavior of the polymerization mechanism becomes the dominating factor and a 1:1 alternating copolymer can be formed independent of the monomer feed ratio. The terminal model also provides a useful means to approximate copolymer compositions that are dependent on such factors as the comonomer feed ratio and the reactivities of the comonomers according to the model. The Mayo-Lewis equation [51], which is derived from the terminal model using the assumption of the steady-state radical approximation, can be used to describe the instantaneous copolymer composition:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])}$$

Figure 2.4 Mayo-Lewis copolymer composition equation.

Where r_1 and r_2 are the respective monomer reactivity ratios. $[M_1]$ and $[M_2]$ describe the beginning concentrations in the comonomer feed. The instantaneous mole fractions of the two repeating units in the copolymer is then defined as $d[M_1]/d[M_2]$.

The terminal model, therefore, allows one to predict the instantaneous copolymer composition for a given comonomer feed simply on the basis of the comonomer reactivity ratios. Although the terminal model relies on several assumptions and may not be the most reliable model to describe of a copolymerization process, it is has the advantages of being simple to apply and very useful as a starting point to study a given copolymerization reaction.

2.2.1.2. Penultimate Model

It has been shown that the behavior of the propagating species of some comonomer pairs is significantly influenced by the penultimate monomer unit [52]. The principal feature of the penultimate model is that the penultimate unit (Figure 2.5) in a propagating polymer chain will affect the reactivity of the terminal reactive radical. The exact nature of the penultimate unit of the propagating species will determine the magnitude of this effect. For example, Tirrell and coworkers have reported that in copolymerizations of styrene and acrylonitrile, there is little effect of the terminal radical reactivity when the penultimate units is styrene unit, but there is an appreciable effect when the penultimate unit is acrylonitrile [53].

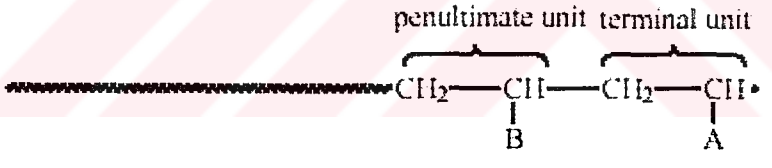


Figure 2.5 Penultimate and terminal units of propagating copolymer chain.

The effect of the penultimate unit on the kinetic of copolymerization was first reported by Merz et al. [54] and later by Ham [55] and Barb. [56] The mathematical model for the penultimate effect involves the use of eight propagating reactions (Figure 2.6) from which four reactivity ratios are defined (Figure 2.7):

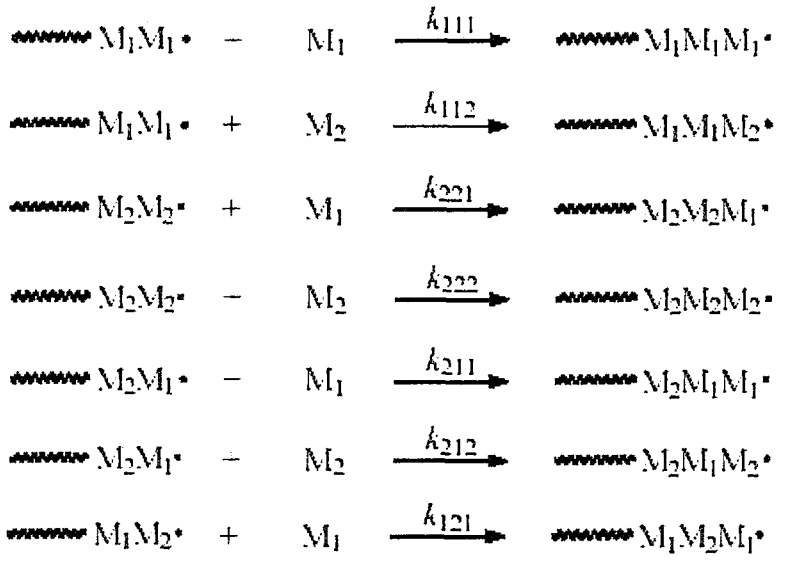


Figure 2.6 Penultimate kinetic model for copolymerization.

$$r_{11} = \frac{k_{111}}{k_{112}} \qquad r_{12} = \frac{k_{122}}{k_{121}} \qquad r_{22} = \frac{k_{222}}{k_{221}} \qquad r_{21} = \frac{k_{211}}{k_{212}}$$

Figure 2.7 Comonomer reactivity ratios based upon the penultimate model.

Each monomer is thus characterized by two monomer reactivity ratios. One reactivity ratio (r_{11} and r_{22}) that represents the propagating species in which the penultimate and terminal monomer units are the same. The other represents the propagating species in which the penultimate and terminal units differ (r_{12} and r_{21}). Several copolymerization processes have been studied where the experimental data agreed better with the penultimate model that the terminal model. However, application of the penultimate model to study copolymerization behavior is significantly more complicated and time consuming than application of the terminal model. Consequently, the study of copolymerizations has been primarily limited to analysis in terms of the terminal model. Comonomers that have been studied using the penultimate model include acrylonitrile,[57] butadiene,[58] maleic anhydride [59], and vinyl chloride [60].

2.2.1.3. Complex Model

The complex model assumes that no free monomers are involved in the kinetic rate of the reaction, but rather the polymer chains propagate by the head-to-tail homopolymerization of comonomer complexes. Copolymerization mechanisms involving complexed comonomers were first introduced to help explain the high degree of alternation observed for some copolymerization reactions [61]. One proposed mechanism is that there is a charge-transfer-complex (CTC) that exists between electron poor/electron rich comonomer pairs and propagation of the copolymer then proceeds via the polymerization of the CTC and not of the individual comonomers[62]. The most studied system is that of styrene-maleic anhydride. The idealized structure of the proposed CTC of the styrenemaleic anhydride comonomer pair is illustrated in Figure 2.8. [63] The validity of complex copolymerization models has been thoroughly debated over the years. The existence of complexes between certain comonomer pairs using spectroscopic techniques has been well documented and accepted. Donor-accepter interactions between monomer pairs can lead to highly colored complexes and the appearance of new absorption bands in the UV-visible spectrum are observed [64]. In addition, charge transfer complexes have been characterized by small chemical shifts in the NMR spectra [65]. However, evidence for the involvement of these complexes in the actual propagation step has been less conclusive and thus undeniable proof for a copolymerization mechanism via a CTC has not been presented [66].

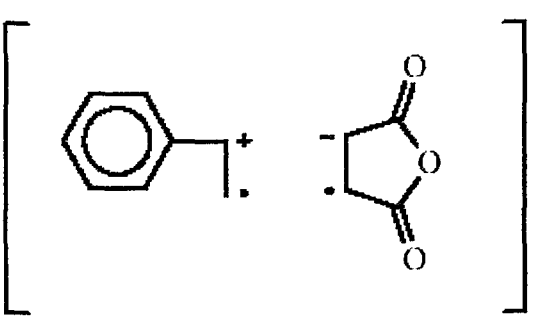


Figure 2.8. Charge-transfer-complex of styrene and maleic anhydride.

Complex copolymerization models have been applied to the study of many electron donor-acceptor comonomer pairs [67]. Electron donating monomers studied include linear dienes, heterocyclic dienes, vinylbenzenes, vinyl esters, vinyl ethers, and vinyl sulfides. Electron accepting monomers include maleic anhydride, maleimides, acrylate esters, cinnamate esters, cyanoethylenes, and fumarate esters. Characteristic features of copolymerizations involving electron donor-accepter pairs include high degrees of alternation, faster copolymerization rates than either homopolymerization rate, and in many cases the strongly electron donating or accepting monomers will not undergo homopolymerization to an appreciable extent. Several complex copolymerization models have been reported to help explain the behavior of copolymerizations involving donoracceptor comonomer pairs. For example, the complex participation model assumes that the comonomer complex that is formed is much more reactive than the uncomplexed monomers and as a result the comonomers are incorporated into the chain as pairs and result in perfectly alternating sequences [68]. The complex participation model considers both propagation of complexed comonomer pairs and also competing propagation of uncomplexed monomers. An alternative model is called the complex dissociation model [69], which also considers propagation of uncomplexed monomers. However, where the complex dissociation model differs is that it assumes the complexed monomer pairs dissociate upon addition to a growing polymer chain and as a result only a single monomer unit is incorporated into the polymer chain. These complex models have been successful in describing the copolymerization behavior of certain donor-acceptor comonomer pairs. However, it is often difficult to differentiate between these models and other higher order models such as the penultimate model, which do not consider the existence of comonomer complexes [70]. In addition, application of complex copolymerization models have been further complicated due to the feature that many of these donor-acceptor pairs undergo spontaneous initiation [71].

2.2.2. Alternating Copolymerization

When two monomers are mixed together in the presence of an initiator there are several ways that the monomers may combine to form a copolymer. In general, the composition of the product rarely follows the monomer feed ratio. Furthermore, the composition resulting from a copolymerization reaction cannot directly be predicted from knowledge of the homopolymerization rates of the monomers [72]. Therefore, the factors that determine the incorporation of repeating units into a copolymer chain are not as trivial as those in homopolymerization reactions. Not only does the homopolymerization rate of the comonomers have an effect, but the rate at which comonomers react with each other is also a determining factor.

Alternating copolymerization is an example of chain copolymerization where each of the monomers adds preferentially to the other, which results in an alternating monomer sequence distribution along the backbone [73]. Monomers that are difficult to homopolymerize are often found to be capable of alternating copolymerization. For example, if a strong electron acceptor is added together with a strong electron donor, regular alternating copolymers may result from either spontaneous initiation or a free radical source [74]. The most widely studied comonomers for producing alternating copolymers is maleic anhydride. Maleic anhydride is a very strong electron acceptor that has been shown to homopolymerize poorly [75], but will react with a number of electron donating monomers to form alternating copolymers [76,77]. Of particular interest is that many 1,2-disubstituted and cyclic olefins that do not homopolymerize by free-radical methods, will form alternating copolymers with maleic anhydride. The copolymerization of *trans*-stilbene with maleic anhydride was first described in 1930 [78]. Later, Bartlett and Nozaki reported that the radical initiated copolymerization of allyl acetate and maleic anhydride resulted in a material with equimolar incorporation of allyl acetate and maleic anhydride into the copolymer regardless of monomer feed [79]. This result led the authors to propose the possibility that electron transfer in an activated charge-transfer-complex (CTC) could account for the observed alternating behavior of these comonomers. The CTC proposed by Bartlett and Nozaki has been thoroughly debated over the years. Early on, several researches supported [80] the CTC while others challenged its existence [81]. The existence of a CTC between donor-acceptor comonomer pairs has typically been illustrated from characterization using ultraviolet-visible spectroscopy [82] and

nuclear magnetic resonance spectroscopy [83]. In addition, experiments studying the effects of temperature and solvent polarity have been utilized to study the effect of the CTC on the behavior of alternating copolymerizations [84]. Following the earlier work of Bartlett and Nozaki, several others have reported the synthesis of materials produced via the alternating copolymerization of maleic anhydride and electron donating comonomers including. Electron donating comonomers that were successfully copolymerized with maleic anhydride include furan [85], conjugated dienes [86], divinyl ether [87], styrene [88], allyl cycloalkenes [89], and methyl vinyl silanes [90]. The results of these investigations demonstrated that the comonomers copolymerized via an alternating copolymerization mechanism. Furthermore, the authors generally supported the CTC concept proposed by Bartlett and Nozaki concluding that propagation occurred following the formation of a CTC between maleic anhydride and the electron donating monomer.

2.3. Controlled / Living Radical Polymerization (CRP)

Free Radical polymerization (FRP) is a very important commercial process for preparing high molecular weight polymers because it can be used for many vinyl monomers under mild reaction conditions, requiring the absence of oxygen but tolerant to water, and large temperature ranges (-20 to 200 °C). In addition, many monomers can easily copolymerize radically leading to an infinite numbers of copolymers with properties dependent on the proportions of the comonomers. The only disadvantage to conventional radical polymerization is the poor control of macromolecular structures including degrees of polymerization, polydispersities, end functionalities, chain architectures and compositions. The synthesis of well-defined polymers has long been of great interest in polymer chemistry. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination. The development during the last decade of various processes for the control of free radical polymerizations (CRP) has lead to new ways of synthesizing polymers with low polydispersities, new architectures, compositions, functionalities and molecular composites (Figure 2.9) [91].

