POLYMERIZATION AND CHARACTERIZATION OF POLY(ETHYL METHACRYLATE)

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ABSTRACT

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In this study, ethyl methacrylate was polymerized by free radical polymerization at 60°C, 70°C, 80°C at open atmosphere; atom transfer radical polymerization, (ATRP), at 80°C in vacuum and in gamma irradiation in vacuum. The polymer obtained was white, hard material. The kinetic curves for free radical polymerization and ATRP by gamma radiation were S-type. However, the curve for polymerization by gamma irradiation raises more smoothly. For ATRP by thermal initiation gives a lineer change of conversion with time. It was observed that the molecular weight can be controlled and low molecular weight polymer could be obtained by ATRP method. The characterization of polymers were made by FTIR, DSC, ¹H and ¹³C NMR techniques.

Key words: ethyl methacrylate, atom transfer radical polymerization, gamma irradiation, free radical polymerization, viscosity.

ÖZ

POLİETİLMETİLAKRİLATIN POLİMERLEŞMESİ VE KARAKTERİZASYONU

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Bu araştırmada etil metakrilatın açık havada 60°C, 70°C, 80°C de serbest radikal polimerizasyonu ve vakum ortamında 80°C de ve vakum ortamında gama radyasyonu ile atom transfer radikal polimerizasyonu , (ATRP), üzerinde çalışıldı. Elde edilen polimer sert ve beyazdı. Serbest radikal polimerizasyon ve gama radyasyonlu atom transfer radikal polimerizasyonda S-tipi kinetik eğrileri elde edildi. Fakat gama radyasyonlu eğrideki eğimin daha yumuşak olduğu görüldü. Termal ATRP zamana göre doğrusal bir dönüşüm gösterdi. ATRP metodu ile moleküler ağırlığın kontrol edilebileceği ve düşük molekül ağırlıkta polimer elde edilebileceği gözlendi. Polimerlerin karakterizasyonları FT-IR, DSC, ¹H ve ¹³C-NMR teknikleri ile yapıldı.

Anahtar Kelimeler: etil metakrilat, atom transfer radikal polimerizasyon, gama radyasyon, serbest radikal polimerizasyon, viskosite.

To my father, Tuncer BAKİOĞLU, my mother, Saadet BAKİOĞLU and my brother Serdar BAKİOGLU

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CHAPTER 1

INTRODUCTION

1.1 SYNTHESIS OF ETHYL METHACRYLATE (EMA)

Acrylic and methacrylic acid compounds are derived from acrylic acid, CH_2 =CHCOOH, the simplest unsaturated aliphatic acid, or methacrylic acid, CH_2 =C(CH₃)COOH, its α -methyl derivative. These compounds are reactive monomers which find their principle use in the manufacture of polymeric products. The availibility of a large group of monomeric materials offers the possibility of tailor-made products with a wide range of physical properties adaptable to the requirements of many different applications. Despite their variety in composition and physical form, the polymers share the common qualities of film clarity, brilliance and out-standing resistance to many chemical agents, atmospheric attack, and degradation by light [1]. Ethyl methacrylate (EMA) is one of the methacrylic compounds with the formula given below.

$$CH_2 = C - CH_3$$

$$|$$

$$C = O$$

$$|$$

$$O - CH_2 - CH_3$$

Ethyl Methacrylate

EMA has formula weight of 114.14, boiling point 117^{0} C, density 0.909 g/ml at 25⁰C and the flash point 35⁰C. EMA is a clear, colorless and flammable liquid with a characteristic odor. Since, EMA polymerize easily, it is stabilized with 15 ppm of monomethyl ether of hydroquinone inhibitor.

In 1843, Redtenbacher oxidized acrolein with an aqueous slurry of silver oxide and isolated an acid, which he named acrylic acid. Beilstein obtained acrylic acid from the distillation of the salts of hydracrylic acid, and Frankland and Duppa dehydrated ethyl α -hydroxyisobutyrate with phosphorus trichloride to form ethyl methacrylate, which was saponified to methacrylic acid [1].

The monomers were first made commercially by improved elimination procedures based on hydroxynitriles as follows:

HOCH₂CH₂Cl
$$\xrightarrow{\text{NaCN}}$$
 HOCH₂CH₂CN $\xrightarrow{\text{ROH}}$ CH₂=CHCOOR (1.1)
H₃O⁺

Methacrylates from acetone cyanohydrin:

$$(CH_3)_2CO \xrightarrow{\text{NaCN}} (CH_3)_2C(OH)CN \xrightarrow{\text{ROH}} (CH_3)_2C(OH)COOR \xrightarrow{\text{PCl}_5}$$

 $CH_2 = C(CH_3)COOR$ (1.2)

The route through the hydroxyisobutyrates was used to produce ethyl methacrylate in 1933 and methyl ester in 1936 but it was soon abandoned in favor of the more efficient synthesis which became the process still employed at present [1].

1.2 PROPERTIES OF POLYMETHACRYLATES

Acrylic and methacrylic polymers have characteristics of brilliance, optical clarity, high transparency, improved mechanical properties, adhesion capability and chemical stability [2]. The photostability of aliphatic acrylic and methacrylic polymers are generally very high. The carbonyl ester groups in the polymer units are not directly photochemically active, but trace impurities in polymer may initiate the photo-induced degradation [3]. Acrylates are more reactive then methacrylates towards oxidation. The light induced oxidation of acrylic and methacrylic polymers are not autocatalytical, but proceed at constant rate of oxygen consumption with direct proportionality of initiation rates on the number of chain ends . The radiation decomposition of polymethacrylates is inversely proportional to the length of ester groups of methacrylate monomers [4].

Although acrylic and methacrylic polymers have a good resistance to hydrolysis, there is some uncertainty in the evaluation of the role of water during their natural ageing; oxidation may be before hydrolysis, or it may take place on the hydrolysis products. Thin films of acrylic based paints obtained from aqueous dispersions were prepared to develop cross-linking and yellowing even when kept in the dark [5].

The physical properties such as solubility, density, and softening point of high polymeric acrylates and methacrylates depend to a large extent on the length and branching of the alcoholic residues. The polymeric esters in which these residues are sizeable are soluble in such solvents as aromatic hydrocarbons, esters, ketones, and halohydrocarbons. The polymers with larger alcohol residues are also soluble in alkanes. Polyacrylates exhibit lower softening points than methacrylates. Among the valuable properties of polyacrylates and polymethacrylates are their clarity, transparency and considerable stability to light. [6]

When Pinacolyl methacrylate polymer is compared with methyl methacrylate polymer in softening point and hardness, methyl methacrylate polymer has the greatest shrinkage and highest refractive index of the series. Hardness and softening point are increased by branching, especially at the second carbon atom from the main chain. This is usually attributed to steric effects, especially better packing of clumped groups. However, Crawford [7] favored the explanation that based on polarity influenced by the number of the electron-repellant methyl radicals. That clumped or cyclic side groups give more rigid macromolecules may result in some cases from restriction of rotation about the carbon-carbon chain. Long alkyl groups have a plasticizing action, promoting randomness of the chains and giving methacrylate polymers a rubber-like elastomeric nature.

