ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ATOM TRANSFER GRAFT COPOLYMERIZATION OF 2-ETHYL HEXYLACRYLATE FROM LABILE CHLORINES OF PVC IN AQUEOUS SUSPENSION

M. Sc. Thesis by

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Programme : Polymer Science and Technology

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MAY 2006

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2-ETİL HEKZİLAKRİLATIN PVC'NİN YER DEĞİŞTİREBİLEN KLORLARI ÜZERİNDEN SULU SÜSPANSİYONDA ATRP İLE GRAFT KOPOLİMERLEŞTİRİLMESİ

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LIST OF SYMBOLS

$\mathbf{M_n}$	**:** Number avarage molecular weight of polymer
$\mathbf{M_w}$	**:** Weight avarage molecular weight of polymer
$\mathbf{M_w / M_n}$	**:** Molecular weight distrubition
$\mathbf{k_{act} / k_{deact}}$	**:** Rate constants of activation and deactivation steps of the initiation in radical polymerization
$\mathbf{k_t / k_p}$	**:** Rate constants of termination and propagation steps in radical polymerization respectively

ABBREVIATION

DP	**:** Degree of Polymerization
ATRP	**:** Atom Transfer Radical Polymerization
PVC	**:** Poly(vinyl chloride)
H-TETA	**:** Hexylated Triethylenetetramine
EHA	**:** 2-Ethyl Hexylacrylate
NMR	**:** Nuclear Magnetic Resonance
GPC	**:** Gel Permation Chromatography
DSC	**:** Differential Scanning Calorimetry
CRP	**:** Controlled Radical Polymerization
RAFT	**:** Reversible Addition Fragmentation Transfer
SFRP	**:** Stable Free Radical Polymerization
NMP	**:** Nitroxide Mediated Polymerization
TEMPO	**:** 2,2,6,6-Tetramethylpiperidinyloxy

ATOM TRANSFER GRAFT COPOLYMERIZATION OF 2-ETHYL HEXYLACRYLATE FROM LABILE CHLORINES OF PVC IN AQUEOUS SUSPENSION

SUMMARY

Poly(vinyl chloride) (PVC) is one of the most important commodity plastics. Due to low flow characteristcs and brittleness of pure PVC, it needs to be modified for its commercial applications.

Copper mediated Atom Transfer Radical Polymerization (ATRP) is one of the most important techniques for controlled living polymerizations because of controlled chain growth, narrow molecular weight distribution and living nature of the polymerization.

Trace amounts of labile chlorines present in PVC structure have been demonstrated to effect as initiation sites for preparing graft copolymers of PVC by ATRP. Copper mediated Atom Transfer Radical polymerization (ATRP) is presented as a versatile tool for graft copolymerization of 2-ethyl hexylacrylate with PVC in aqueous suspension. The use of completely organosoluble copper (I) complex of hexylated triethylene tetramine, in combination with α-methyl cellulose as stabilizer, makes the graft copolymerization possible to occur in dispersed organic phase. Appreciable solubility of PVC in 2-ethyl hexylacrylate (30 %) at temperatures around 130^{o}C makes grafting of the monomer possible from labile chlorines of PVC in aqueous suspensions, without using additional solvent. First order kinetics of percentage mass increase reveals a typical ATRP fashion of the graft copolymerization at low conversions. Nearly spherical green particles are obtained with moderate stirring rates (1000 rpm), at high graft yields. In the study reaction conditions of the grafting have been studied and graft products have been confirmed by common techniques such as ^{1}H-NMR, GPC and DSC. The procedure presented offers an efficient pathway for preparing self-plasticised PVC structures.

2-ETİL HEKZİLAKRİLATIN PVC'NİN YER DEĞİŞTİREBİLEN KLORLARI ÜZERİNDEN SULU SÜSPANSİYONDA ATRP İLE GRAFT KOPOLİMERLEŞTİRİLMESİ

ÖZET

Poli(vinilklorür) (PVC) en önemli plastik eşyalardan birisidir. PVC'nin ticari olarak kullanılabilmesi için düşük akış özelliği ve kırılganlık gibi özelliklerinin değiştirilmesi gerekmektedir.

Bakır varlığında ATRP, kontrollü zincir büyümesi, dar molekül ağırlığı dağılımı ve de yaşayan karakterde bir polimerizasyon sağladığından, en önemli kontrollü yaşayan polimerizasyon tekniklerinden birisidir.

PVC'nin yapısındaki eser miktardaki yer değiştirebilen klorürler, ATRP yolu ile PVC'nin graft kopolimerleştirilmesinde başlatıcı olarak etki göstermektedir. Bakır varlığında ATRP, 2-etil hekzilakrilatın PVC ile sulu süspansiyonda graft kopolimerleştirilmesi için uygun bir yöntemdir. Organik fazda çözünür bakır(1)-hekzillenmiş trietil tetramine kompleks bileşiğinin ve de dengeleyici olarak α-metil selülozun kullanılmasıyla, graft kopolimerizasyon dispers edilmiş organik fazda gerçekleşebilir. PVC'nin 130^{o}C civarında 2-etil hekzilakrilat içerisinde çözünür olması, graft kopolimerizasyonun solvent kullanmadan gerçekleşmesini sağlar. Düşük graft derecelerinde kopolimerleşme, ATRP'den beklenildiği gibi birinci dereceden kinetiğe sahiptir. Yüksek graft derecelerinde, orta kuvvette karıştırma ile (yaklaşık 1000rpm) küresel, yeşil partiküller elde edilmiştir. Bu çalışmada, graft kopolimerizasyonun reaksiyon şartları çalışılmış ve de elde edilen graft kopolimer ürünleri ^{1}H-NMR, GPC ve DSC gibi genel yöntemlerle analiz edilmiştir. Bu prosedür Self-Plasticized PVC hazırlamak için etkili bir yöntemdir.

1. INTRODUCTION

Copper-mediated Atom Transfer Radical Polymerization (ATRP) is one of the most important techniques for controlled living polymerizations [1,2]. Controlled chain growth, a narrow molecular weight distribution and living nature of the polymerization are apparent peculiarities of the method. The living behavior of the polymerization allows preparing many block [3,4] and graft copolymers [5] in well-defined structures.

Copper-mediated ATRP, on the other hand, is unique, especially in graft copolymerization, because only trace quantities of free homopolymer formations are observed while grafting. In other words, chain-transfer reactions are greatly suppressed in the process. As a result, ATRP, when used in grafting-from process, does not yield free homopolymer as undesired byproducts.

The advantage of the method in practice is avoiding the loss of a waste amount of monomer in grafting. Because of this advantage, the method is also applicable even in grafting from solid surfaces [6-8].

This work deals with the graft copolymerization of Poly(vinyl chloride) (PVC) in aqueous suspensions by ATRP. The graft copolymerization of PVC prepolymer has been found to be attractive for imparting plasticizing effect. Although vinyl chloride/vinyl acetate copolymer is commercial product that is being sold under the name of self-plasticized PVC, grafting from pre-existing PVC is of importance to attain materials with different mechanical and chemical properties.

Because chlorines of PVC are chemically inert, these cannot be considered as initiation sites for grafting from PVC by ATRP method.

The first report on the use of ATRP technique for the grafting of PVC is associated with starting from a PVC copolymer containing minute amounts of vinyl chloroacetate as co-monomer . Replaceable chlorines of the comonomer have been used as initiation sites for the grafting by ATRP.

Most chlorine atoms of PVC itself are too inert to initiate ATRP for grafting from the polymer backbone. However, commercial PVC has been demonstrated to have few percent of labile chlorines [9], which arise from structural defects forming during the radical polymerization of vinyl chloride.

Detailed investigations of Percec's group confirmed the presence and formation mechanism of the labile chlorines of PVC [10].

Although reliability of the analytical method given by Caraculacu et.al. [11] for the determination of the labile chlorines is doubtful, we believe that those might be as high as 4%.

The labile chlorines can be considered as reactive enough to initiate ATRP for grafting from nonmodified PVC. Recently, Percec and coworkers showed that naked PVC can be grafted by copolymerization with various vinyl monomers from the labile chlorines [12]. Soon afterwards, Bicak's group have demonstrated that highly plasticizing monomers butylacrylate and 2-ethyl hexylacrylate (EHA) can also be grafted efficiently from PVC in 1, 2 dichloro-benzene as a solvent at 90 ^{o}C [13].

The labile chlorines of PVC prepared by ATRP may also cause complications in making its block copolymers. Percec's group described a versatile method for preparing ABA-type of triblock copolymers containing PVC as the B block. In this method, PVC having iodo groups in both ends is used as initiating site for block copolymerization with various vinyl monomers, by ATRP, under relatively mild conditions [14-16].

Suspension polymerization of water-immiscible monomers is mostly attractive industrially because water is used as the reaction medium. The use of ATRP in aqueous suspension makes it viable method for large-scale controlled polymerizations. However extension of ATRP to suspension process is a difficult

task because of its limitations, such as the water solubility of the copper complexes and the ligands involved. The emulsion polymerization mechanism becomes favored for water-soluble copper complexes, and smaller particles, instead of suspension particles, form, being a few hundred micrometers in diameter.

There appear to be few reports dealing with ATRP in aqueous suspensions. Matyjaszewski's group reported that ATRP in presence of an oil-soluble ligand, 4,4'-di (5-nonyl)-2,2'-bipyridine proceeds with first-order kinetics, and this was ascribed to a suspension mechanism [17]. Additionally, ATRP of methyl metachrylate/dimethacrylate mixture in an aqueous suspension of diphenyl ether has been reported to give crosslinked, spherical bead particles with about 50-100 μm in diameter [18]. The solubility of the copper complex catalyst in the organic phase is crucial in order to perform ATRP in aqueous suspensions. In our previous work, we have demonstrated that hexylated triethylenetetramine (H-TETA) forms oil-soluble copper complexes and provides true suspension conditions in ATRP of methyl metachrylate [19].