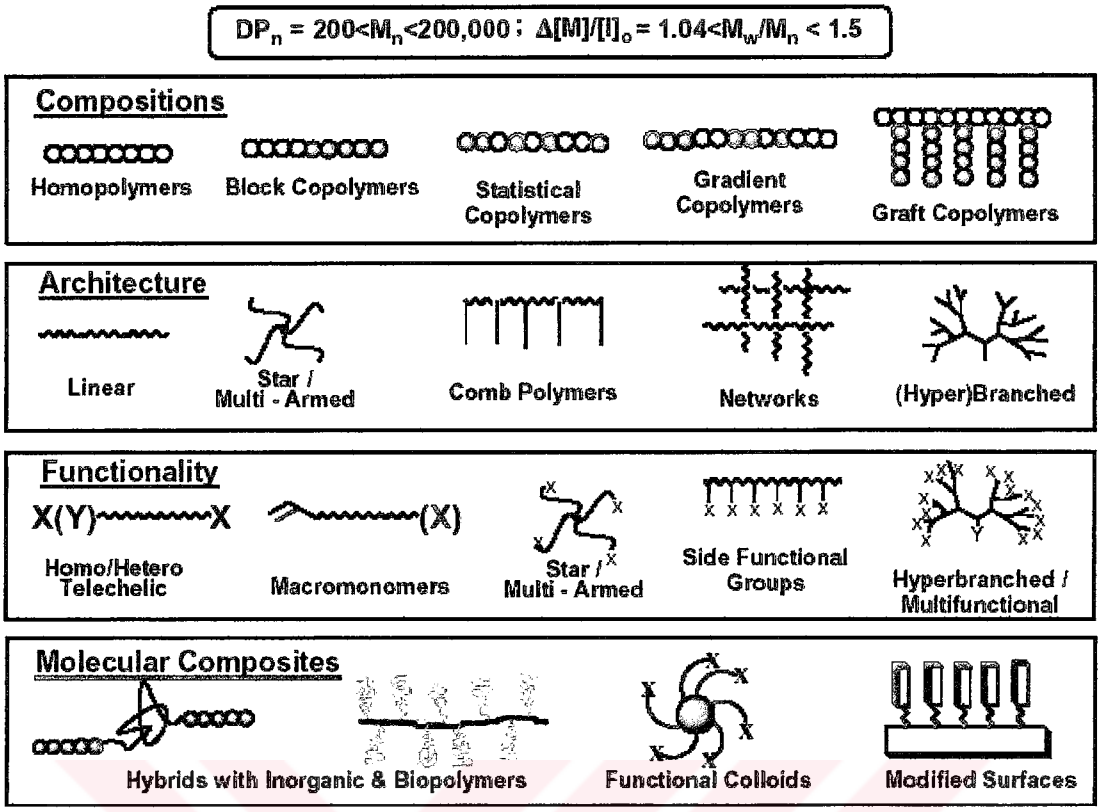


Figure 2.9. Products of Controlled Free Radical Polymerization

To be effective in controlling a radical polymerization, there are two necessary conditions. First, the equilibrium between dormant and active (free radical) species must lie strongly to the side of the dormant species to assure that the overall concentration of propagating radicals will remain very low and that the rate of irreversible termination will be negligible relative to the apparent rate of polymerization. Second, the rate of exchange between dormant and active species must be faster than the rate of propagation to assure that all polymer chains have equal probability of adding monomer. If these conditions are accomplished, then conventional radical polymerization was converted to a controlled/living radical polymerization yielding polymers with a wide range of molecular weights and narrow MWDs is possible [92].

CRP has proved to be a versatile and robust method to prepare well-defined organic polymers. A major difference between conventional radical (i.e., azobis (isobutyronitrile) - or peroxide-initiated processes) and controlled radical polymerizations is the lifetime of the propagating radical during the course of the reaction. In conventional radical processes, radicals generated by decomposition of the initiator undergo propagation and bimolecular termination reactions within a

second. In contrast, the lifetime of a growing radical can be extended to several hours in a CRP, enabling the preparation of polymers with predefined molar masses, low polydispersity, controlled compositions, and functionality for the equilibrium as shown Figure 2.10 [93, 94].

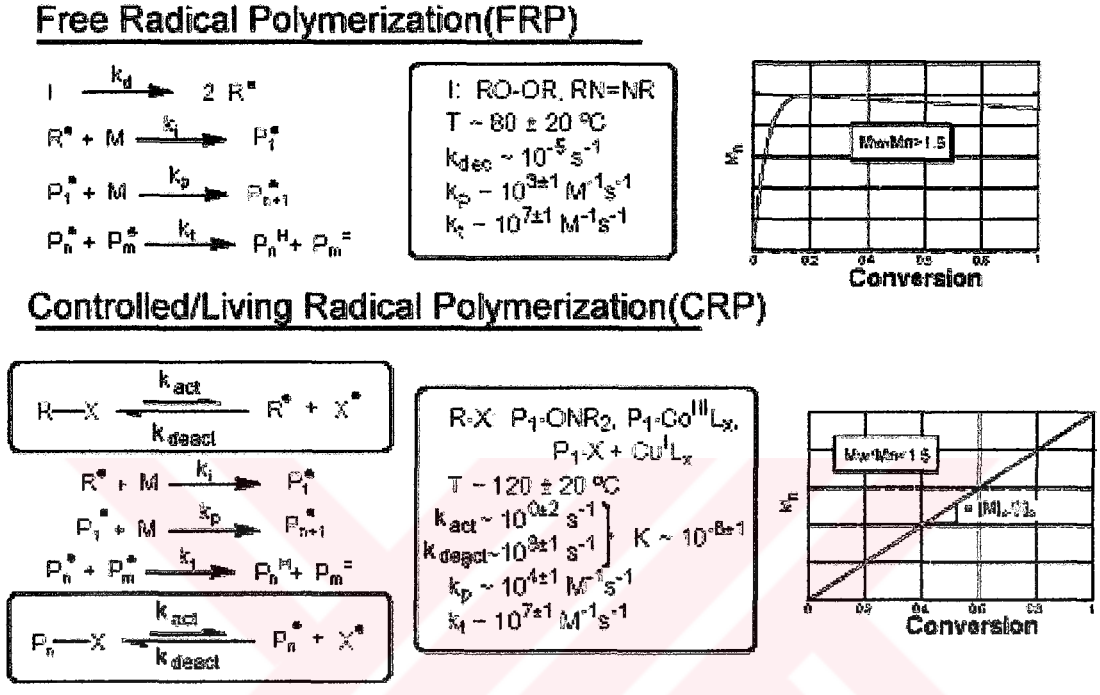


Figure 2.10. Comparison between FRP and CRP

The mechanism invoked in CRP processes to extend the lifetime of growing radicals utilizes a dynamic equilibration between dormant and active sites with rapid exchange between the two states. Unlike conventional radical processes, CRP requires the use of persistent radical (deactivator) species, or highly active transfer agents to react with propagating radicals. These persistent radicals/transfer agents react with radicals (deactivation or transfer reactions with rate constant, k_{deact}) to form the dormant species. Conversely, propagating radicals are generated from the dormant species by an activation reaction (with rate constant, k_{act}) [95]. The use of living radical polymerization (also known as quasi- or pseudo-living radical polymerization) offers the potential to overcome many of these problems.

Three types of radical polymerization have been called "living":

- Polymerizations where the normal termination process of radical-radical reaction is slow or absent because of the physical nature of the reaction medium or the immediate environment of the reactive chain end. Systems in this class include precipitation polymerizations(where the polymer chains being formed are insoluble in the reaction medium), certain template polymerizations and polymerizations in inclusion complexes. Unfourtanetely these systems have little generality and do not have application in the synthesis of high purity block or graft copolymers.

- Systems with reversible termination but where the bond formed by primary radical termination or chain transfer is stable under the conditions of formation. Different reaction conditions are are required to reinitiate polymerization. The aim of the first polymerization step is to synthesize a macroinitiator that serves as a precursor to a block copolymer. Narrow polydispersity polymers are not available by these techiques.

- Systems with reversible termination where the bond formed by primary radical termination or chain transfer is kinetically unstable under the reaction conditions. These polymerizations should be considered as true living polymerizations. It is possible to make block copolymers and narrow polydispersity resins, since all chains grow,though not simultaneously.

In a living process the number of growing chains usually is the same as the number of initiating molecules, and it does not change during propagation until the total monomer consumption. Therefore semilogarithmic kinetic plots and molecular weight conversion dependences are linear, if the initiation is fast.If the exchange reactions between dormant and active species occur fast enough, polymers with low polydispersities can be formed. However some polymerization systems provide well-defined polymers in which chain breaking reactions cannot be totally avoided. Such systems are called controlled or "living" since they do not fulfill criteria of living

polymerization because of the presence of either transfer or termination.Radical polymerization is one of them.

A typical radical polymerization includes four elementary reactions:

Formation of the initiating radicals ,(slow), via the homolytic cleavage (decomposition) of a peroxide, diazo or other similar compound (2.20);

$$I\text{-}I \xrightarrow{k_d} 2\,I^{\bullet} \qquad (2.20)$$

Initiation by relatively fast reaction of primary radicals with monomer to generate the first growing species. Since $k_d < k_o[M]$, the decomposition remains the rate – determining step(2.21):

$$I^{\bullet} + M \xrightarrow{k_o} P_1^{\bullet} \qquad (2.21)$$

Propagation characterized by k_p (2.22);

$$P_n^{\bullet} + M \xrightarrow{k_p} P_{n+1}^{\bullet} \qquad (2.22)$$

Termination (very fast) between growing radicals via coupling or disproportionation k_t (2.23);

$$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_t} P_{n+m} / (P_n^{=} + P_m - H) \qquad (2.23)$$

Transfer reactions are usually less important unless transfer agents are present. Synthesis of high molecular weight polymers requires slow initiation to produce a low momentary concentration of growing radicals that terminate in a bimolecular process. The ratio of the rate of propagation to the rate of termination decraeses with $[P^{\bullet}]$ since propagation is a first-order process, but termination is a second order process with respect to $[P^{\bullet}]$. The proportion of chains marked by termination increases with the chain length. Therefore well-defined polymers from radical polymerization may be formed only if chains are sufficiently short and concentration of free radicals is low enough.

The synthesis of well-defined polymers by controlled polymerization should occur in systems with a low momentary (stationary) concentration of growing radicals that

should be reversibly deactivated to provide a relatively large number of macromolecules. There are three methods to realize these conditions:

1) Reversible homolytic cleavage of covalent species

$$P\ R \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P\cdot + R\cdot \qquad (2.24)$$

An initiator with the structure of P-R is the adduct of the model of growing radical P., capable of propagation, and the scavenging or the dormant radical (R.), which ideally should react only with (P.) but not with the monomer itself.

This case probably is the most postulated in controlled radical polymerization. As examples of (R.); Otsu and Yoshida [96] used dithiocarbamate radicals, Georges et al. [97-98] used nitroxyl radicals and Borsing et al. [99] used triaryl methyl species.

The problem with this method is that except nitroxyl radicals, the others may participate in side reactions leading to degenerative transfer.

2) Reversible homolytic cleavage of persistent radicals

$$P\cdot + X \rightleftharpoons (P{-}X)\cdot \qquad (2.25)$$

The role of a scavenger radical may be also played by a neutral species. The persistent radical, (P-X)· , should only cleave homolytically to form (P.) and the species X, but it should not react with monomer. X should be inert compound capable of reacting only with (P.). X may be elementoorganic or organometalic species with an even number of electrons. Some success have been reported with group XIII and XV elements such as aluminum [100] and phosphorus [101] as well as with organometalic derivatives of Co [102], Cr [103], and other transition metals. In some cases not only radical but also ionic and coordinative polymerization may

take place. The pathway of the polymerization is dependent on the nature of metal or elements, ligands and medium effects.

