ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

GRAFT COPOLYMERIZATION OF N-BUTYL ACRYLATE AND 2-ETHYL HEXYL ACRYLATE FROM LABILE CHLORINES OF PVC BY ATRP

M.Sc. Thesis by

Mesut ÖZLEM

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

Supervisor : Prof.Dr. Niyazi BIÇAK

JANUARY 2004

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Mesut ÖZLEM
(515001118)

Date of submission : 22 December 2003
Date of defence examimation : 13 January 2004

Supervisor (Chairman) : Prof.Dr. Niyazi BIÇAK

Members of the Examining Committe : Prof.Dr. Yusuf YAĞCI (İTÜ)

Prof.Dr. Tunccer ERCİYES (İTÜ)

JANUARY 2004

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PVC' NİN LABİL KLORÜRLER ÜZERİNDEN N-BUTİL AKRİLAT VE 2-ETİL HEXİL AKRİLAT İLE ATRP YOLUYLA GRAFT KOPOLİMERLEŞMESİ

YÜKSEK LİSANS TEZİ

MESUT ÖZLEM
(515001118)

Tezin Enstitüye Verildiği Tarih : 22 Aralık 2003
Tezin savunulduğu Tarih : 13 Ocak 2004-02-08

Tez Danışmanı : Prof.Dr. Niyazi BIÇAK

Diğer Jüri Üyeleri : Prof.Dr. Yusuf YAĞCI (İTÜ)

Prof.Dr. Tuncer ERCİYES (İTÜ)

OCAK 2004

ACKNOWLEDGEMNT

This master study has been carried out at Istanbul Technical University, Polymer Science and Technology Department of Science & Letter Institute.

I am indebted to my supervisor Prof. Dr. Niyazi BIÇAK for being helpful and sharing his deep knowledge and experiences throughout my research.

I would like to thank to Assoc.Prof.Dr. Filiz ŞENKAL, Mustafa GAZİ, Bünyamin KARAGÖZ, and İnan KÜÇÜKKYA for their help during my study.

Finally I would like to thank to my family. I owe much to my family for all their self-sacrifice, patience and support during all my education.

December 2003 Mesut ÖZLEM

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LIST OF SYMBOLS

$\mathbf{T_g}$	**:** Glass transition temperature of polymer
W	**:** Weight fraction of the corresponding monomer in the copolymer
A, B	**:** Two different types of repeating unit in the copolymer
ε	**:** Grafting efficiency in %
$\mathbf{U_G}$	**:** Grafting sucess in %
π	**:** degree of grafting in %
$\mathbf{M_n}$	**:** Number average molecular weight of polymer
$\mathbf{M_w}$	**:** Weight average molecular weight of polymer
$\mathbf{M_w/M_n}$	**:** Molecular weight distribution
$\mathbf{k_{act}/k_{deact}}$	**:** Rate constants of activation and deactivation steps of the initiation in radical polymerization
$\mathbf{k_t/k_p}$	**:** rate constants of termination and propagetion step in radical polymerization respectively
I, M	**:** Initiator and monomer respectively

GRAFT COPOLYMERIZATION OF N-BUTYL ACRYLATE AND 2-ETHYL HEXYL ACRYLATE FROM LABILE CHLORINES OF PVC BY ATRP

SUMMARY

Poly(vinyl chloride)(PVC) is one of the most important commodity plastics. Due to low, flow characteristics and brittleness of pure PVC it needs the use of relatively large amount of plasticiser.

An alternative solution, internal plasticisation involves of copolymerisation of vinylchloride monomer with vinyl acetate lowering the glass transition temperature. Grafting has also been considered to obtain processible material. This has been achieved by treating with diethyl dithiocarbomate salt and following irradiation or heating in a monomer to be grafted .

The new emerging polymerization technique, atom transfer radical polymerization(ATRP) yielding controlled/living chain growth has been used grafting of some acrylate monomers from PVC. But this has been achieved any by means of suitable comonomer having replaceable halogen atoms. Because such a grafting from the chlorine atoms on PVC itself has been described as too inert to initiate ATRP. However some authors C. Bonnans et al demonstrated that small amounts (i.e. less than 1 %) of labile chlorine atoms on the main chain of PVC. This study will be devoted to grafting of poly acrylate esters from the labile chlorine atoms by copper-mediated ATRP.

Trace amounts of labile chlorines present in PVC structure have been demonstrated to effect as initiation sites for preparing graft copolymers of PVC by copper-mediated Atom Transfer Radical Polymerization (ATRP) methodology. High grafting yields can be attained in graft copolymerization of n-butyl acrylate (%161.8) and 2-ethyl hexyl acrylate (51.2 %) in 7.5 h of reaction periods. In both cases the grafting proceeds with first order kinetics with respect to the monomer concentrations, which is typical for ATRP. GPC (Gel permeation chromatography) traces of the resulting products do not exhibit additional peaks attributable to free homopolymer formation. The procedure presented offers an efficient pathway for preparing self-plasticised PVC structures.

PVC' NİN LABİL KLORÜRLER ÜZERİNDEN N-BUTİL AKRİLAT VE 2-ETİL HEXİL AKRİLAT İLE ATRP YOLUYLA GRAFT KOPOLİMERLEŞMESİ

ÖZET

Poli(vinil klorür) en önemli plastik eşyalardan birisidir. PVC düşük akış özellikleri ve kırılganlığı sebebiyle büyük miktarlarda plastikleştiricilerle beraber kullanılmak zorunda.

Vinil klorür monomeri vinil asetat ile kopolimerleştirilerek camsı geçiş sıcaklığı düşürülür. Graft kopolimerleşme ile de işlenebilir malzemeler elde edilebilir. PVC' yi dietil ditiokarbomat tuzu ile etkileştirip daha sonra bir monomerde radyasyonla veya ısıtarak graft kopolimerleşme yapılabilir.

Yeni bir polimerleşme tekniği olan atom transfer radikal polimerizasyonu (ATRP) ile bazı akrilat monomerleri PVC ile graft kopolimerleşmesi yapmakta. ATRP kontrollü/yaşayan zincir büyümesi verir. Fakat PVC' nin kendisi ATRP' yi başlatmak için çok inert. Bunun için PVC' nin yapısında halojenini kolayca verebilecek uygun bir komonomer kullanılmakta. Bununla beraber bazı yazarlar tarafından (C. Bonnans) PVC'nin ana zincirinde %1'den daha az miktarda labil klorür olduğu tespit edilmiştir. Bu çalışmada PVC'nin labil klorürler üzerinden poli akrilat esterleri ile ATRP yoluyla bakır varlığında graft copolimerleşmesi konu edinmekte.

PVC'nin yapısındaki eser miktardaki labil klorürler, bakır varlığında ATRP yoluyla graft kopolimerleşmede başlatıcı olarak etki etmekte. Yüksek graft verimi ile n-butil akrilat (%161.8) ve 2-etil hexil akrilatın 7.5 saatlik reaksiyonları sonunda graft kopolimerleri elde edildi. Her iki durumda da graft kopolimerleşme, ATRP'den beklendiği gibi birinci dereceden kinetiğe sahip. GPC (Jel Geçirgenlik Kromotografisi) sonuçları homopolimer oluşumunu gösteren ikinci pike sahip değil. Bu prosedür self-plasticized PVC hazırlamak için etkili bir yöntem.

1. INTRODUCTION

Copper mediated Atom Transfer Radical Polymerization (ATRP) has been one of the most efficient methods of controlled / living polymerizations, since it was introduced by Matyjaszewski [1]. Controlled chain growth and living nature of the ATRP method make it very useful for preparing well-defined block and graft copolymers [2, 3]. Another advantage of the method over common radical initiation methods is that only negligible homopolymer formation is observed when employed in graft copolymerizations [4,5]. Because of this fact the method is also very efficient in grafting from solid surfaces without sacrifying a vaste amount of monomer yielding homopolymer as a by-product [6-8].

This work is aimed at preparing graft copolymer of PVC by ATRP method. Main purpose of the grafting on PVC is to impart plasticising effect. Mixing with a liquid plasticiser and self-plasticizing by copolymerization of vinyl chloride with vinyl acetate are commercially important methods of plasticizing of PVC [9].

Partial modification of PVC by sodium diethyl dithiocarbamate and subsequent heating [10] or UV irradiation [11, 12] have also been demonstrated to be efficient in grafting of acrylate and N-vinyl pyrrolidone monomers from PVC.