To the best of our knowledge, no reports have been published on application of ATRP in graft copolymerization in aqueous suspension so far. In fact, grafting in a suspension by ordinary initiation methods is not a successful approach because of large quantities of free homopolymer formed as a byproduct [20]. In one of the successful reports, styrene was graft-copolymerized in a suspension from thiol containing chitin in high yields [21]. In another publication, the graft copolymerization of vinyl chloride monomer from poly (butyl acrylate) in suspension has been demonstrated to give soft polymers [22].

İn the present work, we have studied for the first time, the use of ATRP for the grafting of EHA from PVC in aqueous suspension. In this work, H-TETA [23] has been chosen as a proper ligand because it is hydrophobic enough to extent ATRP for grafting in an aqueous suspensions. Another requirement is an additional solvent to dissolve the prepolymer to be grafted. Fortunately, PVC is highly soluble in this monomer around 130 oC, and this makes grafting possible without the use of additional solvent. Because all the prerequisites for a successful grafting in

suspension are being fulfilled, we thought that ATRP could work in the graft copolymerization of EHA from labile chlorines of PVC in an aqueous suspension.

In this study, characteristics and kinetics of the graft copolymerization have been studied and structures of graft products have been investigated by conventional techniques such as nuclear magnetic resonance (NMR), gel permation chromatography (GPC), and differential scanning calorimetry (DSC).

2. THEORETICAL PART

2.1. Controlled Living Polymerization

The synthesis of polymers with well defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. One of the greatest contributions to this field from synthetic polymer chemists is the living polymerization methodology, which allows the preparation of macromolecules with the maximum degree of structural and compositional homogeneity. Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination and ring-openig polymerizations. Among the numerous polymerization techniques, free radical polymerization is a widely used process from the view point of industrial production and applications [24]. This technique is relatively easy to since it does not stringent purification of the reagents, except the elimination of the dissolved oxygen. It generally leads to high molar mass polymers under relatively mild conditions. Many different processes can be applied such as bulk, solution, suspension or emulsion polymerization. Moreover, a wide range of functional monomers can polymerized by a radical mechanism and copolymerizations have provided a great variety of random copolymers with many structures and properties. The main limitations of radical polymerization are the lack of control over the molar mass, the molar mass distribution, the end-functionalities and the macromolecular architecture. Mainly for that reason, the recent emergence of many so-called 'living' or controlled radical polymerization (CRP) processes has opened a new area in this old polymerization method that had witnessed relatively small progress in the previous years [25]. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer

chemistry, as a radical process is more tolerant of functional groups and impurities and is leading the industrial method to produce polymers [26].

The terms of 'living polymerization' and 'living polymers' were introduced by Szwarc in 1956, although prior to his classical work, Ziegler and Flory [27] also described similar concepts. By definition, a living polymerization is a chain polymerization that proceeds without irreversible chain breaking processes, i.e. chain transfer and termination. This ideal case, however, has only been achieved in a few anionic polymerization systems [28-29]. In reality, most of the so-called living polymerizations, especially those proceeding via cationic or radical mechanism, are not exempt from chain transfer or termination. To differentiate these imperfect polymerizations from the ideal living polymerization, terms such as controlled 'living', pseudo-living, quasi-living and many others have been used in literature, which initiate an ongoing debate over the nomenclature.

There are several approaches to control free radical polymerization by suppressing the contribution of chain breaking reactions and assuring quantitative initiation. All of these approaches employ dynamic equilibration between growing free radicals and various types dormant species. These reactions are described as controlled radical polymerization (CRP) or controlled /living radical polymerizations rather than as true living radical polymerizations, due to the presence of unavoidable termination, which is intrinsically incompitable with concept of living polymerizations .

2.1.1. Classification of CRPs

Controlled/living radical polymerization employs the principles of equiliration between growing free radicals and various types of dormant species. There are several approaches to achieve good control over molecular weights, polydispersities, and end functionalities in these systems. They can be classified depending on the mechanism and the chemistry of the equilibration/exchange process, as well as on the structure

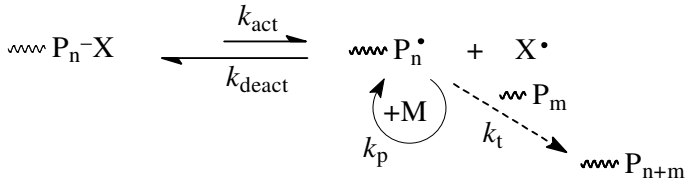
of the dormant species. Some of them are catalyzed and some are not, some of them exhibit the persistent radical effect and some do not .

It is possible to group CRPs into several categories, depending on the chemistry of exchange and structure of the dormant species. Althought it may be simplier to divide CRPs based on the structure of the dormant species, the mechanistic classification may be more appropriate, since it enables better correlation of the rates, molecular weights and polydispersities of the obtained polymers with the concentration of the involved reagents. Thus, mechanistically, CRPs can be reversible addition fragmentation transfer (RAFT), atom transfer radical polymerization(ATRP), stable free radical polymerization (SFRP), and nitroxide mediated polymerization (NMP) .

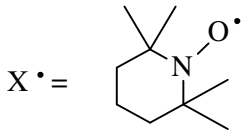
All of these methods are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in reversible addition fragmentation chain transfer processes (RAFT), alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP), and potentially even orgonometallic species. Free radicals may be generated by the spontaneous thermal process (NMP, SFRP) via a catalyzed reaction (ATRP) or reversibly via the degenerative exchange process with dormant species (DT, RAFT) [30].

2.1.1.1. Stable Free Radical Polymerization

Nitroxide mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations (SFRP). In this type of process, the propagating species (Pn·) reacts with a stable radical (X·) as seen in reaction (2.1-2.2) [31]. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn· forms it can then react with a monomer, M, and propagate further.



(2.1)



TEMPO (2,2,6,6-tetramethyl-piperidinyloxy) (2.2)

2.1.1.2. Reversible Addition-Fragmentation Chain Transfer Polymerization

In terms of polymerizable monomers, RAFT is at present the most versatile technique for conducting CRP, that is, it can be applied to a larger range of monomers than SFRP and ATRP. In contrast to NMP and ATRP, this system relies on chain transfer for the exchange between active and dormant chains (2.3, 2.7). The chain end of a dormant chain carries a thiocarbonylthio moiety, which is chain-transfer–active. Upon chain transfer, the thiocarbonylthio moiety is transferred to the previously active chain, which now becomes dormant, and the previously dormant chain carries the radical activity and is able to propagate.

There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: (1) dithioesters (Z = aryl or alkyl), (2) trithiocarbonates (Z = substituted sulfur), (3) dithiocarbonates (xanthates) (Z = substituted oxygen), and (4) dithiocarbamates (Z = substituted nitrogen). Representative examples of thiocarbonylthio RAFT agents are shown in Figure 2.2.

To some extent the choice of RAFT agent determines the degree of control obtained. The general structure of a RAFT agent is depicted in Figure 2.1, where the Z group is the activating group, and R is the homolytically leaving group. To a large extent, the Z group determines the rate of addition, and the R group determines the ate of fragmentation. The choice of Z and R groups is dependent on the nature of the monomer to be polymerized.

RAFT polymerization is performed by adding a chosen quantity of an appropriate RAFT agent (Figure 2.1) to a conventional free radical polymerization mixture and

yields polymers of predetermined chain length and narrow polydispersity. Polydispersity indices of less than 1.1 can be usually achieved under optimal conditions. The RAFT process offers the same versatility and convenience as conventional free-radical polymerization being applicable to the same range of monomers (e.g., (meth)acrylates, styrenes, acrylamides, vinyls), solvents, functional groups (e.g., OH, CO2H, NR2, NCO) and reaction conditions (e.g., bulk, solution, suspension and emulsion). The RAFT process yields thiocarbonylthio-terminated polymers (or 1,1-disubstituted alkene-terminated oligomers if macromonomers are used as RAFT agents) that can be chain extended to yield a variety of copolymers (e.g., AB, ABA blocks, gradient).