3) Degenerative transfer

$$P_n\cdot + P1\text{-}R \xrightarrow{k_{tr}} P1\cdot + P_n\text{—}R \qquad (2.26)$$

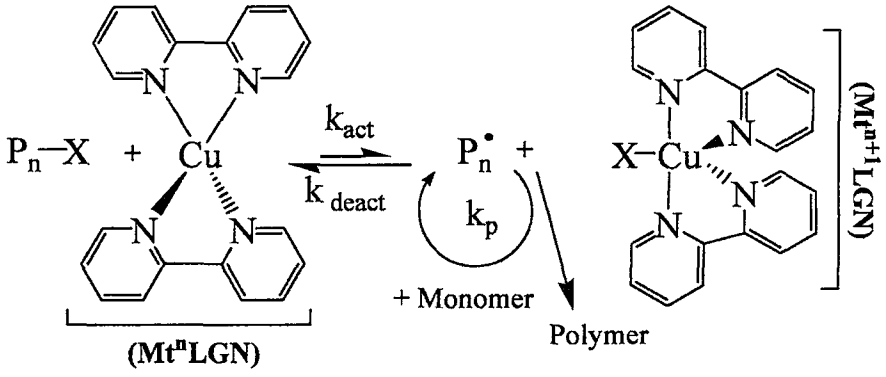
In this case growing radical (P_n.) reacts rapidly and selectively with a transfer agent (P1-R) to exchange the R group and form a dormant species (Pn-R) and a new radical (P1.), which is capable of chain growth. (P.) would be generated by a classical initiator such as AIBN, BPO and redox reactions. (P.) can react with monomer, for propagation, with (P-R), for degenerative transfer, and can also react one with another, for termination.

In the 1990s, several methods were developed that enable controlled radical copolymerization. These methods include stable free-radical polymerization (SFRP) [104], atom transfer radical polymerization (ATRP) [105], and reversible addition–fragmentation chain transfer (RAFT) [106]. Using these polymerization methods, the molecular weight of the polymers linearly increases with conversion and the polydispersities are well below 1.5

2.3.1. Atom Transfer Radical Polymerization (ATRP)

ATRP is one of the most versatile controlled radical polymerization method.This method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal (M_t^n complexed by ligands LGN) reacts with an alkylhalide (P_n-X) to generate a radical ($P_n^{\bullet}$) and a higher oxidation state metal complex ($XM_t^{n+1}LGN,k_a$). This radical then adds monomer to generate the polymer chain (k_p).The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal (k_d) as seen in (2.20). The molecular weight is controlled because both initiation and deactivation are fast, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. Termination cannot be totally avoided; however, the proportion of chains terminated compared to the number of propagating chains is

small [84]. Several metal/ligand systems have been used to catalyze this process and a variety of monomers including styrene, methacrylates, and acrylonitrile have been succesfully polymerized [85-87].



(2.27)

The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, Cu(I),and negative first order with respect to deactivator, XCu(II). The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivities with concentrations and composition of the reaction medium.

One of the most important parameters in ATRP is the dynamics of exchange, especially the relative rate of deactivation.If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [XCu(II)]. They,however, increase with the propagation rate constant, k_p, and the concentration of initiator, $[RX]_o$. This means that more uniform polymers are obtained at higher conversion, when the concentration of deactivator in solution is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive and monomer propagates slowly (styrene rather than acrylate) [88].

2.3.1.1. Monomers

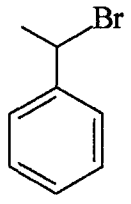
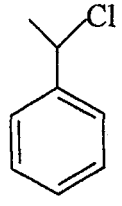
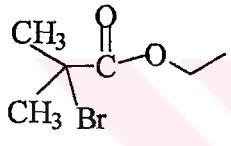
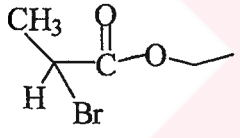
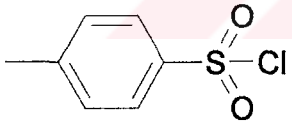
A variety of monomers have been succesfully polymerized using ATRP. Typical monomers include styrenes (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq}=k_{act}/k_{deact}$) determines the polymerization rate.

2.3.1.2. Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system.First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex.When X is either bromine or chlorine, the molecular weight control is the best. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage.

Table 2.2. The most frequently used initiator types in ATRP systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methylmethacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

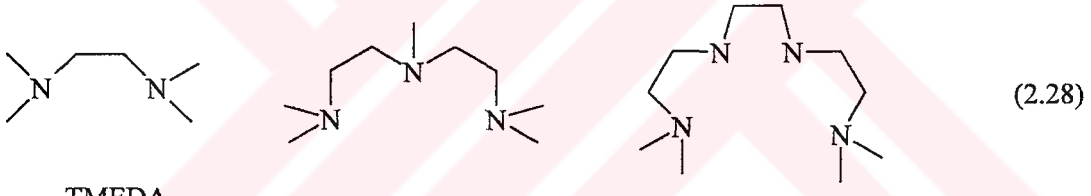
2.3.1.3. Ligands

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRPcatalyst. First fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chainsdormant and produce a low radical

concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate.Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals.

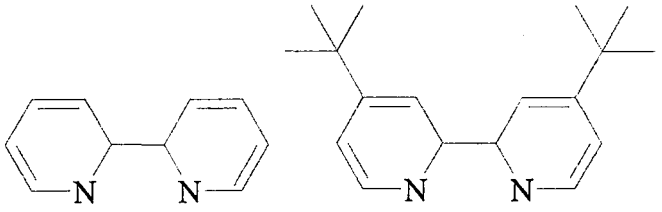
The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine(HMTETA), tris[2-(dimethylamino) ethyl]amine (Me-TREN) and alkylpyridylmethanimines are also used.

Nitrogen based ligands:



TMEDA PMDETA HMTETA (2.28)

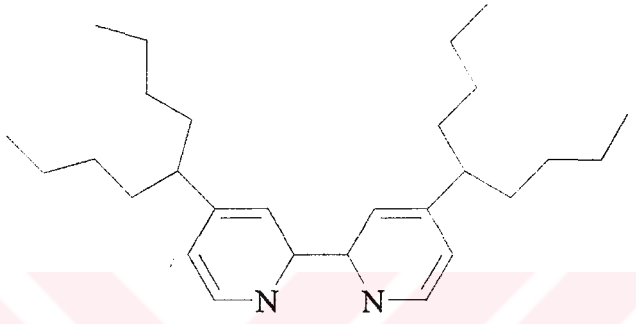
derivatives of 2,2-bipyridine:



Bipy

dTBipy

dHBipy



dNBipy

(2.29)

2.3.1.4. Transition Metal Complexes

Catalyst is the most important component of ATRP. It is the key toATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisities for an efficient transition metal catalyst. First, the metal center must have at least two readily accesible oxidation states separated by one electron. Second the mertal center should have reasonable affinity toward a halogen. Third the coordination sphere around the metal should be expandable upon oxidation to selectively accomodate a (pseudo)-halogen. Fourth the ligand should complex the metal relatively strongly.

The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

2.3.1.5. 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 for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer.

2.3.1.6. Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator (CuX_2 / Ligand).

The rate equation of ATRP is formulated in discussed conditions and given in (2.30).

$$R_p = k_{app}[M] = k_p[P\cdot][M] = k_p K_{eq}[I]_0 \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.30)$$

Results from kinetic studies of ATRP for styrene, methyl acrylate (MA), and methyl methacrylate (MMA) under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations.

If the deactivation does not occur, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in (2.31).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d [RX]_0}{k_p [XCu^{II}]}\right)\left(\frac{2}{p} - 1\right) \qquad (2.31)$$

p= poymerization yield
$[RX_0]$=concentration of the functional polymer chain
$[XCu^{II}]$=concentration of the deactivators
k_d=rate of deactivation
k_p=rate of propagation

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersites are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

b) For the higher ratios of k_p / k_d, higher polydispersities (molecular weight distributions) are usually obtained.

c) Resulting molecular weight distribution decreases as the concentration of the deactivators increases.

2.4. Copolymers

Homopolymers are derived from one species of monomer whereas copolymers are composed of two or more monomer units. Copolymers form two, three, four species of monomers are called bipolymers, terpolymers, quarter polymers etc. Copolymers are subdivided into random,alternating, block, gradient, periodic, segmented and graft copolymers. Block copolymers are polymers which consist of two or more monomers that are segregated into separate regions of the polymer chain, but covalently bound to each other. Gradient copolymers exhibit a compositional gradient along the chain: one end of a bipolymer is enriched in first monomer unit and the other end in second monomer unit. Random copolymers have no continuous change in instantaneous composition. In periodic copolymers, monomeric units are arranged in periodic sequences. Multiblock copolymers with short block lengths are known as segmented copolymers. In graft copolymers, the blocks are connected to the main chain as side-chains.

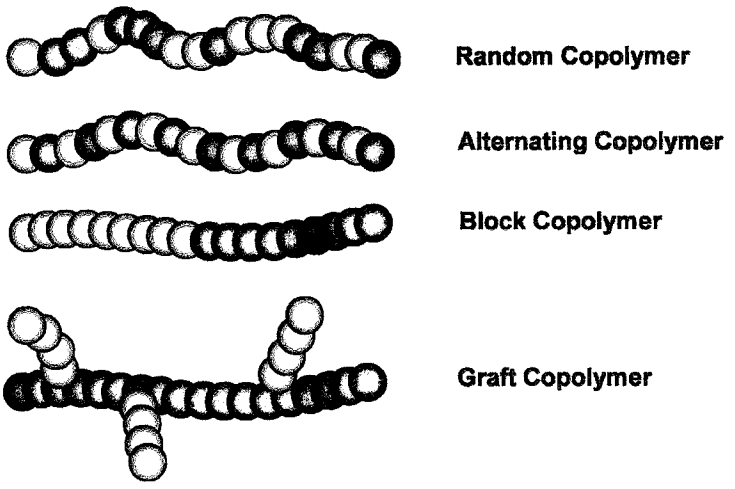


Figure 2.11. Types of copolymers

2.4.1. Graft Copolymers

Graft copolymers represent valuable polymeric materials, as their properties can be tailored by varying the monomers that form the backbone and the side chains. This way, one can obtain impact resistant materials by combining a hard polymer backbone with soft polymer side chains,thermoplastic elastomers where a soft polymer backbone is grafted with hard polymer segments, or amphiphilic copolymers with applications as hydrogels, stabilizers, surface-modifying agents, compatibilizers in polymer blends,etc.[89,90]. Three main methods can be used to prepare graft copolymers:

i) grafting "from", when initiating sites located on the main polymer chain initiate the polymerization of a second monomer

ii) grafting "onto", when a growing polymer or a pre-formed polymer with reactive end groups reacts with pendant functional groups located on another polymer

iii) grafting "through", when a macromonomer is copolymerized with a small molecule comonomer.

Until lately, well defined graft copolymers could be obtained only by using ionic polymerizations or the macromonomer technique. Due to the lack of control of molecular weight and polydispersity, the free-radical methods led to ill-defined polymers, very often accompanied by a certain amount of homopolymer and crosslinked material [89,91,92]. However recent free-radical techniques have also

become available for the preparation of well-defined polymers. The most important types of controlled/"living" radical polymerizations are; stable free radical polymerization (SFRP), which employs stable nitroxyl radicals [93], atom transfer radical polymerization (ATRP), which uses complexes of transition metals in conjuction with alky halides and reversible addition-fragmentation chain transfer polymerization (RAFT), which uses dithioesters together with a free radical initiator[94]. Only SFRP [95] and ATRP have been used to prepare graft copolymers by both grafting "from" and grafting "through" methods.

Two main approaches have been used to prepare copolymers with well-defined grafts: the grafting "through" technique i.e. a well defined macromonomer was synthesized in the first step, followed by its free-radical copolymerization with a small molecule monomer.

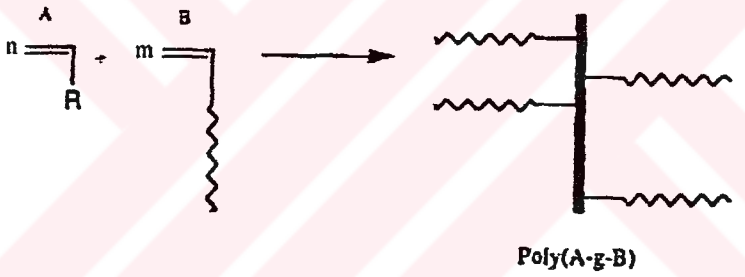


Figure 2.12. Scheme of grafting "through" technique

Grafting "from" technique, i.e. a polymer possesing ATRP-active halogen atoms on its backbone was used as a macroinitiator in the ATRP of a second monomer. Generally these macroinitiators can be obtained directly by copolymerizing a monomer containing a halogen atom that can initiate ATRP or by reacting the functional groups of a polymer with a small-molecule compound possessing active chlorine or bromine atoms.