Brittle points of n-alkyl methacrylate and n-alkyl acylate polymers have been detemined by Rehberg and Fisher. In each series a minimum temperature is reached with increasing length of the R groups. Thus the polymethacrylate from C_{12} to C_{16} long-chain alcohols are less soft and flexible polyoctyl methacrylate at low temperatures. The methyl to n-octyl methacrylate polymers are all higher-softening, harder and higher in the brittle point than the corresponding methyl to n-octyl acrylate polymers [8].

1.3 COMMERCIAL USE OF POLYMETHACRYLATES

Major application of the methacrylates is the manufacture of sheets, tubes, rods. These shapes are used in shatter-resistant glazing for aircraft and buildings, signs, decorative panels, electrical lighting fixtures, showcases, and other applications which take the advantage of the brilliance, sparkling clarity, high transparency, and weathering resistance. Colored products of great beauty can be produced by the incorporation of colorants and pigments into the casting mixtures. Other shapes are made readily by forming the heated plastic under vacuum or with air pressure in suitable molds. The plastics can also be machined and polished with conventional machine tools [1].

Poly-n-butyl methacrylate is elastomeric at room temperature; it is somewhat similar in the softness to polymethyl acrylate. n-Butyl and isobutyl methacrylate polymers have found some use in the optical and other special adhesives. Ethyl methacrylate has been used as an imbedding or mounting medium for biological and other specimens by the application of layer-casting techniques. Polyethyl methacrylate and polybutyl methacrylate of low intrinsic viscosity have been employed in special finishes [8].

Applications for rigid methacrylate polymer products include signs and glazing substitute for safety glass and to prevent vandalism (school, home, and factory windows, patio window doors, aircraft windows and canopies, panels around hockey rinks, bank teller windows, bath and shower enclosures, skylights), indoor and outdoor lightning, lenses, diffusers, and louvers, architectural structures (domes over pools and studio, archways between buildings), bathtubs and sanitary fixtures, optical fibers for light transmission, plastic eyeglass lenses, dentures and dental filling materials, and contact lenses (hard and soft) [9].

1.4 POLYMERIZATION KINETICS OF METHACRYLATES

1.4.1 FREE RADICAL POLYMERIZATION

Free radical polymerization is widely used in industry; because generation of a radical is easy, many polymers can be polymerized, and radical polymerizations are tolerant to the impurities (moisture, protic solvents), that normally would terminate an ionic polymerization. The drawback of radical polymerizations, however, is that while it is easy to generate a reactive radical that can initiate polymerization, the polymerization itself is difficult to control. A radical will readily react with another radical, either through disproportionation or through a coupling reaction. The former will produce both a saturated and an unsaturated chain end, while the latter will produce a single dead chain. Another major limitation for conventional radical polymerizations is that the molecular weight of the polymer chains is poorly controlled. Most free radical initiators have an initiator efficiency is less than unity. There have been attempts to remedy this situation. Chain transfer agents can be used to limit the molecular weight of the polymer. These additives react with the growing polymer chain, limiting the degree of polymerization without affecting the polymerization rate. Transfer agents can introduce functionality to polymer chain ends that will allow for post-polymerization reactions

Acrylate and methacrylate esters polymerize readily under the influence of heat, light and catalysts. Industrially, the use of heat or light alone for initiating polymerization of acrylic esters is seldom encountered, and peroxide type free-radical catalysts such as benzoyl-peroxide are most frequently employed [10].

Benzoyl peroxide may be taken as a typical free radical initiator. Two reactions commonly used to produce radicals for polymerization are the thermal or photochemical decomposition of benzoyl peroxide (BPO). It produces benzoate and phenyl free radicals on decomposition, the proportions depending on the experimental conditions, particularly the nature of the solvent.

$$(C_6H_5COO)_2 \rightarrow 2 C_6H_5COO^{\cdot} \rightarrow 2 C_6H_5^{\cdot} + 2CO_2$$
 (1.3)
benzoate phenyl

Although thermal decomposition is a common means of generating radicals, it has a disadvantage because the rate of generation of free radicals cannot be controlled properly due to the exothermic nature of polymerization of acrylates.

The chain mechanism of the addition of free radicals to double bonds was clearly defined by Kharash and by Hey and Waters in 1937, and was applied quantitatively to the chain-growth polymerization of olefin monomers by Flory in the same year. Flory showed that a free radical polymerization reaction, like other radical processes, was a typical chain reaction requiring three distinct steps: initiation, propagation and termination [11].

1.4.1.1. Initiation:

Initiation in a free-radical polymerization of poly(ethyl methacrylate) consists of two steps;

a. Dissociation of the initiator, I, to form two radical species.

$$\begin{array}{rcl} \text{Ph-COO-OOC-Ph} & \rightarrow & 2 \ \text{PhCOO}^{\,\cdot} & \rightarrow & 2 \ \text{Ph}^{\,\cdot} + & \text{CO}_2 \\ \\ \text{benzoyl peroxide} & & & & & \\ \end{array}$$

$$I \qquad \xrightarrow{k_d} \qquad 2R \cdot \qquad R_i = 2 f k_d [I] \qquad (1.4)$$

where k_d is the dissociation rate-constant.

In an ideal case the initiator fragments add onto monomer molecule in the actual initiation of the chain reaction. There are two radicals per molecule of initiator; consequently, the rate of initiation is twice the rate of initiator decomposition. In real reaction, some radicals are lost because of recombination and induced decomposition. Thus, the efficiency f of the initiator is less than unity; usually, it is between 0.5 and 0.7, but it may be much smaller if the induced decomposition is extensive or when redox initiators or promoters are used [11].

b. Association, addition of a single monomer molecule to the initiating radical.

$$R \cdot + CH_{2} = C \xrightarrow{CH_{3}} RCH_{2} - C \cdot \xrightarrow{|} CH_{3}$$

$$R \cdot + CH_{2} = C \xrightarrow{|} RCH_{2} - C \cdot \xrightarrow{|} C \cdot \xrightarrow{|} C = O \xrightarrow{|} C = O \xrightarrow{|} OC_{2}H_{5}$$

$$R' + M \xrightarrow{k_a} RM' \qquad (1.5)$$

In the presence of the ethyl methacrylate monomer when free radicals are generated, the radical adds to the double bond with regeneration of another radical.

1.4.1.2. Propagation:

In this step; the chain radical formed in the initiation step is added to successive monomers.

$$RM' + M \longrightarrow RMM'$$
(1.6)

$$RMM' + M \xrightarrow{k_p} RM_nM' \qquad (1.7)$$

where k_p is the propagation rate constant. The rate of propagation is as follows:

$$\mathbf{R}_{\mathbf{p}} = \mathbf{k}_{\mathbf{p}} \left[\mathbf{M} \right] \left[\mathbf{M}^{\cdot} \right] \tag{1.8}$$

1.4.1.3. Termination:

In the absence of inhibitors and transfer agents, the propagation of a polymer chain will continue until it is interrupted by chain termination. Chain termination involves a reaction between two growing radicals leading to nonradical products. Two reactions are possible between two radicals: combination and disproportionation [11].

a. Termination by combination:

Two active polymer chains combine together to neutral polymer chain.

$$P_{n}-CH_{2}-CH_{2}^{-} + P_{m}CH_{2}-CH_{2}^{-} \rightarrow P_{n}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-P_{m}$$
(1.9)

b. Termination by disproportionation:

One growing polymer chain will abstract one hydrogen atom from another growing polymer chain and becomes neutral, while making the other polymer chain unsaturated.

$$P_{n}-CH_{2}-CH_{2} + P_{m}-CH_{2}-CH_{2} \rightarrow P_{n}-CH_{2}-CH_{3} + P_{m}-CH_{2}-CH_{2} \quad (1.10)$$

The rate of termination will be;

$$\mathbf{R}_{t} = \mathbf{k}_{t} \left[\mathbf{M}^{\cdot} \right]^{2} \tag{1.11}$$

where $k_t = k_{tc} + k_{td}$ with rate constant of termination by combination (k_{tc}) and rate constant of termination by disproportionation (k_{td}).

