POLYMERIZATION AND CHARACTERIZATION
OF
2-HYDROXYETHYL ACRYLATE

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Approval of the Graduates School of Natural and Applied Sciences

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ABSTRACT

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2-HYDROXYETHYL ACRYLATE

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Poly(2-Hydroxyethyl acrylate), PHEA, is used as hydrophilic polymeric gels which have been studied because of its great importance for agricultural or biomedical applications. Biomedical applications of hydrogels include soft contact lenses, artificial corneas, soft tissue substitutes and burn dressings. In this study, it was aimed to synthesis the polymers with well-defined molecular weights, polydispersities and cahin topologies. Bulk, solution and atom transfer radical polymerization (ATRP) techniques at different temperatures were examined. The polymerization in bulk form was carried in vacuum and in open atmosphere. The polymerization curves showed autoacceleration mechanism. The polymers obtained were insoluable in most common solvents because of having high molecular weights and are crosslinked. So in order to overcome this problem, 2-hydroxyethyl acrylate was polymerized by solution and ATRP methods. The activation energy for bulk polymerization was found from Arrhenius plot. The polymer was characterized by FT-IR, DSC, TGA, ^{1}H and ^{13}C NMR techniques, Tensile tests were also examined for PHEA.

Key words: 2-hydroxyethyl acrylate, bulk polymerization, solution polymerization, ATRP, activation energy, characterization.

ÖZ

2-HİDROKSİETİL AKRİLATIN POLİMERLEŞTİRİLMESİ VE KARAKTERİZASYONU

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YL., Polimer Bilimi ve Teknolojisi Bölümü
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Hidrofilik polimerik jel olarak kullanılan poli(hidroksietil akrilatın),PHEA, tarımsal ve biyomedikal uygulamalarındaki öneminden dolayı çalışıldı. Hidrojellerin biyomedikal kullanım alanları içerisinde yumuşak kontak lensler, yapay kornealar, yumuşak doku sübstituentleri ve yanık sargısı yer alır. Bu çalışmada, iyi tanımlanmış molekül ağırlıklı, çok dağılımlı ve zincir topolojisi uygun polimerlerin sentezlenmesi amaçlandı. Farklı sıcaklıklarda kütle, çözelti ve atom transfer radikalik polimerleşme (ATRP) teknikleri kullanıldı. Kütle polimerleşmesi vakum ve açık atmosferde uygulandı. Polimerleşme eğrileri oto-ivmelenme gösterdi. Elde edilen polimerler yüksek molekül ağırlığı ve çapraz bağlanmalardan dolayı bilinen çoğu yaygın çözücülerde çözünmedi. Bu sorunun üstesinden gelebilmek için 2-hidroksietil akrilat, çözelti ve ATRP metodları ile polimerleştirildi. Kütle polimerleşmesi için aktivasyon enerjisi Arrhenius grafiğinden bulundu. Polimerin karakterizasyonu

FT-IR, DSC, TGA, ^{1}H-NMR ve ^{13}C-NMR teknikleri ile yapıldı. Ayrıca PHEA için çekme-kopma testleri uygulandı.

Anahtar Kelimeler: 2-hidroksietil akrilat, kütle polimerleşmesi, çözelti polimerleşmesi, ATRP, aktivasyon enerjisi, karakterizasyon.

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To my.family.

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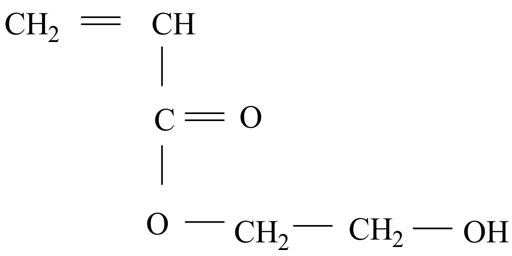
INTRODUCTION

1.1 2-HYDROXYETHYL ACRYLATE

2-Hydroxyethyl acrylate, HEA is an asymmetrically substituted ethylene, with the following formula:

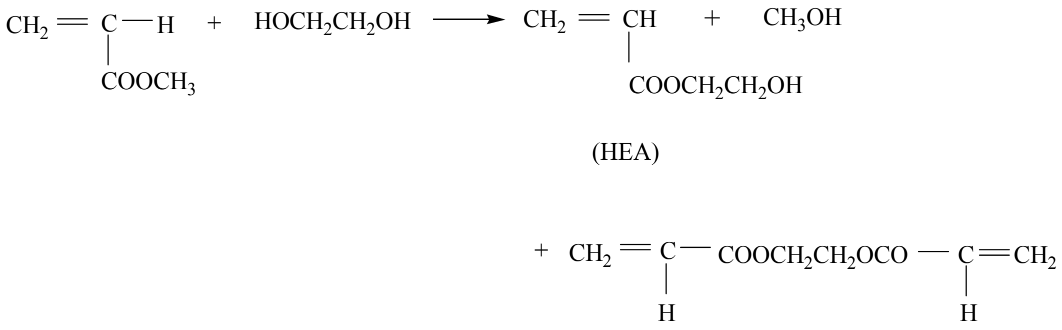


$CH_2=CH-C(=O)-O-CH_2-CH_2-OH$

2-Hydroxyethyl acrylate

The monomer boils at 82°C, has a density of 1,106 g/mL at 25°C and the flash point of 99°C. HEA is a clear, colorless, dangerous environmental pollutant and a toxic liquid of a penetrating and disagreeable odor. It is stabilized by 200 to 400 ppm of hydroquinone monomethyl ether (MEHQ) and it has to be handled under cold conditions.

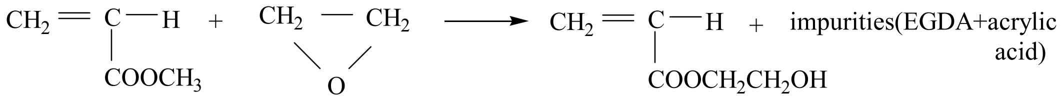
Commercial HEA can be synthesized in a single step from methyl acrylate or acrylic acid by a transesterification reaction with ethylene glycol or ethylene oxide.



$$CH_2{=}C(COOCH_3){-}H + HOCH_2CH_2OH \longrightarrow CH_2{=}CH(COOCH_2CH_2OH) + CH_3OH + CH_2{=}C(H){-}COOCH_2CH_2OCO{-}C(H){=}CH_2$$

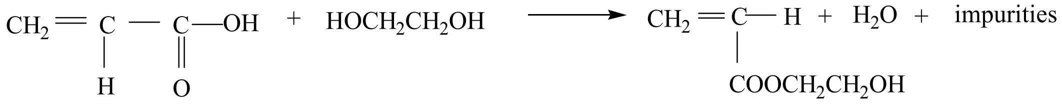
(HEA)

(EGDA)



$$CH_2{=}C(COOCH_3){-}H + CH_2{-}CH_2(O) \longrightarrow CH_2{=}C(COOCH_2CH_2OH){-}H + \text{impurities(EGDA+acrylic acid)}$$

(HEA)



$$CH_2{=}C(H){-}C({=}O){-}OH + HOCH_2CH_2OH \longrightarrow CH_2{=}C(COOCH_2CH_2OH){-}H + H_2O + \text{impurities}$$

Commercial HEA monomer always contains impurities such as ethylene glycol, acrylic acid and ethylene glycol diacrylate (EGDA). Especially the presence of EGDA leads to crosslinking, and in the presence of large amounts of acrylic acid, no polymerization is observed. Polymerizations of the unpurified or poorly purified monomer may be either slow and incomplete or lead to insoluble solids [1]. So it is essential that the monomer must be purified prior to polymerization.

1.2. HISTORY AND COMMERCIAL USE OF POLYACRYLATES

In 1873 methyl, ethyl and allyl acrylate were prepared but only allyl acrylate was observed to polymerize. However, Kahlbaum reported the polymerization of methyl acrylate in 1880. Fitting found that methacrylic acid and some of its derivatives polymerize readily. Ethyl methacrylate was prepared in 1891 [2]. In 1901 in Tuebingen, Germany, Dr. Otto Röhm published his doctoral thesis in which he described the chemical structure of the liquid condensation products obtained from the action of sodium alkoxides on methyl and ethyl acrylate, and characterized in some detail the solid polymeric material formed simultaneously. As a result of this work, a patent was issued in 1912 describing rubber substitutes made by vulcanizing polyacrylates with sulfur. A polyacrylate rubber is actually being manufactured as an out-growth of work by the Eastern Regional Research Laboratory of the U.S. Department of Agriculture [3].

In 1927, Röhm and Haas in Darmstadt began limited production of polymethyl acrylate under the trade names Acryloid, as a suggested ingredient for surface finishes and lacquers, and Plexigum, for use as a safety glass interlayer.

Methyl methacrylate soon became the most important member of the acrylic family. Research on cast sheets from methyl methacrylate was carried out during the 1930's by Röhm&Heas A.-G. in Germany, and by Imperial Chemical Industries Ltd. in England.

Hill of Imperial Chemical Industries discovered that methacrylate ester polymers, especially MMA polymers, were rigid, optically clear plastics suited to replace glass in such applications as aircraft windows.

The elastomeric acrylic ester polymers and higher alkyl methacrylate polymers are becoming increasingly important in a wide variety of applications. They are used in textile sizing, in special adhesives and lacquers and as oil additives [2].

Acrylics are sometimes referred to as “plastic glass” which have not only captured the novelty trade for costume jewelry, pocketbooks, hairbrushes, umbrella handles, trays and ornaments, but also have found more practical purposes in many industrial and commercial products for every day use, such as outdoor signs, patio-roofs, watch crystals, airplane windows, automobile tail light, sky light, sun glass lenses, dentures, and acrylic-water-latex paints.

The industrial applications of solutions or emulsion of acrylic ester polymer as coating or impregnants are many and varied. The inherent stability, durabilty and pigment binding characteristics of acrylic polymers have been important factors in selection of such systems in various coating applications such as in leather and textile finishing. Acrylic ester emulsion polymers are used in the paper industry as pigment binders, saturants, fibers and wet-end additions for high strength paper [4].

Poly(2-hydroxyethyl acrylate), PHEA, is used as hydrophilic polymeric gels which have been studied because of their great importance for agricultural or biomedical applications. The biomedical field is favoured because of the biocompatibility, which is based on the possibility of an interchange between the water of the hydrogel and the body fluids. Hydrogels are polymer networks, which absorb and retain water without dissolving.

Biomedical applications of hydrogels include soft contact lenses, artificial corneas, soft tissue substitutes and burn dressings. Furthermore, the application of hydrogels to a variety of substrates leads to the production of thrombo-resistant coatings, catheters or blood detoxicants. Hydrogels are impregnated with biologically active agents, such as antibiotics, enzymes, contraceptives, drug antogonists, anticancer drugs etc. and may serve as systems for the controlled release of the agents absorbed to a specific size of the body [5].

Controlled release of proteins and peptides from hydrogels synthesized by gamma-ray-induced PHEA was studied by Coliceti et. al. [6]. Inukai et. al. [7] studied the preparation and characterization of hyaluronate-hydroxyethyl acrylate blend hydrogel as a controlled release device.

Mengoli and Martina [8] obtained protective coatings on metallic sheets by in situ polymerization of 2-HEA.

Zubarev et. al. [9] are synthesized the nematic liquid-crystalline polymer network based on 4-(4-cyano-4'-biphenylyoxy) butyl acrylate and 2-HEA. They studied the effects on the conditions of network formation, its topology and the structure of junctions in the phase transition nematic-isotropic phase of this copolymer.

1.3 PROPERTIES OF POLYACRYLATES

The acrylate and methacrylate esters provide a series of monomers whose polymers vary from soft, rubberlike materials to hard plastics. Polymethyl acrylate is a tough, rubbery and moderately hard polymer and having little or no tack at room temperature. Polyethyl acrylate is considerably softer, more extensible, more rubberlike and not quite as tough as polymethyl acrylate. The polymer of n-butyl acrylate is still softer and rather tacky at room temperature. These trends to tackier, softer polymer continue to n-dodecyl (lauryl) ester [3].

Andreopoulos [5] studied hydrogels based on poly(2-hydroxyethyl acrylate)crosslinked with 1,4-butanediol dimetacrylate with respect to their swelling and mechanical behaviour. The modulus of elasticity was found to increase with BGDMA concentration.

Pradas et. al. [10] prepared porous poly(2-HEA) hydrogels by HEA and EGDMA (as crosslinking agent) and macroscopic pores are formed due to the segregation of the solvent from the polymer. The elastic modulus and loss tangents were measured by the dynamic mechanical relaxation process. The main feature found in the dynamic mechanical spectroscopy is the decrease of the elastic modulus in the rubber-like region as the porositiy of the sample increases.

Dielectric relaxation properties of PHEA hydrogel were examined by Gomez et. al. [11]. They explained that PHEA presents two relaxation zones, labelled γ and α, when it is completely dry. The temperature of the maximum of the γ relaxation, as well as its apparent activation energy, are somewhat higher than in poly(hydroxyethyl metharylate), PHEMA, a fact that could be explained by higher intermolecular interactions in the series of polyacrylates than in the series of polymethacrylates. The absorption of even slight traces of water causes a new relaxation to appear. The intensity of which increases with the content of water, while at the same time the intensity of the γ relaxation decreases. This fact suggests the formation of an association of the water molecules with the polar groups of the side chains in the polymer, in such a way that the internal motions in the group resulting from this association are further hindered, producing a different relaxation. The characterization of the α relaxation is difficult because of the high d.c. conductivity component of the permittivity. Its temperature suggests the presence of hydrogen bonds, which render the main chains rigid.

Depolarization thermocurrent and dielectric relaxation spectroscopy in PHEA/water hydrogels were studied by Kyritsis et. al. [12-13]. PHEA hydrogels with water contents varying in a wide interval were studied by differential scanning calorimetry (DSC) and thermally stimulated depolarization currents (TSDC). The TSDC measurements reveal the influence of water on the secondary relaxations when the water content is higher than 0.3%. The dependence of the glass transition temperature and the temperature of the main dielectric relaxation had been determined as a function of the water content. Detailed investigations on the dielectric relaxation mechanisms in PHEA, by means of the TSDC method in the temperature range 77-300 K were reported. There was particular interest in the dependence of the dielectric relaxation mechanisms on the water content, h, h=0-0.5 w/w, in an attempt to contribute to a better understanding of the physical structure of water in the PHEA hydrogels.

Permeability in the amorphous state of polyacylates increase as the side chain length becomes longer but shows mixed trends in the crystalline state. Permeability decreases in the amorphous state when the backbone stiffens. The effect of the main chain versus side chain crystallinity on the permeation is more. The influence of a compositional change in the amorphous phase upon melting on the gas permeability of side-chain crystalline polymers is also considerable [14].

Toshiaki et. al. [15] reported the selectivity of the liquid polymer hybrid membrane composed of carbon tetrachloride and 2-hydroxyethyl acrylate-acrylonitrile graft copolymer for ethanol-water mixture. A membrane with selective permeability for ethanol was designed for the separation of ethanol from its aqueous solution by pervaporation on the basis of the differences in solubility between the two components of the membrane. A liquid membrane was introduced to extend this difference and the ethanol in the liquid membrane was isolated by the polymer membrane; that is, a liquid-polymer hybrid membrane was formed. Carbon tetrachloride was used as a liquid membrane, and a HEA-AN graft copolymer membrane was used as a polymer membrane. The effects of the microphase separated structure of the graft copolymer membrane on permselectivity was studied.

Kyritsis et.al. [16] studied polymer-water interactions in PHEA hydrogels by dielectric, calorimetric and absorption isotherm measurements. PHEA hydrogels with water contents up to 0.96 (g water/g dry material) were studied with equilibrium and dynamic water absorption isotherm measurements, DSC, TSDC and broad-band a.c. dielectric relaxation spectroscopy. The results showed that for water contents lower than about 0.20-0.30, the hydrogel is a homogeneous system in the temperature range down to -100°C. At higher water contents phase separation occurs.