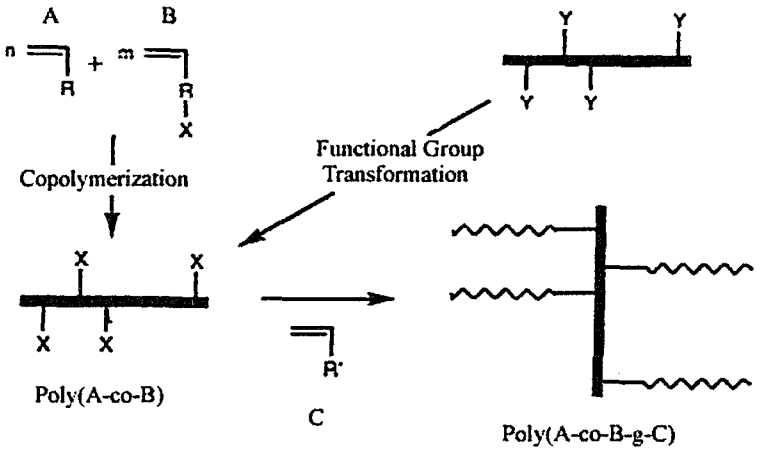


Figure 2.13. Scheme of grafting "from" technique

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Purification of Materials

3.1.1.1. Monomers

Styrene (St) (Fluka)

Washed with aq. 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure (50^0C / 25 mmHg). Middle fraction was collected and immediately used.

Methylmethacrylate (MMA) (Fluka)

Washed with aq. 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure .

3.1.1.2. Solvents

Tetrahydrofuran (THF) (J.T.Baker)

Dried and distilled over CaH_2, then it was let mixing over sodium/benzophenon ketyl, and was distilled prior to use.

Chloroform (Lab Scan)

Shaken with several portions of conc. H_2SO_4 washed throughly with water and dried with $CaCl_2$ before filtering and distilling (61^0C / 760 mmHg).

Toluen (Merck)

Refluxed over CaH_2 for 24 hours. Then distilled over sodium prior to use.

Ethylacetate (J.T.Baker)

It was distilled over CaH_2 prior to use.

Ethanol (J.T.Baker)

It was distilled prior to use.

Methanol (Lab Scan)

It was used without further purification.

Anisole (Acros)

It was used without further purification.

3.1.1.3. Other Chemicals and Reagents

Formaldehyde (Acros)

It was used without further purification.

Triethylamine (TEA) (Acros)

It was used without further purification.

2 – Bromopropionyl Bromide (Aldrich)

It was used without further purification.

Maleimide (MI) (Fluka)

It was used without further purification.

Copper (I) Bromide (Aldrich)

It was used without further purification.

2,2'-Dipyridyl (Bpy) (Aldrich)

It was used without further purification.

Sodium Hydroxide (Acros)

It was used without further purification.

3.2. Equipments

3.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

H-NMR analysis were recorded on a Bruker 250 MHz Spectrometer.

3.2.2. Gel Permeation Chromatography (GPC)

GPC analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and four Waters Styragel Columns (HR 5E, HR 4E, HR 3, and HR2). THF was used as the eluent at a flow rate of 0,3 ml/min at 30^0C. The molecular weights of the polymers were calculated with the aid of polystyrene and polyMMA standards.

3.2.3. Differential Scanning Calorimeter (DSC)

The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (TA DSC Q10) in a flowing nitrogen atmosphere at heating rate 10^0C / min.

3.2.4. Ultra-Violet Spectrophotometer (UV)

The UV spectra of products were determined by Pharmaspec UV-1700 Shimadzu spectrophotometer.

3.2.5. Infrared Spectroscopy

Infrared spectra were recorded on KBr with a Jasco model FT-IR – 5300 fourier transform spectrophotometer.

3.3. Synthesis of Chemical Compounds

3.3.1. Preparation of [(1-hydroxymethyl)-1*H*-pyrrole-2,5-dione)] (N-Methylolmaleimide)

N-Methylolmaleimide was prepared to the method of Tawney et al.[6]. To a suspension of 14.4g (0.15 mol) of maleimide in 11.9 ml of 37 % formaldehyde, 0.44 ml of 5 % sodium hydroxide was added at 30^0C. Within 10 min. all of the maleimide had dissolved and a mildly exothermic reaction had raised the temperature to 35^0C. Seperation of the product began promptly. After 2.5 hours at room temperature the

solution was filtered , dried in vacuo. One recrystallization was made from ethyl acetate.

3.3.2. Preparation of (2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate (MBr)

Under nitrogen 6.24 ml (0.059 mol) 2-bromopropionyl bromide was added dropwise to a stirring mixture of N-Methylolmaleimide (6 g, 0.047 mol) and triethylamine (8.22 ml, 0.058 mol) in 140 ml of $CHCl_3$ in an ice bath for 1 hour. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 hour. The reaction mixture was washed with water (3×140 ml) and then dried over $MgSO_4$. After filtration and evaporation of $CHCl_3$ gave a greasy dark red product. It was dried under vacuum and recrystallized from ethanole (yield 58 %).

3.3.3. General Polymerization Procedure for CFRP of Styrene and MBr

An empty 50 ml dry schlenk flask with a stirring bar was cycled between vacuum and nitrogen three times to remove the oxygen. While the nitrogen was passing through the schlenk, required amounts of monomers (St , MBr) and initiator (AIBN) were introduced in the flask and dissolved in solvent. The flask sealed and then was immersed in an oil bath held by a termostate at required temperature. After reacting for variable time periods, the polymer was precipitated by addition of a ten-fold excess of methanole with rapid stirring to precipitate the product. The precipitated polymer was filtered and washed throughly with methanole, purified by reprecipitation from the THF solution into excess methanole. The polymer was then dried in vacuo for several hours. The amounts of monomers St and MBr, initiator AIBN, reaction times, and conversions for the different preparations of macroinitiators C1, C2, C3, and C4 are collected in Table 4.1

3.3.4. General Copolymerization Procedure for ATRP of Poly(MBr)-alt-Poly(St) with MMA

To a schlenk tube equipped with a magnetic stirrer, vacuum and dry nitrogen was applied three or four times, then certain amounts of MMA, anisole, ligand, bpy and macroinitiator poly(MBr)-alt-poly(St) were added in the order mentioned under

nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then tube was immersed in an oil bath and held by a termostate at 110^0C, with rigorous stirring. The copolymerization was performed for a determined time. Then the tube was cooled to room temperature and the contents were dissolved in large amount of THF. The THF solution was passed through a short neutral alumina column to remove Copper complex and then excess THF was removed by evaporation. The polymer was precipitated into excess methanole and isolated by vacuum filtration. The polymer was dried for 24 hours under vacuum. The conversion was determined gravimetrically. Copolymerization conditions are given in the following tables.

4.RESULTS AND DISCUSSION

4.1. Synthesis of [(1-hydroxymethyl)-1*H*-pyrrole-2,5-dione)] (N-Methylolmaleimide)

N-Methylolmaleimide [(1-hydroxymethyl)-1*H*-pyrrole-2,5-dione)] was synthesized according to the procedure reported by Tawney et. al. [6] yielding 75 % of product melting at 103 ^{0}C. One recrystallization from ethyl acetate raised the melting point of material to 104 ^{0}-105 ^{0}C.

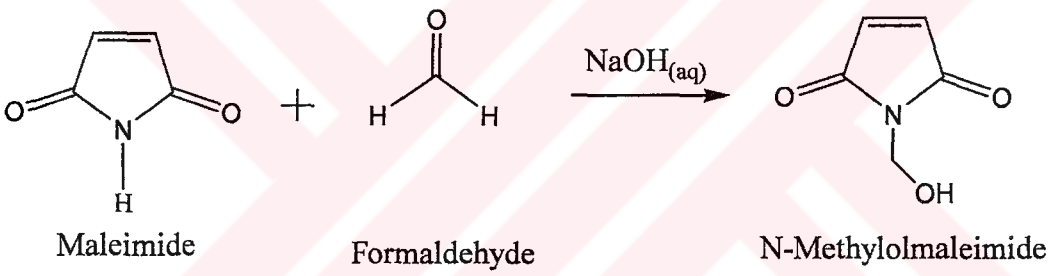


Figure 4.1. Synthesis of N-Methylolmaleimide

The structure of product was characterized by FT-IR and ^{1}H-NMR spectrum and also UV spectra was recorded. The FT-IR spectrum of N-Methylolmaleimide in Figure 4.2 exhibits the characteristic broad band of OH stretch (ν = 3200-3600 cm^{-1}). $H_2C{=}CH_2$ stretch at ν = 3094, 3165 cm^{-1} , C = O stretch at ν = 1699 cm^{-1} and C-N stretch at ν = 1456 cm^{-1} in the imide ring.

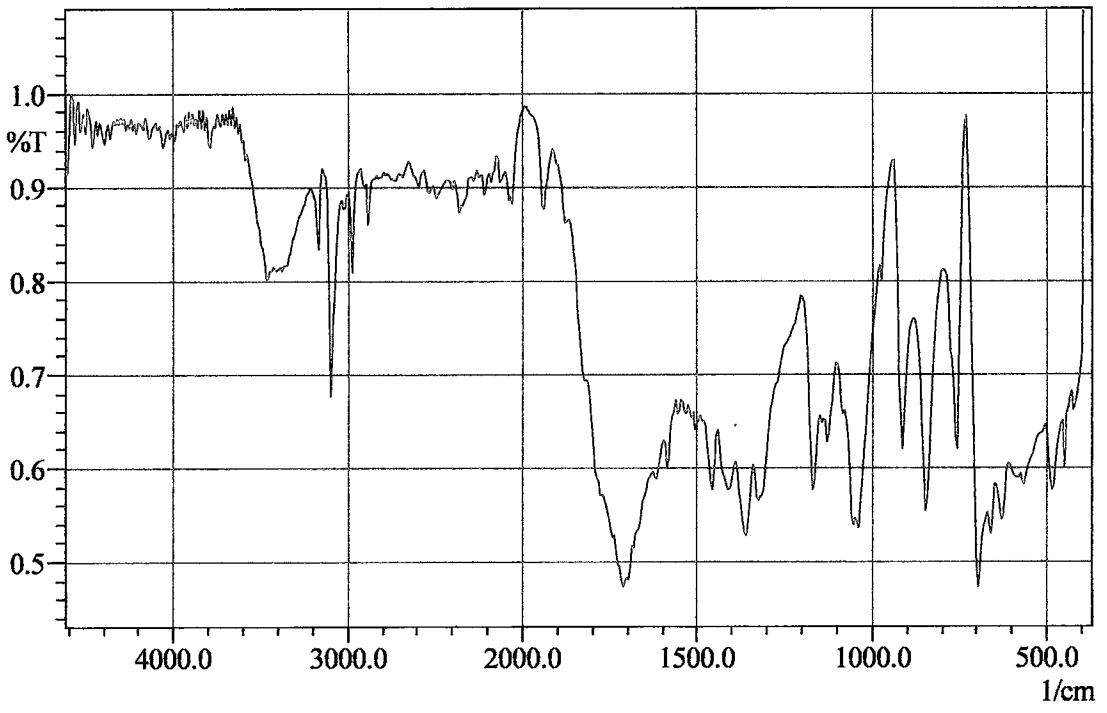


Figure 4.2. FT-IR Spectrum of N-Methylolmaleimide

^{1}H-NMR spectrum of N-Methylolmaleimide was taken in DMSO-d_6. OH proton was seen at δ = 4.76 ppm (b) , CH_2 protons at δ = 6.27, 6.30 ppm (a) and $H_2C{=}CH_2$ protons at δ = 7.05 , 7.07 ppm (c) . Also we know that N-H protons of pure maleimide give signal at δ = 10.8 ppm. In the spectrum there is no signal of N-H protons.