For a steady state kinetic, the radicals must be generated at the same rate as they are consumed, or rate of initiation must equal the rate of termination.

$$\mathbf{R}_{i} = \mathbf{R}_{t} \tag{1.12}$$

$$2 f k_{d} [I] = k_{t} [M']^{2}$$
(1.13)

or
$$[M^{\cdot}] = [\frac{2fk_d[I]}{k_i}]^{1/2}$$
 (1.14)

The concentration of radical in equation (1.9) is substitute into rate equation for propagation (1.5).

$$R_{p} = -\frac{d[M]}{dt} = k_{p} [M] [\frac{2 f k_{d} [I]}{k_{t}}]^{1/2} = k [M] [I]^{1/2}$$
(1.15)

The integration will give the general kinetic equation as follows:

$$\ln \frac{[M]_0}{[M]} = k [M] [I]^{1/2} t$$
(1.16)

1.4.2 ATOM TRANSFER RADICAL POLYMERIZATION

Free radical polymerization is the most important industrial process to prepare high molecular weight polymers. However, conventional free radical polymerization methods lack the control because of chain transfer and termination processes. This precludes conventional radical polymerization from synthesizing well-defined polymers with low polydispersities and complex architecture [12]. One of the main goals in modern synthetic polymer chemistry is to prepare polymers with controlled molecular weight and well defined architecture. Living polymerizations developed in the past forty years, including cationic, anionic, and group transfer polimerizations, provide the opportunity to reach that goal [13]. The concept of living polymerizations started in 1956 when Szwarc found that in the anionic polymerizations of styrene the polymer chains grew until all the monomer was consumed, and that chains continued growing when another batch of monomer was added. The addition of another monomer resulted in the formation of block copolymers. These polymerizations proceeded without termination or chain transfer occuring in the system. Prior to this work, the conditions used for the polymerizations had not been stringent enough to keep the active species alive and allow observation of this type of behavior. The polymer molecular weights were predictable based on the ratio of monomer to initiator and the polydispersities were low, indicating the polymerization was well controlled [14].

Later, other living systems were also achieved. These include ring opening polymerization and carbocationic systems. In the carbocationic systems the high reactivity of the active species required that an aquilibrium between the "active" species and a "dormant" species be formed, thus alowing control over polymerization. This approach was subsequently extended to controlled/living radical polymerizations (CRPs) [15]. Conceptually, if there is only a tiny amount of chains that are active at any given point in time while the others are dormant, this lessens the overall effect of termination. Although termination cannot be avoided, at the same polymerization rate, the same number of chains terminate, but the percentage of dead chains relative to the total number of growing chains would be very small (<10%). This is because while the total number of chains in the conventional process equals the sum of dead and propagating chains, in CRP the total number is the sum of dead, propagating and dormant chains.

New methods were developed in the mid-1990s based on the idea of establishing an equilibrium between the active and dormant species. Three approaches were the most succesful:

- 1. Control via a reversible homolytic cleavage of a weak covalent bond leading to a propagating radical and its stable free radical. They are generally called stable free radical polymerizations (SFRP) or nitroxide mediated processes (NMP).
- 2. Control via a reversible redox reaction between alkyl halides and transition metal complexes, i.e., atom transfer radical polymerization (ATRP).
- 3. Degenerative chain transfer with alkyl iodides or dithioesters (RAFT or MADIX).

The concept of using transition metal complexes to mediate radical polymerizations developed out of atom transfer radical addition reactions (ATRA). It also referred to as the Kharasch reaction, in which originally light was used to generate a radical. Later, transition metal complexes were used to promote halogen addition to alkenes through a redox process. A lower oxidation state metal abstracts a halogen from an activated alkyl halide, which can then add across the double bond of an alkene. The newly formed radical reabstracts the halogen from the higher oxidation state metal to form an alkene-alkyl halide adduct and regenerate the lower oxidation state metal. In efficient ATRA, trapping of the product radical should be faster than the subsequent propagation step and reactivation of the adduct should be very slow, maximizing the yield of the targeted product. This technique has been used extensively with various metal catalysts. [14]

Gaining control over radical polymerization has become one of the most important topics in contemporary polymer chemistry. In methodology similar to controlled/"living" cationic polymerization, free radical polymerization has been shown to be controlled under conditions in which a fast, dynamic equilibrium between the active and dormant chains, and only a low and stationary concentration of the active species exist [15]. Several examples of systems that have shown the ability to control radical polymerizations include nitroxyl-mediated polymerization of styrene [16], ruthenium(II)/aluminium based polymerization of methacrylates [17], Co^{II}-mediated polymerization of acrylates [18], and polymerization of styrene using a degenerative transfer method [19]. Controlled/"living" free radical polymerization can also be obtained through atom transfer radical polymerization (ATRP). [20, 21]

To promote a polymerization, the newly formed carbon-halogen bond must be capable of being reactivated and the new radical must be able to add another alkene. This was accomplished for the radical polymerizations of styrene and methyl acrylate (MA), which were initiated by 1-phenylethyl bromide and catalyzed by a Cu(I)/2,2'-bipyridine (bpy) complex [20, 21, 22]. The process was called "Atom Transfer Radical Polymerization" (ATRP) to reflect its origins ATRA [20]. A succesful ATRP relies on fast initiation, where all initiator is consumed quickly, and fast deactivation of the active species by the higher oxidation state metal. The resulting polymers are well defined and have predictable molecular weights and low polydispersities [14].

ATRP utilizes a transition metal, e.g., Cu/Bipyridine complex, as a halogen atom transfer reagent between the dormant and the active polymer chains with the rate constants of activation and deactivation, k_{act} and k_{deact} , respectively.

$$P_{n}-X + Cu(I)/2L \xrightarrow{k_{act}} P_{n}\bullet + Cu(II)X/2L$$
(1.17)

$$k_{deact} \xrightarrow{k_{deact}} P_{m}\bullet + Cu(II)X/2L$$
(1.17)

$$k_{p} \xrightarrow{k_{t}} P_{m}\bullet +$$

The concentration of growing radicals, which propagate with the rate constant of propagation k_p , is sufficiently low to significantly reduce the contribution of radical-radical termination (with rate constant k_t) and provide well-defined polymers with low polydispersities and novel architectures [23] using various monomers, initiators, and ligands [19,24].