Interaction between water and polymer chains in PHEA hydrogels was also examined [17]. Polymer networks of different cross-linking densities were prepared by copolymerization of HEA and ethylene glycol dimethacrylate. The average molecular weight between crosslinks as well as the polymer chain mobility were characterized by means of a dynamic-mechanical spectroscopy. Equilibrium absorption isotherms and the water uptake in immersion in liquid water allowed the determination of the Flory-Huggins interaction parameter between water molecules and polymer chain segments, which decreased with the water activity in the hydrogel and increased with the crosslinking density as a consequence of the hydrophobic character of the crosslinking agent.

Mangaraj et. al. [18] investigated the solution properties of polyacrylates. The presence of bulky substituents on the monomer affects not only polymerization rate parameters, but also the solvent-polymer interaction to a large extent. They showed that the cohesive energy density decreases with the increase in alcoholic chain length of acrylic and methacrylic esters. The dilute solution properties of these polymers and the interaction parameters such as χ, the second virial coefficient Γ_2 and the end-to-end distance of the polymeric chain are affected by the increase in the alcoholic chain length, and are also largely influenced by the interaction between the α-hydrogen atom of the polymer and the carbonyl group of the solvent.

The electrical conductivity of PHEA, hydrogels was studied by means of a dielectric relaxation spectroscopy in wide ranges of frequency (5Hz-2GHz), temperature (173-363K) and water content (0.065-0.46 g of water/g of dry material) [19]. The data were analyzed within the formalisms of permittivity, impedance and modulus. The results are discussed in terms of temperature –and water- induced effects, shape of the response, fragility and homogeneous-heterogeneous nature of the hydrogels. The dc conductivity of the PHEA hydrogels was determined as a function of the temperature and water content from Z plots. Its temperature dependence is described by the VTF equation at h<0.30 (h=water content) and by the Arrhenius equation in larger water contents.

1.4 POLYMERIZATION OF ACRYLATES

The polymerization of acrylic ester monomers are usually carried out by the free radical process. The polymerization can be performed in homogeneous media either in bulk or in solution or in heterogeneous media either emulsion or suspension. Because of the tough, adhesive properties of most acrylic ester polymers, suspension polymerization is not feasible and cast polymers can not be removed readily from molds. For this reason, solution or emulsion polymerization are most practical for commercial use. The methods used in this work are summerized as follows:

1.4.1 Bulk Polymerization

The conversion of a monomer to a polymer in the absence of dilutant or dispersing agents is termed as “bulk” polymerization. Advantages of this technique include high yield per reacting volume, easy polymer recovery and the option of casting the polymerization mixture into final product form. Limitations are the difficulty of removing the last traces of monomer and the problem of dissipating heat produced during polymerization.

Polymerizations of acrylic and methacrylic esters are highly exothermic. Generally, the heats of polymerization of acrylates are greater than those of methacrylates. Under similar conditions with peroxide catalysts at moderate temperatures methyl acrylate polymerizes more readily than methyl methacrylate and ethyl acrylate. Methyl acrylate shows a much greater tendency to form branched, cross-linked partially insoluble polymers than does methyl methacrylate because of the available alpha-hydrogen atom.

Frequently, even if as little as 20% of the monomer has polymerized, an auto accelerating polymerization effect will take place. This may manifest itself in an increase in the heat evolved as the process nears completion. The viscosity of the polymerization medium will be very high after a certain degree of conversion that limits the diffusion of long-chain radicals. This prevents the chain termination. Thus, the radical concentration in the medium increase and therefore the rate of polymerization also increase. The diffusion of monomer molecules to the propagation sites is less restricted. This means that the termination rate decreases more rapidly than the propagation rate and so the overall polymerization rate increases. The auto acceleration process is also called “Trommsdorff” or “gel” effect [20].

Since the density of a polymer is substantially higher than that of the corresponding monomer, there is a considerable shrinkage of the volume of the material. It may be overcome to some extent by use of molds which have flexible spacers, by preparing solutions of polymers in monomer (casting syrups).

In most cases, a small amount of unreacted monomer remains in the polymer. This residual monomer may be converted by a post-treatment of the polymer at elevated temperatures.

1.4.2 Solution Polymerization

Polyacrylate and polymethacrylate esters of the lower alcohols are, in general, soluble in aromatic hydrocarbons, esters, ketones and chloro-hydrocarbons. They are more or less insoluble in aliphatic hydrocarbons, ethers and alcohols [3].

The solvents with the highest chain transfer activity give polymers with the lowest molecular weight. The molecular weight of the polymer prepared by solution polymerization is influenced not only by the type of the solvent, but also monomer/solvent ratio. In general, the higher this ratio, the higher the molecular weight of the polymer, since the chain transfer activity of the solvent is dependent upon concentration.

Advantages of this method are to prevent the system from becoming viscous during reaction, easy heat control and allow longer chains to be formed. The principal problems encountered in solution polymerization are chain transfers to the solvent and removal of the solvent for isolation of the polymer. Gel effects are also possible depending upon the quality of the solvent and on the concentration used. Because of the solvent-removal problem, solution polymerization is generally not used on a large scale unless the application under consideration involves the direct use of the polymer in solution.

Chain transfer has an effect on the overall rate of a polymerization reaction, on induced decomposition of the initiator, and on the molecular weight of the polymer. However, nonreactive solvents, which are not susceptible to chain transfer reactions, may also influenced either the rate of polymerization or the structure of the polymer formed. As an example of the latter, the stereochemistry of polymer formed in the free-radical polymerization of vinyl chloride may be strongly dependent on the dielectric constant of the solvent present. Furthermore, poly(vinyl chloride) prepared in the presence of aldehydes reportedly shows an unusually higher order of stereoregularity, although the results appeared to be strongly dependent on molecular weight [21].

1.4.3 Atom Transfer Radical Polymerization (ATRP)

Free radical polymerization is an integral part of polymer chemistry. It has become a widely used industrial methodology because generation of a radical is easy, many monomers can be polymerized, and radical polymerizations are tolerant to the impurities that normally would terminate an ionic polymerization (moisture, protic solvents), making it an economically attractive alternative to the rigorous purification needed in the ionic process. 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. Termination reactions cannot be eliminated in radical polymerizations because termination reactions involve the same active radical species as propagation; therefore, eliminating the species that participates in termination would also result in no polymerization. To grow polymer chains with a degree of polymerization of 1000, the rate of propagation must be at least 1000 times faster than the rate of termination (which under steady state condition is equal to the rate of initiation). This requires a very low concentration of radicals to minimize the influence of termination. However, termination eventually prevails and all the polymer chains produced in a conventional free radical process will be “dead” chains.

Another major limitation in conventional radical polymerizations is that the molecular weight of the polymer chains is poorly controlled. Most free radical initiators have an efficiency < 1. There are several reasons for this, including the cage effect and primary radical termination. As a consequence of using thermally activated initiators for the polymerizations, which have a long half lifetime at a given temperature, very few polymer chains are initiated at the onset of polymerization and initiation continues throughout the polymerization, resulting in a broad distribution of chain lengths and ill-defined polymers. Typical initiators include 2,2'-azobisizobutyronitrile (AIBN) which has a half lifetime of ~ 10 h at 65ºC. This means that only half of the initiator will be consumed after ~ 10 h, leaving a significant portion that will continue to decompose and begin new chains. If the temperature is increased to enhance the decomposition rate, the termination rate will also increase because the termination rate is dependent on the concentration of radicals, leading to a significant decrease in the molecular weight.

There have been attempts to remedy this situation. Chain transfer agents can be used to limit the molecular weight of the polymer chains. These additives react with the growing polymer chain, limiting the degree of polymerization without affecting the polymerization rate. Transfer agents can be introduced functionality to polymer chain ends which will allow for post-polymerization reactions. New methods were developed in the mid-1990s based on the idea of establishing equilibrium between the active and dormant species, which is the control via a reversible redox reaction between alkyl halides and transition metal complexes.

The concept of using transition metal complexes to mediate radical polymerizations developed out of atom transfer radical addition reactions (ATRA), also referred to as the Kharasch reaction, which originally used light to generate a radical. Later, transition metal complexes were used to promote halogen addition to alkenes through a redox process. As shown in Scheme 1, 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 re-abstracts 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.

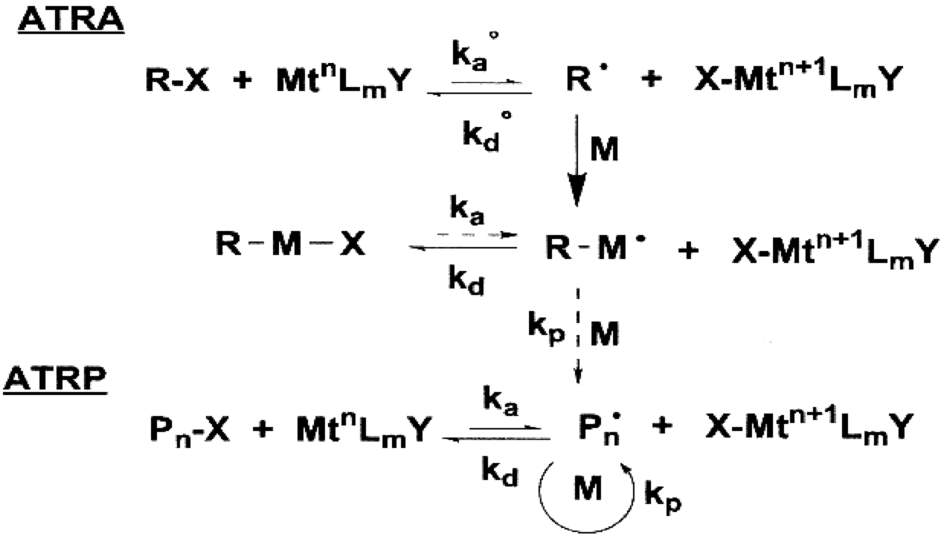


Figure 1.1 **ATRA and ATRP**

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 (St) and methyl acrylate (MA), which were initiated by 1-phenylethyl bromide and catalyzed by a Cu(I)/2,2'-bipyridine (bpy) complex. This process was called "Atom Transfer Radical Polymerization" (ATRP) to reflect its origins in ATRA. A successful ATRP relies on fast initiation, where all the 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 [22-23].

2-Hydroxyethyl acrylate was polymerized by Coca et. al. [1] using the ATRP method. The polymerizations exhibit first-order kinetics and molecular weight increased linearly with conversion. Polydispersities remain low throughout the polymerization (Mw/Mn ~1.2). Reactions were conducted in bulk and in 1:1 (by volume) aqueous solutions; the latter demonstrates the resilience of ATRP to protic media. Analysis of PHEA by MALDI-MS and ^{1}H-NMR shows $M_{n,exp}$ to be much closer to $M_{n,th}$ than those observed by SEC using polystyrene standards.

Mühlebach et. al. [24] synthesized the amphiphilic block copolymers by ATRP. They reported the controled / "living" radical polymerization of n-butyl acrylate (n-BA) and 2-trimethylsilyl-oxyethyl acrylate (TMS-HEA) by ATRP. Di and triblock copolymers with predefined block lengths and low polydispersities were obtained, using methyl-2-bromopropionate as the initiator, Cu^1Br as catalyst and N,N,N'.N'',N''-pentamethyldiethylenetriamine as the ligand. Hydrolysis of the TMS groups led to block copolymers with n-BA and HEA units which were characterized by SEC, ^{1}H-NMR, and DSC. Diblock copolymers of n-BA and HEA could also be obtained by succesive addition of the two monomers, in that order. The amphiphilic di- and triblock copolymers formed dispersions in water.

1.5 FREE RADICAL POLYMERIZATION KINETICS (STEADY-STATE)

Free radical polymerizations are chain polymerizations which can be divided into three distinct stages; initiation, propagation and termination.

1.5.1 Initiation

This stage involves creation of a free-radical active center and usually takes place in two steps. The first is the formation of free radicals from an initiator.

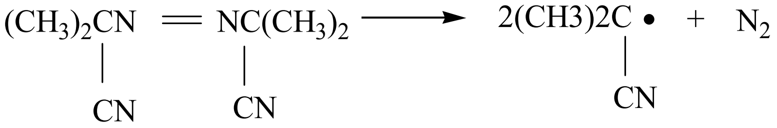
Free-radicals can be generated in a number of ways including;

i) thermal decomposition of organic peroxides/hydroperoxides or azo/diazocompounds.
ii) light (ultra-violet)
iii) high-energy radiation.

Benzoyl peroxide,(BPO), and azobisisobutyronitrile,(AIBN), are most commonly used initiators to produce free-radicals for polymerization. Thermal or photochemical decomposition of BPO produces benzoyloxy and phenyl radicals, the phenyl radical is more reactive than the benzyl radical [25].

$$(C_6H_5COO)_2 \longrightarrow \underset{\text{benzoyloxy}}{2C_6H_5COO^{\cdot}} \longrightarrow \underset{\text{phenyl}}{2C_6H_5^{\cdot}} + CO_{2(g)} \qquad (1.5.1)$$

Azobis isobutyronitrile (AIBN), decomposes at lower temperatures;



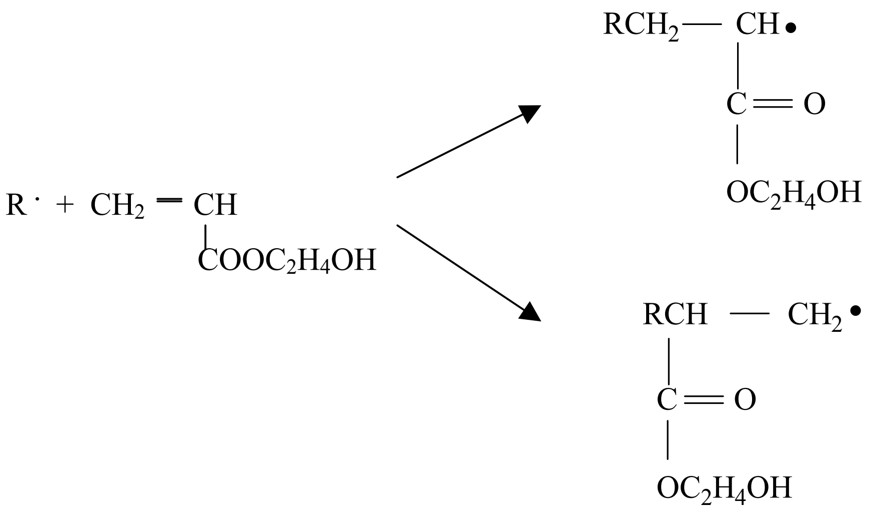
$$\underset{\displaystyle CN}{\underset{|}{(CH_3)_2C}}N = N\underset{\displaystyle CN}{\underset{|}{C}}(CH_3)_2 \longrightarrow 2\underset{\displaystyle CN}{\underset{|}{(CH3)2C}} \bullet + N_2 \qquad (1.5.2)$$

The initiator, I, decomposes into two free-radicals,$R^{\cdot}$;

$$I \xrightarrow{k_d} 2R^{\cdot} \qquad R_i = 2\, f\, k_d\, [\, I\,] \qquad (1.5.3)$$

where k_d is a temperature dependent rate constant for initiator decomposition. The decomposition proceeds with an efficiency, f.

The second is the addition and attack of one of these free radicals to the π-bond of a monomer. There are two possible modes of addition:



(I)

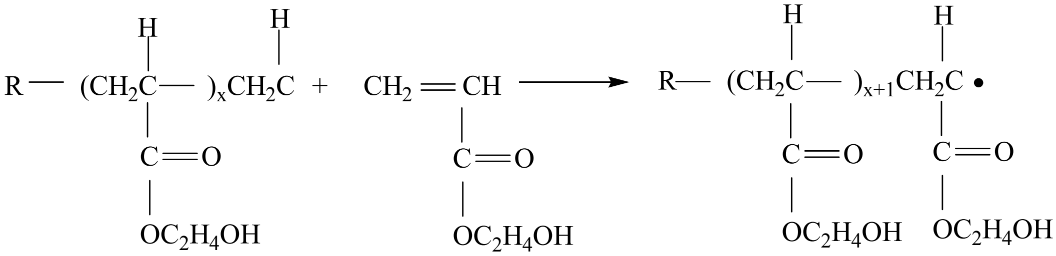
(II)

$R^{\cdot} + CH_2{=}CH(COOC_2H_4OH) \rightarrow RCH_2{-}\dot{C}H(COOC_2H_4OH)$ (I) or $RCH(COOC_2H_4OH){-}CH_2^{\bullet}$ (II)

Mode (I) predominates because attack by the methylene carbon is less sterically-hindered and yields a product free radical that is more stable because of the effects of the adjacent $COOC_2H_4OH$ group [26].