Graft copolymer of PVC has also been prepared ATRP method starting from a PVC copolymer possessing few percent of vinyl chloroacetate segments [13]. The chloroacetyl groups of the polymer have been used as initiation sites for ATRP, due to inertness of chlorine atoms of PVC itself for the ATRP initiation. Indeed PVC differs from single alkyl halides that chlorine atoms of PVC do not readily undergo substitution reactions, in ordinary conditions. In drastic conditions dehydroclorination takes place to give conjugated polyene structures. However commercial PVC contains minute amounts (around 1%) of labile chlorine atoms which are responsible for initiation of the thermal dehydrochlorination [14, 15]. 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 chain 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 [16]. Those labile or active chlorines have shown to be very useful for cationic graft co-polymerization with some vinyl monomers including isobutylene, using dialkyl aluminum catalyst [17]. The same catalysis mechanism has been employed for quantitative allylation via active chlorines of PVC [18]. Caraculacu et.al suggested an analytical procedure for determination of the labile chlorines in PVC [19]. The method relies on substitution with sodium salt of dithiocarbonic acid through the labile chlorines of PVC and amount of replaced chlorines is assigned by determination of sulfur content of the resulting product. However reliability of the method is doubtful. Because the labile chlorine content found is not constant and increases (up to 4.0 %) with contact times of the reagent.

In this study we have investigated utility of ATRP in grafting of butyl acrylate and 2- ethyl hexyl acrylate by initiation from the labile chlorines of PVC. More recently Percec and coworkers [20, 21] have succeeded grafting of styrene and butyl methacrylate monomers from labile chlorines of PVC in diphenyl ether at 120 ^{0}C. In the present work we have studied graft copolymerization of n-butyl acrylate (BA) and 2-ethyl hexylacrylate (EHA) from labile chlorines of PVC by copper mediated ATRP, using 1, 2- dichlorobenzene at 90 C. Hexylated triethylenetetraamine (H-TETA) was used as ligand which forms organo-soluble copper complexes. This ligand provides entirely homogeneous ATRP conditions [22]. In the study, kinetics of the copolymerization was investigated and structures of the resulting of copolymers were confirmed by NMR spectroscopy.

2. THEORITICAL PART

2.1. Graft Copolymers

2.1.1. Background

Polymers which contain more than one type of structural unit are called as copolymers [23]. The objective is usually to achieve a modified set of physical properties, not achievable in economic fashion, or at all, from a homopolymer. For example poly (vinyl chloride) can be made more easily soluble and lower softening by copolymerization with vinyl acetate, polyacrylonitrile more dyeable with vinyl pyridine, and polyisobutylene sulfur-vulcanizable with isoprene [24].

Copolymerization has often been seized on as a panacea for any adverse property of a homopolymer, but the reality is usually that one or more valuable properties of the homopolymer are compromised, e.g., a reduction of brittleness may also be accompanied by a decrease in tensile strength, chemical resistance, surface hardness, and melting point, not all or any of which may be tolerable. The synthetic polymer chemist must decide, usually in collaboration with nonchemists who must market the product, which losses and how much can be tolerated. The effect of copolymerization on polymer properties is perhaps seen fundamentally in its effect on crystalinity and glass-transition temperature T_g. Because the development of crystalinity is due to molecular symmetry and/or intermolecular association, it is not surprising that simple copolymerization should reduce or obliterate an ability of polymer chains to crytallize. Similarly, the T_g in amorphous and crystalline polymers is modified by copolymerization, but in a different way. The general tendency is for T_g in a copolymer to lie between the glass-transition temperatures of the parent homopolymers; and for random (further defined below), a weighted contribution of each parent is sometimes observed, according to the relationship 2.1 [24],

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \qquad (2.1)$$

where T_{g1} and T_{g2} are in degrees absolute (K) and W_1 and W_2 are the weight fractions of the corresponding monomers in the copolymers.

There are several categories of copolymer, each being characterized by a particular form of arrangement of the repeating units along the polymer chain. For simplicity, these different categories will be illustrated here by copolymers containing only two different types of repeating unit (A and B) (Fig. 2.1) [25].

The copolymer with a relatively random distribution 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 sequences 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. In a graft copolymer, the distinguishing feature of the side chains is constitutional, i.e., the side chains comprise units derived from at least one species of monomer different from those that supply the units of the main chain. In a graft copolymer a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain or graft. In graft copolymers the backbone and side chains may both be homopolymeric, the backbone may be homopolymeric and side chains copolymeric or vice versa, or both backbone and side chains may be copolymeric but of different chemical compositions [26].

2.1.2. Nomenclature

Two types of nomenclature are recommended; namely systematic and simplified. The systematic naming of graft copolymers can be used for any graft copolymer, however complex its structure. The alternative, more concise nomenclature is suitable only for graft copolymers with relatively simple structures. The simplest graft copolymer can be represented by A_k-graft-B_m, and its corresponding systematic name is polyA-graft-polyB, or simplified, graft-copoly(A/B). For example, polybutadiene-graft-polystyrene or graft-co-poly(butadiene-styrene) or poly(butadiene-g-styrene) is the name for polystyrene grafted to polybutadiene [26].

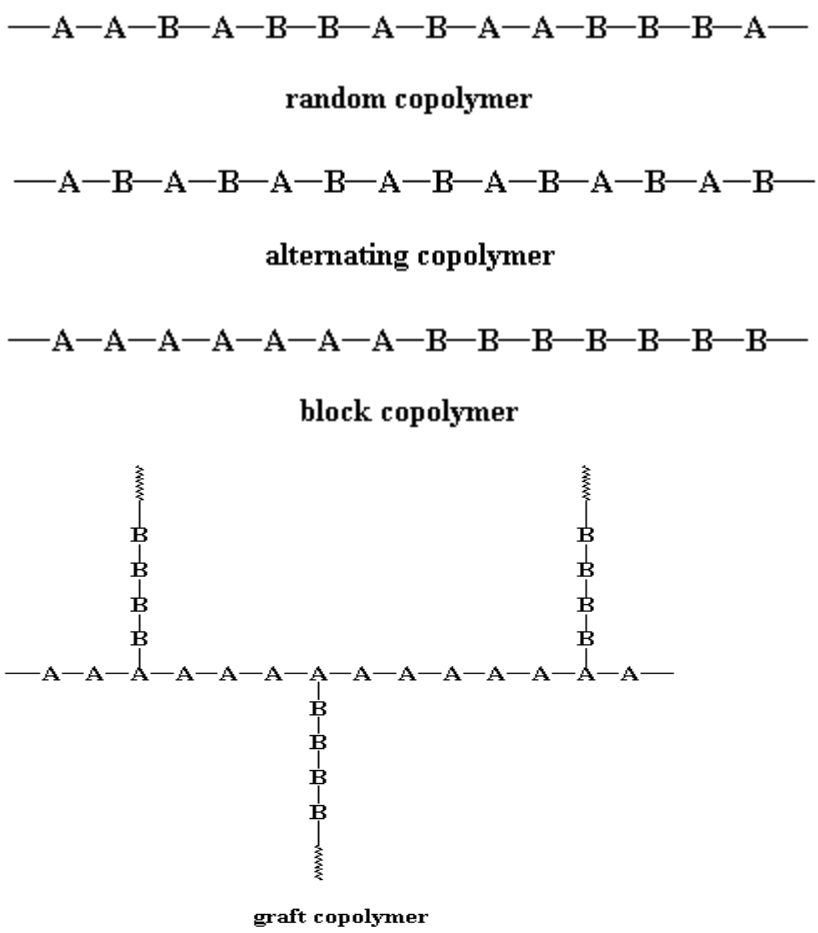


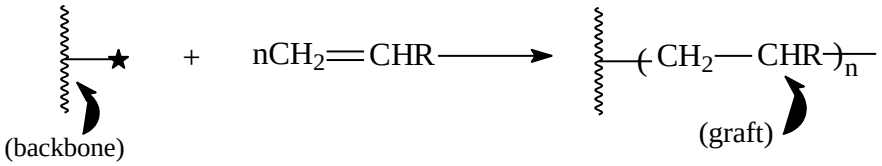
Figure 2.1 Representation of copolymers.

2.1.3. Principles of Graft Copolymer Synthesis

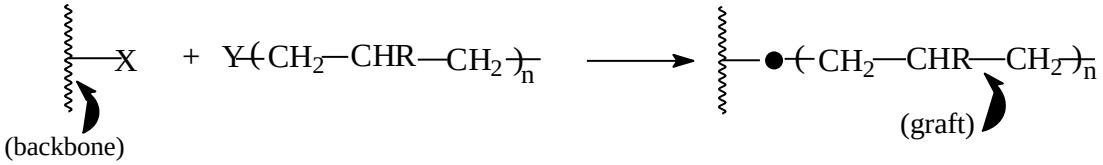
Graft polymerization is a common method for modifying polymer properties. Because the main chain and the branch chain are usually thermodynamically incompatible, most graft copolymers can be classified as multiphase polymers in the solid state, analogous to polymer blends, block copolymers, interpenetrating polymer networks [26]. As the interest in graft copolymers has increased over the years, owing to their diversified applications in many different domains, a large variety of methods have been developed for their synthesis [27].