The living process found in ATRP based on the Cu(I)/Cu(II) redox proces results from two phenomena: (i) the presence of the low stationary concentration of radicals; (ii) the fast reversible equilibration between the growing radicals and the dormant species. Several parameters, such as the nature of the transition metal, the structure and property of ligands, the polymerization conditions, etc., may strongly affect the course of living ATRP [21]. Molecular weights increase linearly with conversion, polydispersities initially decrease with conversion, an excess of persistent radicals reduces polymerization rates, oxygen inhibits polymerization, and water generally does not affect polymerization. In addition chemoselectivity (reactivity ratios and transfer coefficients), regioselectivity, and stereoselectivity (tacticity) are similar to those conventional radical polymerizations. However, the presence of transition metals in the reaction requires very careful examination of the reactive intermediates and the mechanism of propagation [12].

Initiator efficiency is of prime importance for successful controlled/ "living" polmerization through ATRP. Suitable initiators require an observed initiation rate constant greater than (or at least equal to) the observed propagation rate constant. These initiators also need to show little or no tendency to undergo side reactions. The homogeneous controlled/ "living" ATRP of MMA using Cu¹X/4,4'-di(5-nonyl)-2,2'-bipyridine catalytic systems (X=Cl, Br) with various initiators R-X provides examples of how structural differences of initiators affect the energetics of the C-X bonds, the electrochemistry of the initiating radicals, and therefore the efficiency of the initiation step. It is found that a variety of factors play a role in determining initiator efficiency. e.g., steric, polar, redox properties [12]. Since aromatic and aliphatic sulforyl chlorides tolerate a variety of functional groups in their structure and maintain quantitative and faster initiation than propagation for styrene and methacrylates, they provide a much broader versatility for chain end functionalization by initiation than alkyl halide initiators [27].

There are several important criteria for the successful design of ATRP catalysts : (i) the metal must possess an accessible one-electron redox couple, (ii) the oxidation potential should be low, (iii) there should be good reversibility between the reduced and oxidized forms of catalyst, (iv) the metal center must be sterically unencumbered in its reduced form to allow a halogen atom to be accommodated [28]. For a successful ATRP using a good ligand is necessary. Use of a suitable ligand not only increases the solubility of inorganic salt but can also faciliate the abstraction of a halogen atom from initiator, and form the dormant polymeric halide, with the formation of initiating and growing radicals [21]. Multidentate amines are less expensive, the copper complexes with these ligands generate less color to the system, and rates of polymerization are faster compared to complexes with 2,2'-bipyridine and its derivatives. Controlled/ "living" atom transfer

radical polymerization has been succesfully carried out at ambient temperature using CuBr/tris[2-(dimethyamino)ethyl]amine (Me₆TREN) as the catalyst. The polymers obtained have molecular weights close to the theorotical values and narrow molecular weight distributions [32].

An efficient method for the removal of Cu(I) and Cu(II) complexes in ATRP is accomplished by using ion exchange resins with acidic groups. It was found that the rate of removal of copper complexes was dependent on the solvent polarity, temperature, type of ion exchange resin used, and ionic character and size of the copper complex. In the limit of using a large excess of H^+ sites on the resins, Cu(I) and Cu(II) complexes can be removed from reaction mixtures relatively fast [25].

The homogeneous ATRP using Cu(I)X/L, L = Ligand, such as bpy; X=halide, such as Cl or Br, initiation systems has been proposed to occur by the mechanism illustrated below [26]. It consists of (a) an atom transfer equilibrium at both the initiation and propagation steps, (b) addition of radicals to olefinic monomers at both the initiation and propagating steps, and termination step [12].

Initiation:

$$R-X + Cu(I)X/2I \longleftarrow R \bullet + Cu(II)X_2/2L \qquad (1.18)$$

$$R \bullet + Monomer \qquad \stackrel{K_i}{\longrightarrow} P_1 \bullet \qquad (1.19)$$

Propagation:

$$P_{n}-X + Cu(I)X/2L \checkmark P_{n}\bullet + Cu(II)X_{2}/2L \qquad (1.20)$$

$$P_{n} \bullet + Monomer \xrightarrow{k_p} P_{n+1} \bullet$$
 (1.21)

Termination:

$$P_{n}\bullet + P_{m}\bullet \xrightarrow{k_{t,d}} P_{m}^{=} + P_{n}^{H}$$
(1.22)

$$P_{n}\bullet + P_{m}\bullet \xrightarrow{k_{t,c}} P_{m+n} \qquad (1.23)$$

In ATRP of ethyl methacrylate, M, P-Toluene Sulfonyl Chloride $(C_7H_7ClO_2S)$ was used as initiator, R-X, 4,4' Dimethyl 2,2' Bipyridine $(C_{12}H_{12}N_2)$ was used as ligand, L, and Copper(I)Chloride (CuCl) was used as catalyst, Cu(I)X, in this study.

Initially, the transition metal species, Cu(I)X/L, abstracts the halogen atom X from the organic halide, R-X, to form the oxidized species, Cu(II)X₂/L, and the carbon centered radical R•. In the subsequent step, the radical, R•, reacts with alkene, M, with the formation of the intermediate radical species, P₁•. The reaction between Cu(II)X₂/L and P₁• results in the target product, P_n-X, and regenerates the reduced transition metal species, Cu(I)X/L, which further reacts with R-X and promotes a new redox cycle.

The high efficiency of the transition metal catalyzed atom transfer reaction in producing the target product, P_n -X, in good to excellent yields,

often >90%, suggests that the presence of such a Cu(I)X/L / $Cu(II)X_2/L$ redox process can effectively induce a low concentration of free radicals, resulting in less significant termination reactions between radicals. If polymeric halides, P_n -X, are reactive enough toward Cu(I)X/L and the monomer is in excess, a number of atom transfer radical additions, i.e., a possible "living"/controlled radical polymerization, may occur. [21]

The reaction mechanism for ATRP is proposed above, which consists of the atom transfer equilibrium followed by the addition of radicals to olefinic monomers at both initiation and propagation steps and the termination step. Assuming a fast initiation, insignificant termination reactions and a steady concentration of propagating radicals, the following rate laws were derived.

$$\mathbf{K}_{eq} = \frac{k_{act}}{k_{deact}} = \frac{\left[\mathbf{P} \bullet \right] \left[Cu(II) X \right]}{\left[\mathbf{P} X \right] \left[Cu(I) \right]}$$
(1.24)

$$R_{p} = k_{app}[M] = k_{p}[P\bullet][M] = k_{p} K_{eq}[In] \frac{[Cu(I)]}{[Cu(II)X]}[M]$$
(1.25)

A fast equilibrium is necessary condition to observe the low polydispersivity in controlled/"living" free-radical polymerization. [29]

Reverse ATRP differs from normal ATRP in its initiation process, where a conventional radical initiator, such as AIBN is used. As shown below, in the initiation step, once generated, the initiating radicals or propagating radicals, I• or I-P₁•, can abstact the halogen atom X from the oxidized transition metal species, XM_t^{n+1} , to form the reduced transitionmetal species, M_t^n , and the dormant species, I-X or I-P₁-X. In the subsequent steps, the transition-metal species, M_t^n , promotes exactly the same ATRP process as normal ATRP where $R-X/M_t^n/L_x$ are used as the initiation system. Instead of first activation of a dormant species, R-X, with M_t^n , as in the case of normal ATRP, reverse ATRP originates from the deactivation reaction between radicals, I• or I-P₁•, and XM_tⁿ⁺¹ [30].