1.5.2 Propagation

This involves growth of the polymer chain by rapid sequential addition of monomer to the active center.



$R{-}(CH_2CH(COOC_2H_4OH){-})_xCH_2\dot{C}H(COOC_2H_4OH) + CH_2{=}CH(COOC_2H_4OH) \longrightarrow R{-}(CH_2CH(COOC_2H_4OH){-})_{x+1}CH_2\dot{C}H(COOC_2H_4OH)$

$$RM^{\cdot} + M \xrightarrow{\mathbf{k_p}} RMM^{\cdot} \qquad (1.5.4)$$

$$RMM^{\cdot} + M \xrightarrow{\mathbf{k_p}} RM_nM^{\cdot} \qquad (1.5.5)$$

where kp is the propagation rate constant. The rate of propagation is as follows;

$$R_p = - d[M]/dt = k_p\,[\,M\,]\,[\,M^{\cdot}\,] \qquad (1.5.6)$$

1.5.3 Termination

If all transfer reactions are neglected and the supply of monomer was exhausted, termination can take place by combination or disproportionation.

$$M_n^{\cdot} + M_m^{\cdot} \longrightarrow M_{n+m} \qquad R_t = k_{tc}\,[M_n^{\cdot}][M_m^{\cdot}] \qquad (1.5.7)$$

$$M_n^{\cdot} + M_m^{\cdot} \longrightarrow M_n + M_m \qquad R_t = k_{td}\,[M_n^{\cdot}][M_m^{\cdot}] \qquad (1.5.8)$$

In equation (1.5.8) one of M_n and M_m is saturated and one has an unsaturated end group. The overall termination rate will be,

$$R_t = 2\,k_{tc}\,[M_n^{\cdot}][M_m^{\cdot}] + 2\,k_{td}\,[M_n^{\cdot}][M_m^{\cdot}]$$

or taking $k_t = k_{tc} + k_{td}$ and $[M_n^{\cdot}] = [M_m^{\cdot}] = [M^{\cdot}]$

$$R_t = 2\,k_t\,[M^{\cdot}] \qquad (1.5.9)$$

A steady-state hypothesis can be applied, stating that the rate of initiation and termination are equal (Ri = Rt) to each other.

$$2fk_d[I] = 2k_t[M^{\cdot}]^2 \quad \text{or}$$

$$[M^{\cdot}] = [\,\frac{f\,k_d[I]}{k_t}\,]^{1/2} \qquad (1.5.10)$$

the concentration of the radical in equation (1.5.10) is substituted into therate equation for propagation (1.5.6).

$$R_p = -\frac{d[M]}{dt} = k_p [M] [\frac{f k_d [I]}{k_t}]^{1/2} = k [M] [I]^{1/2}$$

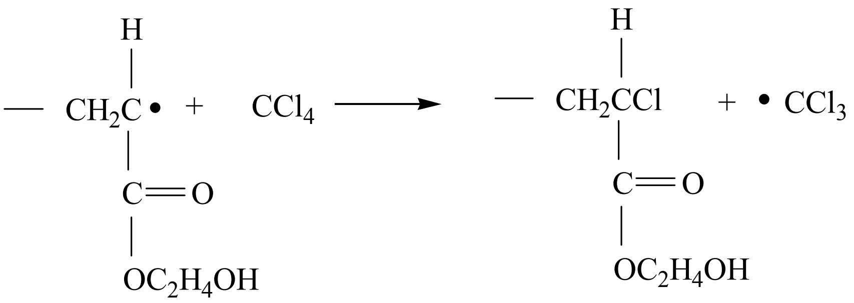
where $k = k_p (fk_d/k_t)^{1/2}$ and the integration will give the general kinetic equation:

$$\ln\frac{[M]_0}{[M]} = k[I]^{1/2} t \qquad (1.5.11)$$

In this case, conversion time data should be plotted as ln [M] vs. time. The intercept of the line will give us ln $[M]_o$ and the slope $k [I]^{1/2}$.

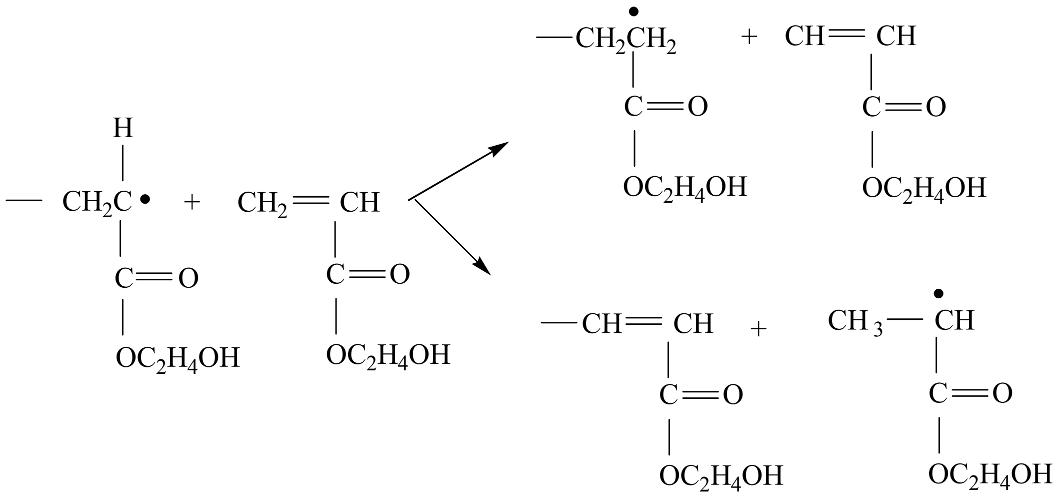
1.5.4 Chain Transfer

It was recognized by Flory that the reactivity of a radical could be transfered to another species. The reaction involves the transfer of an atom between the radical and the molecule. If the molecule is saturated, like a solvent or other additive, the atom must be transferred to the radical. For example, when the polymerization of HEA is taken place in CCl_4 solution, the chain transfer reaction will be as follows:



$$—CH_2C(H)(COOC_2H_4OH)\bullet + CCl_4 \longrightarrow —CH_2CCl(H)(COOC_2H_4OH) + \bullet CCl_3$$

If the molecule is unsaturated, like a monomer, the atom transferred (usually hydrogen) can go in either direction.



The major effect of chain transfer to a saturated small molecule (solvent, initiator or an added chain transfer agent) is the formation of additional polymer molecules for each radical chain initiated. Transfer to polymer and monomer with subsequent polymerization of the double bond lead to the formation of branched molecules.

The degree of polymerization is;

$$\overline{P}_n = \frac{rate\, of\ growth}{\sum rates\, of\ all\, reactions\ leading\, to\, dead\ polymer}$$

$$\frac{1}{\overline{P}_n} = \frac{fk_d[I] + k_{tr,M}[M][M\bullet] + k_{tr,S}[S][M\bullet] + k_{tr,I}[I][M\bullet]}{R_p}$$

In the presence of a solvent, there is a relationship between the degree of polymerization, the monomer and the solvent concentrations as follows:

$$\frac{1}{\overline{P_n}} = \left(\frac{1}{\overline{P_n}}\right)_0 + C_s \frac{[S]}{[M]}$$

where $\frac{1}{\overline{P_n}}$ is the reciprocal of degree of polymerization, C_s is the transfer constant, [S]/[M] is the molar ratio of solvent to monomer and $\left(\frac{1}{\overline{P_0}}\right)_0$ combines the polymerization and transfers to monomer terms. So there is a linear dependence of $\frac{1}{\overline{P_n}}$ on [S]/[M] [27].

1.6 LITERATURE SURVEY OF PHEA

The main handicap of hydrogels is their poor mechanical properties, mainly in the swollen state. Consequently reinforcement is needed for medical applications. Increasing the crosslinking density, copolymerization with a more resistant hydrophobic system, crystallization (when possible) are among the ways to reinforce hydrogels, as well as the formation of interpenetrating polymer networks, IPNs. IPNs are systems formed by two or more chemically independent polymer networks interpenetrated in space. These systems are indeed binary systems composed of two mixed polymers, each of which is individually cross-linked, even when both initiating monomers are completely miscible, the thermodynamical stability of the monomer mixture is soon lost as the polymerization reaction proceeds, and phase separation takes place [28]. Rault et. al. [29] studied the thermal transitions in hydrogels based on interpenetrating networks of poly(ethyl acrylate) and poly(hydroxyethyl acrylate). The IPNs based on the hydrophobic PEA and the hydrophilic PHEA form hydrogels when swollen with water. For a 2% concentration of crosslinking agent the xerogel has an equilibrium water uptake of c=0.346 (swelling ratio s=0.530). The effect of water is to lower the value of the hydrogel's Tg, as any low molecular weight substance, homogeneously mixed with the polymer would do.

Sequential poly(methyl acrylate) / poly(hydroxyethyl acrylate) interpenetrating polymer networks with different PHEA contents were prepared by free radical polymerization of hydroxyethyl acrylate inside the previously polymerized poly(methyl acrylate) network [30]. DSC on dry samples showed that IPNs exhibit phase separation, and no differences are found between the glass transition temperatures of the two phases present in the IPN and those of the pure components TSDC experiments were used to study the influence of water sorption on the mobility of the different molecular groups in the PHEA phase of the IPN. Diffusion coefficients of water in the IPNs were obtained by means of dynamic sorption experiments.

Degiorgi et. al. [31] obtained polymers by gamma irradiation of 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylate at -78˚C in the presence of water and glycerol as well as poly(vinyl alcohol) cyrogels obtained by freezing –thawing cycles were examined as carriers for immobilization of bacterial cells in experiments of metal decontamination. Bacterial strains capable of growing in the presence of heavy metals were selected from soil and water from the Rio de la Plata coasts, Argentina, and cultured in the hydrophilic membranes with the aim of the bioremedation of standard contaminated solutions. The results obtained indicate that removal from free bacteria was more efficient for Pb(II) and Cd(II) that for Cr(III) and Cu(II).

Hydrophilic sponges based on PHEA were prepared by copolymerization of HEA and ethylene glycol dimethacrylate in solution [32]. The porous structure of the sponge is due to the segregation of the solvent from the polymer network during the polymerization process as the result of a large excess of solvent. The influence of the solvent and the monomer/solvent ratio on the formation of the porous structure was studied. The morphology of the samples was examined by a scanning electron microscope equipped with a cyro unit using the low temperature freeze drying technique cyrogenic scanning electron microscope (cyroSEM).

The nature of water-macromolecule interactions in aqueous model polymers had been investigated using quantitative measurements of magnetizations transfer by Gochberg et. al. [33]. Crosslinked polymer gels composed of 94% water, 3%N,N'-methylene-bis-acrylamide, and 3% functional monomer (acrylamide, methacrylamide, methacrylic acid, HEA, HEMA) were studied. Water-macromolecule interactions were modified by varying the pH and specific functional group on the monomer.

Kamakura [34] prepared and characterized the hydrophilic monodisperse microspheres by radiation precipitation polymerization. A preparation method for monodisperse polymer microspheres with a hydrophilic property had been investigated by utilizing an irradiation method. Hydrophilic microspheres were synthesized by radiation precipitation copolymerization using polyethyleneglycol dimethacrylate, hydroxyethyl acrylate, hydroxyethyl methacylate, methacrylic acid monomer. The diameter of the microspheres prepared was 0.3-1μm, in which the irradiation was carried out without a catalyzer at room temperature for 1 hr at a dose rate of 10 kGy/hr with γ-rays from a Co-60 source. The diameter of the microspheres increased with increasing hydrophilicity of monomer.

Sun and Yamauchi [35] examined the polymer bearing an S-Sulfate side chain. Vinyl mercaptoacetate S-Sulfate sodium salt (VMAS) was prepared with a yield of 74% from a reaction of vinyl chloroacetate and sodium thiosulfate. Polymerization of VMAS with 2-hydroxyethyl acrylate (HEA) in the presence of ammonium persulfate and N,N,N',N'.-tetramethylethylenediamine afforded a colorless copolymer bearing the $S\text{-}SO_3^- Na^+$ group in 3.2-4.3 mol% and having a Mw of $2.4\text{-}13 \times 10^4$. The polymer was water-soluble but, upon treatment with an oxidizing agent, was transformed quickly into a water-tolerant material. It again became water-soluble with the addition of a reducing agent. The unique solubility alternation was explained by the formation and fission of a S-S bond crosslinking in the polymer.

The copolymerization reaction between 2-hydroxyethyl acrylate and itaconic acid has been studied with a range of solvents [36]. In a series of reactions in protic solvents, i.e. water, methanol, ethanol, isopropanol and n-butanol, the reactivity ratios (r_1 and r_2) showed a distinct dependence on the solvent used. Copolymerizations in an aprotic solvent, dimethyl formamide, again yielded different r_1 and r_2 values, but the copolymerization behaviour was very similar to the reactions carried out in water.

Guan et. al. [39] studied the grafting of HEA on polyurethanes. PU with functional groups (amide, hydroxyl, carboxyl) on surfaces were prepared by grafting monomers such as acrylamide (AAm), hydroxyethyl acetate (HEA), and methacrylic acid (MAA) onto the PU membranes.

The radiation polymerizations of ethyl acrylate (EA) and hydroxyethyl acrylate (HEA) monomers in aqueous solutions were studied [37]. For pulse radiolytic experiments, optical detection was used to measure the concentration of intermediates.

1.7 AIM OF THIS WORK

The detailed kinetic study of 2-hydroxyethylacrylate polymerization has not been reported. In this work, free radical polymerization of HEA under different conditions will be studied. Polymer obtained will be characterized and possible molecular weight control will be investigated. The work will be continued in the future to copolymerize HEA with other monomers to obtain suitable hydrogels for different applications. However, before block copolymer synthesis methods have to be found to control the molecular weight of PHEA.

CHAPTER 2

EXPERIMENTAL

2.1 PURIFICATION OF MATERIALS

Monomer : Commercial HEA always contains impurities, such as ethylene glycol, acrylic acid and ethylene glycol diacrylate (EGDA). Purification has to be done to remove diacrylate and acrylic acid. The presence of diacrylate leads to crosslinking and in the presence of large amounts of acrylic acid, no polymerization is observed. Therefore, polymerizations of unpurified or poorly purified monomer may be either incomplete and slow or lead to insoluble solids. HEA (Acros, 97%) was dissolved in water (25% by volume) and the solution was extracted 10 times with hexane to remove diacrylates. The aqueous solution was then salted (200g of NaCl / L) and the monomer was separated from the aqueous phase by ether extraction (4 times) to remove acrylic acid. Finally, $MgSO_4$ (3 wt %) drying agent was used to remove traces of water before evaporation of the ether phase in a rotary evaporator. The purified monomer was distilled under vacuum immediately prior to use for polymerizations.

Solvents : Methanol, carbontetrachloride (Merck), hexane (Merck), diethyl ether (Riedel de-Haen), benzyl chloride (Aldrich 99%) were all reagent grades and used without further purification.

Solids : 2,2'-bipyridine (Fluka), benzoyl peroxide (Merck), CuCl (Riedel de-Haen) were all reagent grades and used without further purification.

2.2 INSTRUMENTATION

2.2.1 Polymerization Tubes

The tubes 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 facilitates connection to the vacuum line using fittings.

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 5-6 hours was applied.

a) Duo-Seal Vacuum Pump

It is a product of "Sargent-Welch Scientific Co." Model 1399 and capable of pressure reduction 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 110 cm., diameter 4.53 cm. was employed. It was connected to the first trap by a high vacuum cockstop and to the sample holder tubes to high vacuum cockstops 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 Infrared Spectrometer

Infrared spectra of monomer and the polymers obtained with different polymerization techniques were taken from KBr pellets by using Nicolet 510 FT-IR Spectrometer. The data was processed by the OMNIC computer program.