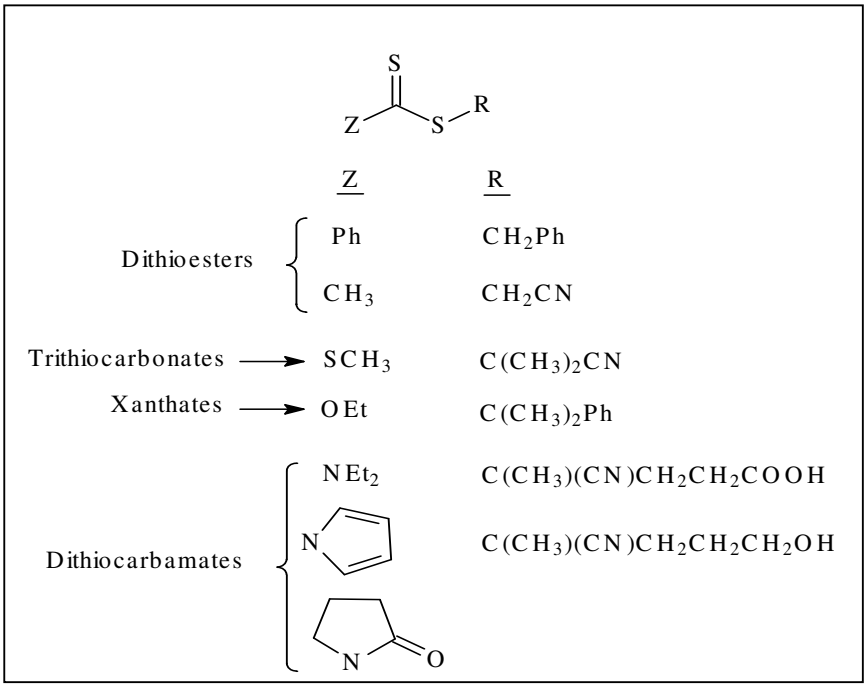
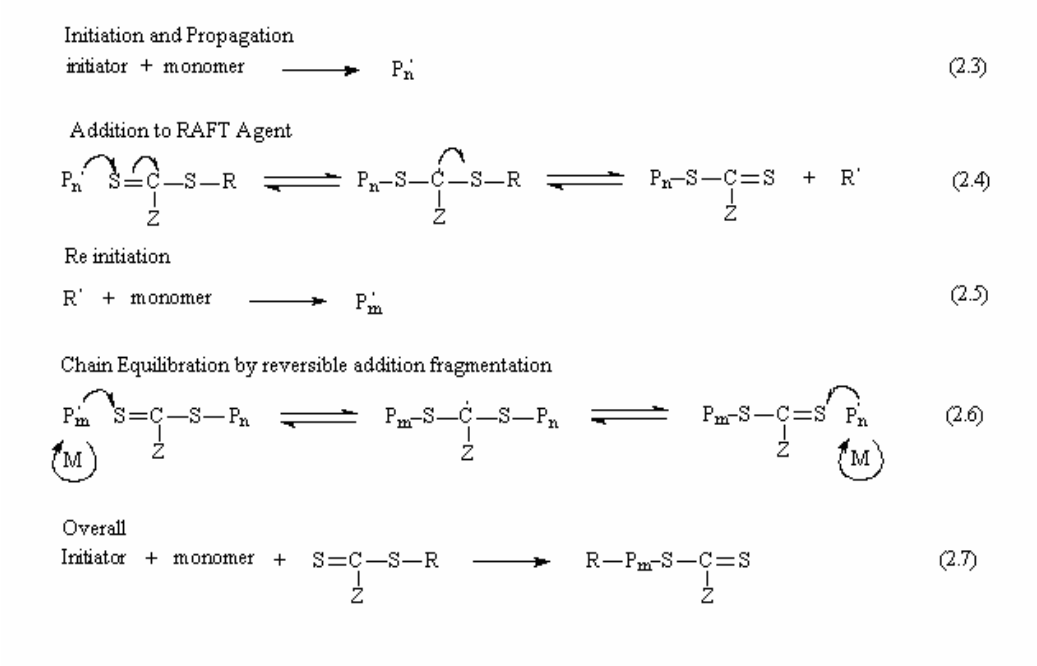
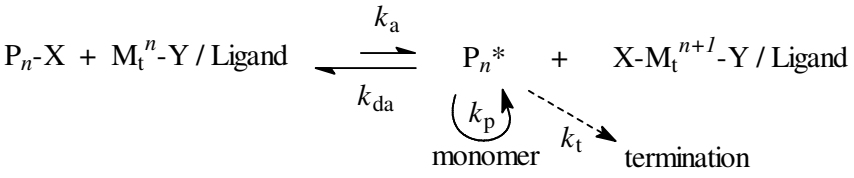


Figure 2.1: Examples of the different classes of thiocarbonylthio RAFT agents



2.1.1.3. Atom Transfer Radical Polymerization (ATRP)

The name atom transfer radical polymerization comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [32]. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [33,34].



(2.8)

A general mechanism for ATRP is represented by (2.8). The radicals, i.e., the propagating species Pn*, are generated through a reversible redox process catalyzed by a transition metal complex (activator, Mtn –Y / ligand, where Y may be another

ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, Pn–X. Radicals react reversibly with the oxidized metal complexes, X–Mtn+1 / ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, ka, and deactivation kda, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, kp. Termination reactions (kt) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below [35]. (2.9-2.11)

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [36]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

Initiation

$$\text{R-X} + \text{M}_\text{t}^{n}\text{-Y / Ligand} \underset{k_{da}^{o}}{\overset{k_a^{o}}{\rightleftharpoons}} \text{R} + \text{X-M}_\text{t}^{n+1}\text{-Y / Ligand}$$

$$\text{R} + \text{M} \xrightarrow{k_i} \text{P}_1 \qquad (2.9)$$

Propagation

$$\text{P}_n\text{-X} + \text{M}_\text{t}^{n}\text{-Y / Ligand} \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} \text{P}_n + \text{X-M}_\text{t}^{n+1}\text{-Y / Ligand} \qquad (2.10)$$

$$\text{P}_n + \text{M} \xrightarrow{k_p} \text{P}_{n+1}$$

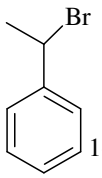
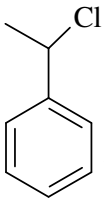
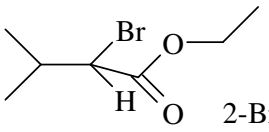
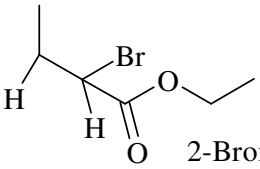
Termination

$$\text{P}_n + \text{P}_m \xrightarrow{k_t} \text{P}_{n+m} \quad \text{or} \quad \text{P}_n^{=} + \text{P}_m^{H} \qquad (2.11)$$

Monomers: In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. However, 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 dispropor- tionation, the magnitude of the equilibrium constant (Keq=kact/kdeact) determines the polymerization rate. ATRP will not occur or occur very slowly if the equilibrium constant is too small. In contrast, too large an equilibrium constant will lead to a large amount of termination because of a high radical concentration. This will be accompanied by a large amount of deactivating higher oxidation state metal complex; which will shift the equilibrium toward dormant species and may result in the apparently slower polymerization [37]. Each monomer possesses its own intrinsic radical propagation rate. Thus, for a specific monomer, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain polymerization control. However, since ATRP is a catalytic process, the overall position of the equilibrium not only depends on the radical (monomer) and the dormant species, but also can be adjusted by the amount and reactivity of the transition-metal catalyst added.

Initiators: A variety of halogenated initiators and macro initiators activated by various types of aryl, sulfonyl and carbonyl groups can be used in ATRP systems.

Table 2.1: Types of initiators used in ATRP sytems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethyl isobutyrate	Methylmethacrylate
 2-Bromo ethyl propionate	Methacrylate and other acrylates

The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator at full monomer conversion.

Catalysts: Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the

dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

1. The metal center must have at least two readily accessible oxidation states separated by one electron.
2. The metal center should have reasonable affinity toward a halogen.
3. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo) halogen.
4. The ligand should complex the metal relatively strongly.
5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [38].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [39], Ni [40], Ru [41], etc have been used to some extent. Recent work from Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [42].

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

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N′,N″,N″ pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me_6-TREN). Examples of ligands used in copper-mediated ATRP are illustrated below [43,44].

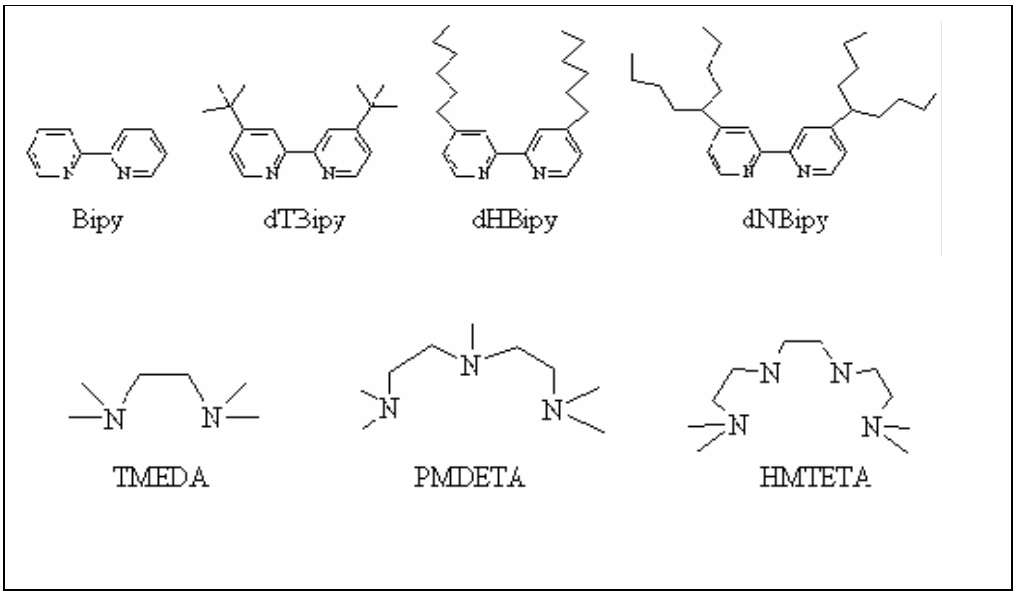


Figure 2.2: Examples of ligands used in copper mediated ATRP.

Solvents: ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [45] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, [46] should be minimized.

Temperature and Reaction Time: The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher kp/kt ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more

pronounced at elevated temperatures [46-52]. In general, the solubility of the catalyst increases at higher temperatures; however, catalyst decomposition may also occur with the temperature increase [53-54]. The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight.

At high monomer conversions, the rate of propagation slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration indepedent. Prolonged reaction times leading to nearly complete monomer conversion may not increase the polydispersity of the final polymer but will induce loss of end groups [55]. Thus, to obtain polymers with high end-group functionality or to subsequently synthesize block copolymers, conversion must not exceed 95% to avoid end-group loss.

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 usually negative first order with respect to the deactivator (CuX_2 / Ligand).

The rate equation of ATRP is obtained by the aid of some assumptions such that the contribution of termination on the rate of the polymerization is ignored, the initiating molecules are completely consumed in the initiation step and fast equilibrium, which is necessary for getting low polydispersities, is ensured. The rate of polymerization is formulated in discussed conditions and given in (2.12).

$$R_p = k_{app} [M] = k_p [P\bullet] [M] = k_p K_{eq} [I]_o \frac{[Cu(I)]}{[Cu(II)X]} [M] \qquad (2.12)$$

Control of the polymerization and thus the resulting polymer depends not only on the concentration of the growing radicals but also on the rate of propagation and deactivation steps in atom transfer radical polymerization. If the deactivation does not occurs, 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 (2.13).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d[RX]_o}{k_p[XCu^{II}]}\right)\left(\frac{2}{p} - 1\right) \qquad (2.13)$$

p = polymerization yield

$[RX]_o$ = concentration of 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 kp / kd, higher polydispersities (molecular weigh distributions) are usually obtained.