Most of the methods used to synthesize graft copolymers can be classified into three main categories [27]. These processes are grafting from, grafting onto, and grafting through (Scheme 2.1). In these categories graft copolymers can be synthesized by methods involving free-radical polymerization ,ionic polymerization , macromonomers [26], and atom transfer radical polymerization [28].

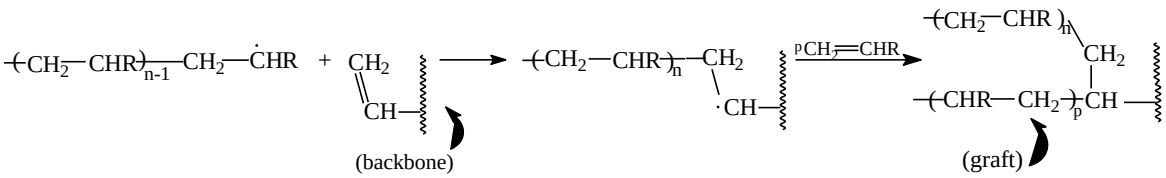
Free-radical polymerization methods are the oldest and most widely used procedures for the synthesis of graft polymers, because they are relatively simple. However, they usually give heterogeneous materials that are difficult to charecteize. Backbones for free- radical graft copolymerization require the presence of an atom or group that can be abstracted or displaced by another radical. Although free-radical graft copolymerization are the simplest, oldest, and most widely used, the least spesific grafting sites and the most poorly defined branches result [26].



Grafting from: a polymer chain carries active sites which are used to initiate the polymerization of a second monomer



Grafting onto: a polymer chain (backbone) carrying randomly distributed reactive functions, is reacted with another molecule carrying antagonist functions located selectively at its chain ends



Grafting through: a growing polymer chain incorporates a pendant unsaturation belonging to another polymer chain or to a macromonomer

Scheme 2.1 Method used for graft copolymer synthesis

Backbones for ionic or condensation polymerization require a reactive site or functional group capable of participating in specific chemical reactions. The products are well-difened and the properties of the branches can be controlled. Ionic living processes have contributed extensively, but they apply to a limited number of cases only. The recent use of macromonomers for graft copolymer synthesis is also quite promising [27]. Atom

transfer radical polymerization (ATRP), can also been used to produce graft copolymers with well-difened structures [28].

2.1.3.1. Grafting From Process

A polymer chain can have initiating sites attached to it, or functions capable of generating such sites. The polymerization of a second monomer can then be initiated from the backbone chain to yield the grafts, provided that initiation occurs by addition to the incoming monomer [29, 30]. This method is quite general. The sites created on the backbone can be of free radical, anionic, cationic, or Ziegler- Natta type. These methods are generally referred to as 'grafting from' processes, to stress that the backbone is made first and that the grafts are grown from it in a second polymerization process. Though these methods are quite efficient in a number of cases, no accurate knowledge of the molecular structure of the graft copolymer formed is provided. The number of grafts is not accessible experimentally, and their length may fluctuate very much within a sample. Moreover, the graft copolymers often contain a fair amount of both homopolymers [27].

In addition to chemical modification or copolymerization to introduce reactive monomer units into the backbone polymers, redox reactions generate radical initiation sites singly on the backbone polymer without any accompanying small radicals that can initiate homopolymerization [26]. In the recent years ATRP is also used to prepare graft copolymers by "grafting from" processes [13, 31-33].

2.1.3.2. Grafting Onto Processes

Grafting may also result from the reaction between a polymer molecule carrying one reactive site at a chain end, and another polymer with attached antagonist functions distributed at random along its chain. In these cases grafting does not involve a chain reaction. However, it does imply that access of the functional chain end to the grafting sites is permitted. This is not obvious, owing to the well known incompatibility between polymers of different chemical natures. Such reactions are best carried out in a common solvent for both constituents to provide homogenity of the reaction medium [27]. An advantage of these methods is that they allow a structural characterization of the graft copolymers formed, as backbone chain and grafts are made separately and can be

characterized individually. Knowing the molecular weight of each of them, and the overall composition of the graft copolymer, it is possible to evaluate the number of grafts per chain, and the average distance between two successive grafts along the backbone. However, the absence of ungrafted homopolymer should be checked for [27]. These 'grafting onto' reactions have gained interest as the ionic 'living' polymerization methods have become commonplace, giving access to polymers fitted with reactive sites at the chain ends. Their domain of application now extends far beyond these eases [34, 35].

2.1.3.3.Grafting Through Processes

If the polymerization of a monomer is performed in the presence of a polymer carrying pendant unsaturations which can participate in the process, then grafting results. However, such reactions can involve formation of links between individual molecules, if a growing site happens to incorporate unsaturations belonging to two (or more) different backbones. Consequently, the process may result in crosslinked material. Measures have to be taken to avoid gel formation if soluble species are required. In any case, these methods cannot be considered as ways of access to tailor-made graft copolymers.Another type of 'grafting trough' process has attracted much interest in recent years. It involves, in a first step, the synthesis of a polymer species with a terminal polymerizable unsaturation, and referred to as a macromonomer (or macromer). Copolymerization of these species with suitable comonomer allows easy access to graft copolymers. Each macromonomer molecule incorporated forms a unit carrying a graft [36, 37]. As the macromonomer is made separately, it can be characterized independently. The backbone chain is formed upon copolymerization of the macromonomer with a suitable comonomer, using free radical initiation, and a rondam distribution of the grafts can be anticipated. An alternative way is to synthesize a polymer having two functions (such as –OH or $–CO_2H$) at one chain end and to build the backbone chain by a step growth (polycondensation) reaction with appropriate bifunctional compounds [38]. In the recent years ATRP is also used to prepare graft copolymers by "grafting through" processes [39-41].

2.1.4. Characterization

It must be assumed that the products of intended graft copolymerizations are mixtures of graft copolymer, unreacted backbone, and homopolymer of the graft. The first step in the characterization of a graft copolymer is the determination of whether any graft copolymerization has occurred and if so, how much. Sometimes careful analysis reveals only mixtures of homopolymers. The first step in the characterization of a graft copolymers the determination of whether any graft copolymerization has occurred and if so, how much [26]. For the successful detailed studies on the grafting reactions the following requirements apply [42]:

1. The boiling point of the monomer should not be lower than the depolymerization temperature of the polymer.
2. Identification of the grafted polymer should be easy.
3. Solubility differences in the products should allow separation of graft and homopolymer.

Furthermore, grafting with monomers preferring combination termination can lead to combination of two growing chains and therefore to crosslinking or doubling of the molecular weight. Purification and analysis of the product has to be done carefully to allow statements on the characteristic values for grafting processes: grafting efficiency ε, grafting success U_G, and degree of grafting π [42].

grafting efficiency in %: $\varepsilon = [(g/(g+h)]x100$ (2.2)

grafting success in %: $U_G = [(p-n)/p]x100$ (2.3)

degree of grafting in %: $\pi = [(g-p)/g]x100$ (2.4)

conclusions can be drawn from the ε-values with respect to reactivity of the various radicals: high ε means low reactivity of the free radical in homopolymerization of monomer. U_G=100% implies that each backbone contains at least one grafted side chain. P is polymer to be grafted, h is homo-polymer formed as by product, g is graft copolymer, and n is non-grafted perpolymer remained unreacted. Most purification methods are based solubility differences between the graft copolymer and impurities. Graft copolymers often act as emulsifiers to reduce the incompatibility of chemically

different polymer species; this makes their separation difficult [26]. Complete characterization of a graft copolymer requires knowledge of the molecular weight and molecular-weight distribution of both backbone and branches, of the number and location of the branches on each macromolecule, and of the chemical composition of both backbone and branches [26]. IR,NMR,GPC, DSC, Viscosimeter are used for characterization.

2.2. Atom Transfer Radical Polymerization (ATRP)

2.2.1. Historical

The polymerization techniques can been classified as conventional polymerization techniques and controlled/living polymerization techniques. The conventional polymerization mechanisms are chain polymerization (free-radical, anionic, and cationic polymerizations) and condensation polymerization. Atom Transfer Radical Polymerization (ATRP) is one of the controlled/living radical polymerization.

The synthesis of polymers with well-defined structure has long been of great interest in polymer science. It was not possible to synthesize these polymers by conventional polymerization techniques.

One of the greatest contributions to this field from synthetic polymer chemists is the development of living polymerization methodology, which allows the preparation of macromolecules with the maximum degree of structural and compositional homogeneity. As a consequence, well-defined polymers with precise molar masses, compositions, topologies and functionalities can be tailor-made. This is a significant step toward the ultimate goal of polymer synthesis, when the design of novel materials is only limited by the imagination of human beings [45].