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Initiation:

$$I - I \xrightarrow{\Delta} 2I \bullet$$
 (1.26)

$$I \bullet + XM_t^{n+1} \longrightarrow I - X + M_t^n$$

$$k_t + M \qquad (1.27)$$

$$I - P \bullet + X M_t^{n+1} \longrightarrow I - P_1 - X + M_n^n$$
(1.28)

Propagation:

$$I - P_n - X + M_t^n \longleftarrow I - P_n \bullet + XM_t^{n+1}$$
(1.29)
$$\swarrow + M \qquad k_p$$

In the homogeneous reverse ATRP initiated by azo compounds and peroxides are different from each other. In the former process, reverse ATRP occurs efficiently in the presence of CuBr₂/2dNbpy, which can scavenge initiating/growing radicals and form CuBr/2dBpy and RBr species. In addition, initiating/growing radicals do not interact with CuBr/2dBpy species. In contrast, CuBr₂/2dBpy is an inefficient component of reverse ATRP initiated by benzoyl peroxide (BPO). This is due to electron transfer from Cu(I) to BPO and coordination of benzoate anions to copper. Such an induced decomposition reoxidizes Cu(I) back to Cu(II) species and disables the catalytic reaction. However, the polymerization initiated by BPO can be controlled in the presence of a sufficient amount of CuBr. After the induced decomposition of BPO, the growing radicals are deactivated by Cu(II) species to produce bromine-terminated oligomers and

Cu(I) species. Both $Cu(O_2CPh)$ and CuBr complexed by the ligand can then succesfully catalyze ATRP [31].

1.5 BULK POLYMERIZATION OF ETHYL METHACRYLATE

Bulk polymerizations represent the simplest polymerization system. All of them are characterized by an initial homogenity and consist of monomer with or without added catalyst or other modifying agents. Once the polymerization has been initiated, bulk polymerizations may exhibit different modes of behavior; (a) polymer is soluble in monomer, (b) polymer is insoluble in monomer. [33]

Poly(ethyl methacrylate) is soluble in its monomer at all stages of conversion. Here initiation occurs in the monomer, because the system contains nothing but monomer and initiator. A monomer-soluble initiator would be used. As the polymerization progresses, the viscosity increases noticeably, and the propagation takes place in a medium of associated polymer chains dissolved in, or swollen by the monomer until the monomer is consumed. Termination in a free-radical bulk polymerization can occur in two ways: by the combination of two growing chains or by chain transferring [34]. When viscosity is high, the termination reaction is hindered, since the macroradicals are unable to diffuse readily in the viscous medium. In contrast, the monomer may diffuse quite readily and high molecular weight macroradicals are produced as the result of propagation in the absence of termination. This autoacceleration, called Norris-Trommsdorff, or gel effect, causes the formation of unusually high molecular weight polymers [35].

Advantages of this technique include high yield per reacting volume, easy and high purity polymer recovery, and the option of casting the polymerization mixture into final product form. The principal difficulties are removal of dissolved gases, adjustment for the shrinkage in volume, and adequate control of the highly exothermic polymerization reaction in the early stages, especially after the material has reached the gel consistency [10].

1.6 VISCOSITY AVERAGE MOLECULAR WEIGHT DETERMINATION

The viscosity of a fluid is simply a measure of its resistance to flow and as such reflects the frictional forces between the molecules. In a solution one would therefore expect these frictional forces to increase with the size of the solute, so that viscosity measurements provide a measure of molecular weight as Staudinger realized in the very early days of polymer science [36].

Measurement of the viscosity of dilute polymer solutions is one of the most frequently used, and easily available methods, for the characterization of the average molecular weights of polymers. Viscosity of solvent and solutions are usually determined in capillary viscometers. Viscosity is measured by determining the flow time of the solvent or the solution between two marks on the glass capillary [37].

The experimental procedure consists of measuring the efflux time, t, it takes a given volume of polymer solution to flow through a capillary tube and relating into the corresponding efflux time t_0 for the solvent. This leads to the following expressions:
Realtive viscosity, η_r :

$$\eta_r = \frac{t}{t_0} \tag{1.30}$$

Specific viscosity, η_{sp} :

$$\eta_{\rm sp} = \eta_{\rm r} - 1 = \frac{t - t_0}{t_0} \tag{1.31}$$

Reduced viscosity, η_{red} :

$$\eta_{\rm red} = \frac{\eta_{sp}}{C} \tag{1.32}$$

Inherent viscosity, η_{inh} :

$$\eta_{\rm inh} = \frac{\ln \eta_r}{C} \tag{1.33}$$

Intrinsic viscosity, $[\eta]$:

$$[\eta] = \left(\frac{\eta_{sp}}{C}\right)_{C=0}$$
(1.34)

where C is the concentration.

The viscosity data as a function of concentration are extrapolated to infinite dilution by means of the Huggins or Kraemer equation.

$$\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c \qquad (\text{Huggins, 1942}) \qquad (1.35)$$

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \qquad (Kraemer, 1938) \qquad (1.36)$$

Where k' and k'' are constant for a series of polymer of different molecular weight in a given solvent. The extrapolation gives intrinsic viscosity $[\eta]$. The k' + k'' = 0.5 indicates a good solvent for the polymer.

The intrinsic viscosity being dependent of concentration by virtue of extrapolation to zero concentration can be used for molecular-weight determinations. Mark-Houwink expressed this in the relationship:

$$[\eta] = KM^{\alpha} \tag{1.37}$$

where K and α are constants determined from a double logarithmic plot of intrinsic viscosity and molecular weight. The emprical relation ship is validonly for linear polymers, which is a limitation of the method [34].

1.7 AIM OF THE WORK

In this study, the polymerization of ethyl methacrylate was carried out in bulk system for different time periods to get the percent conversions. In order to obtain polymers that can be processable and have lower molecular weight, the polymerization was carried by Atom Transfer Radical Polymerization. ATRP has caused a decrease in molecular weight. Therefore, polymerization in different initiation systems was examined. The molecular weight of samples was measured by viscosity method. Nuclear Magnetic Resonance, Infrared Radiation Spectroscopy and Differential Scanning Calorimetry were applied for the polymer characterization.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Monomer

Ethyl Methacrylate (Aldrich) was used as monomer without further purification.

2.1.2 Ligand

4,4'Dimethyl 2,2'bipyridine (Fluka) used as ligand for atom transfer radical polymerization.

2.1.3 Catalyst

Copper(I)chloride is used as catalyst for atom transfer radical polymerization.

2.1.4 Initiators

P-toluenesulfonylchloride is used as initiator for atom transfer radical polymerization and benzoyl peroxide is used as initiator for free radical polymerization.

2.1.5 Solvents

Methanol and toluene were all reagent grades and used without further purification.

2.2 INSTRUMENTATION

2.2.1 Polymerization Tubes

The tubes used for ATRP were 1-3 cm. in diameter, 10 cm. in length Pyrex tubes. The open ends of the pyrex tubes were attached to another tube of smaller diameter, which allows to be connected to the vacuum line with ease. For free radical polymerization 10 ml. capacity with TFE stopcock tubes were employed.