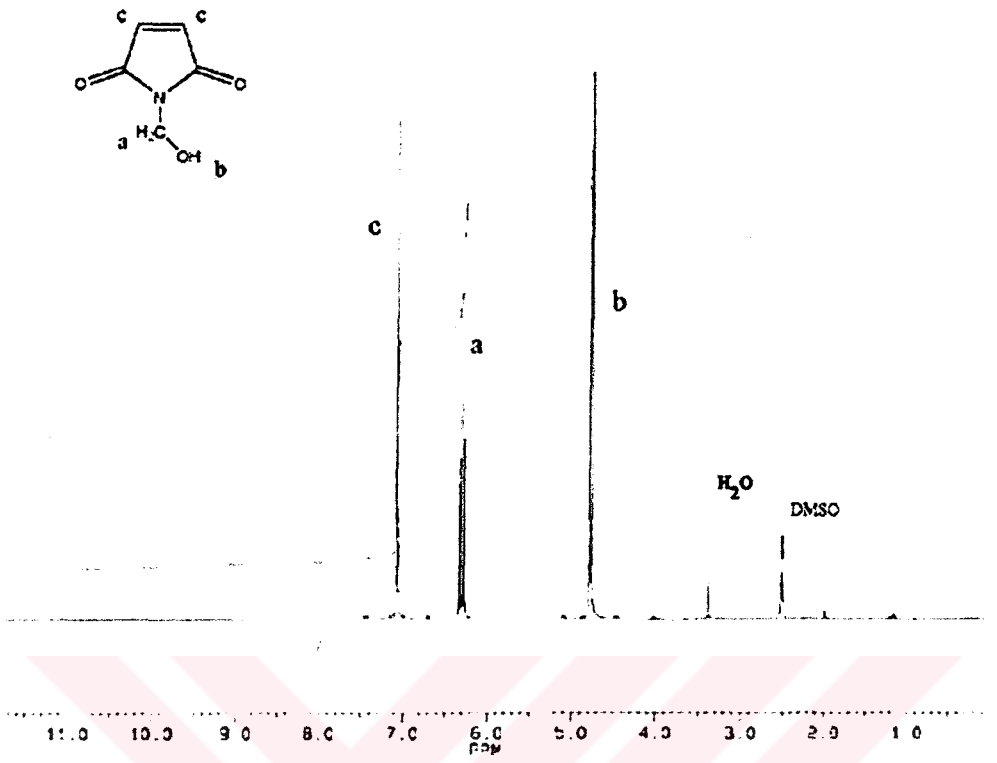
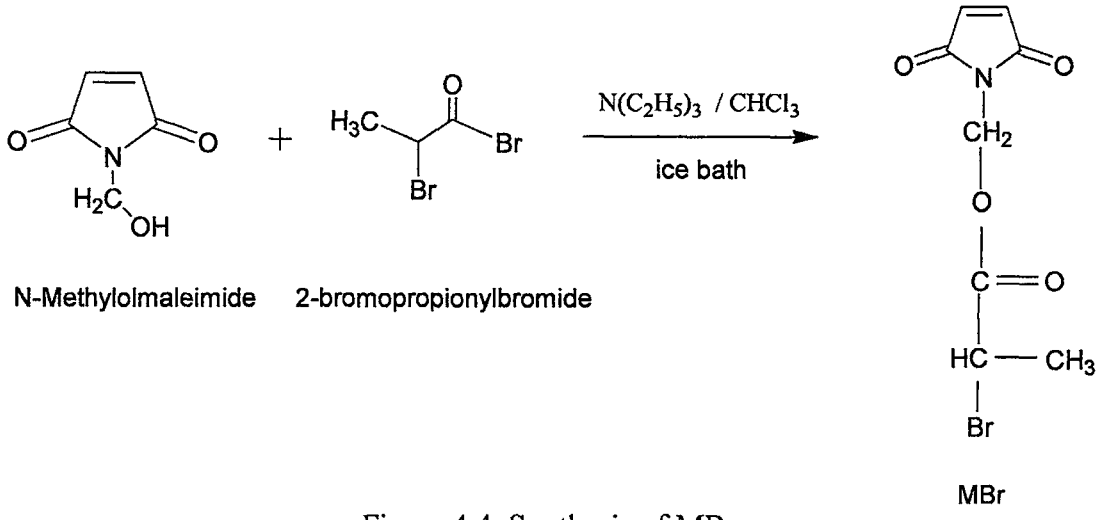


Figure 4.3. ^{1}H-NMR Spectrum of N-Methylolmaleimide

4.2. Synthesis of (2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate (MBr)



N-Methylolmaleimide 2-bromopropionylbromide MBr

Figure 4.4. Synthesis of MBr

(2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate (MBr), was synthesized according to the modified method of Paik et al.[119]. MBr was prepared from esterification reaction of N-Methylolmaleimide and 2-bromopropionylbromide with 47 % yield. The obtained product was then characterized by ^{1}H-NMR spectrum (Figure 4.5). Spectra of MBr prove the expected structure of the product. According to the spectrum, the signals originating from esterificated Br end group of MBr were discerned at δ = 4.2-4.3 ppm (c) , CH_3 protons at δ = 1.6-1.8 ppm (b) , CH_2 protons at δ = 5.5-5.6 ppm (d) , and monomeric maleimide protons at δ = 6.8 ppm (a).

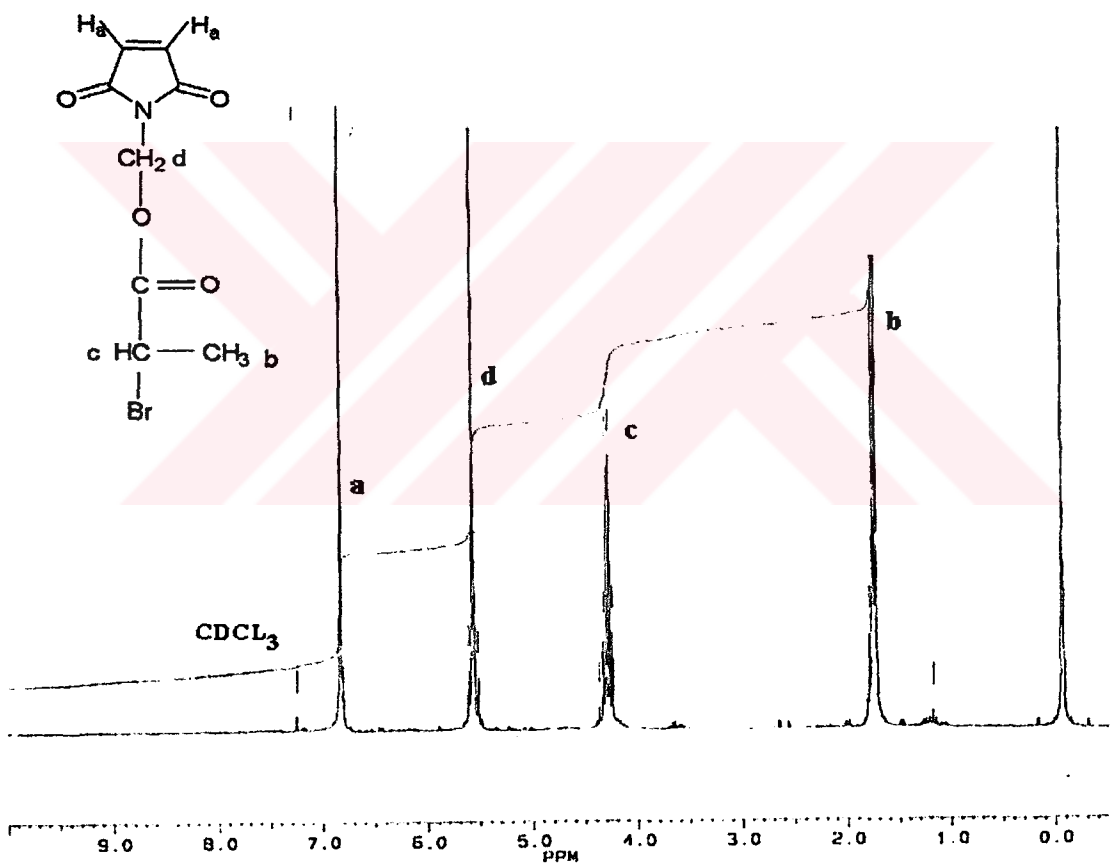


Figure 4.5. ^{1}H-NMR Spectrum of MBr

FT-IR Spectra of MBr also showed no signal corresponding to –OH protons of the starting N-Methylolmaleimide, indicating quantitative esterification (Figure 4.6). Also C-Br stretching was discerned at $\nu = 694\ cm^{-1}$

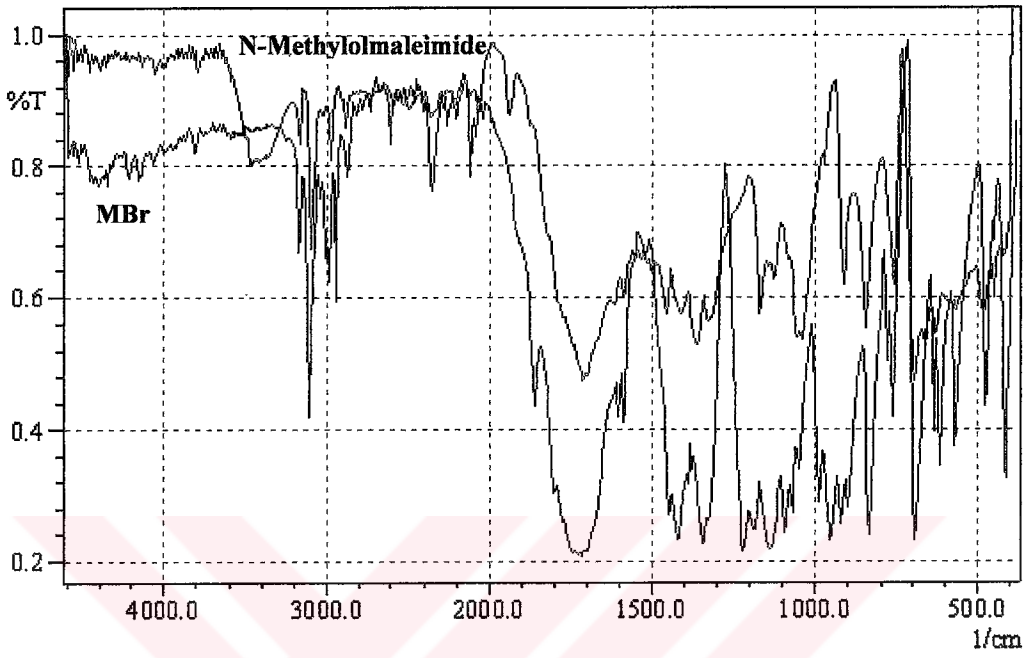


Figure 4.6. FT-IR Spectrum of MBr and N-Methylolmaleimide

4.3. Conventional Free Radical Copolymerization of Styrene and MBr

Alternating copolymers were obtained from the conventional free radical copolymerization of Styrene and (2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate (MBr). Styrene is an electron donor and maleimide is an electron acceptor monomer so they formed a charge transfer complex together at propagating step to give alternating copolymer.