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

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control over the molecular weights and the molecular weight distributions of the resulting polymers. Additionally, since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

2.2. Application of Copper Mediated ATRP

2.2.1. Graft Copolymers

Polymers which contain more than one type of structural unit are called as copolymers. The copolymer with random distrubution of the different mers or repeating units in its structure is commonly referred to as a random copolymer. In the alternating copolymer the two mers alternate in a regular fashion along the polymer chain. A block copolymer is a linear polymer with one or more long uninterrupted squence of each mer in the chain. A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points (Fig. 2.3). Graft copolymers represent valuable polymeric materials, since a variety of molecular parameters can be varied: i) main and side chain polymer type, ii) degree of polymerization and polydispersities of main and side chain, iii) graft density (average spacing in-between the side chains) and iv)distrubition of the grafts (graft uniformity). Using special polymerization techniques tailor-made graft copolymers can be afforded according to specific needs.

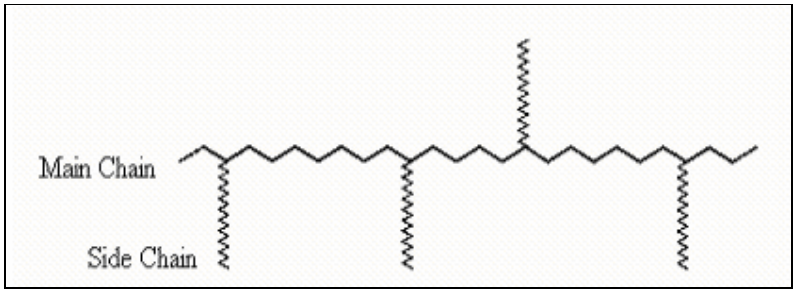


Figure 2.3: Graft Copolymer

By controlling the molecular parameters, 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 for applications as hydrogels, stabilizers, surface-modifying agents, dispersants and compatibilizers in polymer blands, etc [56,57]. Three main methods can be used to prepare graft copolymers : i) “grafting through”,

where a macromonomer is copolymerized with a low molecular weight comonomer; ii) “grafting from”; in this case a macroinitiator with predetermined initiation sides is used to initiate the polymerization of a second monomer; iii) “grafting onto”, where an end-functional or a living polymer with reactive end-group is coupled with functional groups located on another polymer.

Until recently, well-defined graft copolymers could be obtained only by using ionic polymerizations or the macromonomer route. Due to the lack of control of molecular weight and polydispersity, the free radical polymerization methods (FRP) lead to poorly defined polymers, very often accompanied by a certain amount of homopolymer and crosslinked material [56,58]. Free radical techniques though have become available for the preparation of well-defined polymers. So far only SFRP [59] and ATRP have been used to prepare graft copolymers by both “grafting through” and “grafting from” methods.

ATRP has been applied in the synthesis of several well-defined graft copolymers. Two main approaches have been adapted: i) the “grafting through” technique; i. e. A well defined macromonomer was synthesized in the first step by ATRP, followed by its free-radical or controlled radical copolymerization with a low molecular weight comonomer (Figure 2.3); ii) the “grafting from” technique, i. e. a polymer possesing ATRP-active halide atoms as side groups was used as a macroinitiator in the ATRP of a second monomer. Generally, these macroinitiators can be obtained directly by copolymerizing a monomer containing ATRP-initiator group using a polymerization mechanism that is different from ATRP (FRP, SFRP, ring opening polymerization ROMP)) or by copolymerization of a monomer carrying a precursor that can be transformed to an ATRP-initiating group.

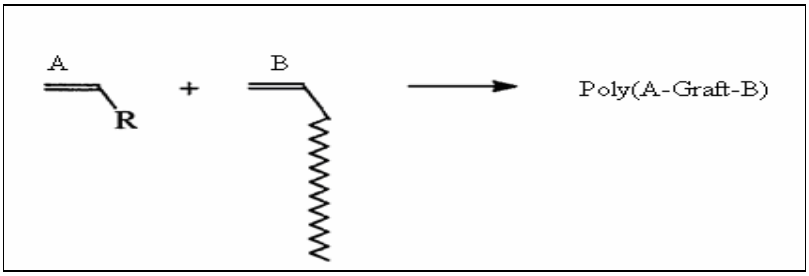


Figure 2.4: Grafting through approach

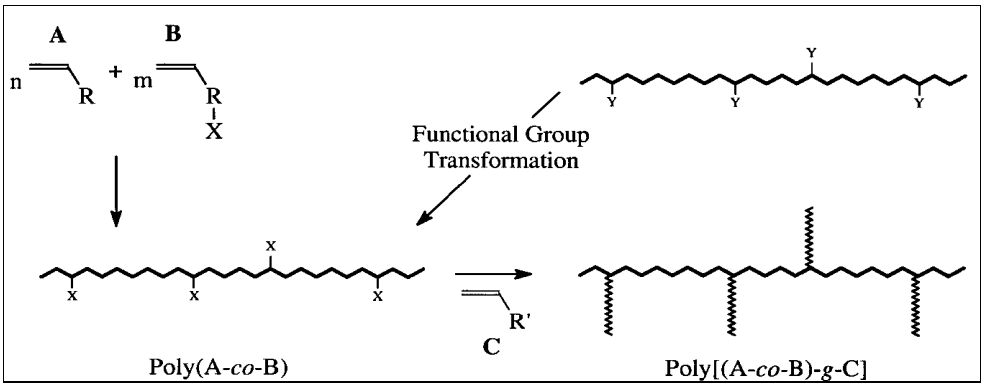


Figure 2.5: Grafting from approach

2.2.1.1. Graft Copolymers by the "Grafting Through" Approach

The "grafting through" approach is the most common route to controlled graft copolymers[60, 61]. The copolymerization of macromonomers (MM) with low molecular weight comonomer allows good control of the polymer side chain parameters (DP, M_w/M_n) by using living or controlled polymerization methods fort he MM synthesis. The polymer main chain parameters (DP, M_w/M_n) can be controlled by a living copolymerization of the MM with a low molecular weight comonomer. The avarage side chain density is determined by the reactivity ratio of the MM in the copolymerizaiton and by the ratio of the MM in the feed. The spacing distribution of the side chains is the most crucial parameter to control. It is influenced by the diffusion differences of MM in comparison to the low molecular weight comonomer [62], by the inherent reactivity of MM and comonomer [63] and by the potential incompatibiliy of the side chain polymer with the main chain polymer[64].

2.2.1.2. Graft Copolymers by the "Grafting From" Approach

The "grafting from" approach uses a macroinitiator (MI) that carries initiation groups to start a polymerization reaction of a monomer. The synthesis of the MI allows the control of the main chain parameters (DP, M_w/M_n) as well as the pre-determination of side chain density and side chain distribution. The main difficulty in this approach is to ensure a uniform propagation of the side chains and furthermore to supress chain coupling reactions.

The method is not restricted to linear MI, particles [65,66] and surfaces [67,68] were also succesfully functionalized with initiating groups and used as MI to get Access to e.g. inorganic organic hybrid materials.

In conclusion, atom transfer radical polymerization (ATRP) was used to synthesize a variety of graft copolymers, differing in main and side chain polymer types. Using "grafting through" and "grafting from" methods, the molecular parameters such as the degree of polymerization of and the polydispersity of main and side chain polymer, graft density and graft distrubition could be controlled.

2.2.2. Living/Controlled Radical Polymerizations in Dispersed Phase Systems

Living/controlled radical polymerization provides a route to synthesize materials with designed microstructure and narrow weight distrubition. Extensive research has been conducted into homogeneous bulk and solution living radical polymerizations, but investigations into aqeous dispersed phase system (suspension, emulsion and microemulsion) have only recently appeared. There are a number of incentives to use suspension or emulsion polymerization on a commercial scale, including ease of mixing and good heat transfer. However, adaptation of living radical chemistry to aqeous dispersions poses several advantages relating to maintainining effective control over the growth of living chains. Furthermore, there currently exists substantial investment in suspension polymerization facilities throughout the world, and therefore there is considerable interest in adapting living polymerizations to suspension based polymerization systems.

2.2.2.1. Aqueous Dispersed Phase Polymerizations

A number of terms have been used to describe different heterogeneous polymerizations, such as suspension, emulsion. miniemulsion, dispersion, and precipitation. The criteria to classify these systems depends on i) the initial state of the polymerization mixture; ii) the kinetics of the polymerization; iii)the mechanism of particle formation; and iv) the shape and size of the final polymer particles[69-71].

Suspension Polymerization: A relatively water insoluble monomer is dispersed in the continuous aqueous phase as liquid droplets by vigorous stirring. An oil soluble

initiator is employed to initiate polymerization inside the monomer droplets. During the course of polymerization, the coalescence of monomer droplets and the adhesion of partially polymerized particles are hindered by a small amount of stabilizers. The latter may be either water soluble polymers, such as poly(N-vinylpyrrolidone) (PVP) and poly(vinyl alcohol-co-vinyl acetate), or insoluble inorganic salts such as talc, calcium and magnesium carbonates, silicates and phosphates.

The average number of radicals per particle (π) is on the order of 102-106, therefore each particle behaves as an isolated micro reactor and the kinetics resemble those of bulk polymerization (or solution polymerization if the monomer phase contains diluent). Consequently, the droplet size and the amount of stabilizer do not affect the polymerization rate. The continuous aqueous phase serves only to decrease the viscosity and to dissipate heat generated from the polymerization.The diameters of the particles obtained from suspension polymerization are usually in the range of 20-2000 μm depending on the stirring speed, volume ratio of the monomer to water, concentration of the stabilizer, the viscosities of both phases and the design of the reaction vessel. With a properly designed reactor and a well-stabilized suspension, monodisperse particles can be produced in agreement with theoretical predictions [72, 73].

Another important property that is directly related to the application is the surface and bulk morphology of the individual particles. Particles with the polymer soluble (or swellable) in its own monomer have a smooth surface and a relatively homogeneous texture, like polystyrene and poly(methyl methaclylate). When the polymer is not soluble (or swellable) in its own monomer, the particles will have a rough surface and a porous morphology, like poly(vinyl chloride) and polyacrylonitrile. Using a suitable monomer diluent can control the degree of porosity and the pore structure of the particles, which is of particular interest in the production of crosslinked ion exchange resin and polymer supports.