2.2.4 Differential Scanning Calorimeter (DSC)

Thermal properties of samples were analyzed using Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S. All the measurements were done under N_2 atmosphere in a temperature range of 25ºC to 250ºC with 10ºC/min heating rate.

2.2.5 Thermogravimetric Analysis (TGA)

Thermal stability of PHEA was characterized by Dupont 951 Thermogravimetric Analyzer. Thermograms were recorded under N_2 atmosphere in a temperature range of 30ºC to 600ºC with 5ºC/min heating rate.

2.2.6 Nuclear Magnetic Resonance

The H^1 NMR Spectra of monomer and polymer were taken on an Ultrashield 400 MHz Digital NMR Bruker, NMR Spectrometer.

2.2.7 Mechanical Testing Apparatus

LLOYD NK5 Computerised Testing machine was used for the mechanical tests.

2. 3 EXPERIMENTAL PROCEDURE

2.3.1 Bulk Polymerization under vacuum

1,5 ml of HEA and 0,0016 g of benzoyl peroxide were placed into the vacuum tubes and High Vacuum System was applied for about 6 hours at 10^{-4} to 10^{-5} mmHg in order to evacuate the tubes. The tubes were then put into a water bath at a constant temperature (50°C, 60°C, 70°C).

The tubes were then broken open and polymerization was terminated by the addition of methanol and removal of the monomer. The polymer was dried to constant weight under vacuum and conversions were calculated gravimetrically.

Furthermore, bulk polymerization were carried out by γ-radiation. The results were similar and not included in text.

2.3.2 Bulk Polymerization at Open Air

Again the same amounts of monomer and initiator were put into tubes and they were sealed with a flame without applying vacuum. Polymerization was carried out similar to vacuum polymerization (2.3.1).

2.3.3 Solution Polymerization

4 ml solutions of hydroxyethyl acrylate at 10, 20, 30, 40, 50, 60, 70, 80, 90 % v/v concentrations were prepared in carbontetrachloride.

After applying high vacuum, they were polymerized for 2 hours at 60^0C and the % conversions were calculated.

Also 20% (v/v) HEA solutions in CCl_4 were prepared and after applying high vacuum they were polymerized at different time periods in order to obtain the percent conversion versus time graphs.

Additionally, solution polymerization were carried out by using other solvents, such as; methanol, dichloromethane, benzene, toluene and water. The results were similar and not included in text.

2.3.4 Atom Transfer Radical Polymerization

ATRP employs a Cu(I) halide, which is complexed with ligands (2,2'-bipyridine), to form a "CuX/2L" complex. Halogenated initiators are used for polymerization. The Cu(I) complex reversibly activates dormant polymer chains (and the initiator) by transfer of the halogen end group.

In a reaction tube, 0.0337 g of bpy, 0.0154 g CuCl, 12 μL benzyl chloride and 2 mL of HEA were combined and degassed via three freeze-pump-thaw cycles on the high vacuum system. The tube was then sealed under vacuum and placed in an oil bath at 90°C for the desired time. The tube was then immediately frozen in liquid nitrogen and opened. A part of the contents was dissolved in d-DMSO for NMR inverstigation.

2.3.5 Tensile Tests

Tensile tests were performed by a LLOYD LR 5K Computerised testing machine for all specimen groups. Tests were performed according to ASTM D638M-91a, (Standard Test Method for Tensile Properties of Plastics). The speed was 20 mm/min. The shape and the dimensions of the specimens are illustrated in Figure 2.1.

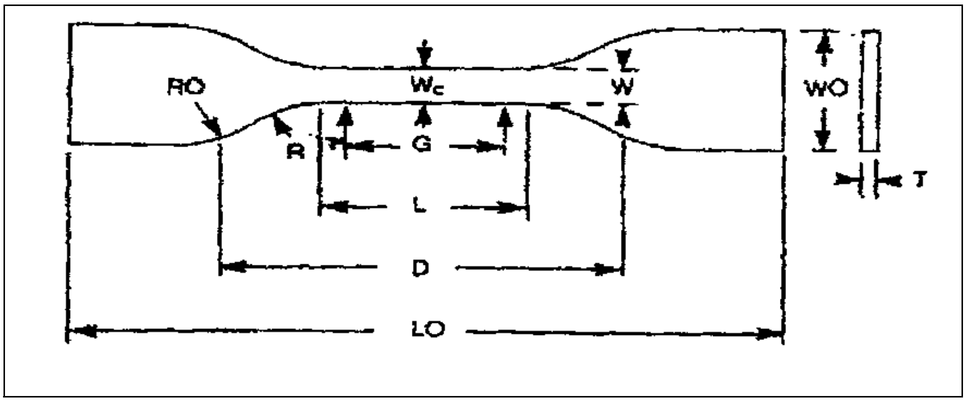


Figure 2.1 Tensile Test specimen

W = Width of narrow section

L = Length of narrow section

W_0 = Width overall (3.00 mm)

L_0 = Length overall

G = Gauge length (3.10 cm)

D = Distance between grips

T = Thickness (2.70 mm)

W_c = Width at the center

CHAPTER 3

RESULTS AND DISCUSSION

3.1 BULK POLYMERIZATION OF 2-HYDROXYETHYL ACRYLATE UNDER VACUUM

The percent conversions versus time for bulk polymerization of monomer are given in Table 3.1 and the percent conversions are plotted against time in Figure 3.1.

The polymerization reaction is highly exothermic and the heat of polymerization could not be dissipated readily from the viscous medium and this causes over heating of the reacting mixture. Homopolymerization of HEA at 70°C is so fast that it was completed in just a few minutes and system became highly viscous shortly after the reaction started. Then the reaction temperatures were reduced to 60°C and 50°C. The percent conversion versus time values of bulk polymerization are given in Table 3.2 and Table 3.3 at 60°C and 50°C, respectively. The percent conversions are plotted against time in Figure 3.2 and Figure 3.3.

Table 3.1 The percent conversion vs. time for the bulk polymerization of HEA in vacuum at 70°C.

Time (min.)	% Conversion	$\ln[M_0] / [M]$
1	8.1	0.084
2	16.3	0.178
3	44.7	0.592
4	65.1	1.053
6	73.9	1.343
10	84.8	1.884
15	90.1	2.313
20	92	2.526
25	91.2	2.043
30	94.8	2.956
35	95.4	3.079
40	98.3	4.075
45	98	3.912
50	99.2	4.828
55	100	
70	100	

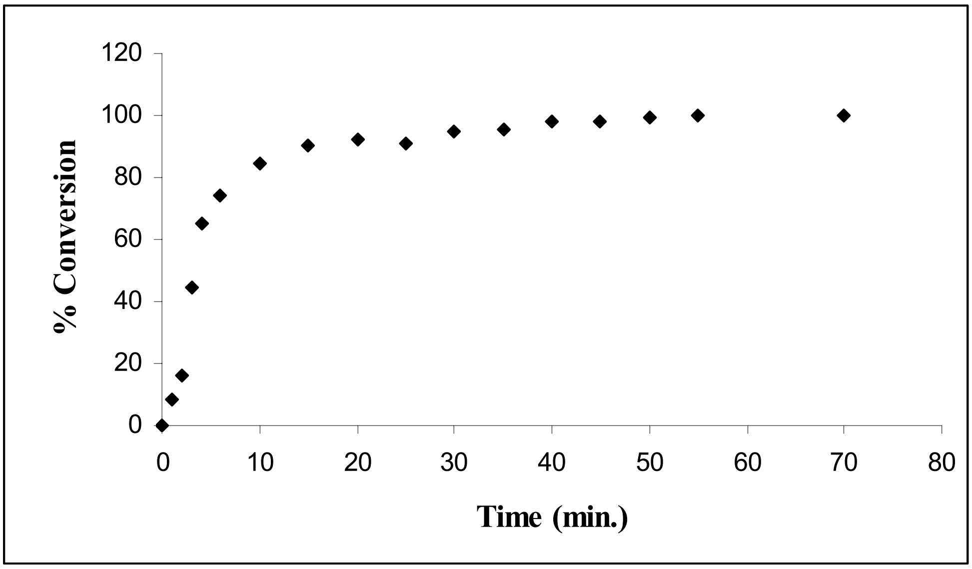


Figure 3.1 **% Conversion vs. time graph for bulk polymerization of HEA at 70^0C under vacuum.**

Table 3.2 The percent conversion vs. time for the bulk polymerization of HEA in vacuum at 60°C.

Time (min.)	% Conversion	$\ln[M_0] / [M]$
3	3.7	0.0377
5	6.3	0.065
6	9.4	0.099
10	10.5	0.111
13	13.7	0.147
16	47.2	0.639
20	79.7	1.595
25	86.5	2.002
33	88.9	2.198
40	89.6	2.263
50	89.2	2.226
60	92.8	2.631
70	93.5	2.733
90	96.9	3.474
105	98.5	4.199
150	100	
175	100	

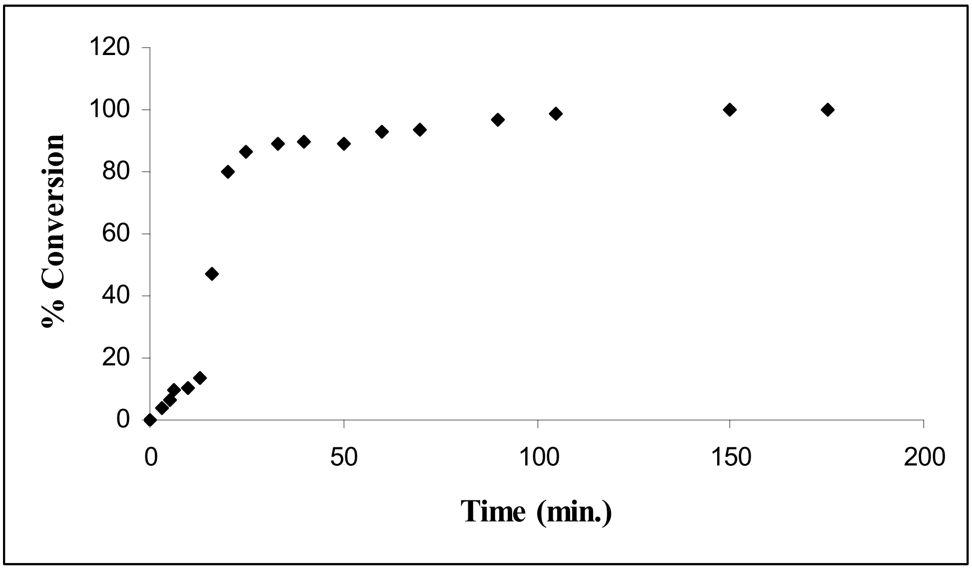


Figure 3.2 **% Conversion vs. time graph for bulk polymerization of HEA at 60^0C under vacuum**

Table 3.3 The percent conversion vs. time results for the bulk polymerization of HEA in vacuum at 50°C.

Time (min.)	**% Conversion**	**ln[M_0] / [M]**
5	**3.8**	**0.039**
8	**5.7**	**0.059**
11	**7.6**	**0.079**
13	**10.3**	**0.109**
17	**14.0**	**0.151**
19	**14.2**	**0.153**
25	**15.3**	**0.166**
30	**22.0**	**0.248**
35	**25.1**	**0.289**
45	**43.3**	**0.567**
55	**54.6**	**0.789**
65	**71.7**	**1.262**
75	**81.4**	**1.682**
80	**85.7**	**1.945**
95	**92.5**	**2.590**
120	**98.3**	**4.075**
190	**94.6**	**2.919**
240	**100.0**	

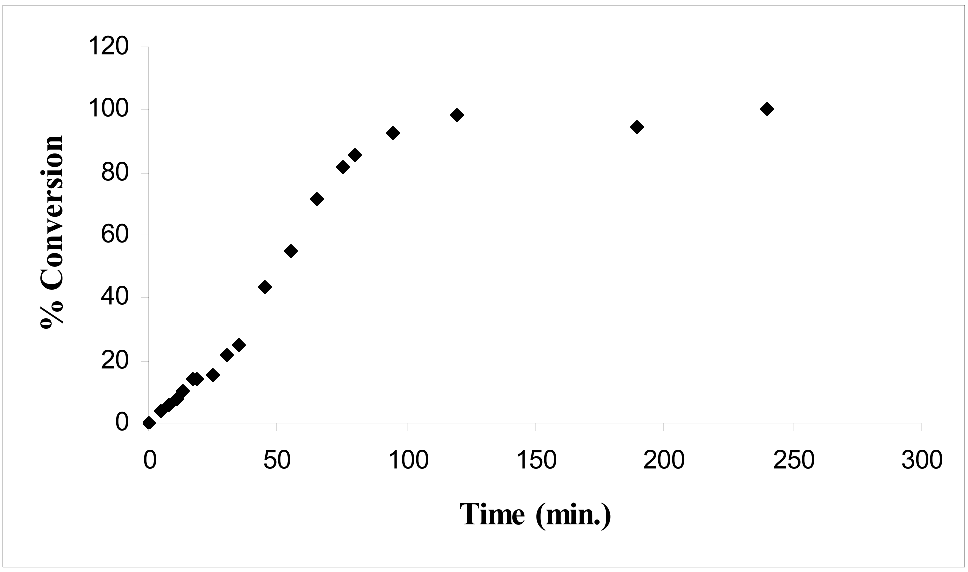


Figure 3.3 **% Conversion vs. time graph for bulk polymerization of HEA at 50^{0}C under vacuum**

HEA homopolymerization exhibits a strong gel effect in early stage of polymerization. Bulk polymerization of HEA at 70°C is so fast that high conversion levels were achieved at the beginning of the reaction. This can be explained by the effect of temperature on the decomposition rate of the initiator. If the temperature is increased to enhance the decomposition rate, the termination rate will also increase because the termination rate is dependent on the concentration of radicals. An increase of about 10°C in temperaute leads to a nearly three-fold increase in rate. In order to see the differences of the bulk polymerization at these three different temperatures, the percent converisons versus time graphs are shown in Figure 3.4.