2.2.2 High Vacuum System

In order to evacuate the vacuum tubes containing the monomer, high vacuum system at 10^{-4} to 10^{-5} mmHg pressures for about 2-3 hours was applied.

a) Duo-Seal Vacuum Pump

It is a product of "Sargent-Welch Scientific Co." Model 1399 and capable of pressure reduction and down to 1.5×10^{-2} mmHg

b) Mercury Diffusion Pump

It is a water-cooled one-stage diffusion pump with an approximate capacity of 200 ml of mercury. Mercury was heated by a 143 W metallic bond resistive heater operating at 130 V, which is a product of "Pliz Co." Type 62

c) Main Manifold

A Pyrex glass tube of length 11 cm., diameter 4.53 cm. was employed. It was connected to the first trap by a high vacuum stopcock and to the sample holder tubes to high vacuum stopcocks with standard joints.

d) Liquid Nitrogen Traps

Two Pyrex traps were used to protect the pumps from the chemicals evaporating at low pressures and placed before the connection of each pump.

2.2.3 Gamma Radiation

Irradiation was made in a "220 model Gamma Cell" made "Atomic Energy of Canada Limited". In this gamma cell unit the cobalt is in the form of a yellow cylinder into which the sample is introduced by means of the moving drawer; spiral tubes through the drawer allow wires and small tubes to be led into the irradiation cavity without the escape of irradiation. The "Gamma Cell 220" used contains 12400 curies of Cobalt-60 with a radiation intensity of 0.011 MRads/hour. (on April 2003)

2.2.4 Viscometer

Viscosities of different concentrations of polymer solutions were measured with Ethyl acetate as a solvent at 35 ^oC by using Ubbelohde glass viscometer. The driving pressure in this viscometer was determined by measuring the distance from the level of the liquid in the bulb to the level, which is the bottom of the capillary

2.2.5 Infrared Spectrometer

Infrared spectra of monomer and the polymers obtained with different polymerization techniques were taken from KBr pellets by using Perkin Elmer Spectrum-One FT-IR Spectrometer.

2.2.6 Differential Scanning Calorimetry

The thermal analyses of the samples were recorded by TA-DSC 910S differential scanning calorimeter. Heating rate 10° C/min. from -50° C to 250° C under nitrogen gas atmosphere.

2.2.7 Nuclear Magnetic Resonance

The molecular structure of PEMA was determined by using Magnetic Resonance Spectrometer, Ultrashield 400 MHz Digital NMR Bruker, with ¹H and ¹³C Spectrometers.

2.3 EXPERIMENTAL PROCEDURE

2.3.1 Free Radical Polymerization at Open Atmosphere

2.0 ml of EMA and 0.0020g of benzoyl peroxide were put into the 10 ml tubes with PTFE stopcock. After polymerizing at 60° C, 70° C, 80° C at different time periods, the tubes were open and the contents first dissolved in toluene, then polymer precipitated in methanol. The polymer were transferred into a crucible and they were put into the drying oven at 60° C under vacuum until constant weight. The conversions were calculated gravimetrically.

Conversion % =
$$\frac{mass of polymer}{mass of monomer} \ge 100$$
 (1.38)

2.3.2 ATRP at High Vacuum System

0.0037g 4,4'dimethyl 2,2'bipyridine as ligand, 0.0010g Copper(I)chloride as catalyst, 0.0038g p-toluenesulfonylchloride as initiator and 2 ml EMA were put into the vacuum tubes and High Vacuum System was applied for about 3 hours at 10⁻⁴ to 10⁻⁵ mmHg in order to evacuate the tubes and they were sealed with flame. After polymerizing with Gamma Radiation or thermally at 80^oC at different time periods, the tubes were broken opened and the same procedure as 2.3.1 was applied.

2.3.3 Viscosity Measurement

Viscosity was measured in Ubbehlohde viscometer at 35° C using ethyl acetate as solvent. About 50 mg of polymer was dissolved in 25 ml. of solution and filtered after complete dissolution. Then 15 ml of this solution was transferred into viscometer in constant temperature water-bath. The experiments were repeated by diluting 15 ml PEMA solutions 4 times by adding 5 ml of solvent ethyl acetate each time. Then specific viscosity to concentration ratio, (η_{sp} /c), was plotted against concentration (c), the intercept of the straight line gives intrinsic viscosity [η] by means of the Huggins equation (1.35). Similarly ln n_r / c vs concentration were plotted according to Kraemer's equation (1.36). The k' and k'' values from slopes were found and k' + k'' calculated. The relation between molecular weight and intrinsic viscosity is given in equation (1.37).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. POLYMERIZATION OF EMA

3.1.1 FREE RADICAL POLYMERIZATION IN BULK AT OPEN ATMOSPHERE

Ethyl methacrylate was polymerized in constant temperature oven at 60° C, 70° C and 80° C for different time periods using benzoyl peroxide as the initiator. The percent conversions with time at 60° C, 70° C and 80° C are given in Table 3.1, Table 3.2, Table 3.3 and the percent conversions are plotted against time in Figure 3.1, Figure 3.2, Figure 3.3 respectively.

Table 3.1	Time-percent	conversions t	for the free	radical	polymerization
of EMA a	t 60 ⁰ C.				

Time (hour)	% Conversion
6.0	0.0
8.0	1.1
12.0	15.5
14.0	19.8
16.0	15.3
16.5	16.0
17.0	38.1
17.5	62.4
18.0	94.4
20.0	100.0
22.0	96.7





Table 3.2 Time and percent conversion results for the free radical polymerization of EMA at 70° C.

Time (hour)	% Conversion
2.0	0.0
4.0	8.4
6.0	14.1
7.0	39.9
7.3	45.5
8.0	88.0
10.0	100.0
12.0	100.0





Table 3.3 Time and percent conversion results for the free radical polymerization of EMA at 80° C.

Time (hour)	% Conversion
2.00	11.5
2.50	19.1
2.75	23.0
3.00	48.8
3.25	86.4
3.50	91.6
4.00	98.0
4.50	100.0





The polymerizations of PEMA under open atmosphere showed induction periods. This is because of inhibiting effect of molecular oxygen on the polymerization. The oxidation of organic compounds with atmospheric oxygen is often termed auto oxidation because the rates of these reactions almost always show an autoacceleration. Oxidation reactions are free radical in mechanism. The autooxidation of hydrocarbons is a twostep chain-reaction sequence leading primarily to the formation of hydroperoxide groups. The two steps are: (1) a radical combination reaction, assuming oxygen to be a diradical in the ground state, and (2) a hydrogen abstraction reaction.

 $R^{\cdot} + O_2^{\cdot} \longrightarrow RO_2^{\cdot}$

 RO_2 ·+ RH \longrightarrow RO_2H + R·

The overall reaction rate depends on the hydrogen abstraction reaction, which is usually much slower than the rate of formation of peroxy radicals in the preciding step. One hydroperoxide functional group is formed in each sequence, and this group can subsequently act as an initiator for the generation of new radicals. Hydroperoxides so formed are particularly susceptible to decomposition either by metal ions or by absorption of thermal or ultraviolet light energy. Polymerization occurs only after free oxygen is removed by reaction to form peroxides.