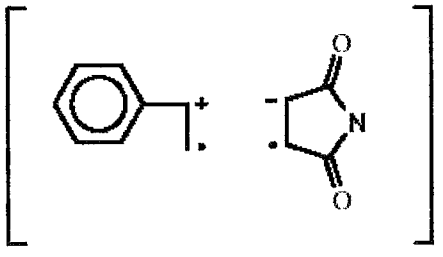


Figure 4.7. Charge Transfer Complex of St and Maleimide

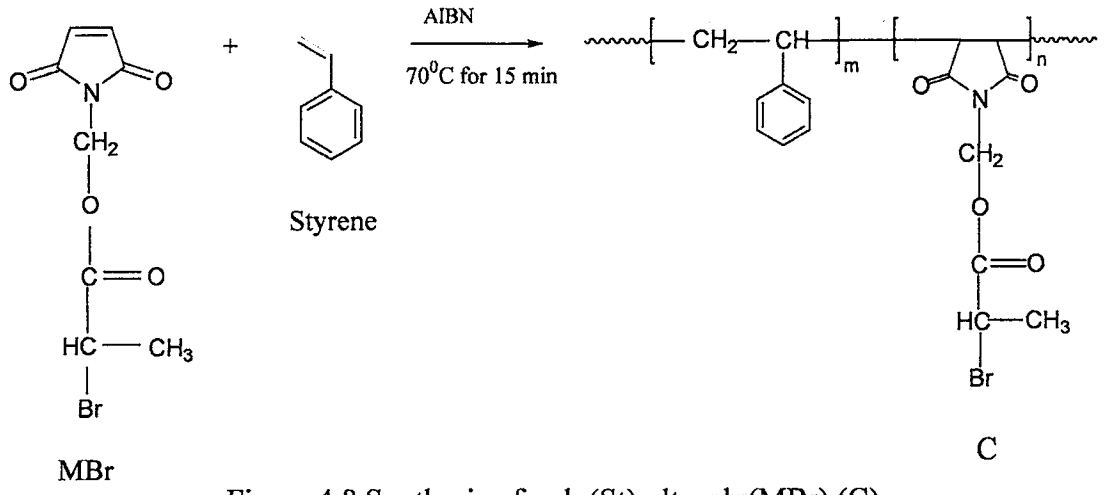


Figure 4.8 Synthesis of poly(St)-alt-poly(MBr) (C)

C copolymers with different molecular weights were synthesized via FRP in solvent using AIBN as initiator. The results of the polymerization reactions are summarized in Table 4.1. Ratio of the monomer units in alternating copolymer was determined by the integral areas in the ^{1}H-NMR spectrum.

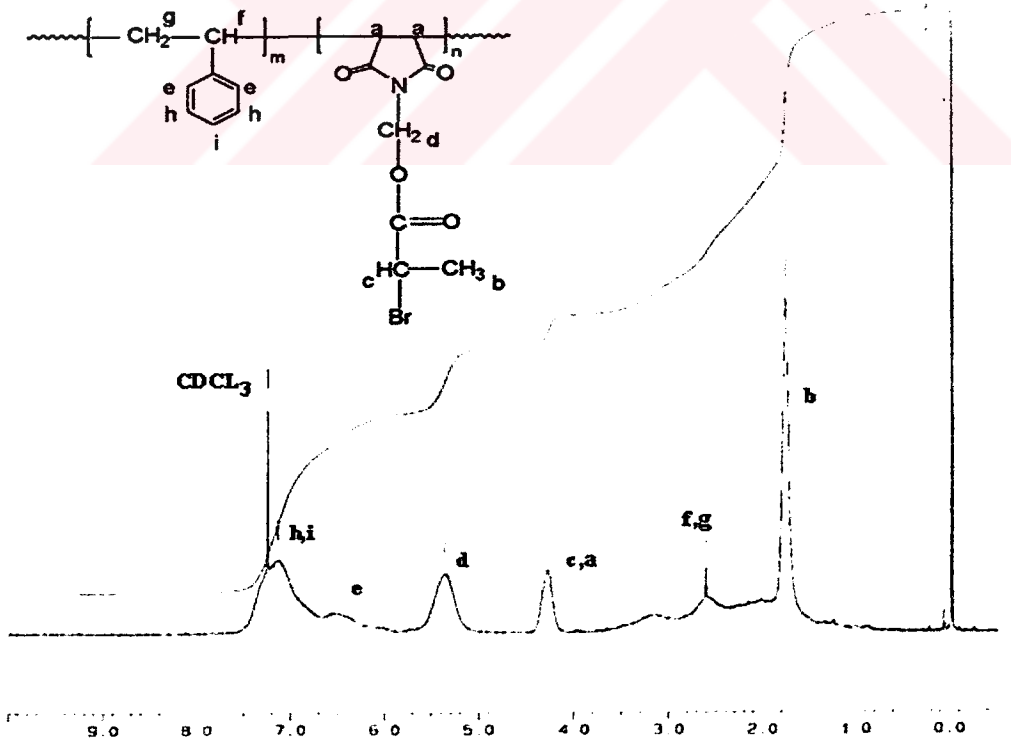


Figure 4.9. ^{1}H-NMR Spectrum of poly(St)-alt-poly(MBr)

The ^{1}H-NMR Spectrum of poly(St)-alt-poly(MBr) (Figure 4.9.) displays signals at δ = 1.7 ppm (b) , δ = 2.3-2.6 ppm (f, g) , δ = 4.3 ppm (c,a) , δ = 5.3 ppm (d) , and aromatic protons δ = 6.5-7.1 ppm (e, h, i).

These macroinitiators (C1,C2,C3,C4) with initiation sites for ATRP at each repeat unit along the copolymer were subsequently used to initiate ATRP of MMA in the presence of a copper catalyst at the different reaction conditions. Solubility in toluene was beter than THF, so the polydispersity of the obtained copolymer in toluene gave beter results (Table 4.1).

Table 4.1. FRP of St and MBr by using AIBN[a]

Run No	MBr (mol/l)	St (mol/l)	AIBN (mol/l)	Solvent	Time (min)	Conv. (%)	M_n[b]	M_n[c]	M_w/M_n[b]	(MBr/St)
C1	0.896	0.896	0.394	Toluene	15	88	16804	19090	4.4	0.55/0.45
C2	0.790	2.380	0.034	THF	120	70	32602	17036	5.2	0.42/0.58
C3	0.790	2.380	0.034	THF	30	67	37090	20038	6.4	0.61/0.39
C4	0.572	1.739	0.549	Toluene	15	54	16907	18300	3.6	0.50/0.50

[a] T ; 70 °C

[b] Determined from GPC, based on PSt standarts

[c] Determined from ^{1}H-NMR Spectrum

4.4. Preparation of Graft Copolymers of MMA by using ATRP Mechanism

poly(St)-alt-poly(MBr)-g-MMA(C-G) copolymers with different molecular weights and polydispersities were synthesized via ATRP of MMA in anisole at 110^0C using CuBr complexed by Bpy as the catalyst and poly(St)-alt-poly(MBr) as the initiator.

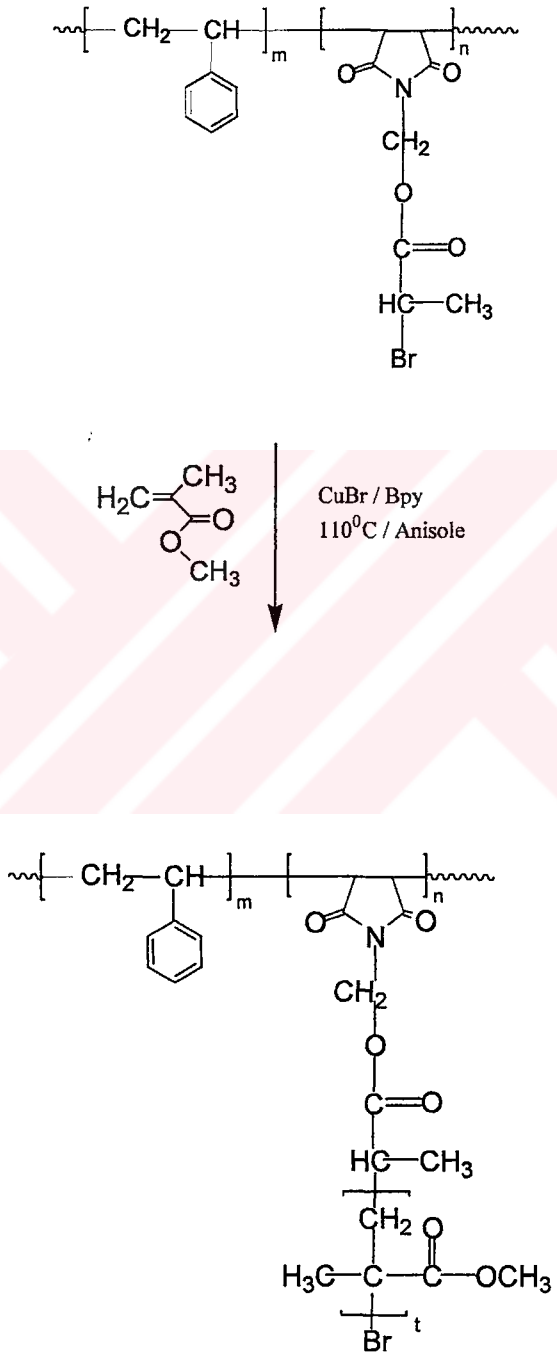


Figure 4.10. Synthesis of poly(St)-alt-poly(MBr)-g-polyMMA

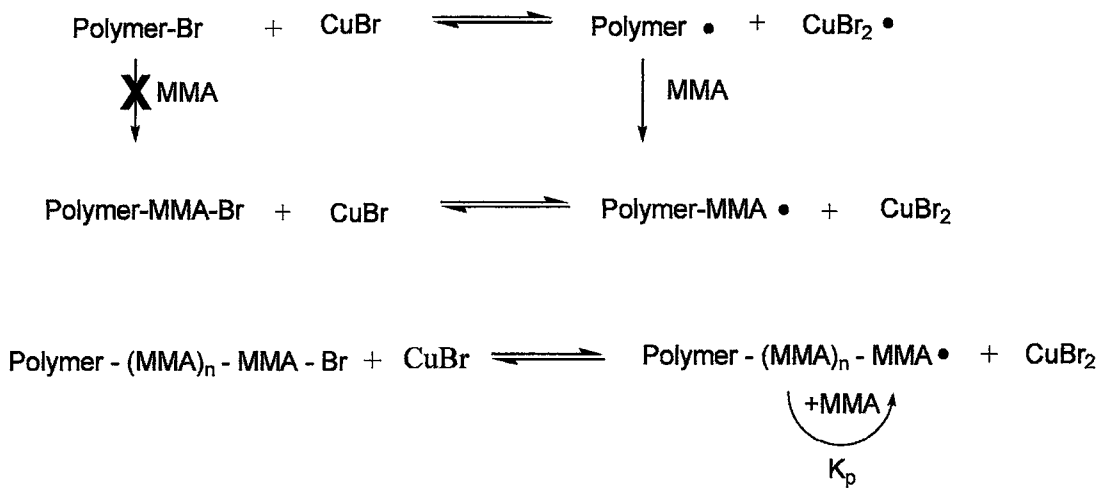


Figure 4.11. The Mechanism of Graft Copolymerization of MMA via ATRP

When the poly(St)-alt-poly(MBr) was used as a macroinitiator, the Bromine in the poly(St)-alt-poly(MBr) would in situ react with CuBr/bpy to produce polymeric radicals which could initiate the polymerization of MMA to form graft PMMA chains as described in Figure 4.11. It is essential for graft-from polymerization. Thus ATRP has provided the means to prepare densely grafted macromolecules with more well-defined dimensions.