In the beginning, to synthesize the polymers with well-defined structure living ionic polymerization techniques were employed. But these techniques have some drawbacks [46]. Since Staudinger [47] proposed the concept of a chain polymerization and the basic structure of a polymer molecule eight decades ago, polymer science and technology has experienced an immense development that has revolutionized the look of the world and the life of human beings. Among the numerous polymerization techniques, free-radical polymerization is a widely used process from the viewpoint of

industrial production and applications [48]. This technique is relatively easy to perform since it does not require 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 polymerizations. Moreover, a wide range of functional monomers can be 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. This is caused by the unavoidable fast radical–radical termination reactions. 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 [45]. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is the leading industrial method to produce polymers [49].

The terms of `living polymerization' and `living polymers' were introduced by Szwarc [50] in 1956, although prior to his classical work, Ziegler [51] and Flory [52] also described similar concepts. By definition, a living polymerization is a chain polymerization that proceeds without the occurrence of irreversible chain breaking processes, i.e. chain transfer and termination. For nearly 30 years after Szwarc reported his insightful work, living polymerization of vinyl monomers had been restricted to anionic polymerization systems. But in 1960s and 1970s, several cationic ring-opening polymerizations of heterocyclic monomers were found to proceed with most undesirable side reactions yielding virtually absent of active chain-end. It was discovered that if a dynamic equilibrium between an active and dormant species was formed, it allowed for fine tuning of the polymerization of tetrahydrofuran. This concept of dynamic equilibrium was eventually extended to vinyl monomers in early 1980s, triggering the breakthrough discovery of cationic vinyl polymerizations that proceeded in a controlled fashion under certain restrictive conditions. Since then, extensive investigations of various CLP mechanisms has been conducted. The late 1980s and the entire 1990s witnessed a rapid expansion of the scope of CLP. To date, the major classes of chain polymerization, i.e. anionic, cationic, ring-opening metathesis, coordination and radical

polymerization, can become living or controlled under appropriate conditions. However, most of these polymerization techniques are not exempt from chain transfer or termination reactions. 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 initiated an on going debate over nomenclature [45].

There are several approaches to controlling 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 of dormant species . These reactions are described as controlled radical polymerizations (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 [53].

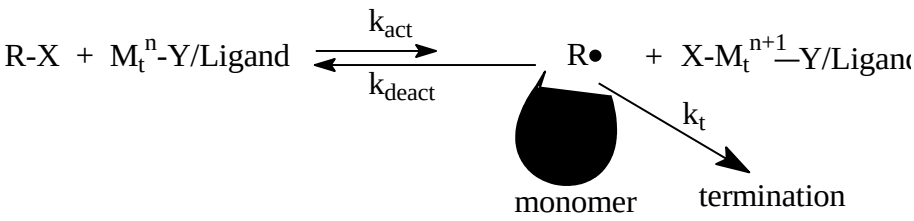
2.2.2. Classification of CRPs

Controlled/living radical polymerization employs the principle of equilibration between growing free radicals and various types of dormant species. There are several approaches to achieve good control over molecular weights, polydispersities and end functinalities in these systems. They can be classified depending on the mechanism and chemistry of the equilibriatio/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 [53].

It is possible to group CRPs into several categories, depending on the chemistry of exchange and structure of the dormant species. Although 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 classified into four different cases: Reversible addition fragmentation chain transfer(RAFT), atom transfer radical polymerization (ATRP), stable free radical polymerization(SFRP), and nitroxide mediated polymerization (NMP) [53].

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 organometallic 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) [28].

The name atom transfer radical polymerization (ATRP) originates from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. A general mechanism for ATRP shown in Scheme 2.2.



Scheme 2.2 Transition Metal-Catalyzed ATRP

2.2.3. Components of ATRP

As a multicomponent system, ATRP is composed of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration[28].

2.2.3.1. Monomers

Various monomers have been successfully polymerized using ATRP: styrenes [13,54], (meth)acrylates [13,55,56], (meth)acrylamides [57], acrylonitrile [59], dienes, and other monomers which contain substituents that can stabilize the propagating radicals.

2.2.3.2. Initiators

Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized.

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 in a living polymerization (2.5) [28]. The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion.

$$DP = [M]_0/[initiator]_0 \times conversion \quad (2.5)$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the 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. Thus far,when X is either bromine or chlorine, the molecular weight control is the best [28]. When the initiating moiety is attached to macromolecular species, macroinitiators are formed and can be used to synthesize block/graft copolymers [60].

2.2.3.3. Catalyst (Transition –Metal Complexes)

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. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)halogen. Fourth, the ligand should complex the metal relatively strongly.

Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system [28].

Transition metal complexes are perhaps the most important components of ATRP and also the most obscure. Molibdenyum [61], chromium [62], rhenium [63], rutheenium [64], iron [65], nickel [66], rhodium [67], paladium [68], and copper [69,70] complexes can been also used as ATRP catalysts.

The first copper-based ATRP system was reported in 1995 [1,71]. Copper catalysts are superior in ATRP in terms of versatility and cost. Styrenes, (meth)acrylate esters and amides, and acrylonitrile have been successfully polymerized using copper-mediated ATRP [69,70,72].

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 appropriate reactivity and dynamics for the atom transfer[73].

Ligands may be even more important than metal centers. Catalytic activity and selectivity is strongly ligand dependent. They can fine-tune selectivities and force the complex to participate in a one electron transfer process needed for ATRP in comparison with the preferred two-electron-transfer process. Ligands serve several purposes. In addition to primary roles of tuning atom transfer equilibrium constants and dynamics as well as selectivities, they control solubilities in the reaction mixture and ensure stability of the complexes in different monomers, solvents, and temperatures. This is especially important in polymerization of acidic monomers and monomers which can strongly complex transition metals such as pyridine-, amide-, or amine-containing monomers. Proper design of ligands is especially important in polymerization under heterogeneous conditions, in water or ionic liquids. Partition coefficients and their dependence on temperature will define the efficiency of the catalyst for ATRP. Ligands may also facilitate the removal and recycling of the catalyst. They may allow the immobilization of the catalyst and also distribution between two phases[28].

Nitrogen and phosphorus ligands are used in ATRP succesfully. Nitrogen ligands have been used in copper- and iron-mediated ATRP [73,74]. For copper-mediated ATRP,

nitrogen-based ligands work particularly well. Both monodentate (e.g., N(nBu)3) and bidentate (e.g., dNbpy) ligands have been applied to iron mediated ATRP. For copper-based ATRP, the coordination chemistry of the transition-metal complex greatly affects the catalyst activity.

2.2.3.4. Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). A solvent is sometimes necessary, especially when the obtained polymer is insoluble in its monomer (e.g., polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. 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 [28].

2.2.3.5. 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 k_p/k_t ratios and better control may be observed at higher temperatures. 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 independent. 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 [28].

2.2.4. Kinetics, Molecular Weight, and Molecular Weight Distribution

ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the

polymerization conditions such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [1,20,70,71]. 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 [60,69,70,72,75,].

ATRP employs an equilibrium between dormant alkyl halids and active propagating radical to maintain a low concentration of active species. The activated radical species can either propagate or be deactivated to reform the dormant species [13].

A general mechanism for ATRP shown in Scheme 2.5. The radicals, or the active species, are generated through a reversible redox process catalyzed by a transition metal complex (M_t^n -Y/Ligand, where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, R-X. This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. 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, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination [77]. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

The kinetics of ATRP is discussed here using copper-mediated ATRP as an example. Mechanistic investigations into ATRP based upon other metal systems are anticipated to yield similar results. According to Scheme 2.2 using the assumption that contribution of termination becomes insignificant due to the persistent radical effect [77,78] (PRE) (especially for the chain-length-dependent PRE [79] and using a fast equilibrium

approximation, which is necessary for observed low polydispersities, the rate law for ATRP can be derived as by Equation 2.6.

$$R_p = k_p [M][P^\bullet] = k_p K_{eq} [M][I]_0 - [Cu^I] / [X - Cu^{II}] \quad (2.6)$$

Figure 2.2 shows a typical linear variation of conversion with time in semilogarithmic coordinates. Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. However, since termination occurs continuously, the concentration of the Cu(II) species increases and deviation from linearity may be observed. For the ideal case with chain length independent termination, PRE kinetics implies the semilogarithmic plot of monomer conversion vs time to the 2/3 exponent should be linear [77]. Nevertheless, a linear semilogarithmic plot is often observed. This may be due to an excess of the Cu(II) species present initially, a chain-length- dependent termination rate coefficient, and heterogeneity of the reaction system due to limited solubility of the copper complexes. It is also possible that self-initiation may continuously produce radicals and compensate for termination [80]. Similarly, external orders with respect to initiator and the Cu(I) species may also be affected by the PRE [81].