Because of the effect of oxygen, the polymerization of PEMA has started after about 6 hours at 60° C, about 2 hours at 70° C and about 1 hour at 80° C while all the oxygen was consumed. The difference in the induction periods are due to the thermal energy difference between 60° C, 70° C and 80° C. As the thermal energy is higher at 80° C, the decomposition of hydroperoxides occur faster than decomposition at 70° C and correspondingly, the decomposition of hydroperoxides at 70° C is faster than the decomposition at 60° C.

There are smooth increases in the percent conversions after induction periods in each polymerization temperature. Then a rapid increase occurs in the percent conversions because of Norris-Trommsdorff or gel effect, which is a result of high viscosity that prevents diffusion of macroradicals in viscous medium while the monomers diffuse quite readily and high molecular weight macroradicals are produced in the absence of termination reaction. After this autoacceleration period 100 % conversion is reached in a short time.

The times required to reach some certain percent conversions at 60^{0} C, 70^{0} C and 80^{0} C was compared in Table 3.4 and the differences in the % conversion vs. time graphs due to temperature difference are compared in Figure 3.4.

Table 3.4 Comparison of the time required getting the same % conversion for the free radical polymerization of EMA at open atmosphere 60° C, 70° C and 80° C.

	% conversions						
	15	40	60	100			
Time required for free radical polymerization of EMA at 60 ^o C (hour)	12	17	17.5	20			
Time required for free radical polymerization of EMA at 70 ^o C (hour)	6	7	7.7	10			
Time required for free radical polymerization of EMA at 80 ^o C (hour)	2.25	2.9	3.1	4.5			





3.1.2 ATRP UNDER VACUUM

Ethyl methacrylate was polymerized in an oven at 80° C for different time periods using CuCl/4,4'dimethyl 2,2'bipyridine as catalyst system and p-toluenesulfonylchloride as the initiator and the percent conversions are calculated. The percent conversion change with time at 80° C is given in Table 3.5 and the percent conversions are plotted against time in Figure 3.5.

Polymerization curve showed an induction period and conversion changed linearly with time. Autoacceleration stage is not observed. Thus the rate of reaction can be controlled better and gel effect is eliminated.

Time (hour)	% Conversion
20.0	17.0
25.0	31.8
30.0	35.6
35.0	39.4
40.0	57.6
46.5	63.3

Table 3.5 Time and percent conversion results for the ATRP of EMA at 80^oC in vacuum.





3.1.3 ATRP BY GAMMA IRRADIATION UNDER VACUUM

Ethyl methacrylate was polymerized in an oven at 80^oC for different time periods by using CuCl/4,4'dimethyl 2,2'bipyridine as catalyst system and p-toluenesulfonylchloride as the initiator and the percent conversions are calculated. The percent conversion change with time by gamma irradiation is given in Table 3.6 and the percent conversions are plotted against time in Figure 3.6.

In this case, the kinetic curve is typical to a radiation initiated polymerization showing S-type. There is a relatively long induction period. Thus the effects of complex is less and initiation of monomer is mostly with radiation rather than radical initiator.

Table 3.6 Time and percent conversion	results	for	the	ATRP	of	EMA
by gamma irradiation in vacuum.						

% Conversion
6.0
19.2
23.8
69.0
89.5
99.2
100.0





3.2 MOLECULAR WEIGHT DETERMINATION BY VISCOSITY

Viscosity measurements are carried out for each type of polymerization systems. For PEMA K and α values are 8.6 x 10⁻³ ml/g and 0.71 respectively at 35^oC in ethyl acetate [38]. In the free radical polymerization of EMA in bulk at 80^oC obtained viscosity average molecular weight values are increasing from 5.3 x 10⁵ to 10.3 x 10⁵ as conversion increases and there is a small decrease at higher percentages conversions due to the chain degradation. The molecular weight changes with percent conversion results for free radical polymerization at 80^oC is given in Table 3.7 and the molecular weights are plotted against percent conversion in Figure 3.7.

Table	3.7 I	Molecula	ar weight	and	percent	conversion	results	for	the	free
radica	l pol	ymeriza	tion of El	MA a	at 80ºC.					

% Conversion	[η]	$\dot{k} + \dot{k}$	$M_{\rm w} \ge 10^{-5}$
11.5	100.8	0.55	5.3
19.1	109.3	0.59	6.0
23.0	110.4	0.63	6.1
48.8	170.1	0.65	11.2
86.4	160.2	0.69	10.3
91.6	156.7	0.65	10.0





The viscosity average molecular weights of the polymer obtained ATRP of EMA at 80° C in vacuum are between 0.6 x 10^{5} to 1.3 x 10^{5} increasing with the percentage conversion linearly. The molecular weight change with percent conversion results for ATRP of EMA at 80° C in vacuum are given in Table 3.8 and the molecular weights are plotted against percent conversion in Figure 3.8.

At 17.0 % conversion molecular weight is about 6 x 10^4 , which is much lower than the molecular weights obtained by conventional free radical polymerization. (e.g. 10 times smaller than that reported in table 3.7)

 Table 3.8 Molecular weight and percent conversion results for the

 ATRP of EMA at 80°C in vacuum.

% Conversion	[η]	$\dot{k} + \dot{k}$	$M_{\rm w} \ge 10^{-5}$
17.0	22.4	0.27	0.6
31.8	22.5	0.29	0.6
39.4	24.3	0.35	0.7
57.6	31.9	0.39	1.1
63.3	36.7	0.45	1.3





In the ATRP of EMA by gamma radiation in vacuum obtained viscosity average molecular weight values are increasing from 1.4×10^5 to 31.5×10^5 as conversion increases and there is a small decrease at higher percentages conversions due to the chain degradation. The molecular weight change with percent conversion results for ATRP of EMA by gamma radiation in vacuum is given in Table 3.9 and the molecular weights are plotted against percent conversion in Figure 3.9.

The molecular weight shows similar changes as that of radiation polymerization. Initially ATRP mechanism is noticeable and molecular weight is lower but at higher conversions, gamma rays becomes more functional compared to ATRP.

Table	3.9	Molecular	weight	and	percent	conversion	results	for	the
ATRP	of H	EMA by gan	nma irra	ndiati	on in vac	uum.			

% Conversion	[η]	$\dot{k} + \dot{k}$	$M_{\rm w} \ge 10^{-5}$
6.3	39.6	0.41	1.4
19.2	24.2	0.78	0.7
23.8	30.0	0.62	1.0
68.3	285.0	0.68	23.2
89.0	354.4	0.64	31.5
98.2	300.0	0.63	25.0





When viscosity average molecular weights were compared, it was seen that the smallest values and changes in molecular weights were obtained with thermal ATRP at 80^oC and the increase in molecular weight was lineer. Although ATRP with gamma irradiation showed similar molecular weight values at the lower percent conversions with thermal ATRP, as the conversion increase the highest value of molecular weights of all three experiments reached. In both experiments lower molecular weight values were obtained than classical free radical polymerization. The percentage conversions required to reach some certain molecular weights with free radical polymerization, thermal ATRP and ATRP with gamma irradiation was compared in Table 3.10 and the differences in the viscosity average molecular weight versus percentage conversion are compared in Figure 3.10.