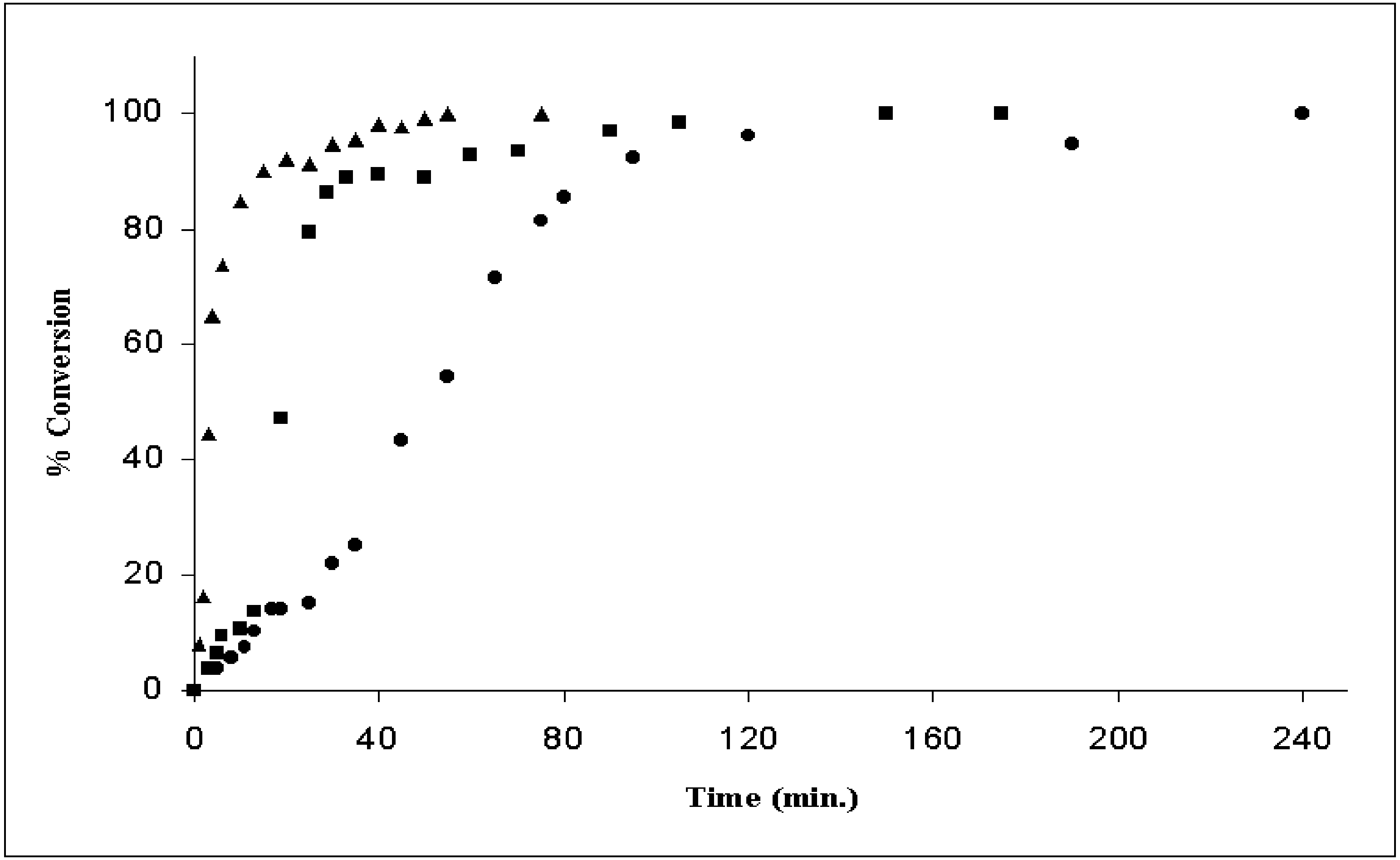


Figure 3.4 **Comparison of the graphs for bulk polymerization of HEA (▲ 70ºC, ■ 60ºC, ● 50ºC)**

Activation energy of polymerization were calculated from Arrhenius plot using rate constant for each of temperature of polymerization. The rate constants were calculated by application of kinetic equation (1.5.11). ln $[M]_o$ / [M] values were plotted against time(t) and curves were illustrated in Figure 3.5, 3.6 and 3.7 slopes (k values) were calculated from straight lines for each of polymerization temperature studied.

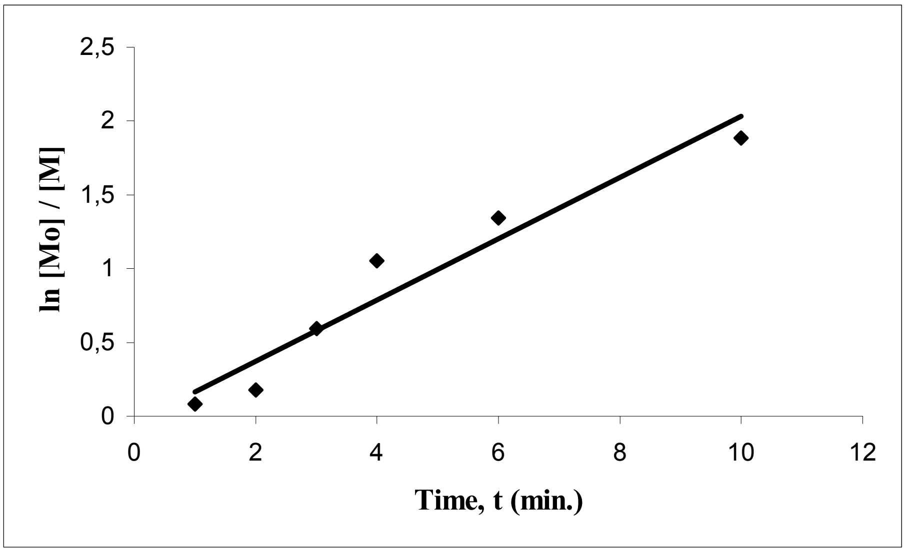


Figure 3.5 **The plot of ln$[M_0]$/[M] vs. time for bulk polymerization at 70°C.**

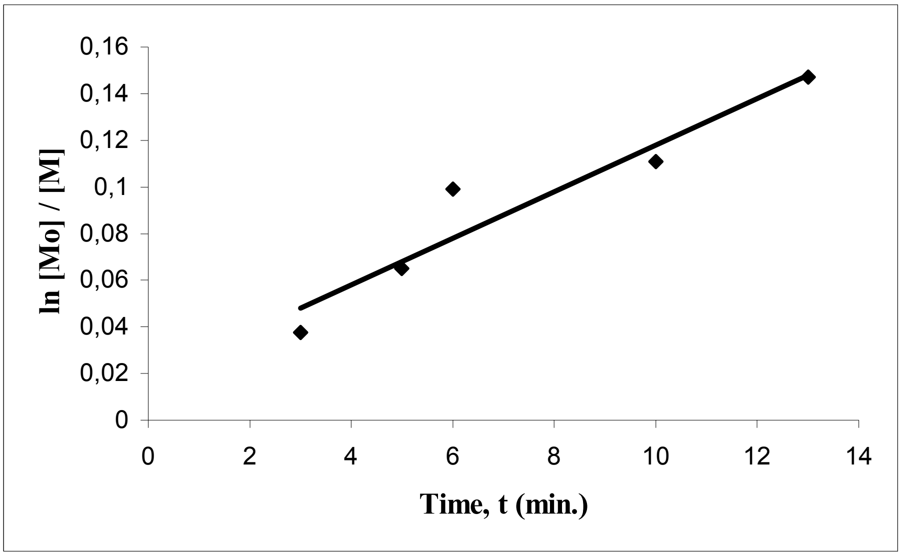


Figure 3.6 **The plot of ln[M_0]/[M] vs. time for bulk polymerization at 60°C.**

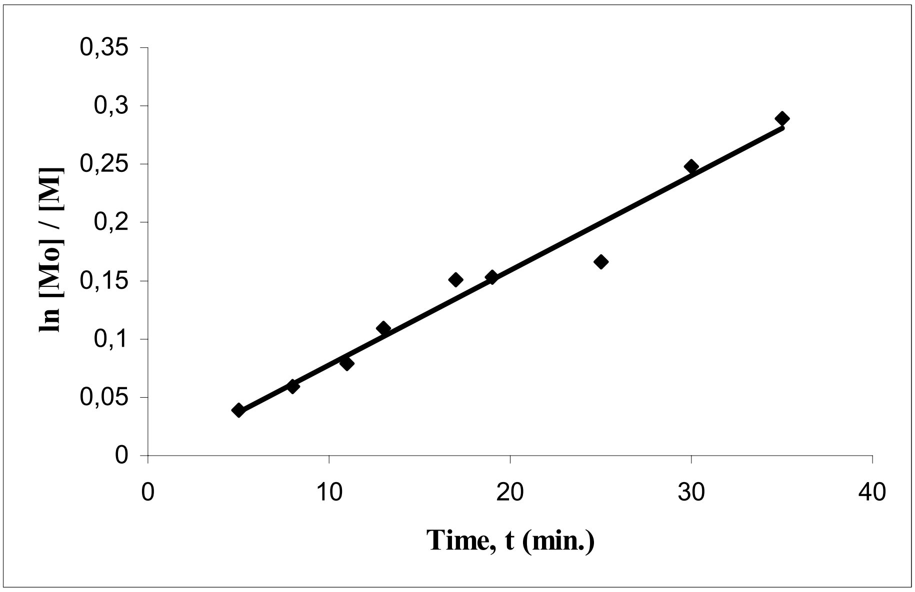


Figure 3.7 **The plot of ln[M_0]/[M] vs. time for bulk polymerization at 50°C.**

The ln of rate constant against 1/T was plotted in Fig. 3.8 the slope of straight line obtained was equal to E_a / R (8.314 J / K.mol) and E_a calcuated from slope is 155.8 kj / mol.

Table 3.4 Reaction rate constants for bulk polymerization of HEA at different temperatures.

T (K)	**1/T (K^{-1})**	**k=Slope (min^{-1})**	**ln k**
323	0.00309	0.0081	-4.8159
333	0.00300	0.0100	-4.6052
343	0.00292	0.2077	-1.5717

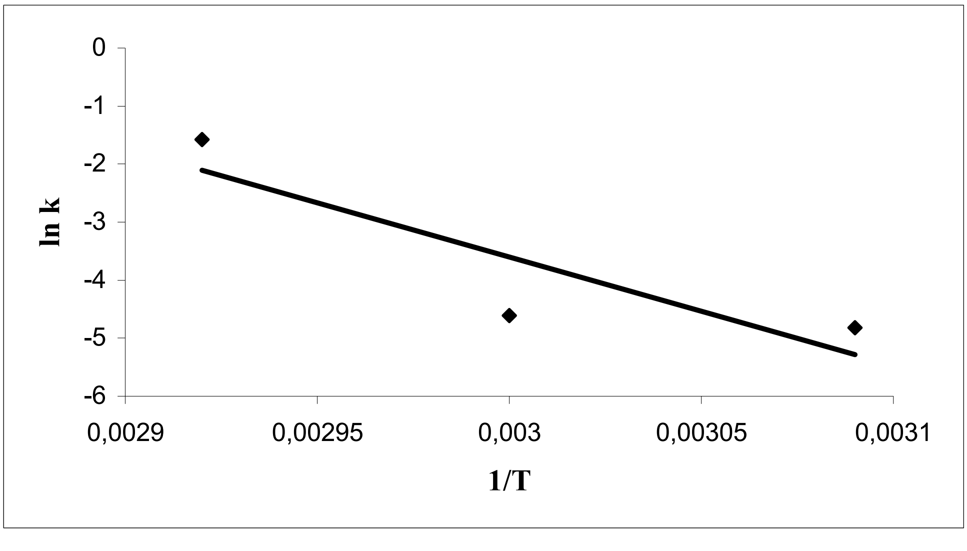


Figure 3.8 **ln k vs. 1 / T**

3.2 BULK POLYMERIZATION OF HEA IN OPEN AIR

Bulk polymerization of 2-HEA was also carried out in water bath at 60°C without vacuum. Ampoules were sealed and polymerized for different time intervals by benzoyl peroxide. The % conversions change with time is given in Table 3.5 and the % conversions are plotted against time in Figure 3.9.

Table 3.5 % Conversions vs. time for the bulk polymerization of HEA at 60°C in open air.

Time (hour)	% Conversion
34.0	10.79
43.0	13.00
47.2	27.81
48.0	33.42
49.0	57.11
49.4	64.49
50.0	73.27
50.2	80.08
51.0	87.92
53.0	93.20
57.1	91.50
63.0	95.80
70.5	100.00
82.0	100.00

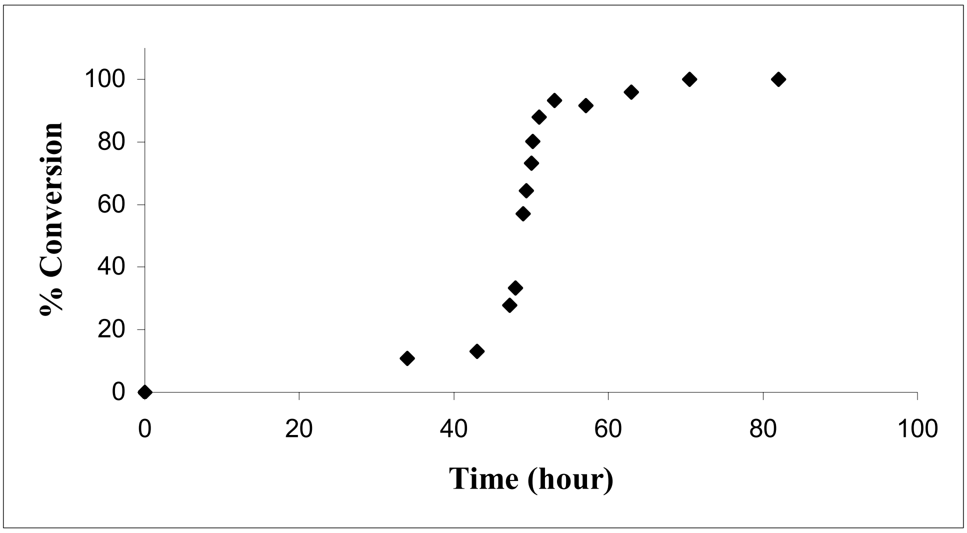


Figure 3. 9 **% Conversion vs. time graph for bulk polymerization HEA at 60°C at open air.**

In the presence of the oxygen, polymerization has an induction period. This is due to the inhibiting effect of the oxygen in the medium. Peroxide formation was assumed to occur in preference to polymerization as long as free oxygen was available, thus destroying active centers or activated molecules which otherwise would have initiated chain growth.

$$\mathrm{M} \xrightarrow[\text{heat}]{\text{light or}} \mathrm{M}^* + \mathrm{O}_2 \rightarrow \underset{\text{peroxide}}{\mathrm{MO}_2}$$

$$\mathrm{M}^* + \mathrm{M} \rightarrow \mathrm{MM}^* \ldots\ldots \rightarrow \text{polymer}$$

where, M represents the HEA.

After induction period, the polymerization curve is superimpossible to that of vacuum polymerization at 60°C. Thus, after oxygen in the medium is completely consumed, the polymerization progress as in vacuum.

3.3 SOLUTION POLYMERIZATION OF 2-HEA

Polymers obtained by bulk polymerization were insoluble in common solvents even for the low conversions because of the high molecular weight and it is reasonable to suspect the crosslinking. Polymer samples swollen in methanol to a certain extent but still remained as gel. Therefore, 2-HEA was polymerized in CCl_4 in order to dilute the viscous medium and reduce the molecular weight by chain transfer.

The solvent was chosen due to the facts that; both the initiator and monomer were soluble in it, acceptable chain-transfer characteristics of the solvent and suitable melting and boiling points for the conditions of the polymerization and subsequent solvent removal steps.

Solutions of HEA at different (v/v) % concentrations in CCl_4 were polymerized in water bath at 60°C for 2 hours.

The percent conversions obtained in CCl_4 are lower than the conversions in bulk polymerization. From Table 3.2, the percent conversion in bulk polymerization for 150 minutes at 60°C, is about 100 %, which is reduced to lower values in CCl_4 given in Table 3.6. The plot of % conversion versus % HEA (v/v) is given in Figure 3.10.

Table 3.6 % Conversion vs. % HEA for polymerization of HEA in CCl_4 at 60°C.

% HEA (v/v)	% Conversion
10	4.96
20	11.34
30	20.64
40	30.66
50	40.98
60	50.52
70	53.54
80	78.57
90	79.01

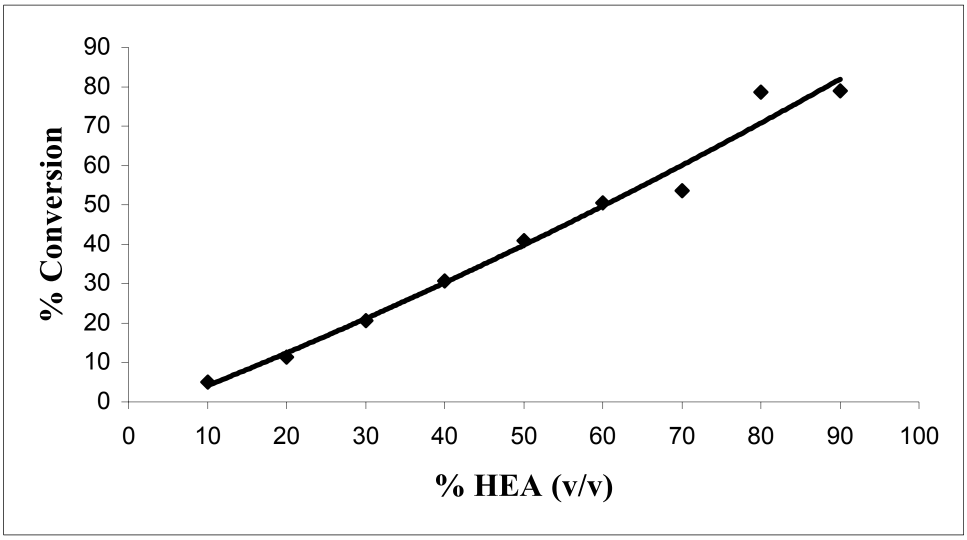


Figure 3.10 **The plot of % conversion vs. % HEA in CCl_4**

The percent conversion increased with the % HEA, almost linearly. Polymerization of 20% (v/v) HEA in CCl_4 solution was also carried out for different polymerization times and results are given in Table 3.7.