Some typical polymers produced by suspension polymerization include polystyrene, poly(vinyl chloride), polyacrylates, poly(vinyl acetate) and their copolymers.

Emulsion Polymerization: Typical emulsion polymerization employs two different ingredients from suspension polymerization: i) The surfactant (or emulsifier) used to impart colloidal stability is composed of both hydrophilic and hydrophobic parts. The stabilization comes from either electrostatic effect (anionic and cationic surfactants), steric effect (nonionic surfactans) or both (polyelectrolytes). The monomer is present in the micelles (5-15 nm) as well as in large droplets (10^3-10^4 nm). ii) The initiator is water-soluble and the radicals are produced in the continuous aqueous phase. Accordingly, emulsion polymerization is distinguished from suspension polymerization by nucleation proceeding outside monomer droplets (in micelles or in the aqueous phase) and π is on the order of 10-1-100 due to the small size of the particles (50-300 nm). The polymerization takes place in the monomer-swollen particles, and monomer droplets serve primarily as reservoirs to supply the consumed monomer within particles.

The number of polymerization sites ($l0^{17}$-10^{18} cm^{-3}) is usually much larger than the number of radicals generated (10^{13}-10^{15} $c\,m^{-3}$ s^{-1}), therefore radicals tend to be isolated in separate particles without direct access to each other. This compartmentalization effect has a profound influence on the kinetics and the nature of the polymers formed in an emulsion polymerization. A resultant distinctive feature is that both polymerization rate and degree of polymerization can he simultaneously increased, which is of particular interest to industrial applications. In homogeneous or suspension systems, however, the enhancement of the polymerization rate is always accompanied with a reduction of the molecular weight [73, 74, 75].

Miniemulsion Polymerization: The concept of minimulsion polymerization is to produce a latex which is a 1:1 copy of the original droplets so as to achieve a direct control over the number of particles. This is accomplished by reducing the monomer droplets to submicronic size (50-500 nm) using a strong shear force such as ultrasonication. An enhanced stabilization of these tiny monomer droplets comes from the addition of the so called "co-surfactant" (usually ultra hydrophobes such as hexadecane and hexadecanol). The function of the co-surfactant is to retard the diffusion of monomer out of the monomer droplets (Ostwald ripening) with a balanced osmotic pressure and the Laplace pressure[75].

Because of the dramatically reduced sizes, the total interfacial area of droplets is significantly increased, which allows droplets to compete readily with monomer-swollen micelles for radical capture. In fact, most miniemulsion polymerizations are carried out with a surfactant concentration below the critical micellar concentration (cmc), so that monomer droplets become the principal locus of particle nucleation (homogeneous nucleation is still possible).

2.2.3. Atom Transfer Radical Polymerization in Aqueous Dispersed Media

2.2.3.1. Criteria for A Successful ATRP in Aqueous Dispersed System

ATRP from the organic homogeneous system to the aqueous heterogeneous system is not straightforward. One of the biggest challenges comes from the multi-phase medium. In general, to obtain a living/controlled radical polymerization in multi-phase systems, not only water-borne (mini)emulsions or suspensions, but also dispersion polymerizations in non-solvents such as alkanes or supercritical CO_2, all of the components of the reaction (monomer,growing/dormant chain end, radical mediator) must be in the same phase at some point. If these components are not in the same phase, then there will either be no reaction or an uncontrolled reaction.

To explore this in ATRP, consider that if the catalyst were to be confined to the aqueous phase, but the monomer and initiator were solely in the organic phase of an emulsion. Since the catalyst can not interact with the initiator to generate a radical, then initiation does not occur and there is no polymerization. Similarly, if the initiator and catalyst are water soluble, upon formation of the polymer (and collapse into polymer particles), the growing radical and the deactivator can not come into contact with one another. The result is that there is no reversible deactivation of the growing polymer chain, and thus, the polymerization behaves as a conventional, redox initiated radical polymerization.

The goal then is to have a system where at least some proportion of the components, particularly the activator and deactivator, are available in the organic phase where the polymerization takes place. It is acceptable that the various components may change phase dynamically, as long as the system still allows for rapid activation and

deactivation of all chain ends. The role of adjusting the partitioning behavior of the metal complexes is mainly played by the ligand, and presumably a highly hydrophobic ligand may bring sufficient amount of metal complexes to the organic phase.

Two other keys to the success of ATRP in water-borne systems are the stabilities of the end group on growing chains and the catalytic system in the presence of water and surfactants. Since ATRP utilizes an alkyl halide as an initiator/dormant chain end, the hydrolysis of this group under the polymerization conditions should be minimized, if not totally avoided. From this point of view, acrylates and methacrylates are slightly better than styrene derivatives. Concerning the stability of the catalytic system, the presence of the anionic surfactant impairs the control of the polymerization. This is presumably through the ion exchange with the deactivator. Therefore, to avoid any potential interaction between the surfactants and the catalytic system, nonionic surfactants seem to be a preferred choice. Conversely, water is not a big threat for copper complexes due to its much lower coordination constant to copper compared with the nitrogen ligands commonly used in copper-based ATRP[76]. For iron-based ATRP, however, water does destroy the active catalyst/deactivator, that is why well-defined polymers have not been synthesi zed in water-borne iron-based ATRP systems so far.

2.2.3.2. Atom Transfer Radical Polymerization in Aqueous Dispersed Media

The preparation of well-defined polymers and copolymers by radical polymerization has been an area of intense interest in recent years. This is basically due to a large range of monomers available for radical polymerizations, as well as easily accessible and tolerant polymerization conditions compared with other living/controlled polymerization methods. In particular, atom transfer radical polymerization (ATRP) has been one of the most successful and versatile techniques by radical means, demonstrated with the preparation of a wide variety of novel polymeric materials under nonstrenuous reaction conditions.

Until the early 1998, nearly all living/controlled radical polymerizations were confined to bulk or solution polymerization. Although some reactions had been

conducted in water, either as homogeneous or as biphasic mixtures, few well-defined polymers synthesized by emulsion or suspension systems were reported.

A seeded emulsion polymerization of styrene was conducted with a TEMPO-mediated polymerization system, but the polymerization temperature was above 120°C and thus required high pressure. Furthermore, the seeded polymer was prepared via conventional emulsion polymerization and therefore not well-defined. With a relatively high ratio of the seed used, the separation of the seed from the desired homo- or copolymer would be difficult, which means the resulting bulk polymer was not well-defined.

Addition-fragmentation polymerization, using a macromonomer as the transfer agent, was also applied to emulsion polymerization of methacrylates. The drawback of this method, however, was the preparation of the macromonomer as well as the limited success in the polymerizations of styrene and acrylates.

ATRP was attempted in emulsions as well, but the resulting polymers were not well defined as evidenced by broad molecular weight distributions and the theoretical molecular weights not corresponding with predicted values (DPn = v[M]/[I10).

There have appeared a few reports on the use of ATRP under suspension polymerization conditions. Matyjaszewski et al. reported that the direct ATRP of methyl methacrylate (MMA) in an aqueous suspension proceeded with first-order kinetics in the presence of an oil-soluble ligand, 4,4~-di(5-nonyl)-2,2~-bipyridine, and a nonionic surfactant [22]. This result was ascribed to the suspension mechanism They also presented the polymerizability of styrene by copper-mediated ATRP in a toluene/water mixture [23]. In addition, Percec et al. reported a method for ATRP of vinyl chloride in a two-phase system containing H2O and tetrahydrofuran (THF) initiated with CHI3 and catalyzed by Cu2O/tris(2-aminoethyl)amine or Cu2O/ poly(ethyleneimine) at room temperature [24]. They found that a combination of two processes, liquid–liquid emulsion and solid–liquid dispersion polymerization, was operative. More recently, the copper-mediated ATRP of MMA in an aqueous suspension of diphenyl ether was used to prepare crosslinked hollow polymer particles about 50–100 ~m in diameter [25]. Zhu et al.reported ATRP of MMA in an

aqueous suspension and found a typical ATRP behavior under direct suspension conditions, although they used a water-soluble catalyst system (CuCl/bipyridine). However, this system was not found to be successful in reverse ATRP[26].

2.3. Graft Copolymerization of PVC

2.3.1. General Properties Of PVC

Poly(vinyl chloride) (PVC) is, in volume, the second most widely used plastic in the world today(the first is low-density Polyethylene (LDPE). Despite many technical, economic, and environmental concerns, PVC production still increases worldwide at a rate of more than 4% per year [77].

The history1of PVC dates back to 1835, when Liebig and Regnault first discovered the monomer, vinyl chloride (VC), as a product of the reaction of ethylene dichloride with alcoholic potassium hydroxide [77-80]. Baumann observed the light-induced polymerization of VC in 1878. And nearly 35 years later, in 1913, Klatte polymerized VC with organic peroxides. PVC is widely used in construction, packaging, electronics, and transportation. But the properties of PVC is not appropriate to make useful materials. So, to improve the properties of PVC is very important for its commercial use. Owing to the difficulties in processing and the thermal instability of PVC, the first commercial products were copolymers. Between 1928 and 1930, Union Carbide and Du Pont copolymerized VC with vinyl acetate, and IG-Ludwigshafen copolymerized VC with vinyl ethers and acrylic esters. The first industrial homopolymerizations of VC were performed between 1930 and 1939 in the USA by Union Carbide, using suspension polymerization, and in Germany by IG, using emulsion polymerization, with an annual production of a few hundred tons. Also, to overcome processing and heat stability problems of PVC, Semon discovered plasticizer for PVC in 1932 [81].