Table 3.10 Comparison of the Molecular weights of the same % conversion for the free radical polymerization, ATRP thermally and ATRP by gamma irradiation.

	% Conversions		
	20	40	60
Molecular weight of free radical polymerization (10^{-5})	6.0	10	11
Molecular weight of ATRP thermally (10^{-5})	0.5	0.8	1.1
Molecular weight of ATRP by gamma irradiation (10 ⁻⁵)	0.7	9	20





3.3 FOURIER TRANSFORM INFRARED SPECTROMETER (FT-IR)

For the characterization of poly (ethyl methacrylate), the fourier transform infrared, FTIR spectra were obtained for the monomer, EMA, and polymer, PEMA, given in Figures 3.11 and 3.12, respectively and both spectras were put into a single figure in Figure 3.13.

In both of the spectra there are some common peaks due to the alkyl groups between 2900 cm⁻¹ and 3000 cm⁻¹. Asymmetric C-H stretching of the methyl groups gives a peak at 2983 cm⁻¹ and C-H stretching of the methylene -C- group gives a peak at 2940 cm⁻¹. Other common peaks are at about 1700 cm⁻¹ for the stretching vibration of the carbonyl compound and a weak peak for the overtone of the carbonyl stretching band.

The main difference between monomer EMA from PEMA is the C=C double bond stretching which should not exist in the PEMA. As observed in the spectrums this double bond gives a peak at 1638 cm⁻¹ and the C-H bonding due to C=CH₂ group comes at 939 cm⁻¹. These peaks are very small at the PEMA spectrum because of the fact that some disproportion occurs in the termination process. Another difference was observed in the carboxylic acid ester groups which were some shifts and broadenings in the related peaks. The ester peak at 1148 cm⁻¹ broadens in the polymer spectrum, also the –O- peaks at 1320 cm⁻¹ and 1296 cm⁻¹ in the monomer shifted to 1269 cm⁻¹ and 1239 cm⁻¹, the –CH₃ peak at 1451 cm⁻¹ in monomer spectrum was at 1448 cm⁻¹ in polymer spectrum, the peak at 1366 cm⁻¹ in monomer spectrum and at 1388 cm⁻¹ in polymer spectrum.













3.4 DIFFERENTIAL SCANNING CALORIMETRY

In the DSC thermograms of PEMA obtained the T_g of the polymer was observed at 44.5°C for the ATRP in gamma irradiated in Figure 3.14, at 38.8°C for the free radical polymerization in Figure 3.15 and, 46.4°C for the ATRP at 80°C in Figure 3.16. The overlaid thermogram of all polymerizations is given in Figure 3.17.

The Tg value for PEMA is given as 12° C for isotactic, 65° C and 66° C atactic and syndiotactic PEMA, respectively [38].

The T_g value changes with number average molecular weight as:

$$\frac{1}{T_g} = \frac{1}{T_{T_{g\infty}}} - \frac{K}{M_n}$$

Therefore, for lower molecular weight the T_g will be low, the values reported are the limiting values of $T_{g\alpha}$. The difference observed are due to different molecular weights. If the tacticity were present, there should be melting peak also in the DSC thermograms.
















3.7 NUCLEAR MAGNETIC RESONANCE

For the characterization of PEMA, ¹H-NMR and ¹³C-NMR spectra of monomer EMA and polymer PEMA are investigated. ¹H-NMR of EMA and PEMA are given in Figures 3.18 and 3.19, and ¹³C-NMR spectra are given in Figures 3.20 and 3.21, respectively.

In the ¹H-NMR spectrum of ethyl methacrylate (Figure 3.18), the methyl group in O-CH₂-CH₃ group gives a triplet at 1.2 ppm because of two protons of methylene in O-CH₂- group and the methylene, $-CH_2$ -, gives a quarted at 4.1 ppm because of three protons of methyl group in O-CH₂-CH₃ and the shift is caused by the electronegative oxygen atom. The α -methyl group of the monomer is seen at 1.85 ppm. The two peaks at 5.45 ppm and 6.0 ppm represents the vinyl group protons, CH₂=C, of the monomer EMA.

In the ¹H NMR spectrum of PEMA (Figure 3.19), the methyl peaks of O-CH₂-CH₃ group is between 1.2 ppm and 0.8 ppm and the methylene, -CH₂-, peak at 4 ppm. with the chemical shift because of electronegative oxygen atom. The vinyl peaks at 5.45 and 6.0 ppm in the PEMA spectra disappeared and instead of these methylene, peak appeared at 2.2 ppm in the spectrum of EMA. The solvent peak is at 7.1 ppm. These show that the polymerization reaction occurs by the opening of vinyl group.









The ¹³C NMR spectra of monomer EMA and polymer PEMA are given in Figures 3.20 and 3.21, respectively.

In the ¹³C NMR spectrum of the monomer (Figure 3.20), ethyl methacrylate, the peak at δ 14.4 refers to the carbon of the methyl in the –O-CH₂-CH₃ group and the peak at δ 60.8 is for the carbon of the methylene group of –O-CH₂. The carbonyl group carbon, C=O, is at the δ 167 and the α -methyl carbon of the monomer gives peak at δ 18.5. The peaks at δ 125.3 and δ 136.9 correspond to the carbons of double bond CH₂= and C=C, respectively. The triplet solvent peak is at δ 77.5.

In the ¹³C NMR spectrum of polymer (Figure 3.21), polyethyl methacrylate, the peaks for the methyl carbon of O-CH₂-CH₃ group at δ 14.2, the methylene carbon of O-CH₂-CH₃ group at δ 61.1, the α -methyl carbon of the monomer at 17.1, the carbonyl group carbon, C=O, at δ 177.8 and the solvent peak at 77.4 are similar to the monomer spectrum. On the contrary the double bond carbons peaks at δ 125.3 and δ 136.9 disappeared instead of these the peaks methylene peak of the polymer backbone, -CH₂-, appears at δ 45.5 as a result of the vinyl opening reaction of the polymerization. Some traces of double bond has seen at δ 129 because of the disproportionation reaction of termination.









CHAPTER 4

CONCLUSIONS

The following results are concluded from this study;

- 1. In bulk polymerization of EMA by free radical at open atmosphere oxygen in the medium cause an induction period.
- 2. In bulk polymerization of EMA by free radical at open atmosphere induction period due to oxygen is inversely proportional with temperatue.
- 3. In bulk polymerization of EMA by free radical at open atmosphere reaction rate is directly proportional with temperature.
- 4. In bulk polymerization of EMA by ATRP under vacuum at 80^oC there is a lineer conversion curve and no autoacceleration observed.
- In bulk polymerization of EMA by ATRP under vacuum in gamma irradiation polymers show similar initiation as ATRP thermally at 80^oC however autoacceleration occurred and S-type conversion observed.

- 6. By ATRP lower molecular weight polymers were obtained than free radical, in thermal ATRP molecular weight increase linearly by conversion and all lower than free radical. However, the molecular weight in Gamma irradiated ATRP distributes from lower values to much higher values than free radical by the increasing conversion.
- 7. Characterization of Polymers in NMR and IR shows that the polymerization is a vinyl opening polymerization.

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