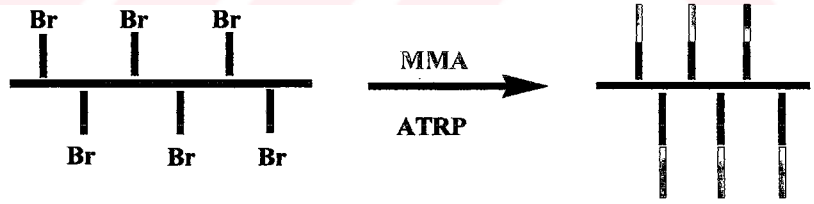


Figure 4.12. Schematic Representation of Graft Copolymerization by ATRP

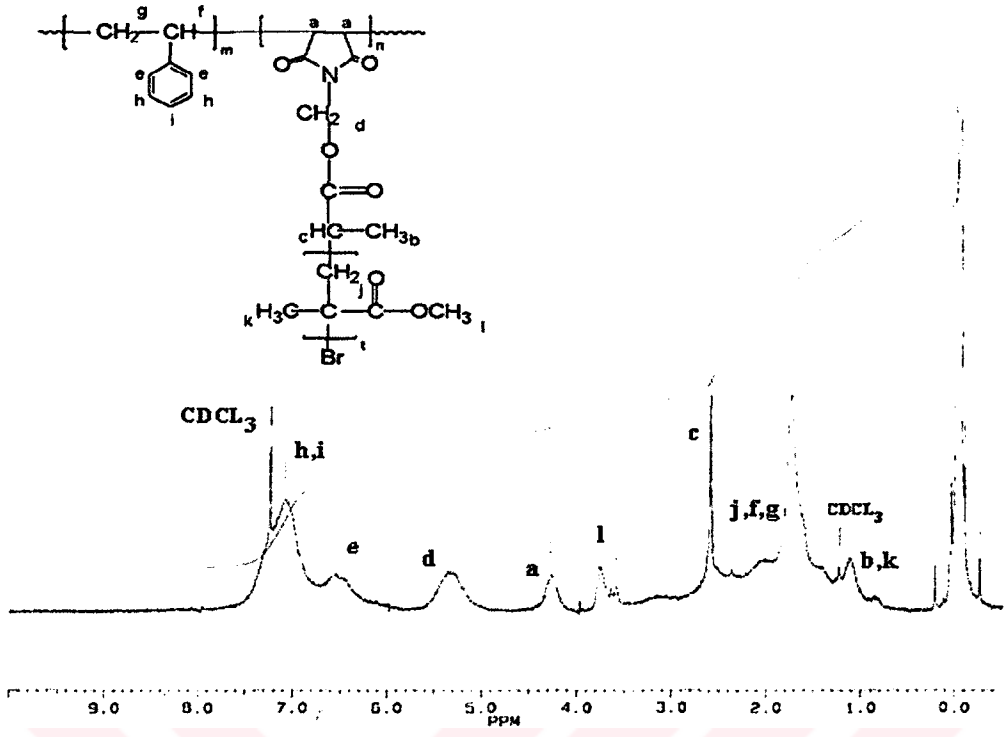


Figure 4.13. ^{1}H-NMR Spectrum of poly(St)-alt-poly(MBr)-g-MMA

^{1}H-NMR Spectrum of resulting graft copolymer implies that polyMMA grafted from the macroinitiator. Spectrum indicates the presence of OCH_3 protons at $\delta = 3.58$ ppm (l). The disappearance of CH-Br signal could not be confirmed for poly(St)-alt-poly(MBr)-g-poly(MMA) , because of overlap of the signal resulting from –CH protons in maleimide. But these protons was shifted to $\delta = 2.0$-2.6 (c) ppm by the consumption of bromine in ATRP.

Table 4.2. ATRP of MMA Initiated by Bromine Terminated Macroinitiator C2[a]

Run No	$[M]_0$ (mol/L)	Time (h)	Conv %	M_n[c]	M_n[d]	M_w / M_n[c]
C2-G1[b]	1.8	12	18.2	74463	46777	2.0
C2-G2[b]	1.8	24	18.4	74897	58295	1.9
C2-G3[b]	1.8	48	18.6	62146	49333	1.8
C2-G4[b]	1.8	72	14.1	45551	48256	1.7

[a] $[I]_o$ / $[CuBr]_o$ / $[Bpy]_o$ / $[MMA]_o$;1 / 4 / 12 / 800 , T;110 ^{0}C

[b] MMA /Anisole ; 1 / 4 (in ml)

[c] Determined from GPC, based on PMMA standarts

[d] Calculated by ^{1}H-NMR

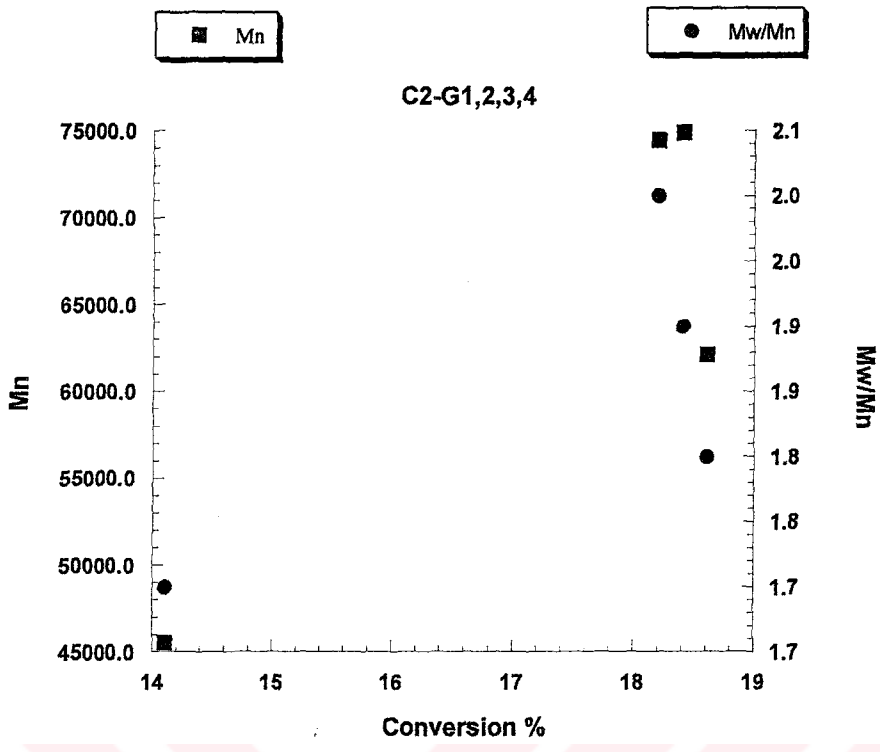


Figure 4.14. The dependence of M_n and polydispersity upon conversion for the copolymerization of MMA with C2 in anisole at 110 ^{0}C; $[MMA]_0$ = 1.8 M , $4[I]_0 = [CuBr]_0 = [bpy]/3 = 9 \times 10^{-3}$ M

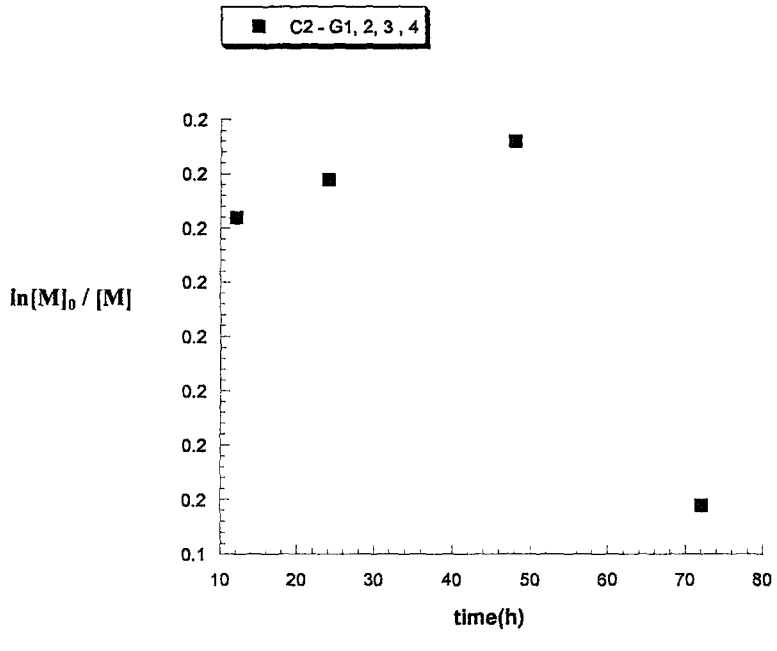


Figure 4.15. Semi-logarithmic kinetics plot for the ATRP with C2

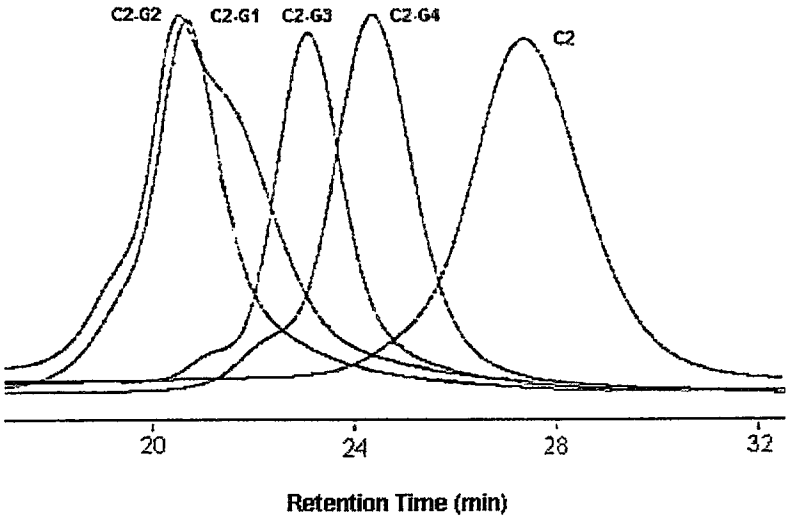


Figure 4.16. GPC Traces of C2 precursor and its graft copolymers

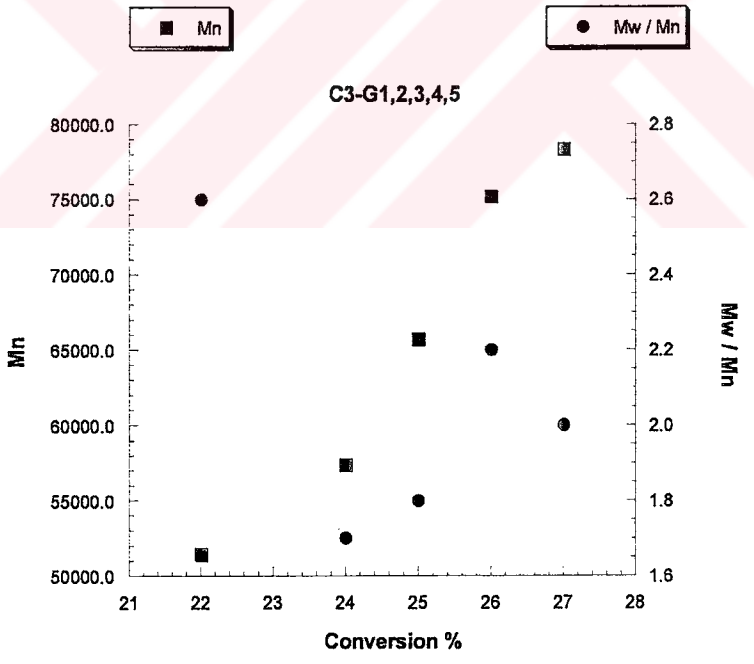


Figure 4.17. The dependence of M_n and polydispersity upon conversion for the copolymerization of MMA with C3 in anisole at 110 ^{0}C ; $[MMA]_0$ = 1.8 M , $4[I]_0 = [CuBr]_0 = [bpy] / 3 = 9 \times 10^{-3}$ M.