There are various processes to modify PVC. These processes can be classified in two main groups; chemical processes and physical processes. Chemical modification can be made by studying the chain structure in PVC and chemical, physical, and mechanical properties and its range of application can be modified by chemical

modification. The chemical modification of PVC has mainly involved dehydrochlorination, reductive dehalogenation, substitution of chlorines by other functionalities, and graft copolymerizaiton using ionic and free radical methods 5. In recent years, Atom Transfer Radical Polymerization is used to modify the PVC 6,7,8. But the chemical modification of PVC is not preferred in the industry. One of the reasons that graft or interpenetrating network polymers have not gained wide commercial success is that PVC can usually be compounded with conventional plasticizers or elastomers (or combination of thereof;) to produce materials with similar properties at a lower cost and over a broader spektrum of property requirements [82].

2.3.2. Plasticizer effect on PVC

Plasticizers are the most common additives. They are less expensive than other additives used in polymer processing and applications. Plasticizers are used in flexible PVC primarily to control softness and flexibility and also to modify processing or physical properties. Plasticizers are low volatility liquids or low MW solids that, when added to the polymer, decrease the intermolecular forces between the polymer chains and segments and therefore the glass transition temperature (Tg). Plasticization increases flexibility, softness, and elongation, while decreasing tensile strength and modulus. Low temperature properties are improved, while processing temperature and melt viscosity are also reduced.

Plasticizers can be either monomeric or polymeric. Monomeric plasticizers consist of mono-, di-, and triesters produced from acids (or anhydrides) and mono- or dibasic alcohols. Polymeric plasticizers with higher MW are produced from polyfunctional acids and alcohols, generating longer chains. The plasticization efficiency of polymeric plasticizers is poor compared to that of monomerics, but resistance to volatility and migration are superior. Typical plasticizers for PVC are the members of the phthalate family, the adipates and the organophosphates. Secondary plasticizers include the chlorinated paraffins and epoxidized soy bean oils. The efficiency of a plasticizer is the level of plasticizer required to achieve a given hardness, flexibility, or modulus of elasticity's. Low-molecular weight phthalate plasticizers are the most efficient plasticizers for PVC materials.

2.3.2.1. Polymer/Plasticizer Interaction

The highly electronegative nature of the chlorine atoms leads to strong dipoles along the polymer chain, resulting in high concentrations of secondary valence forces, and therefore in a reduction of chain flexibility. At the same time, since chlorine atoms are relatively bulky, they separate the chains sufficiently. The simplest model of plasticization envisions the plasticizer molecules, which have polar or polarizable groups, as bonding with the polymer dipoles, while the non-polar parts of the molecules act as shields between polymer dipoles. The result is thus a reduction of dipole bonding between polymer chains, less overall cohesion and a consequent increase in the freedom of molecular movement. For all polymers including plasticized PVC, the theory attempted to explain diminution of the glass transition temperature (Tg) with increased plasticizer content. Sears and Darby summarized the main aspects of the free volume theory in the following ways: "Because an increase of whole free volume permits increased motion of polymer molecules, a study of plasticization is a study of ways to increase free volume. Free volume comes from three principal sources:

1- Increase of the number of end groups.
2- Increase of the number or length of side chains.
3- Increase of the chance of main chain movement.

According to principles, the introduction of plasticizer molecules into the polymer mass implies not only addition of molecules with a Tg lower than that of polymer itself, but the relatively small plasticizer molecules add a great free volume to the system.

2.3.2.2. Migration

When plasticized PVC comes into contact with other materials, plasticizer may migrate from the plasticized PVC into the other material. The rate of migration depends not only on the plasticizer employed but also on the nature of the contact material. The key characteristic for migration is molecular size. The higher the molecular weight of plasticizer the less it tends to migrate. The extreme case is seen by the use of polymeric plasticizers in applications where excellent resistance to

migration is required. There is also a contribution from the linearity of the alcohol component of the plasticizer ester. Phthalates generally do not migrate into air as easily as branched plasticizers. This fact is only true if the volatile loss of plasticizer is considered. However, it was also stated that for plasticizer migration into liquid or solid, branched plasticizers can show less plasticizer loss than linear plasticizers.

2.3.2.3. Processability of Plasticized PVC

The need to switch from one plasticizer to another arises sometimes due to cost considerations or at other times due to their effect on physical properties. A change from one plasticizer to another may result in differences in the processing behavior of PVC. For example a change in plasticizer may result in higher melt temperature, higher pressure build-up in extruders, streaks or surface distortions in extrudates.

The influence of plasticizers on the fusion time and fusion temperature is related to their efficiency. The fusion characteristics are a measure of the ability of a plasticizer to fuse with the polymer to give a product of maximum elongation and softness. Fusion properties are often measured as a processing temperature (the temperature to which the plasticizer and polymer must be heated in order to obtain these properties). Ease of fusion is related to plasticizer polarity and molecular size. The closer the polarity of a plasticizer is to PVC, the greater the attraction to the PVC polymer. The polarity of the plasticizer is determined by both acid type and alcohol chain length. Molecular size also makes a key contributor and explains why molecules of similar polarity can show different fusion properties. The smaller the plasticizer molecule the easier it is for it to enter the PVC matrix; large molecules require more thermal energy to establish the desired interaction with the polymer. Since branching influences molecular size, this too contributes to fusion properties.

2.3.3 The Structure of PVC

Radical polymerization of VC results in the formation of macromolecules containig a number of different isomeric forms and structural defects.these factors are of practical importance, since they effect the color, thermal stability, crystalinity, processing and mechanical properties of the finished material.

Typical PVC moecules contain approximately 1000 vinyl chloride monomer units, joined in predominantly head-to-tail fashion(other structural arrangements are considered to be defects) [83].In this structure, chlorine atoms are inert because of the strong bond between C and Cl atoms. However commercial PVC contains minute amounts (about 1%) of labile chlorines (defect structure). Allylic chlorines and tertiary chlorines at branching points are considered to be labile chlorines. Amount of labile chlorines depends on polymerization conditions of vinyl chloride. Head-to-head monomer addition and following chein transfer to monomer may lead to allylic chloride and branch defects. Branching may also be result of chain transfer to the monomer after backbiting and chain transfer to PVC [84].

2.3.4. Chemical Modification of PVC by Grafting

2.3.4.1. PVC Grafting By ATRP

Chemical modification of PVC by grafting reactions on the base polymer has been an area of great interest. Graft copolymerizations have been carried out mainly to raise the heat-distortion temperature or impact strength and to improve the termal stabiliy of the polymer. These studies have involved cationic, anionic, and free radical grafting techniques; of these the free radical technique has been the most widely studied.

Atom transfer radical polymerization can also been used to prepare grafted PVC. There are a few studies to prepare grafted PVC by ATRP. In these sudies PVC firstly is copolymerized randomly with comomomer (1 mol - % compared to vinyl chloride) and this copolymer can act as a macroinitiator for an ATRP polymerization. Later, the second monomer is added to prepare graft polymer.

There is a patent for producing self-placticized graft PVC industrially. The concept valuated is production of a self plasticized graft PVC by a two suspension copolymerization process. This economic evaluation is based on a product initially produced when exploring the capabilities of controlled polymerization. The process involves copolymerization of vinyl chloride with vinyl chloroacetate in a standart peroxide initiated VCM suspension polymerization producing a copolymer that can

act as a macroinitiator for an ATRP polymerization. Without isolation of the product, a second vinyl monomer, butyl acrylate is added to the suspension polymerization swelling the PVC particle and is grafted from the macroinitiator ina core/shell type of copolymerization using a copper based ATRP catalyst. This particular study is a model for grafting from commodity polymers and should also shed some light on the cost of using existing polymerization equipment and commercially available macroinitiators for controlled polymerization.

More recently, Percec and coworkes have succeeded grafting of styrene and butyl methacrylatemonomers from labile chlorines of PVC in diphenyl ether at 120 ^{o}C [16-17].

The occurance of undesrable side reactions, dehydrochlorination , has been a persistent problem in the stuudies on the chemical modification of PVC. In most cases it has not been possible to prevent these side reactions from occuring, though their levels may have remained witin tolerable limits.

3. EXPERIMENTAL PART

3.1. Chemicals Used

Commercial 2-ethyl hexylacrylate (Fluka) was rendered inhibitor-free by shaking with 0.1 M NaOH solution prior to the graft copolymerization. All the other chemicals; the suspension stabilizer, α-methyl cellulose (Aldrich), polyvinyl chloride (M_n: 22.000 polydispersity index, PDI: 1.95, Aldrich) and solvents were analytical grade commercial products. They were used without any further purification.

Cuprous bromide: this was freshly prepared by the method described in the literature [24].

Preparation of hexylated TETA: The ligand H-TETA [(hexacis 1, 1,4,7,10,10 hexyl 1, 4,7,10 tetraaza decane by IUPAC]: this was prepared by reaction of 1-bromo hexane with triethylene tetramine as reported elsewhere [28].

3.2. Graft Copolymerization of 2-ethyl hexylacrylate in Aqueous Suspension

In a 250 mL volume of three-necked flask, equipped with a reflux condenser and a nitrogen inlet, there was added 20.8 mL (0.1mol) 2-ethyl hexylacrylate (inhibitor free) and 3.125 g PVC (0.05 mol repeat units) under nitrogen atmosphere. The flask was placed in a thermostated oil bath at 130 ^{o}C. The mixture was stirred with a magnetic bar until a clear solution has obtained (about 40 min.). The temperature of the oil bath was adjusted to 90 ^{o}C. Meanwhile a stock solution of α-methyl cellulose was prepared by dissolving 0.5g of α-methyl cellulose in200 mL distilled water. A 100 mL of this solution was heated to boil and added to the flask while stirring vigorously, under nitrogen flow. The stirring rate was adjusted to 1000 rpm.

The ligand H-TETA (0.325 g, 5×10^{-4}mol) and CuBr (0.071 g, 5×10^{-4}mol) were added and the nitrogen inlet was closed. The mixture was stirred for a predetermined time interval. Droplets of the polymer solution became green in about 5 min. and turned to be brown. Kinetics of the grafting was followed by repeating this procedure for various time intervals. The reaction content was poured into 500 mL of cold water and filtered. The gelly-like flakes were filtered and dispersed in 30 mL acetic acid and filtered. The crude products were washed with 30 mL ethanol. The products were finally dried at 40 ^{o}C under vacuum for 48 h and weighed.