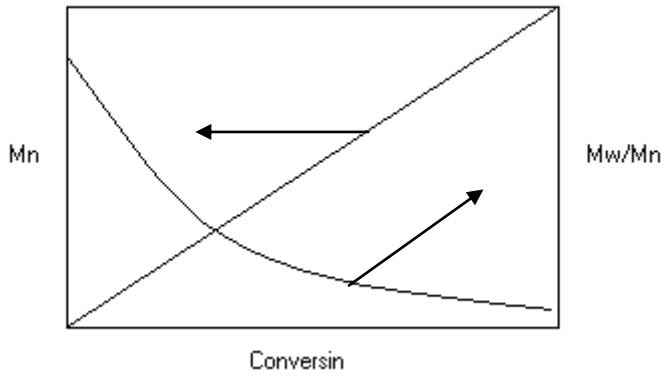


Figure 2.2 Schematic representation of the dependence of the conversion on time in linear and semilogaritmic coordinates.

Results from kinetic studies of ATRP for styrene [82], methyl acrylate (MA) [83], and methyl methacrylate (MMA) [84] under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(l) complex concentrations. These observations are all consistent with the derived rate law (2.6). The

kinetically optimum ratio of ligand to copper in the polymerization of both styrene and MA was determined to be 2:1. Below this ratio the polymerization rate was usually slower, and above this ratio the polymerization rate remained constant. It should be noted that the optimum ratio can vary with regard to changes in the monomer, counterion, ligand, temperature, and other factors [53,84].

The precise kinetic law for the deactivator (X-Cu II) was more complex due to the spontaneous generation of Cu(II) via the persistent radical effect [77,82,83]. In the atom transfer step, a reactive organic radical is generated along with a stable Cu(II) species that can be regarded as a persistent metalloradical. If the initial concentration of deactivator Cu(II) in the polymerization is not sufficiently large to ensure a fast rate of deactivation (k_{deact}[Cu(II)]), then coupling of the organic radicals will occur, leading to an increase in the Cu(II) concentration. This process has been observed experimentally using I H NMR, UV- vis, EPR, and GC-MS techniques [82]. With each radical termination event, 2 equiv of Cu(II) will form irreversibly. Radical termination occurs rapidly until a sufficient amount of deactivator Cu(II) is formed and the radical concentration becomes low enough. Under such conditions, the rate at which radicals combine ($k_t[R^1]^2$) will become much slower than the rate at which radicals react with the copper(II) complex (kdeact[R^1][Cu(II)]) in a deactivation process and a controlled/"living" polymerization will proceed. Typically, a small fraction (~5%) of the total growing polymer chains will be terminated during the early stage of the polymerization, but the majority of the chains (>90%) will continue to grow successfully. If a small amount of the deactivator (~10 mol %) is added initially to the polymerization, then the pro-portion of terminated chains can be greatly reduced [75]. The effect of Cu(II) on the polymerization may additionally be complicated by its poor solubility. Similarly to a typical living polymerization, the average molecular weight of the polymer made by a well-controlled ATRP can be predetermined by the ratio of consumed monomer and the initiator ($DP_n = \Delta[M]/[I]_0$. DP = degree of polymerization) while maintaining a relatively narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$). In addition, precise control over the chemistry and the structure of the initiator and active end group allows for the synthesis of end-functionalized polymers and block copolymers. Well-defined polymers with molecular weights ranging from 1000 to 150 000 have been successfully synthesized. However, termination and other side reactions are also present in ATRP, and they become more prominent as higher molecular weight

polymers are targeted. For example, in the copper-mediated ATRP of styrene, a slow termination process was observed arising mainly from the interaction of the copper(II) species with both the growing radical and the macromolecular alkyl halide. This effect is negligible for low molecular weight polystyrene but could result in an upper limit to styrene ATRP [28].

The rate constants of propagation for acrylates are relatively large, initially, higher polydispersities were observed because several monomer units are added during each activation step. However, with the progress of the reaction, chains become more uniform due to continuous exchange reactions. The polydispersities drop with conversion, as predicted by Equation 2.7. If k_p and the concentrations of initiator and deactivator are known, the rate constant of deactivation can be calculated from the evolution of polydispersities with conversion.

$$M_w / M_n = 1 + ([RX]_0 k_p/k_{deact} [D]) ((2/p)-1) \quad (2.7)$$

The molecular weight distribution or polydispersity (M_w/M_n) is the index of the polymer chain-length distribution. In a well-controlled polymerization, M_w/M_n is usually less than 1.10. Equation (2.7) illustrates how the polydispersity index in ATRP in the absence of significant chain termination and transfer relates to the concentrations of initiator (RX) and deactivator (D), the rate constants of propagation (k_p) and deactivation (k_{deact}), and the monomer conversion (p) [28]. This equation holds for conditions when initiator is completely consumed and degrees of polymerization are sufficiently high; otherwise the Poisson term should be added ($1/DP_n$). Thus, for the same monomer, a catalyst that deactivates the growing chains faster will result in polymers with lower polydispersities (smaller k_p/k_{deact}). Alternatively, polydispersities should decrease with an increasing concentration of deactivator, although at the cost of slower polymerization rates. For example, the addition of a small amount of Cu-(II) halides in the copper-based ATRP leads to better controlled polymerizations with decreased polymerization rates [83]. Perhaps most important, however, is the propagation rate constant; higher polydispersities are usually found for polyacrylates than for polystyrene or polymethacrylates due to a much higher kp for the former monomers [85]. Other predictions from eq. (2.7) include higher polydispersities for shorter chains (higher $[RX]_0$) and a decrease of the polydispersity with increasing

monomer conversion. The implications of eq. (2.7) are in agreement with the experimental results. It is also possible to correlate polydispersities with the rate constant of activation when they are plotted against time rather than conversion [87].

The rate constant of deactivation (k_{deact}) is affected by a number of factors, such as the transition metal, the metal counterion, and the ligand. For the same catalytic system, an important factor is the lability of the X-Mt bond in the deactivator.

In ATRP, the concentration of deactivator increases sharply at the beginning of the polymerization and then increases slowly, but continuously, with mono-mer conversion [87]. The addition of a small amount of Cu(II) halides at the beginning of the polymerization can reduce the proportion of terminated chains and help establish the atom transfer equilibrium. Conversely, the addition of small amounts of copper(0) in copper-mediated ATRP can result in a faster polymerization rate, as "excess" copper(II) is reduced to copper(I) [88]. It should be noted that deactivators may also participate in side reactions [89].

2.2.5. Grafting by ATRP

An early example about grafted polymer by ATRP is grafting from PVC (includes small amount of pendent chloroacetat units) with BA, MA, MMA [67,89]. The purpose of the studies were to chemically incorporate another monomer into the PVC matrix to reduce the brittle nature of that polymer. Traditionally used plasticizers suffer from problems such as leaching and phase separation. Polymerization of the grafts is initiated by chloroacetate moieties attached to the polymeric backbone. Commercial PVC containing 1% (mol) chloroacetate groups was used in ATRP of styrene, MA, n-BA, and MMA. The results of the study, demonstrate that in each case the molecular weight of the copolymer increased above that of the macroinitiator yet the polydispersity remained essentially the same. The polydispersity did not decrease because of the variable quantity of initiating sites per chain. The large increase in the molecular weight distribution for the MMA polymerization may originate from slow ATRP initiation of MMA from the primary alkyl halide sites. Most important, however, was the influence on the glass transition temperatures after incorporation of the grafts. The decreased T_g of the copolymers containing MA and nBA indicates that self-plasticized PVC has been

synthesized. This is especially well illustrated by systems with an increasing content of pnBA. One T_g indicates no microphase separation for these copolymers [28].

2.3. Chemical Modification of PVC

2.3.1. Introduction

Vinyl chloride (VC) was first discovered by Regnault in 1835, and the polymer was first observed in 1838 [90]. Commercial production of PVC first started in German, in the early 1930s using emulsion polymerization.

Poly(Vinyl Chloride) is the second largest volume plastic material (the first is low-density polyethylene LDPE) in the world today. It is the lowest priced among the others and it is important for commercial production. PVC is widely used in construction, packaging, electronics, and transportation. But, the properties of pure PVC is not appropriate to make useful materials. So, to improve the properties of PVC is very important. The first breakthrough to overcome the processing and heat stability problems of PVC came in 1932 when Semon discovered plasticizers for PVC [91].

Polymer modification has became a major route to better polymer properties and wider polymer applicability in the 1990's. The high cost of developing a completely new polymer and the many long-term performance objectives a new polymer must meet have pushed firms to innovate by modification and blending rather than synthesis of a new monomer and polymer. This dependence on modification is not new. Indeed, while the use of stone and clay pottery is a use of polymeric silicates, cooked meat is denatured polymeric protein, and wool or cotton fabric are woven polymers, the first commercial that was not just gathered and processed from nature was a modified cellulose, gun cotton [92].