Table 3.7 % Conversion vs. time results for solution polymerization of HEA at 60°C.

Time (min)	% Conversion
20	0.54
25	1.01
30	1.34
35	2.24
40	2.52
45	2.55
60	2.93
80	5.61

The percent conversions vs. polymerization times of 20% HEA in CCl_4 solutions are plotted in Figure 3.11.

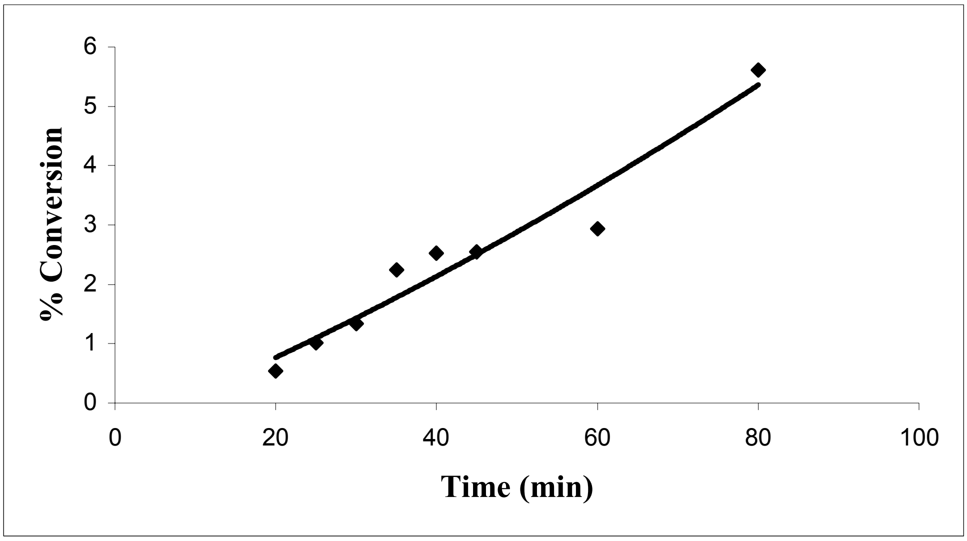


Figure 3.11 **The plot of % conversion of 20 % HEA solutions vs. different polymerization times at 60°C.**

The % conversion of HEA increased with polymerization times. However, % conversion is low because of the concentration of monomer. The autoacceleration stage is not observed in this case. This means that the gel effect was eliminated. However, polymers obtained by solution polymerization were also insoluble in common solvents and they were swollen in methanol but they did not dissolve in it. Therefore, chain transfer constant to solvent, Cs, could not be determined.

3.4 ATOM TRANSFER RADICAL POLYMERIZATION OF 2-HEA

% Conversions versus time for atom transfer radical polymerization of HEA are given in Table 3.8.

Table 3.8 %Conversion vs. time for polymerization of HEA by ATRP method at 90 °C.

Time (min.)	**% Conversion**
1.15	**12.5**
2.00	**22.1**
4.00	**84.6**
4.15	**81.6**

After the % conversion of sample was calculated, part of the content was dissolved in d_6-DMSO for ^{1}H-NMR and ^{13}C-NMR investigation (for all polymers). Parts of the remaining samples were used for DSC analysis.

3.5 FT-IR ANALYSIS

The FT-IR spectra obtained for HEA and PHEA are shown in Figure 3.12 and 3.13, respectively.

In the IR spectrum of monomer, a characteristic carbonyl peak (C=O stretching) is at 1712 cm^{-1}. The peaks for the C=C was observed at 1638 cm^{-1} and at 935 cm^{-1}. The peaks in the range of 2900-3000 cm^{-1} correspond to the aliphatic C-H stretching.The $-CH_2-$ peak is at 1410 cm^{-1} . The peak at 3415 cm^{-1} corresponds to O-H stretching. Furthermore, O-H bending was observed at 1298 cm^{-1} . The ester peak (C-O stretching) of monomer can be seen at 1200 cm^{-1}.

In the spectrum of PHEA, C=O bond stretching appeared at 1719 cm^{-1}. Also an aliphatic C-H stretching was observed at 2946 cm^{-1} and an aliphatic C-H bending ($-CH_2-$) at 1447 cm^{-1}. The broad peak at 3500 cm^{-1} corresponds to O-H bond stretching and also O-H bending can be seen at 1394 cm^{-1} . The ester peak of polymer was observed 1162 cm^{-1}. Peaks belong to double bond were completely dissappeared.

It can be concluded from IR spectra investigation that polymer was successfully achieved and the polymerization proceeds by carbon-carbon double bond opening.

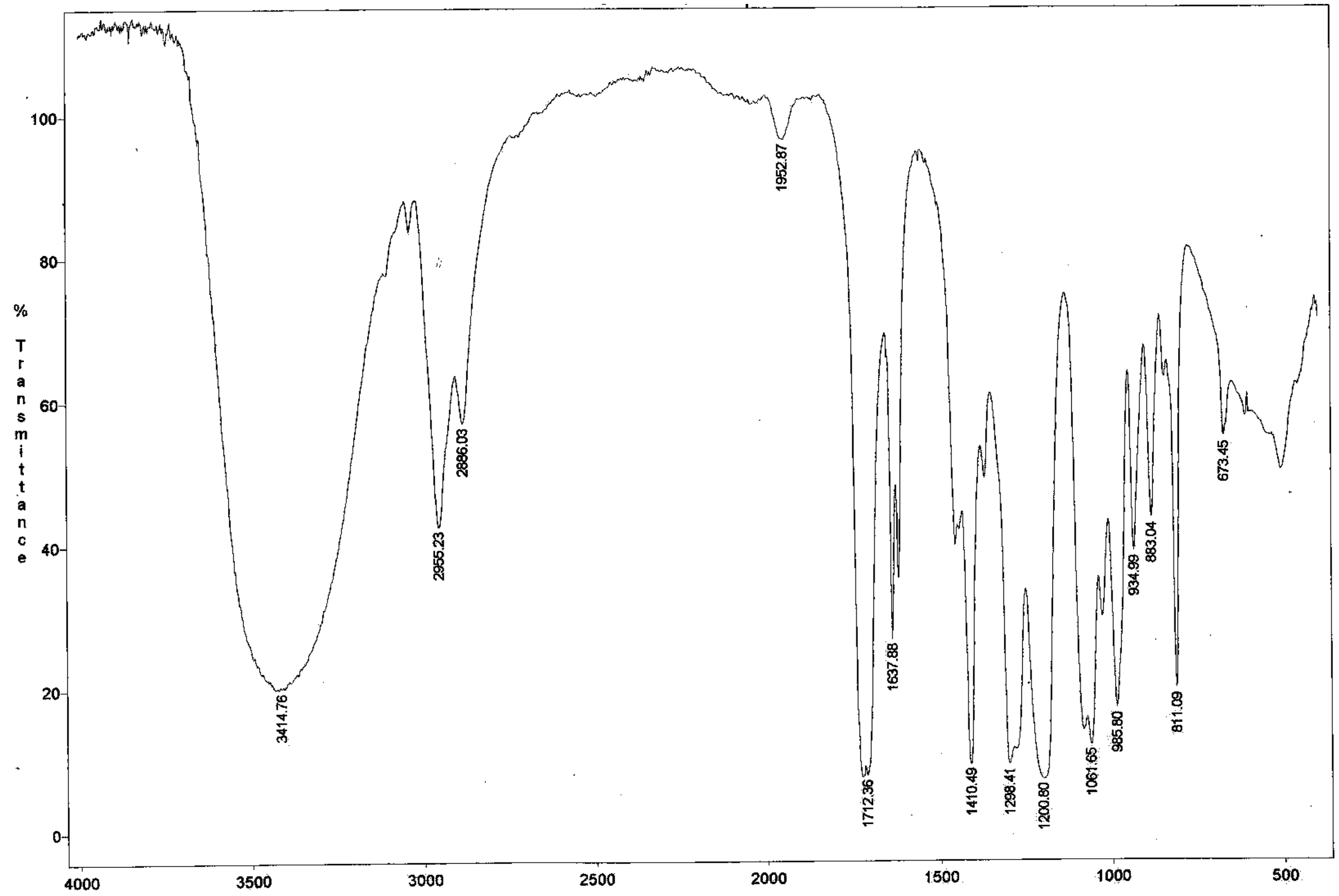


Figure 3.12 **FT-IR Spectrum of HEA**

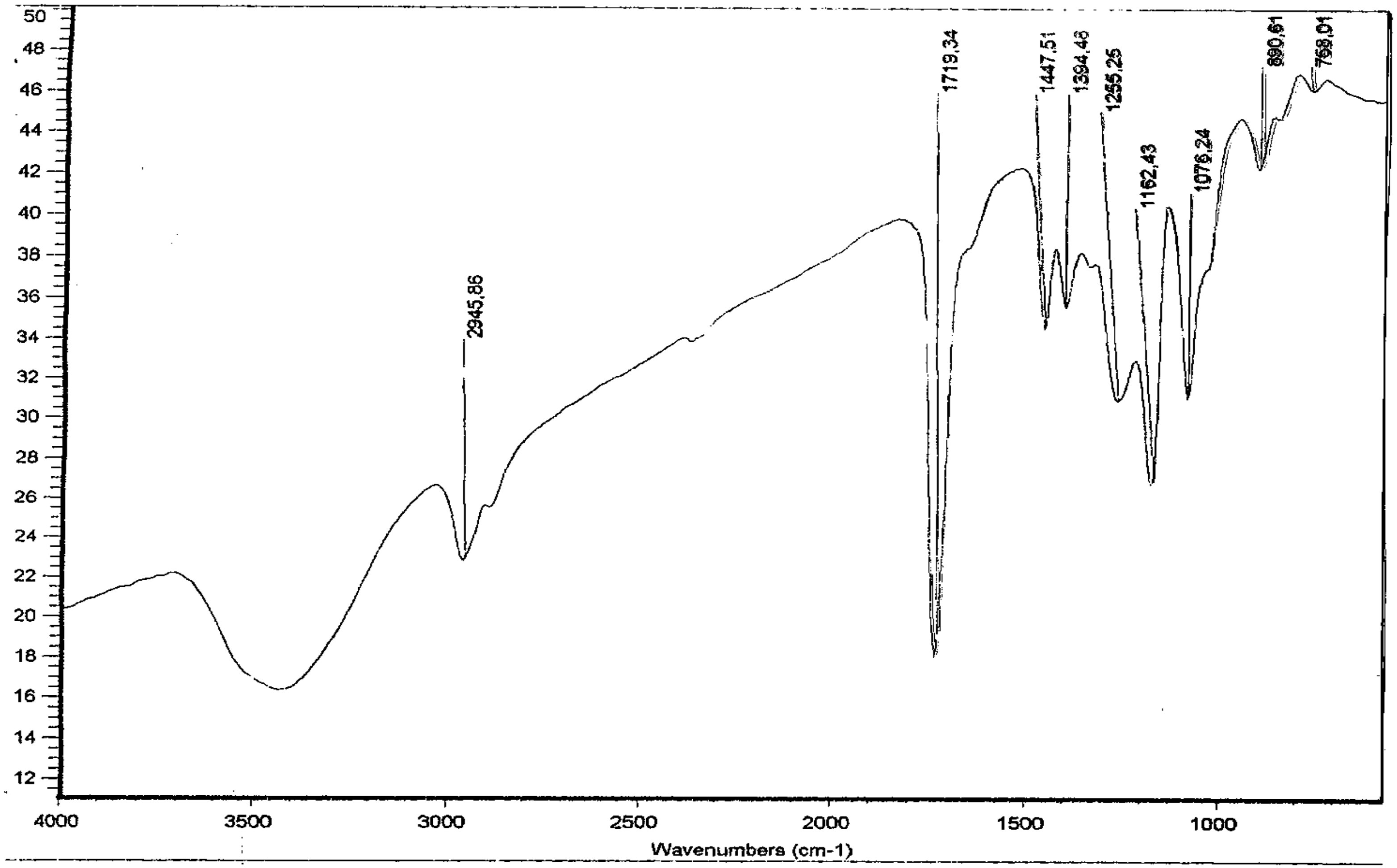


Figure 3.13 **FT-IR Spectrum of PHEA**

3.6 NUCLEAR MAGNETIC RESONANCE

The monomer and polymers were identified by ^{1}H-NMR and ^{13}C-NMR. The spectra are given in Figure 3.14 to Figure 3.17.

In the ^{1}H-NMR spectrum of 2-HEA (Figure 3.14) six different peaks were observed. The assigned protons are shown in formula of molecule and the chemical shifts in Table 3.9.

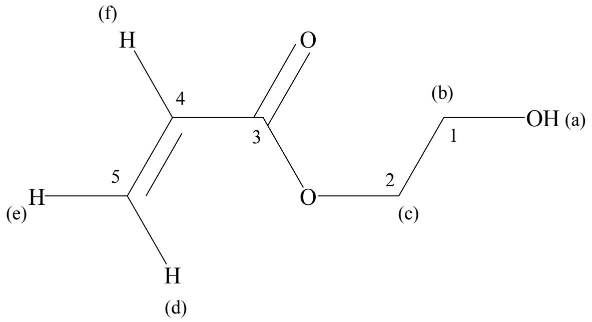


Table 3.9 The ^{1}H-NMR spectrum of HEA

Proton Type	Shift (ppm)	Group
(Ha) OH	3.54	Alcohol
(Hb) CH_2	3.73	Ester
(Hc) CH_2	4.23	Ester
(Hd) H	6.39	Ethylene (cis)
(He) H	5.77	Ethylene
(Hf) H	6.09	Ethylene (trans)

The ^{13}C-NMR spectrum of 2-HEA is given in Figure 3.15 and the peak assignment in Table.3.10.

Table 3.10 ^{13}C-NMR spectrum of 2-HEA

C Type	Shift (ppm)	Group
(1) CH_2	66	Aliphatic
(2) CH_2	71	Aliphatic
(3) C	172	Carboxyl
(4) CH	133	Ethylene
(5) CH_2	137	Ethylene

The ^{1}H-NMR spectrum of PHEA obtained by γ-radiation is shown in Fig. 3.16. The peaks for vinyl groups are not observed and $-CH_2-$ peaks in the range of 0.8-1.4 ppm appeared. This clearly shows that polymerization proceed via opening of vinyl groups. In the structure of polymer, there are repeated $-CH_2-$ groups in the main chain and $-CH_2CH_2OH$ side groups. However, the ^{1}H-NMR spectra of bulk polymerized HEA by free radical polymerization (Figure 3.17) is more complicated and cannot be explained that easily. The polymer is almost insoluble in DMSO and spectra obtained are not very reliable. However, the peaks in the region of 1-2 ppm might be assigned to $-CH_2-$ groups opened in the backbond chain, but other peaks for vinyl groups and ester groups are also available. This is not supported by FT-IR results. Therefore, either the ^{1}H-NMR spectrum of polymer are not corresponding to pure polymer or the structure of polymer is more complicated. The most reasonable explanation might be the presence of residual monomer in polymer that is extracted into solvent and that the spectrum is corresponding to a mixture of polymer and monomer. Similar spectrum was observed for polymers obtained under different conditions including the polymers obtained by ATRP method.