Those graft products were light green in color due to the copper salts remaining. For the viscosity, NMR and GPC analyses, colorless samples were obtained separately by the procedure described below.

3.3. Characterization

Molecular weight of the graft samples were monitored by Gel Permeation Chromatography (GPC). Before the manipulations, the copper residues in the samples were removed by reprecipitation twice in acetic acid-water mixtures (1/1). Thus about 0.2 g light blue samples were dissolved in 10 mL of THF and precipitated 40 mL of acetic acid-water mixtures. The samples dried under vacuum at 40 ^{o}C for 24 h, were white and pure enough to use in NMR and GPC measurements.

Nuclear Magnetic Resonance(^{1}H-NMR) spectra were recorded with a Bruker 250 MHz spectrometer, using DMSO-d6 as solvent and TMS as internal standart.

Gel Permeation Chromatograms (GPC) were recorded by an Agillant 1100 series instrument consisting of a pump, a refractive index-detector and Waters Styrogel (HR4, HR3, HR2) columns. THF was used as eluent at a flow rate of 0.3 mL / min.

Differential Scanning Calorimetry (DSC): The glass transition temperatures (T_g) of the polymers were measured by TA DSC Q10 model instrument in flowing nitrogen atmosphere at a heating rate of 10 ^{o}C /min.

Infrared spectra were taken by Perkin Elmer Spectrum One FT-IR Spectrometer.

Viscosities were determined by capillary viscometer technique using Ubbelohde viscometer.

4. RESULTS AND DISCUSSION

A few percent of labile chlorines existing in commercial PVC serve as initiation sites for atom transfer graft copolymerization (Figure 4.1), as reported previously [18].

Here we present graft copolymerization of (EHA) with PVC in an aqueous suspension by ATRP. Interestingly, PVC (M_n = 22.000 Da) is soluble in EHA at temperatures around 130 °C. Notably, upon cooling to room temperature, the solution becomes gelled again.

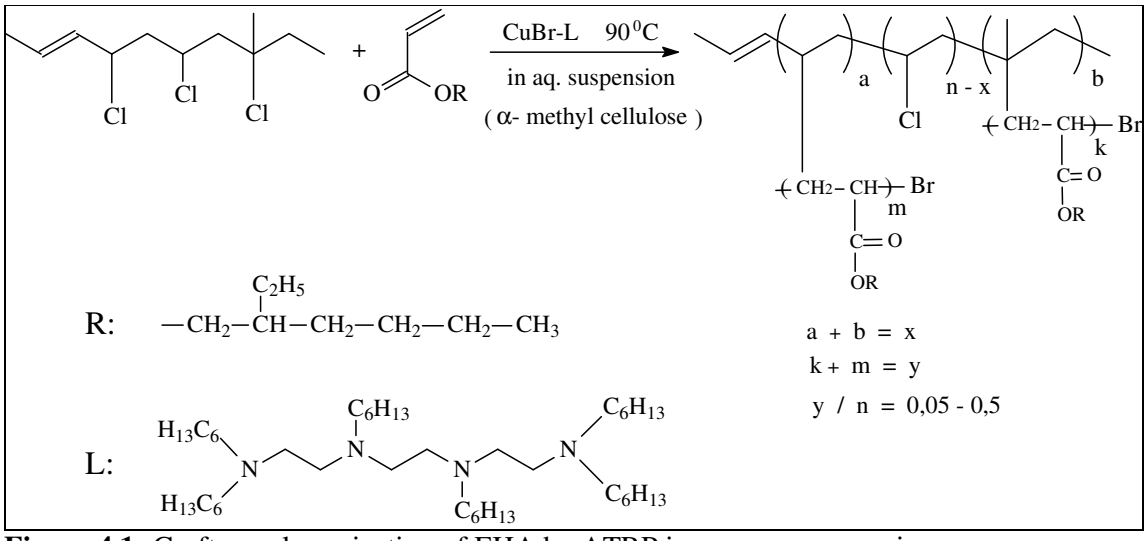


Figure 4.1: Graft copolymerization of EHA by ATRP in aqueous suspension

When the gel is heated up to 100 °C, a homogeneous solution is obtained, again implying physical gelation. The solubility of PVC in the monomer at elevated temperatures allows performing graft copolymerization in a suspension without the use of additional solvent. The monomer, EHA was chosen to induce a plasticizing effect due to the low T_g of the corresponding homopolymer (-84 °C) and its compatibility with PVC.

4.1 Grafting

A viscous solution of PVC in EHA is quite dispersible in hot water containing 0.25 % of α-methylcellulose as a suspension stabilizer. The grafting is effected by the addition of CuBr and the ligand (in 1/ 1 /50 [CuBr] / [H-TETA] / [EHA] molar ratios) to the suspension stirred at 90 ^{o}C.

An immediate coloration of the organic phase takes place in 5 minutes. Only slightly white turbidity is observed in the aqueous phase throughout the polymerization. This behavior indicates that CuBr is being extracted to the organic phase by H-TETA, almost quantitatively, at this temperature, in accordance with our previous report [24].

This may be considered a visual confirmation of true suspension conditions provided by H-TETA.

At the end of predetermined reaction times, the graft product in the organic phase was precipitated in acetic acid which is nonsolvent for PVC and EHA homopolymer. Acetic acid was chosen to remove unreacted monomer as well as copper residues without changing particle shapes of the graft products.

However the products isolated so were still greenish.

4.2 Kinetics

The graft yields (Figure 4.2) based on the total monomer consumption indicate nearly first-order kinetics with a rate constant of $k = 4.2 \pm 0.24 \times 10^{-6}$ s^{-1} for the yields below 126 %. This can be ascribed to controlled chain growth for low graft yields. However, at high conversions, the semilogarithmic plot greatly deviates from linearity. Such a deviation from the first order is common for ATRP at high conversions. A molecular weight/conversion plot of the grafting (Figure 4.3) also gives nearly linear relationship at low conversions but deviates above 20 % monomer consumption. The obtained PDIs are rather high (Table 4.1) in comparison with those for the homopolymerizations in ATRP. This might be largely due to high PDI

(1.95) of the starting PVC. Nearly spherical particles were obtained for the reaction times longer than 6 h, whereas shorter times resulted in sticky and shapeless particles, because of the presence of a large amount of unreacted monomer.

Table 4.1: Physical characteristics of PVC-EHA graft copolymers

Entry	*React. Time (h)*	*Graft yield (%w /w)*	M_n [a]	M_w	*PDI*	η_{inh} [b] *(dL /g)*
1	0	0.0	22.000	43.000	1.95	0.278
2	1	14.0	36.900	69.700	1.88	0.285
3	2	16.1	38.100	71.600	1.87	0.287
4	3	19.2	40.000	72.200	1.80	0.310
5	5	33.5	40.700	71.900	1.77	0.318
6	8	69.0	55.600	110.600	1.99	0.362
7	16	126.3	74.500	170.600	2.29	0.470
8	24	146.0	76.300	171.000	2.24	0.477[a]

[a] from GPC [b] in DMF Soln. (1g/ dL) at 25 ± 1 °C

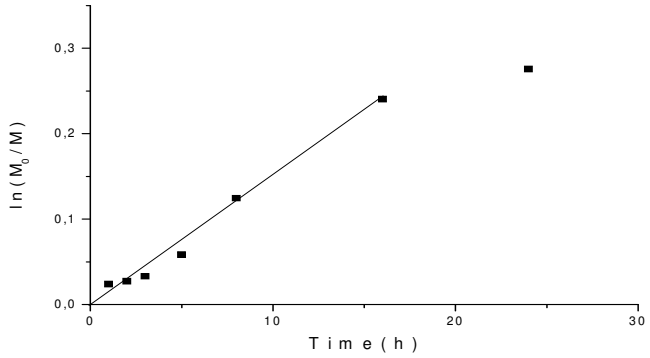


Figure 4.2 : First-order kinetic plot for the graft copoly- merization of EHA in an aqueous suspension (at 90 8Cfor a 1/1/50/100 [H-TETA]/[CuBr]/[PVC]/[EHA] molar ratio).

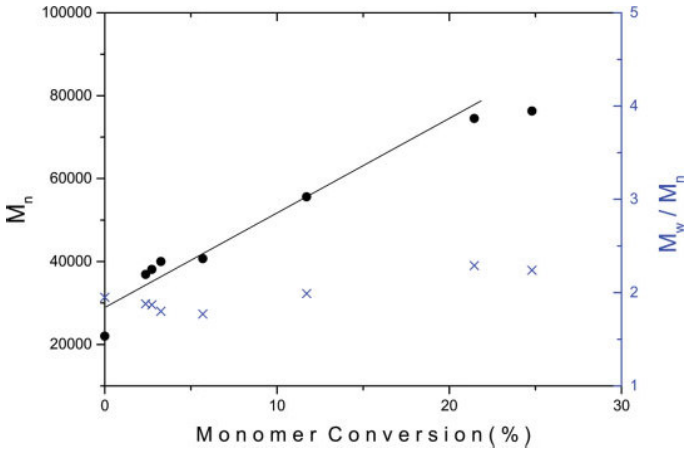


Figure 4.3 : Mn versus (.) the monomer conversion for the grafting and (x) the variation of the PDI with the conversion.

4.3 Structure

Copper-free test samples for GPC analyses and spectral measurements were prepared separately by reprecipitation of the THF solutions in acetic acid twice. Simple

evidence for the incorporation of graft chains into the PVC structure is the characteristic stretching vibration bands of the carbonyl group of EHA component appearing at 1723 cm^{-1} in their FT-IR spectra (Fig.3). In the spectra, other typical peaks of each component are also observed.

The ^{1}H-NMR spectrum (Fig.4) of the graft copolymer sample (from 5-h reaction with a 2/1 monomer ratio) shows proton signals of both PVC and EHA polymer.