The major advances that have enhanced the pace and effectiveness of modification of polymers are:

1. the application of experimental design, statistical design, and combinatorial analysis to allow rapid experimental testing of polymers,

2. advances in the thermodynamics of polymers and the thermodynamics of miscibility,

the development of predictive capacity of polymer properties and behavior based on field models of molecular interactions,

3. development of the theory controlling the processing of polymers,

4. modeling of the polymeric solid, and

6. new methods to form polymers including coextrusion, pultrusion, and production with internal reinforcement [92].

Chemical modification of PVC by postpolymerization reactions on the polymer as a substrate has been a research area of great interest both commercially and academically. An enormous amount of literature, both in magnitude and diversity, has been generated over the years [93].

There are various processes to modify PVC. These processes can been classified into two main groups; chemical processes and physical processes. Chemical modification has been used as a means to modify the chemical, physical, and mechanical properties of PVC and diversity its range of applications. It has been a means of studying the chain structure in PVC. It has been used as a means of identification and quantification of the labile chlorines in PVC, thought to be mainly responsible for the low thermal stability of the polymer. Important inroads have been made into understanding the mechanism of degradation and stabilization of PVC by studies involving chemical modification of the polymer [93].

The chemical modification of PVC has mainly involved dehydrochlorination, reductive dehalogenation, substitution of chlorines by other functionalities, and graft copolymerization using ionic and free radical methods [94]. In the recent years Atom Transfer Radical Polymerization is used [1,20,21] to modify the PVC.

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 spectrum of property requirements [94].

2.3.2. Defects in the Structure of PVC

Radical polymerization of VC results in the formation of macromolecules containing a number of different isomeric forms and structural defects. These factors are of practical importance, since they affect the color, thermal stability, crystallinity, processing and mechanical properties of the finished materials.

Typical PVC molecules contain approximately 1000 vinyl chloride monomer units, joined in predominantly head-to-tail fashion (other structural arrangements are considered to be defects) [95]. In this structure, chlorine atoms are inert because of the strong bond between C and Cl atoms. However commercial PVC contains minute amounts (around 1%) of labile chlorine atoms (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 chain 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 [96].

2.3.3. Analysis of Labile Chlorines

The abnormally low thermal stability of PVC is attributed to labile chlorines, allylic and/or tertiary, present as structural defects in the polymer chain. These serve as initiation sites for degradetion. Chemical modification of PVC has served as an important tool in studying the labile clorine structures [93].

A quantitative method was reported for determination of labile chlorines in PVC based on substitution of labile chlorines by phenol [19,97]. IR and UV have been used for the quantitative determination of the incorporated phenol. The method was tested on models and verified on copolymer with known labile chlorine content. The published data indicate a detection limit of 0.5-2.0 labile chlorines Per 1000 m.u.

Labile chlorines in PVC have also been determined by a crown ether catalyzed acetoxylation of PVC [98] and the thermal degradation characteristic of the modified polymer [99]. The values were found to be comparable with those obtained by the phenolysis method.

Bonnans-Plaisance et al. [15] reported a study of chemical modification of PVC involving the substitution of chlorines by phenythiocarbonylthio groups. They shoved that methyllammonium dithiobenzoate provides a clean substitution reaction of chlorine in PVC without the occurrence of elimination of HCL at 20-30 C. The reaction provides a new method of determining labile chlorines in PVC by extrapolating data to zero time. The extent of labile chlorines was found to be 0.3-0.4 mol % of the total chlorine in the polymer. This is considerably higher than the accepted levels of combined allylic and tertiary chlorines in PVC. This is because of ordinary secondary chlorines in PVC can also behave as labile chlorines depending on their stereochemistry in the polymer chain.

2.3.4. Chemical Modificcation of PVC by Grafting

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 thermal stability 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 [93].

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 studies [1,13] PVC firstly is copolymerized randomly with comonomer (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 [100] for producing self-plasticized graft PVC industrially. The concept evaluated 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 controllod polymerization. The process involves copolymerization of vinyl chloride with vinyl chloroacetate in a standard 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 coworkers [20,21] have succeeded grafting of styrene and butyl methacrylate monomers from labile chlorines of PVC in diphenyl ether at 120 ^{0}C.

The occurrence of undesirable side reactions, dehydrochlorination, has been a persistent problem in the studies on the chemical modification of PVC. In most cases it has not been possible to prevent these side reactions from occurring, though their levels may have remained within tolerable limits.

3. EXPERIMENTAL PART

3.1. Chemicals Used

n-Butyl acrylate (Fluka) was purified by distillation and 2-ethyl hexyl acrylate (Aldrich) was made inhibitor- free by shaking with 0.1 M NaOH solution. Polyvinyl chloride (PVC) (Aldrich Mn= 93 000, polydispersity: 1.718) was used as supplied.

CuBr was freshly prepared according to the procedure described in the literature [101]. The ligand, hexacis-(hexyl triethylene tetramine) (IUPAC name: Hexacis – (1,1,4,7,10,10-hexyl,1,4,7,10, tetraazadecane) was prepared by condensation of triethylene tetramine with 1-bromo hexane as described before [22].

3.2. Characterization

^{1}H-NMR Spectra were obtained by Bruker model 250 MHz NMR spectrometer, using DMSO-d_6 as solvent and TMS as internal standard.

FT-IR Spectra were recorded by Matson 1100 IR spectrometer, using cast films of the polymer samples.

GPC (Gel Permeation Chromatography) traces of the graft copolymer samples were taken by using an Agillant 1100 series consisting of a pump, a RI detector and Waters styrogel (HR 4, HR 3 and HR 2) columns. Tetrahydrofurane (THF) was used as the eluent and the flow rate was 0.3 mL / min. Prior to the manipulations, copper residues in the samples were removed by re-precipitation twice in acetic acid-ethanol mixtures (1 / 1). Thus, about 0.2 g of the light blue products were dissolved in THF (10 mL) and precipitated in 25 mL of the acetic acid-ethanol mixtures. This procedure gave copper-free white polymers, which are pure enough to use in NMR and GPC experiments. By this way trace coppers remained in the samples are transferred into the solution as acetate salt.

3.3. Graft Copolymerizations

The graft copolymers of PVC with n-butyl acrylate and 2-ethylhexyl acrylate were prepared in 1,2 dichloro benzene as solvent at 90 ºC. A typical procedure is as follows:

3.3.1. Graft Copolymerization of n- Butyl Acrylate from Labile Chlorine Atoms of PVC

PVC (6.25 g, 0.1 mol) was dissolved in 100 ml of 1,2-dichlorobenzene. This solution was transferred into a 250-ml flask equipped with magnetic stirrer and a reflux condenser. . Nitrogen was flushed through the solution for 3 minutes. Then 14.3 ml (01 mol) of n-butyl acrylate, 0.325 g (0.001 mol) of hexacis-(hexyl triethylene tetramine) (H-TETA), and 0.08 g (0.001 mol) of Cu(I)Br was added to the flask Graft copolymerization was carried out under nitrogen atmosphere. Then the flask was immersed in a thermostated oil bath and stirred at 90 ±1 ^{0}C with constant stirring rate (400 rpm). Polymerization was continued for 7.5 h. and the reaction kinetics were followed by monitoring progressive mass increases of the aliquots (approx. 5ml of each) taken in predetermined time intervals. These aliquots were poured into THF/acetic acid mixture (15 ml, 10:1) to stop the reaction and remove the copper residues. Then the polymer solutions were precipitated in ethanol (40 ml). The products were filtered by suction and washed with ethanol and water. The samples were dried at room temperature, for 24 hours under vacuum and weighed.

In order to separate free homo polymer from the product it was dissolved in THF (10 ml) and precipitated in n-butanol (25 ml) and filtered. The filtrate was poured into methanol. But no precipitate was observed.

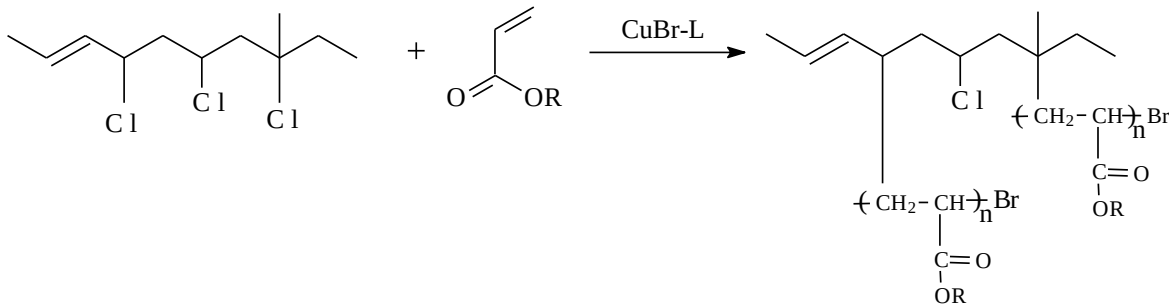
3.3.2. Graft Copolymerization of 2-Ethyl Hexyl Acrylate

The same procedure was followed for grafting of 2-ethyl hexyl acrylate, except the aliquots were precipitated in n-butanol directly, to remove free homopolymer.