Table 4.3. ATRP of MMA Initiated by Bromine Terminated Macroinitiator C3[a]

Run No	$[M]_0$ (mol/L)	Time (h)	Conv. (%)	M_n[c]	M_n[d]	M_w/M_n[c]
C3-G1[b]	1.8	12	22	51448	61815	2.6
C3-G2[b]	1.8	24	26	75176	64000	2.2
C3-G3[b]	1.8	48	27	78344	63628	2.0
C3-G4[b]	1.8	72	25	65708	65568	1.8
C3-G5[b]	1.8	96	24	57372	66142	1.7

[a] $[I]_o$ /$[CuBr]_o$ /$[Bpy]_o$ /$[MMA]_o$;1/4/12/800 , T;110°C
[b] MMA/Anisole ;1/4 (in mL)
[c] Determined from GPC, based on PMMA standarts
[d] Calculated by ^{1}H-NMR

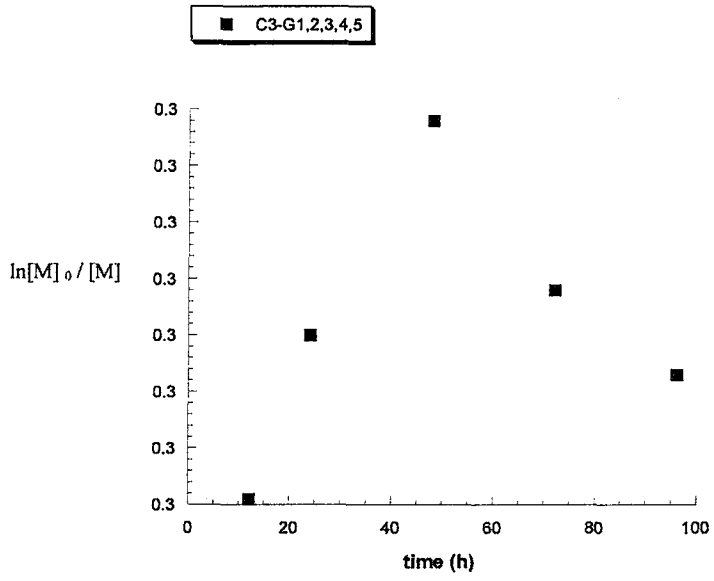


Figure 4.18. Semi-logarithmic kinetics plot for the ATRP with C3

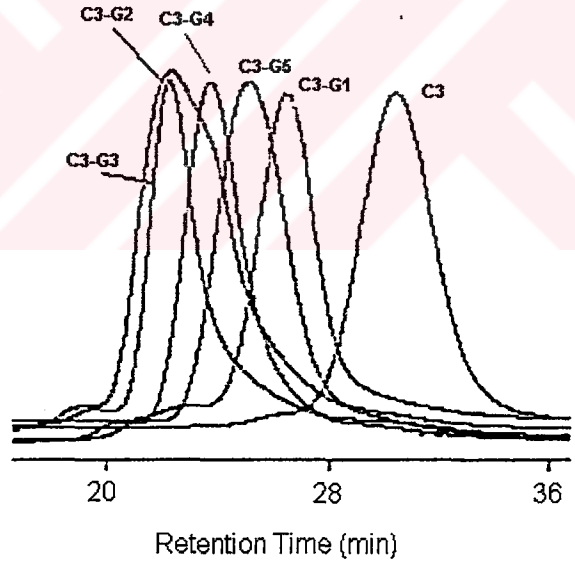


Figure 4.19. GPC Traces of C3 precursor and its graft copolymers

Table 4.4. ATRP of MMA Initiated by Bromine Terminated Macroinitiator C4[a]

Run No	$[M]_0$ (mol/L)	Time (h)	Conv %	M_n[c]	M_n[d]	M_w / M_n[c]
C4-G1[b]	1.8	12	7.8	36027	34854	2.4
C4-G2[b]	1.8	24	8.2	39764	34958	2.1
C4-G3[b]	1.8	48	8.6	33669	28615	2.0

[a] $[I]_o$ / $[CuBr]_o$ / $[Bpy]_o$ / $[MMA]_o$;1 / 4 / 12 / 800 , T;110 ^{0}C

[b] MMA /Anisole ; 1 / 4 (in ml)

[c] Determined from GPC, based on PMMA standarts

[d] Calculated by ^{1}H-NMR

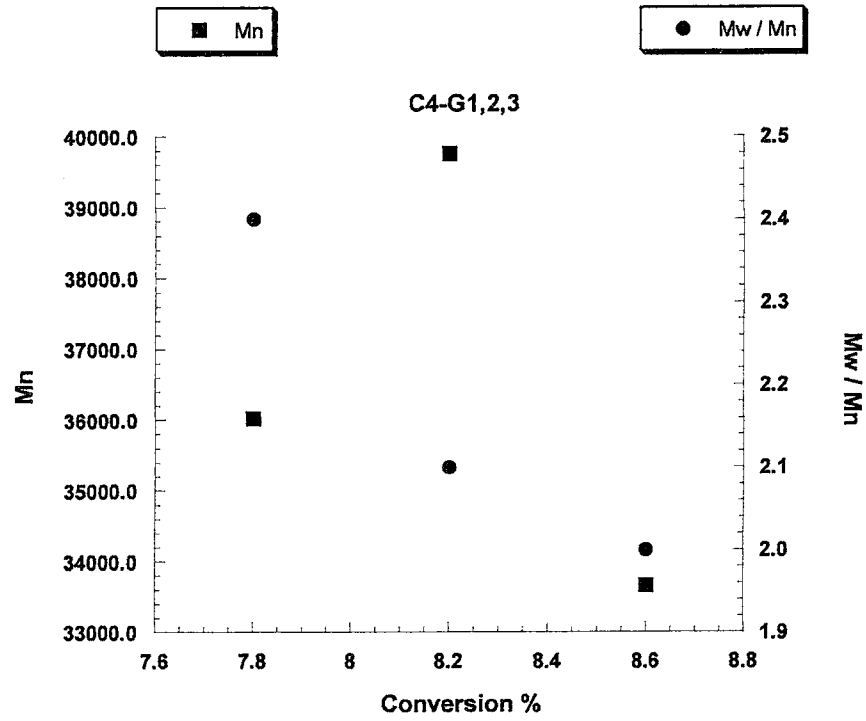


Figure 4.20. The dependence of Mn and polydispersity upon conversion for the copolymerization of MMA with C4 in anisole at 110 ^{0}C; $[MMA]_0$ = 1.8 M , $4[I]_0$ = $[CuBr]_0 = [bpy] / 3 = 9 \times 10^{-3}$ M.

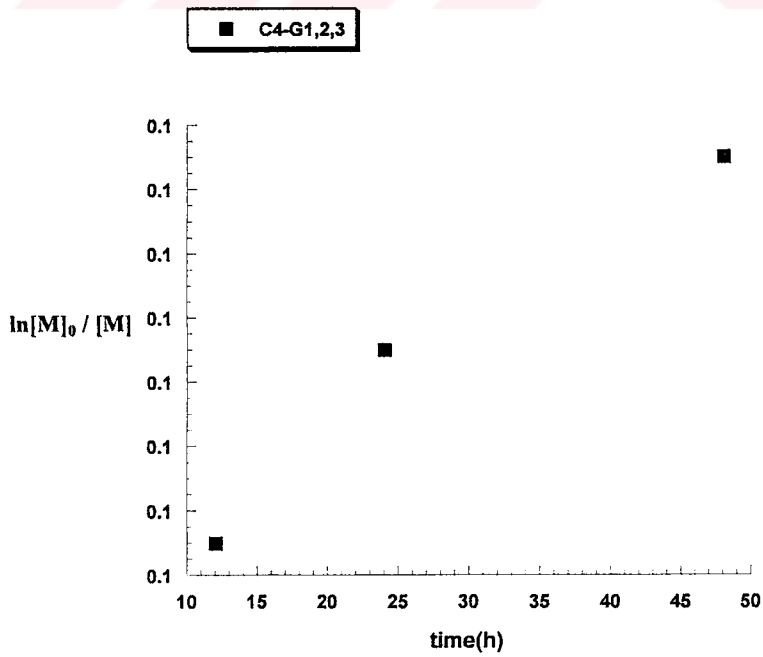


Figure 4.21. Semi-logarithmic kinetics plot for the ATRP with C4

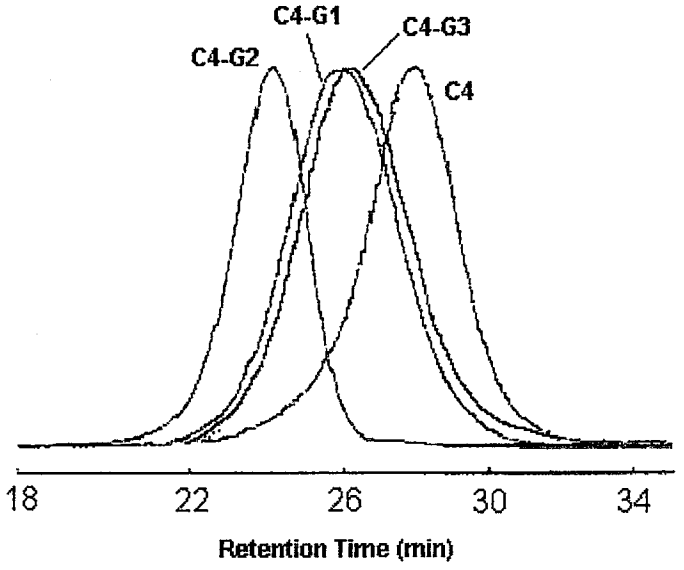


Figure 4.22. GPC Traces of C4 precursor and its graft copolymers

Under typical reaction conditions , a linear semilogarithmic plot of monomer conversion vs time was observed indicating that the apparent propagation rate constant was first-order in the monomer concentration; this implied that the concentration of the growing radicals stayed constant during the polymerization regardless of the initial concentration of the initiator for 48 hour reaction time. However, after 48 hour concentration of the growing radicals began to decrease dramatically. Living free radical character of ATRP reduced the concentration of propagating radicals which inhibits the unwanted termination reactions. However here there could be some intermolecular coupling of the macroinitiator due to the high radical stability. This can cause to form networks in the polymer. This was observed that when the reaction time increased, the solubility of the resulting polymer decreased.

After a certain time conversion was also decreased with a decrease in molecular weight. Probably, some irreversible termination reactions take place and some propagating species have disappeared. In spite of this as the reaction time increased the polydispersity decreased. ATRP is moderately sensitive to oxygen. The

polymerization will proceed in the presence of a small amount of oxygen, since small amounts of oxygen can be scavenged by the catalyst, which is present at a much higher concentration than the growing radicals [120]. However, oxidation of the catalyst reduces the catalyst concentration and slows down the polymerization. In some cases (such as very long reaction times), oxygen may produce peroxides that can actually catalyze the reaction. The polymerization of methacrylates in the presence of small amounts of oxygen and Cu (I) or Cu (II) complexes has recently been reported to yield high molecular weight products with relatively low polydispersities [121].

The GPC traces of polymers obtained using refractive index is reported in Figure 4.16 , 4.19 , 4.22. Molecular weights of the formed graft copolymers increased according to the macroinitiator and traces were shifted to high molecular weight region.

The experimental number avarage molecular weights were determined by GPC based on linear PSt (for macroinitiator) and PMMA (for grafts) standards. Theoretical molecular weights were calculated from ^{1}H-NMR spectrum as follows;

$$M_{n(NMR)} = Mn_{(\text{first monomer})} \left(1 + X \frac{MW_{2\text{nd monomer}}}{MW_{\text{first monomer}}} \right) + Y\, Mn_{(\text{first monomer})}$$

X is the molar ratio of 2nd monomer units to 1st monomer units in copolymer, measured by ^{1}H-NMR. Y is the percent of maleimide unit in alternating copolymer measured by ^{1}H-NMR. The $M_{n\ (\text{first monomer})}$ value is based on the apparent MW of polySt-alt-polyMBr estimated by GPC using polystyrene standards. The calculated values are in tables 4.2 , 4.3 and 4.4.

Thermal behaviours of synthesized alternating and graft copolymers were observed with DSC instrument. For alternating copolymer one Tg was observed at 250 ^{0}C . For graft copolymers two Tg values were obtained 115 ^{0}C for poly MMA segment and 185 ^{0}C for poly MI segment.

The controlled character of the polymerization was proved in the case of polySt-alt-polyMBr-g-polyMMA by the linear increase of molecular weight with conversion and low polydipersities of resulting graft copolymer. DSC measurements revealed that each graft copolymer had two glass-transition temperatures, characteristic to the segments forming the graft copolymer.

The polySt-alt-polyMBr-g-polyMMA has been synthesized through ATRP initiated by a new macroinitiator. It provides a new way to synthesize graft copolymers with well-controlled structure.

5. CONCLUSIONS

ATRP technique is based on a copper / nitrogen based ligand catalyst which is normally employed together with an alkyl halide as initiator.

By using functional polymers containing appropriate alkyl halide along the backbone as an initiator , it is possible to obtain graft copolymers with a well – controlled structure.

In this thesis we describe a new method for the synthesis of poly(St)-alt-poly(MBr) grafted with poly MMA by using ATRP technique. The increase of Mn and monomodal shape of the GPC traces of the copolymers suggest the formation of graft copolymers without homopolymerization. The grafting efficiency as determined from the initial concentration of the bromine groups in the macroinitiator was around 42 - 61 % .

When the reaction was achieved in anisole at higher reaction time and also a narrower molecular weight distribution of graft copolymers was observed. The formation of the graft copolymer was supported by analysis of GPC ,^{1}H-NMR and DSC. This new approach, a copolymer with a large number of sites capable of initiating ATRP using as a macroinitiator can allow for the preparation of new materials.

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