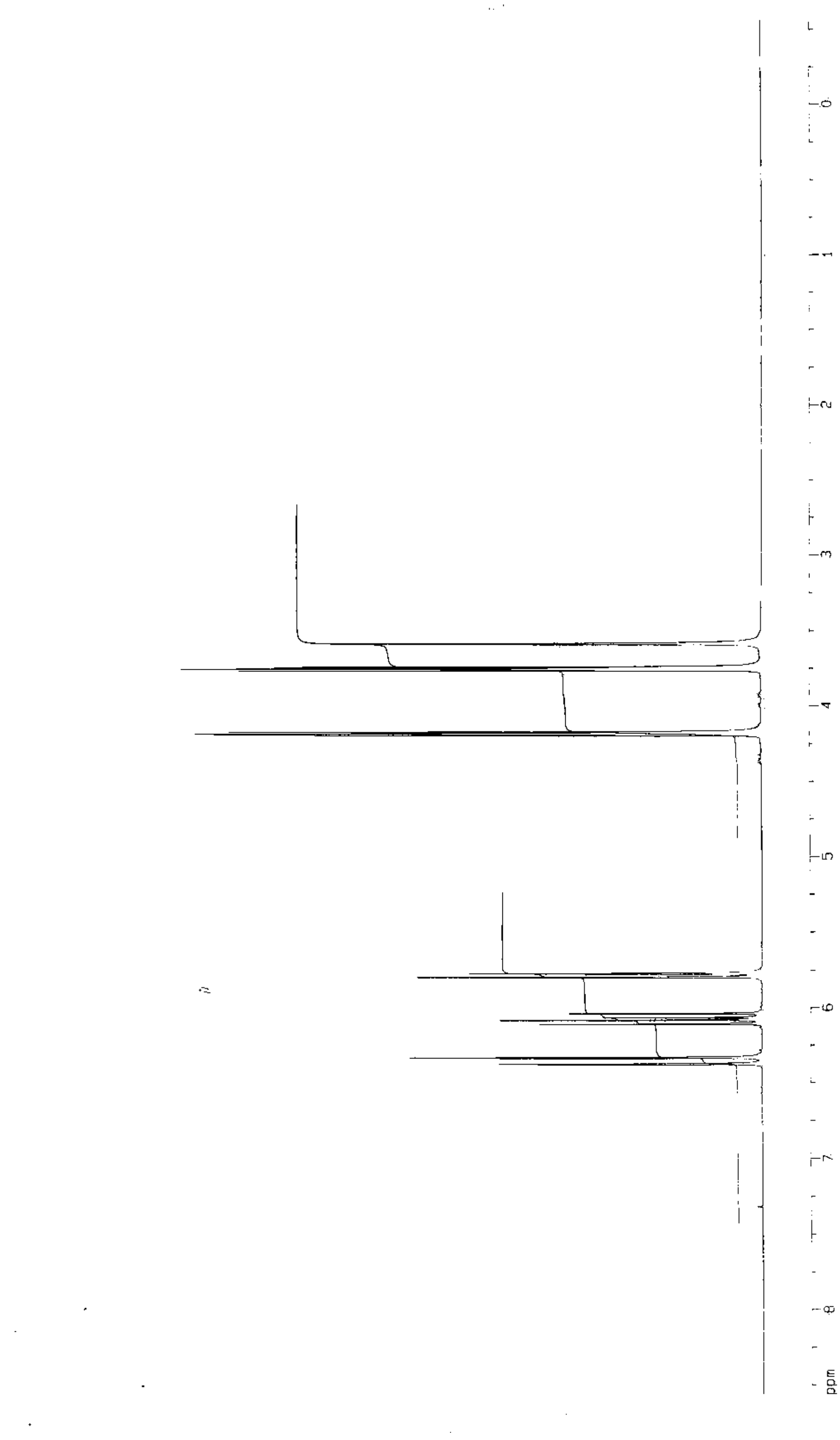


Figure 3.14 **^{1}H-NMR Spectrum of monomer HEA**

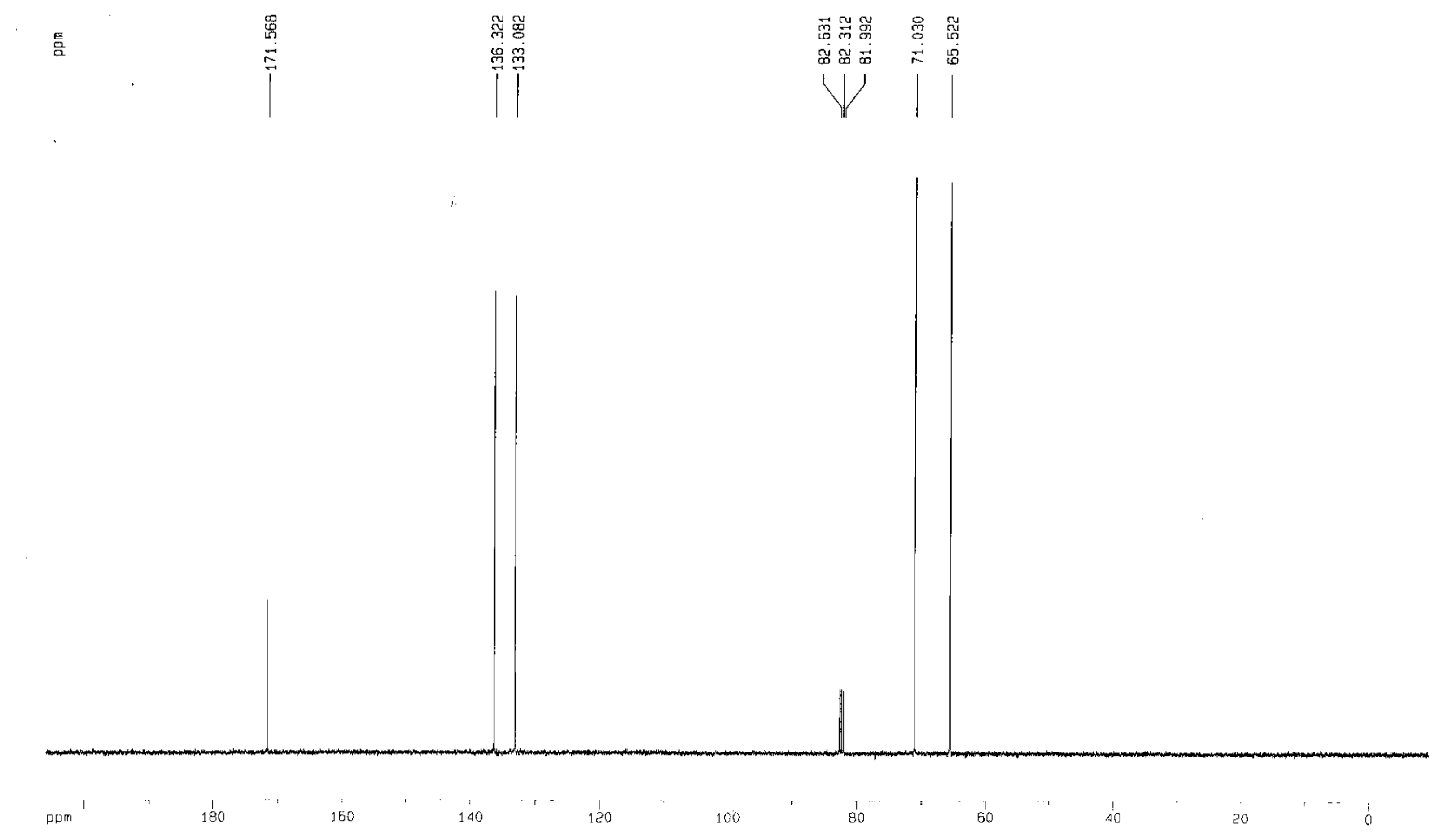


Figure 3. 15 ^{13}C-NMR Spectrum of HEA

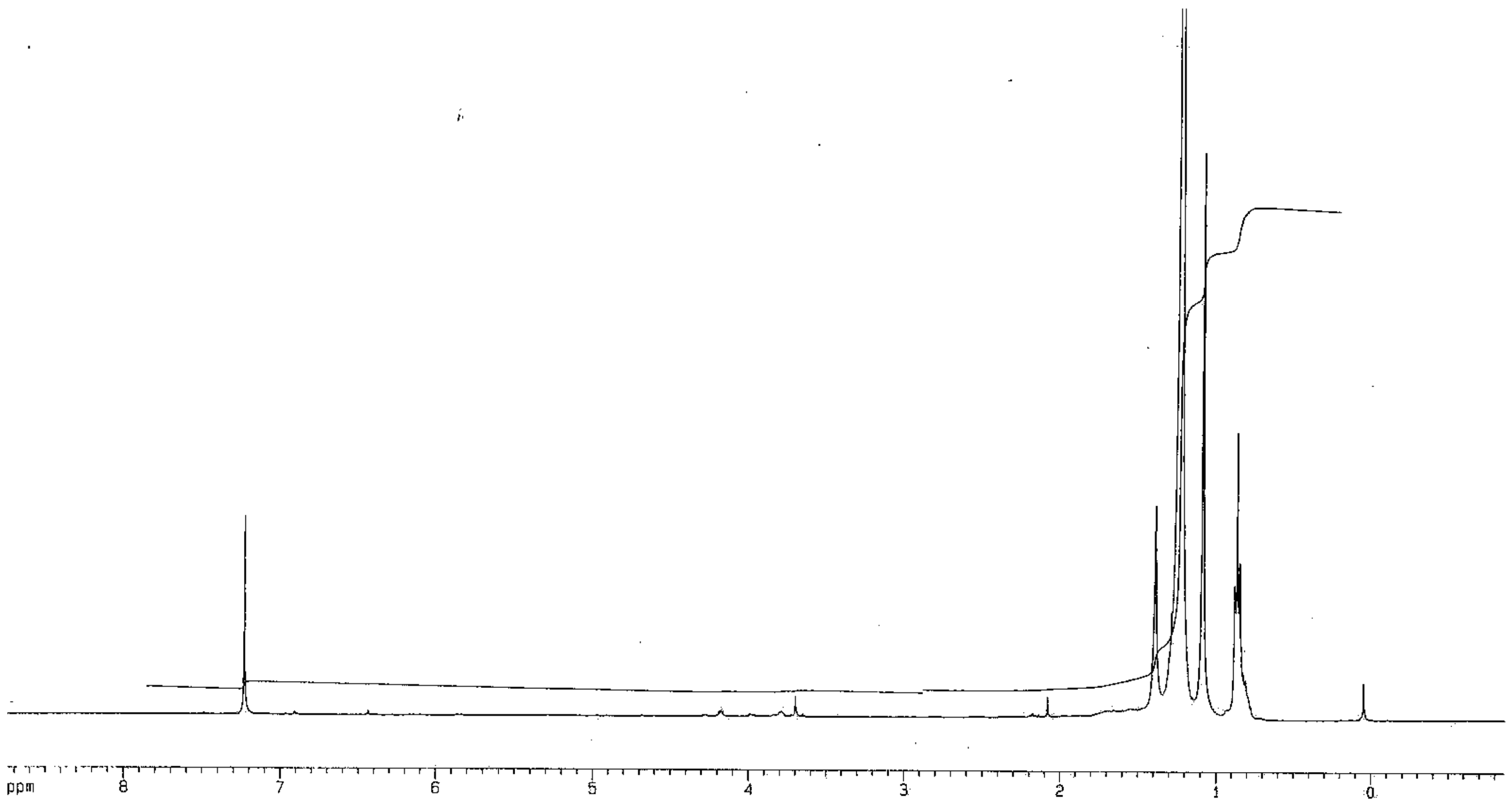


Figure 3.16 ^{1}**H-NMR Spectrum of bulk PHEA under vacuum-gamma source**

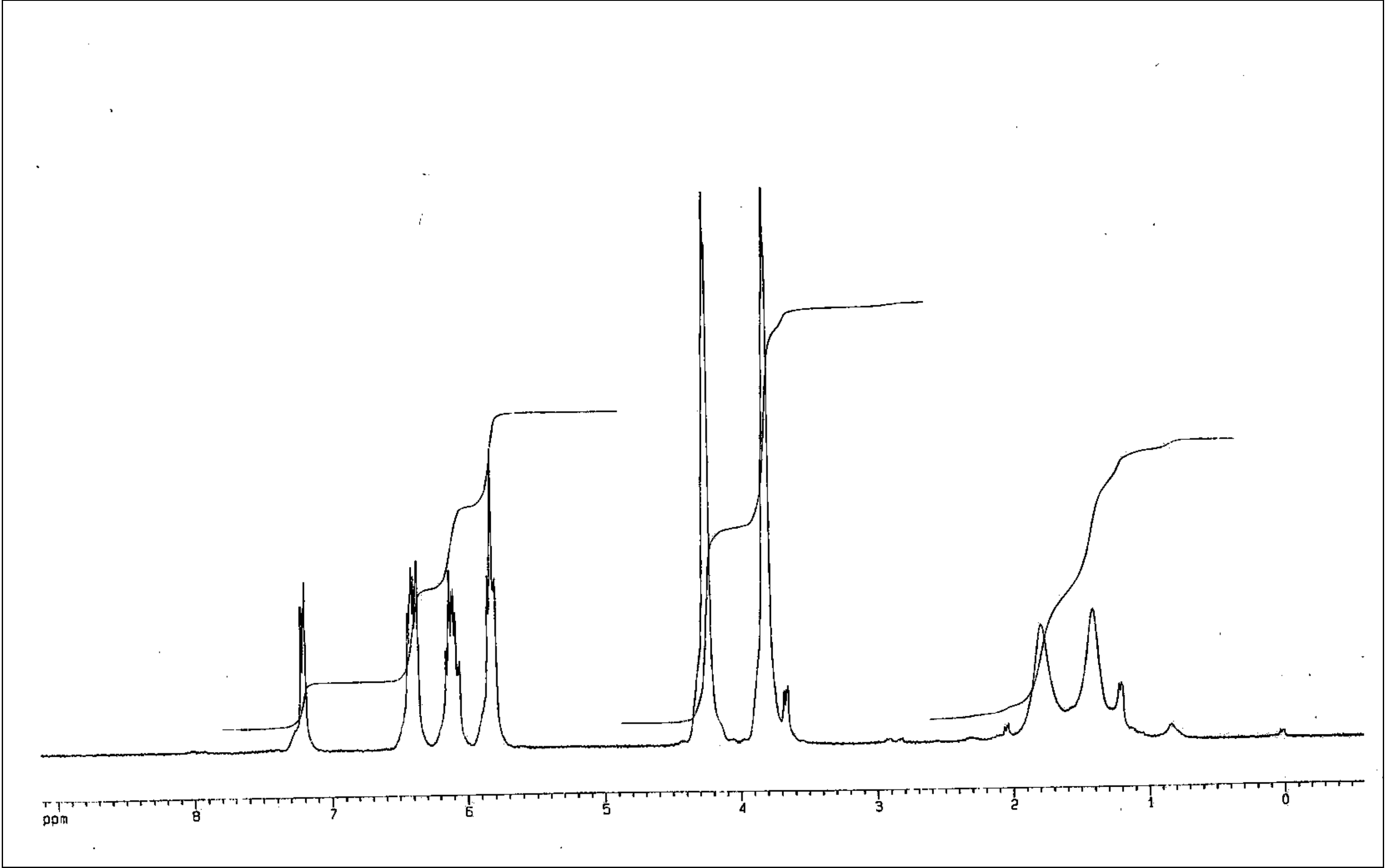


Figure 3.17 ^{1}**H-NMR Spectrum of bulk PHEA under vacuum**

3.7 DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

The DSC measurements were carried out at N_2 atmosphere by heating polymer samples in the temperature range of –150 to 300 °C. Thermograms of samples were shown in Figure 3.18 to 3.23. No melting peak of polymer was observed due to the amorphous structure. The Tg values are given in Table 3.8.

Table 3. 11 Tg values of PHEA

Samples	Tg of polymer /°C	Rheological Flow /°C
PHEA.BULK.at 60 °C	-25.2	185.3
PHEA.BULK. at 70 °C	-3.4	136.6
PHEA.SOLN. %90 at 60°C	-12.4	195.4
PHEA.ATRP. 2.0 at 90 °C	-9.6	142.0
PHEA.ATRP. 4.0 at 90 °C	-24.9	-
PHEA.ATRP. 4.15 at 90 °C	-20.7	137.9

The Tg value depends on number average molecular weight according to the following equation.