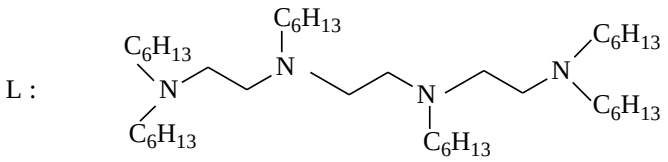
4. RESULTS AND DISCUSSION

Labile chlorines of PVC resulting from structural defects formed during radical polymerization of vinyl chloride can act as initiation sites for direct grafting of PVC by copper mediated ATRP methodology. By this way the graft copolymers; PVC-g-poly (2-ethyl hexylacrylate) and PVC-g-poly (n-butyl acrylate) have been prepared in high conversion yields (Scheme 4.1).

Graft copolymerizations were carried out in 1,2 dichloro benzene as solvent at 90 ºC, constant temperature. In this work 1,2 dichloro benzene was selected as proper solvent for PVC. Other common solvents such as cyclohexanone and methyl ethyl ketone were not chosen to avoid their possible side reactions yielding their brominated derivatives with cuprous bromide.



R : $-C_4H_9$, $-CH_2-CH(C_2H_5)-CH_2-CH_2-CH_2-CH_3$



Scheme 4.1 Grafting of acrylate monomers from labile chlorines of PVC

The ligand used was hexylated triethylene tetramine, which forms completely soluble copper complexes in organic solvents. This formulation enables us to perform ATRP in entirely homogenous conditions.

The graft reaction kinetics was followed by progressive mass increases of the polymer samples taken from the reaction mixture, at different time intervals. Grafting of PVC at 90 ^{0}C is reasonable fast for both monomers. 161.8 % and 51.2 % of graft yields are attained in 75 h of reaction time for BA and EHA monomers respectively (Table 1).

Interestingly, no free homopolymers of BA and EHA were detected throughout the polymerizations. In order to detect any probable free homopolymer formation, the graft copolymers samples were precipitated in butanol and butanol filtrates were added to excess of methanol. No precipitate was observed in each case. These observations clearly indicate that homopolymers do not present in the graft products.

Table 4.1. Graft co-polymerization characteristics of BA and EHA from PVC

M	Initial [(a)] conc.	[M] / [Cu-L] [(b)]	Graft yield [(c)] (%)	First order rate constant	M_n x 10^{-3}	PDI[(d)]
BA	1 M	100 / 1	161.8	$3.34 .10^{-5}$ s^{-1}	130	1.64
EHA	1 M	100 / 1	51.2	$4.48 .10^{-6}$ s^{-1}	106	1.56

(a) : In 1,2-dichloro benzene at 90±1 ^{0}C

(b) : Molar ratio of monomer to the copper complex

(d) : Calculated from mass increase for 7.5 h of reaction time.

(e) : PDI polydispersity index of the graft copolymer.

Moreover, only one peak appears in each GPC traces (Fig.4.1) , which reveals neither unreacted PVC nor acrylate homopolymers present in the reaction products. In the case for 161.8 % of grafting, molar ratio of BA units to the vinyl chloride repeat units (by neglecting minor changes in mass differences arising from replaced chlorines at the initiation sites and added halogens at the chain-ends) would be:

$$\frac{161.8/128}{100/62.5} = 0.79$$

Where, 128 and 62.5 are molecular weights of butyl acrylate and vinyl chloride respectively. In other words 79 BA repeat units per 100 repeat units of PVC.

Similarly, estimation for 51.2 % of grafting with EHA yields 0.174 EHA units per repeating unit of PVC.

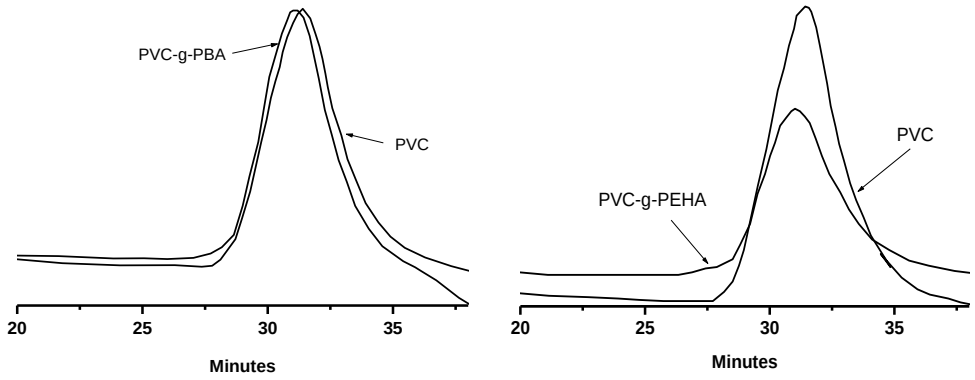


Figure 4.1 GPC traces of the graft copolymers of PVC obtained in 7.5 h of reaction times. PVC-g-Poly(butylacrylate) : (a) , PVC-g-Poly(2-ethylhexylacrylate) : (b).

Almost linear ln (M_0 / M) versus-time plots are obtained for BA and EHA graft reactions (Fig.4.2). Where, M_0 is initial monomer concentration, M is monomer concentration at any time, which is found by differencing amounts of the monomers involved in grafting from the initial monomer concentrations. Linearity of the semi - logarithmic plots implies first order kinetics of grafting for both monomers.

Corresponding rate constant were found 3.3410^{-5} s^{-1} and 4.48 10^{-6} s^{-1} for the case of BA and EHA respectively. Low grafting rate for EHA might be due to high molecular weight of this monomer. Moreover Mn – conversion plots are also linear (Fig.4.3) which are typical behaviour of the copper mediated ATRP. Since polydispersity of commercial PVC used is high (1.718), polydpispersities of the graft co-polymer samples are relatively high and typically lie in 1.99 – 1.56, as shown in Fig.4.4. Sharp rises are observed in the polydpispersities at the beginning of the reactions. These values are around 1.6 at high conversions.

Presences of the attached chains of BA and EHA have also been evidenced by FT-IR and ^{1}H-NMR spectra of the graft products. In the FT-IR spectra appearance of characteristic C=O stretching vibrations of the acrylate repeat units at 1715 cm^{-1} establish the graft structures (Fig. 5).

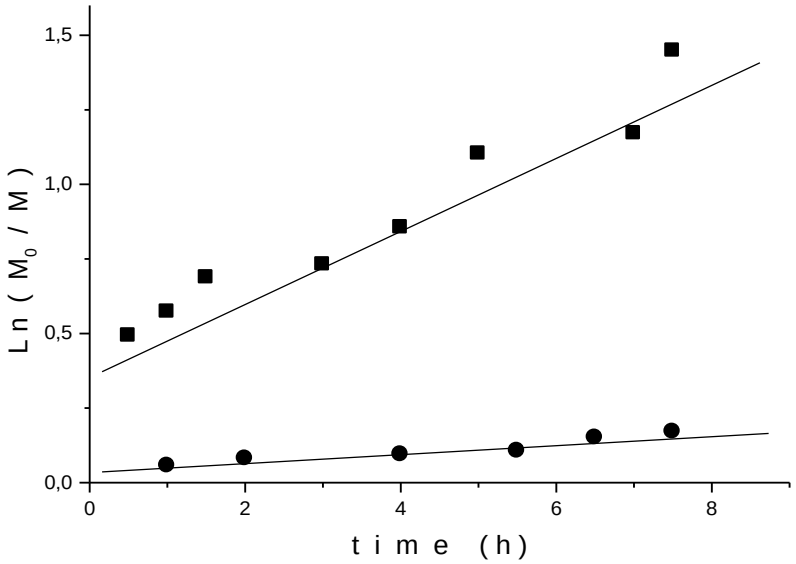


Figure 4.2 First order kinetic plots for graft copolymerization of butylacrylate (■), and 2-ethylhexylacrylate (●) at 90 ^{0}C (CuBr - L / [M] : 0.0018).