Thus, the broad multiplet located in 3.7-4.7 ppm range, represents methine (-CH-Cl) protons of PVC and $–OCH_2$- protons of the EHA grafts. Two methyl protons of 2-ethyl hexyl units give a triplet around 1 ppm. The multiplet in 1.8-2.6 ppm is due to methylene protons of PVC and –CH-COO- protons of polymerized EHA component. The multiplets at 1.2-1.7 ppm arise from all the other CH_2 protons of 2-ethyl hexyl group.

The integral ratio of the multiplets at 3.7-4.7 ppm to those of the other proton signals is 0.31. By neglecting end-group effects and effects of chemical shifts at the graft points, we find that this corresponds to 31.2 % (w/w) of grafting. This value fairly agrees with that obtained by mass increase (33.5 %).

The copper-free samples give no soluble fraction in ethyl acetate, and this indicates the absence of the free-homopolymer of EHA, this is similar to the case for the grafting in 1, 2-dichlorobenzene as described before [15]. This is an important aspect of ATRP graft methodology in comparison with the other techniques yielding free-homopolymers as byproducts. Indeed, GPC traces (Fig.5) represent unimodal peaks for each sample, and this is direct evidence for the presence of only grafted species in the samples.

We have also studied effect of different monomer ratios (i.e. [EHA] /[PVC] = 1 /1; 1.5 /1; 2 / 1; 2.5/1; 3 /1). The graft yields were almost the same for the reaction times shorter than 5 h. However, the kinetic plots showed great deviations from first order kinetics for the monomer ratios lover than 2 /1. For instance, for the case of 1 /1 ratio, the graft yield was 52 % after 6 h. However, the yield did not change practically for rolonged reaction times. This must have been due to rapidly increasing viscosities inside the droplets. For the higher monomer ratios, the droplets were still

soft and sticky, owing to unreacted monomer absorption. However, the presence of unreacted monomer is not desirable in suspension polymerization processes. For this reason, the monomer ratio of 2 /1 was chosen as the optimum ratio.

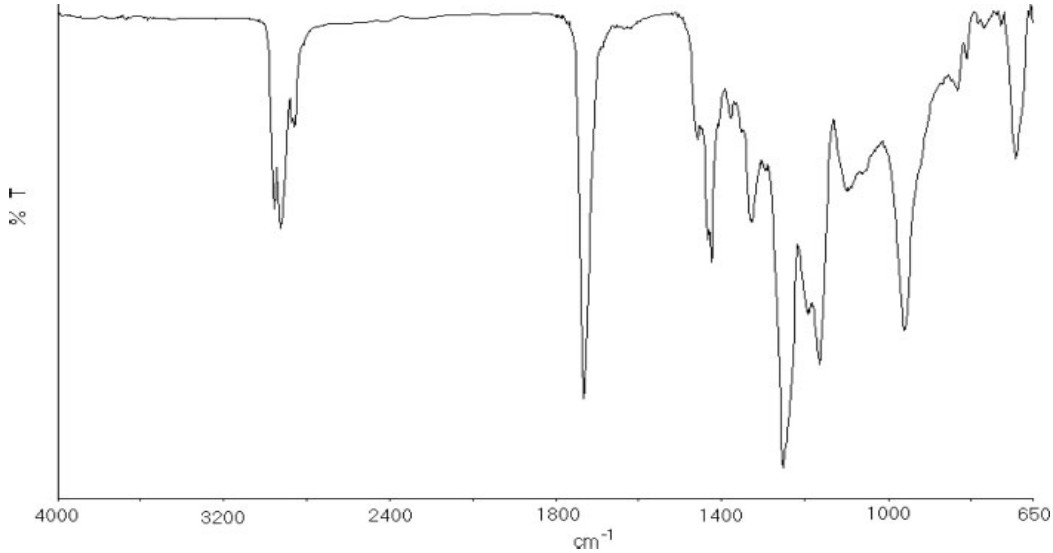


Figure 4.4: FTIR spectrum of a graft copolymer sample.

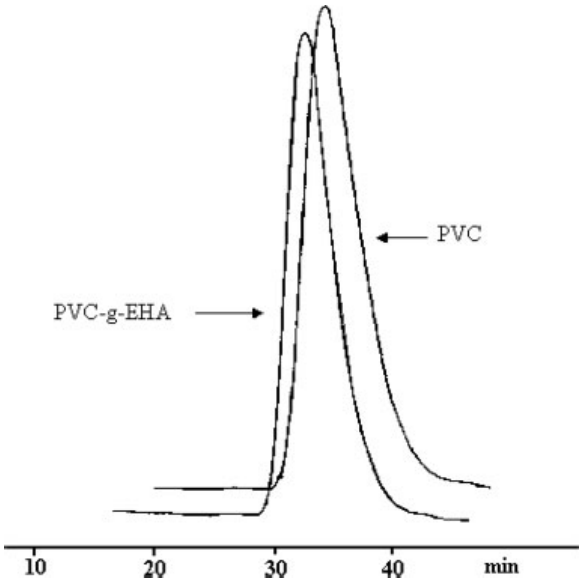


Figure 4.5: GPC traces of PVC and a graft copolymer sample

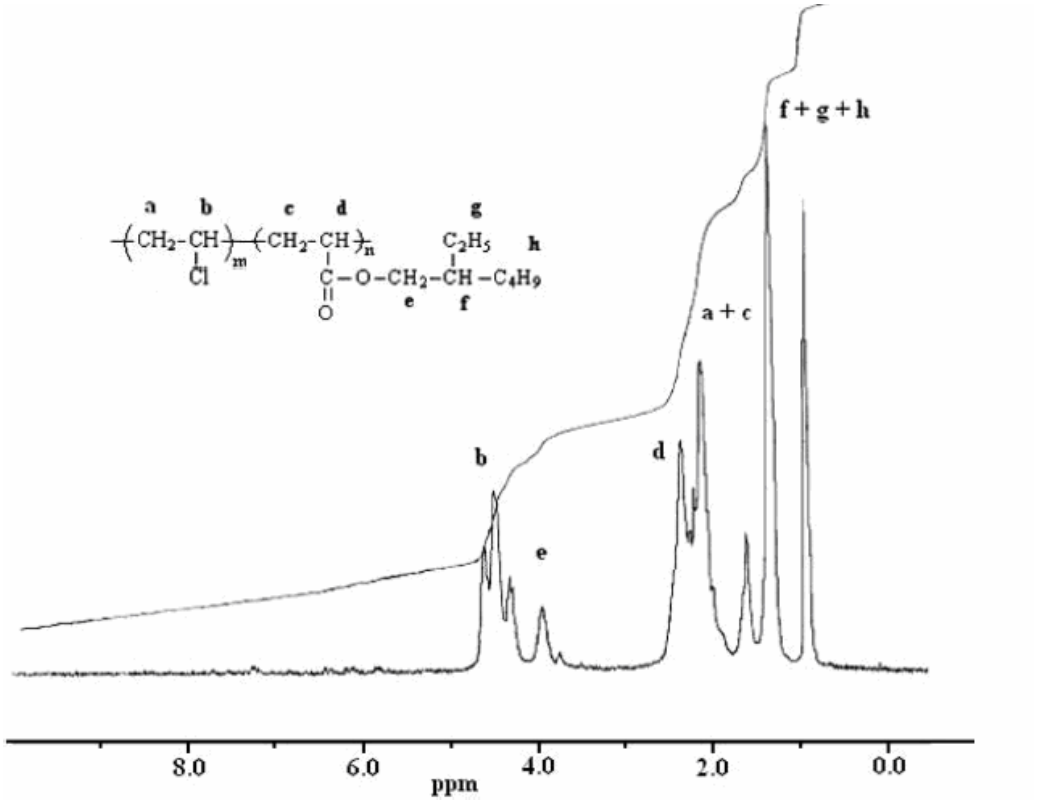


Figure 4. 6: 1H NMR spectrum of a PVC-g-EHA sample

What we expected by grafting with EHA was to bring plasticizing effect to the PVC. To inspect such an effect, we compared DSC traces of PVC and one of the graft samples (the product of 3 h of reaction; Fig.6). T_g of the PVC at 85 ^oC shifts to 58 ^oC after grafting (upper curve). Although it needs further detailed studies for clarifying such effects, this result shows that the graft segments are reasonably compatible with PVC and the plasticizing is being well established.

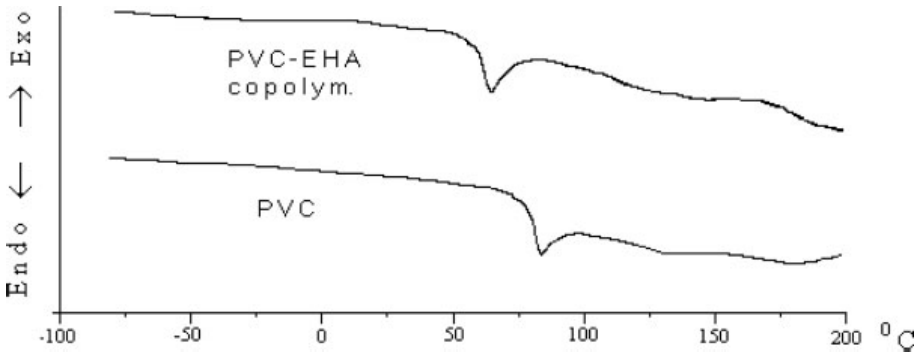


Figure 4.7: DSC curves of PVC and a graft copolymer sample

5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, solubility of PVC in EHA at elevated temperatures makes the graft copolymerization of this monomer possible from the labile chlorines of commercial PVC in an aqueous suspension without the use of an organic solvent.

Beaded products can be obtained at high graft yields by proper adjustment of the stirring rates and the stabilizer concentrations. This work reveals that the presented method seems to be applicable to the large-scale grafting of PVC in aqueous suspensions.

From an industrial viewpoint, the preference is the highest graft yields to minimize unreacted monomer to be recovered. However, the loss of the chain-growth control at high graft yields can be considered as a disadvantage of this procedure. Nevertheless, this procedure might still be useful, even in this case, because the grafting is achieved without formation of free homopolymers, which cannot be attained by other methods.

The only drawback of this procedure is greenish graft products, a common problem in copper-mediated ATRP.

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