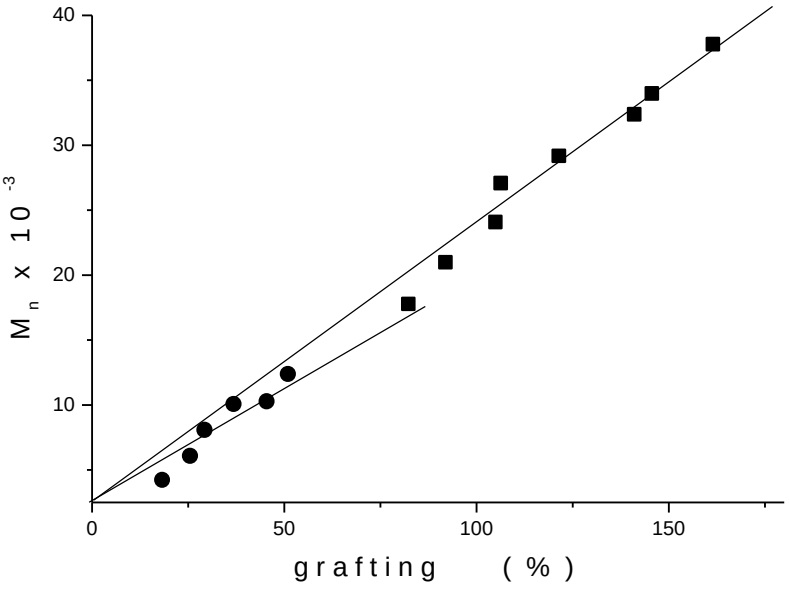


Figure 4.3 Total molecular weights of graft chains accumulated on PVC versus conversion plots for grafting of butylacrylate (■), and 2-ethylhexylacrylate (●) at 90 ^{0}C (CuBr-L/[M] : 0.0018).

The ^{1}H-NMR patterns (Fig. 6) of the graft copolymers seem to be superposition of ^{1}H-NMR spectra of the individual components. Typical signals of the methyl protons of the butyl or hexyl groups are discernible as broadband around 1 ppm, which indicate incorporation of BA and EHA chains into the graft products. All the other proton signals are broadened in 1.5 – 3 ppm and 4 – 4.9-ppm ranges. The former signal must be associated with sum of methine protons of PVC with $–OCH_2$ - protons of the ester groups of the acrylate units. Integral ratio of the signal in 4 – 4.9 ppm range to that of the one at 1 ppm gives 0.75 BA repeat units for each PVC repeat unit. This rough estimation is very close to the value (0.79) obtained from the mass increase.

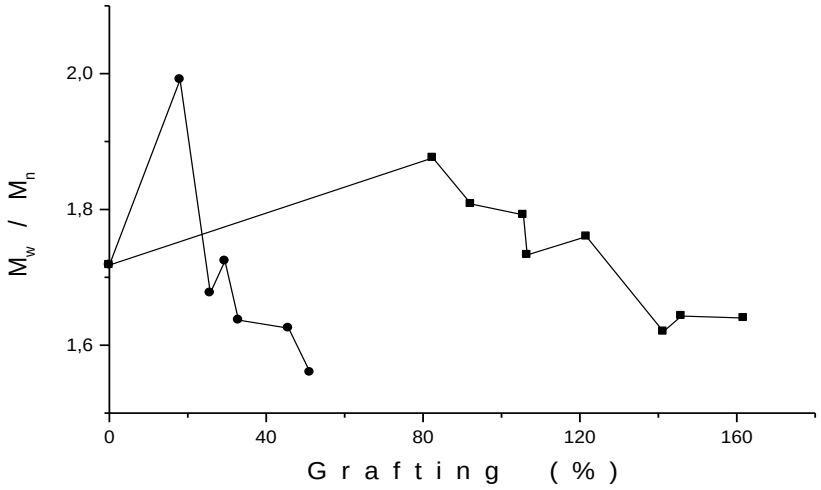


Figure 4.4 Polydispersities (M_w / M_n) as a function of graft yields for butylacrylate (■) and 2-ethylhexylacrylate (●) at 90 ^{0}C (M_w / M_n of the starting PVC is 1.718)

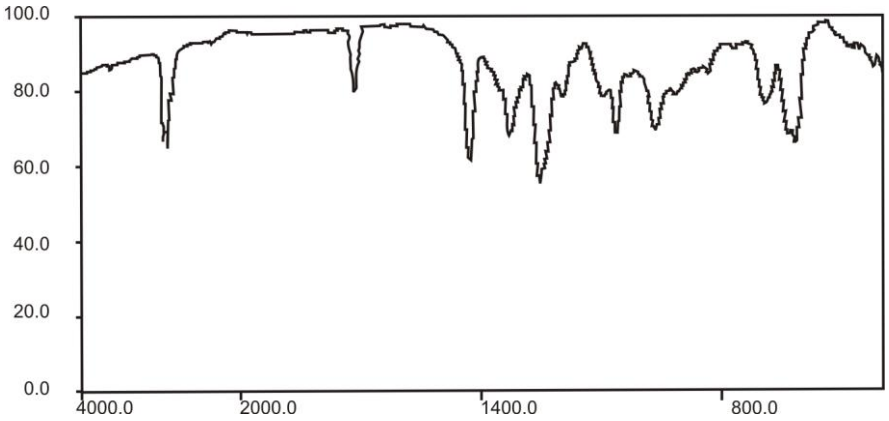


Figure 4.5 FT-IR spectra of poly(VC-g-EHA)

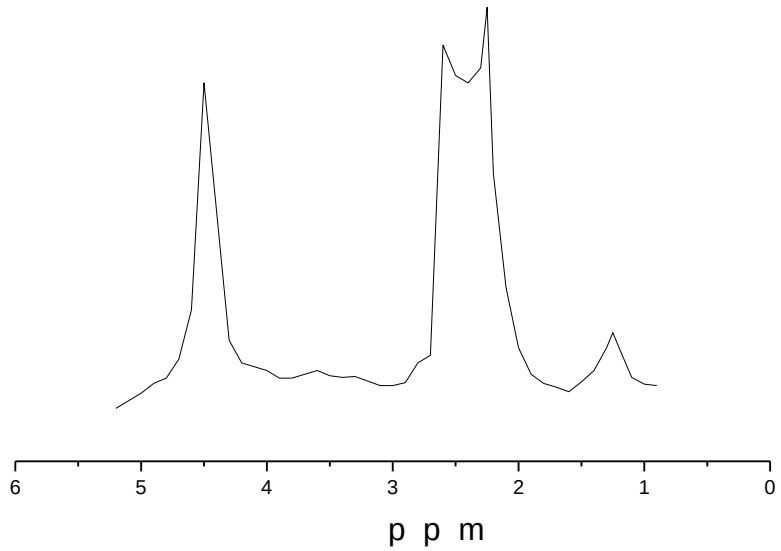


Figure 4.6 ^{1}H-NMR Spectrum of PVC-g-Poly(butylacrylate) obtained in 7.5 h of reaction time.

Similar inspection for the EHA- graft sample obtained 7.5 h of reaction time gives a 14.3 EHA repeat units per 100 repeat units of the PVC. This amount is also comparable with the value (17.4) found by mass increase of the sample. As a result, spectroscopic measurements qualitatively confirm the graft structures expected.

We have also attempted to estimate lengths of the polyacrylate chains by determination of labile chlorine content of the starting PVC using the method suggested by Caraculacu et al [19]. However the values found were in the range of 0 – 2.6 % (mol/mol) and varied depending on both temperature and contact time of the sulfur reagent. For 7.5 h of reaction time at 90 ^{0}C the value (2.6 %) found corresponds to 2.6 of initiation sites in 100 repeat units of PVC. Ratio of the BA repeat units to the number of initiation sites would, then, be 79. / 2.6 = 30.4 In the other words, an average 30 repeat units of BA might present in each graft chain. However reliability of 2.6 values is doubtful. We believe that this assumption is not true because not only unreliability of the labile chlorine content found but also reactivity differences of halogens at the ends of graft chains and labile chlorines on the backbone of PVC.

It is important to note that, prolonged graft reactions (longer than 24h) result in gelation. This might be largely due to formation of additional new primary radicals during the

chain growths. Combination of these radicals is expected to form partially cross-linked gel products for longer reaction times.

5. CONCLUSIONS AND RECOMMENDATIONS

BA and EHA monomers can be grafted from labile chlorines of the commercial PVC, efficiently by the copper mediated ATRP. The process does not need the use of additional comonomers or modified functional groups having active halides for initiation of ATRP.

The process presented offers a relatively simple pathway for efficient grafting of BA and EHA to prepare self-plasticised PVC.

Since the ligand and its copper complexes are almost insoluble in water, the present method seems to be applicable to carry out the graft reaction in suspension polymerization conditions. This needs further studies which are under consideration.

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AUTOBIOGRAPHY

He was born in 1977 in Kırcaali. He completed his undergraduate study in Chemical Engineering Department at Cumhuriyet University in 2000. He attended to his graduate study in the programme of Polymer Science and Technology at Istanbul Technical University, which he is about to graduate at the moment.