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

where, K is a constant depending on the nature of polymer, M_n number average molecular weight, Tg^{∞} glass transition temperature over a certain limiting molecular weight and Tg is the glass transition temperature of a given sample. Different Tg values obtained shows that the samples didn't reach to limiting molecular weights of corresponding Tg^{∞}. These results mean that, PHEA is in the rubbery state at room temperature, demonstrating elastic behaviour.

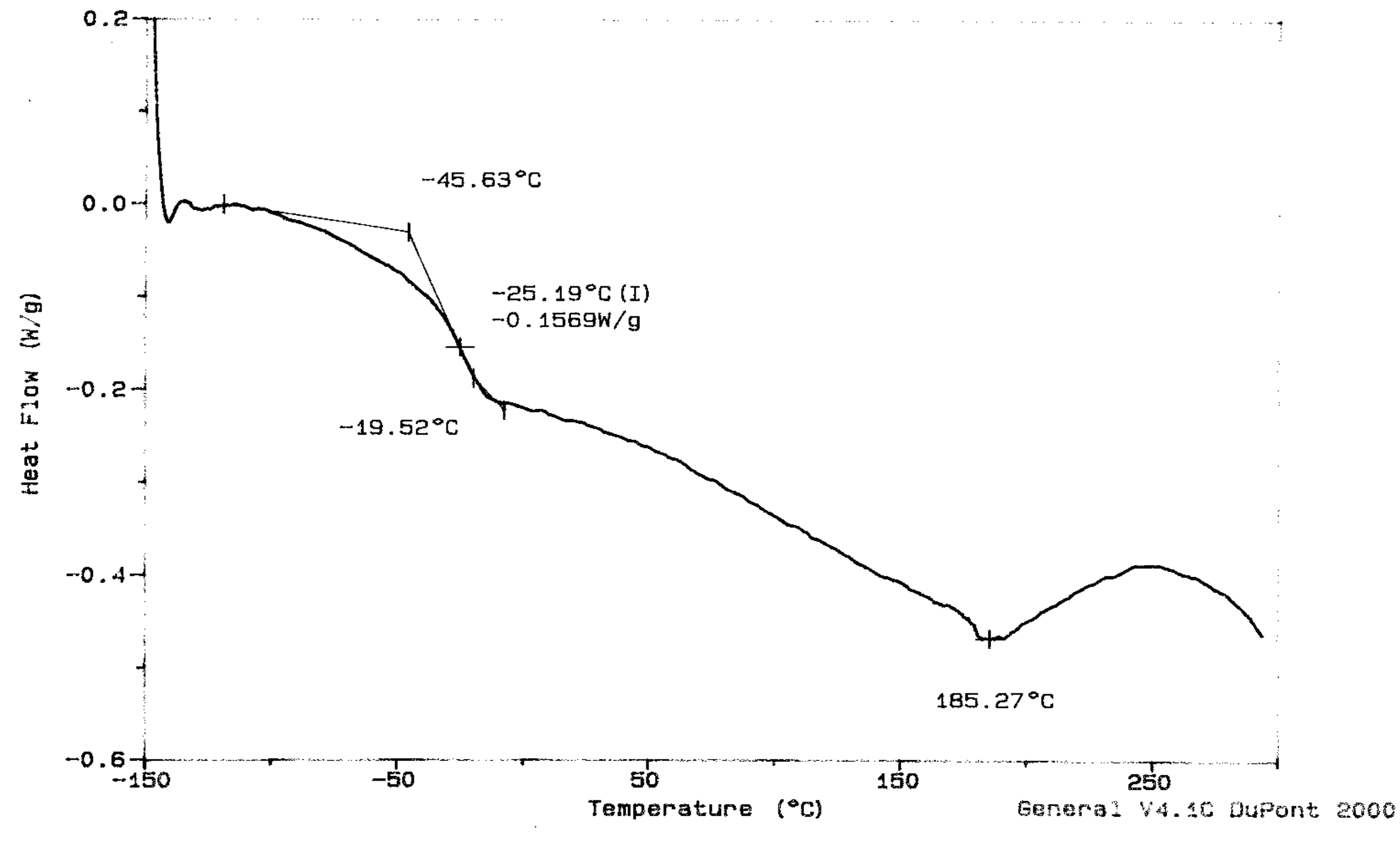


Figure 3.18 **DSC Thermogram of PHEA.BULK.at 60 °C**

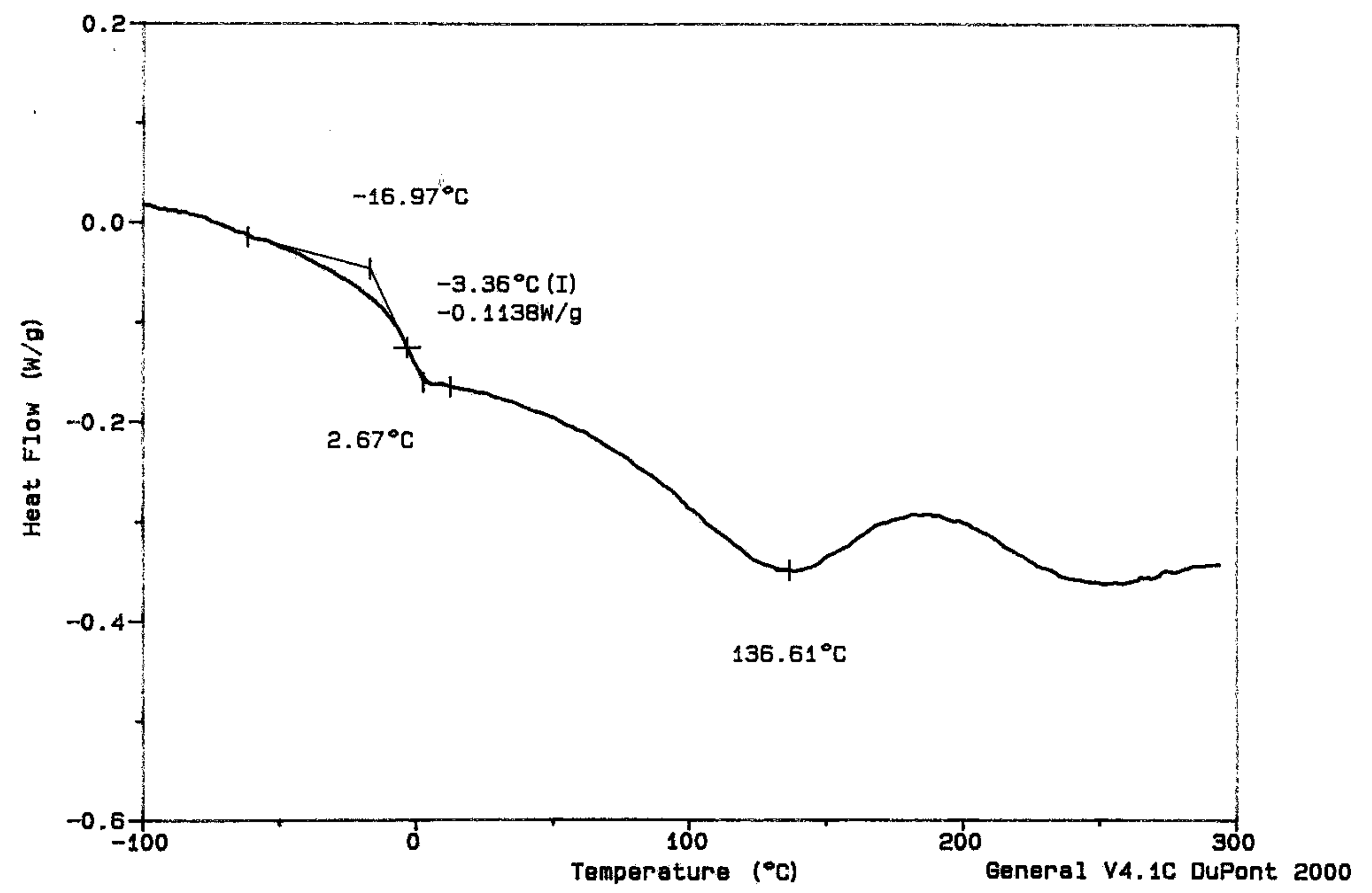


Figure 3.19 **DSC Thermogram of PHEA.BULK.at 70 °C**

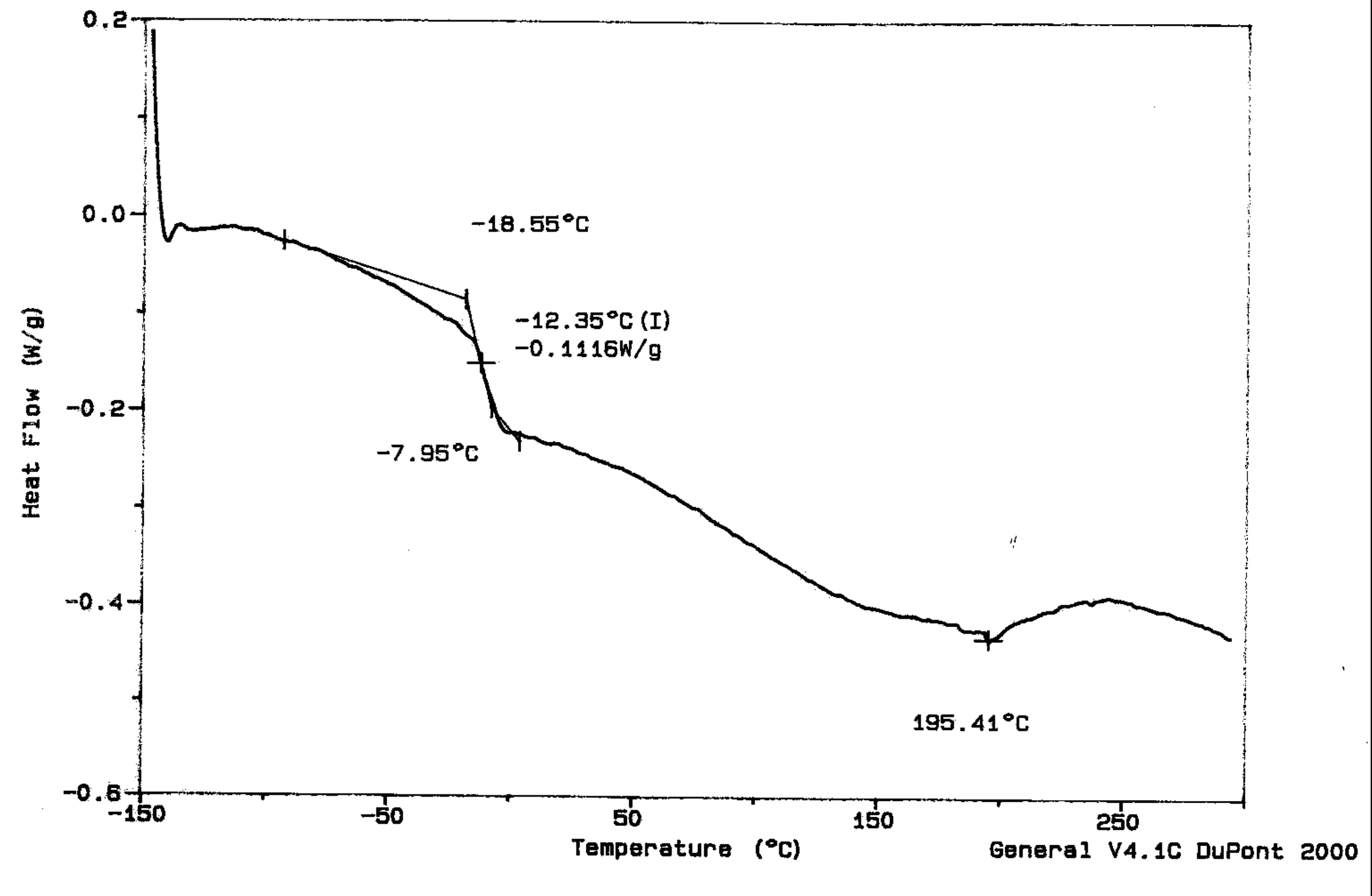


Figure 3.20 **DSC Thermogram of PHEA.SOLN. 90%.at 60 °C**

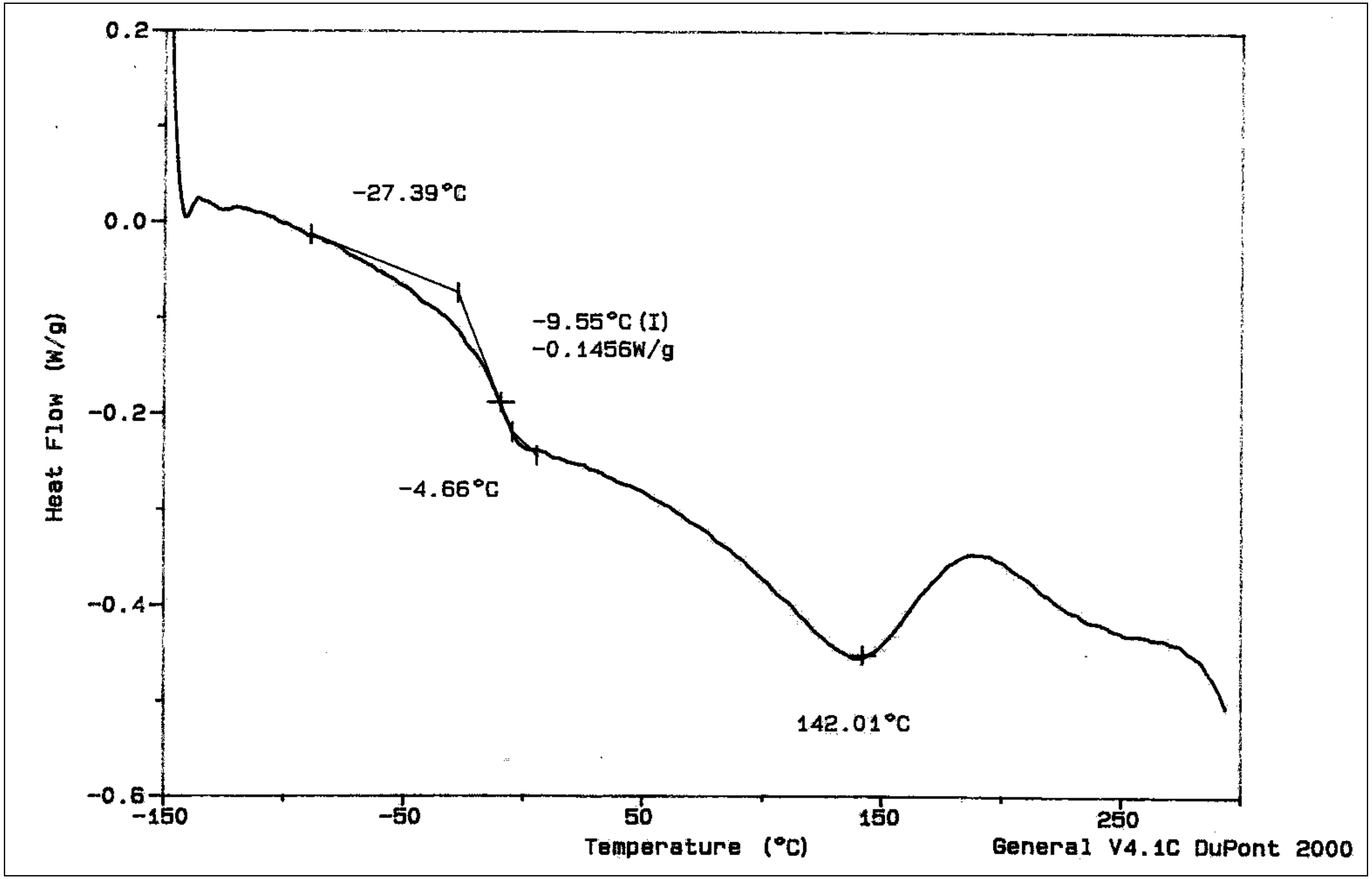


Figure 3.21 **DSC Thermogram of PHEA.ATRP. 2.0 at 90 °C**

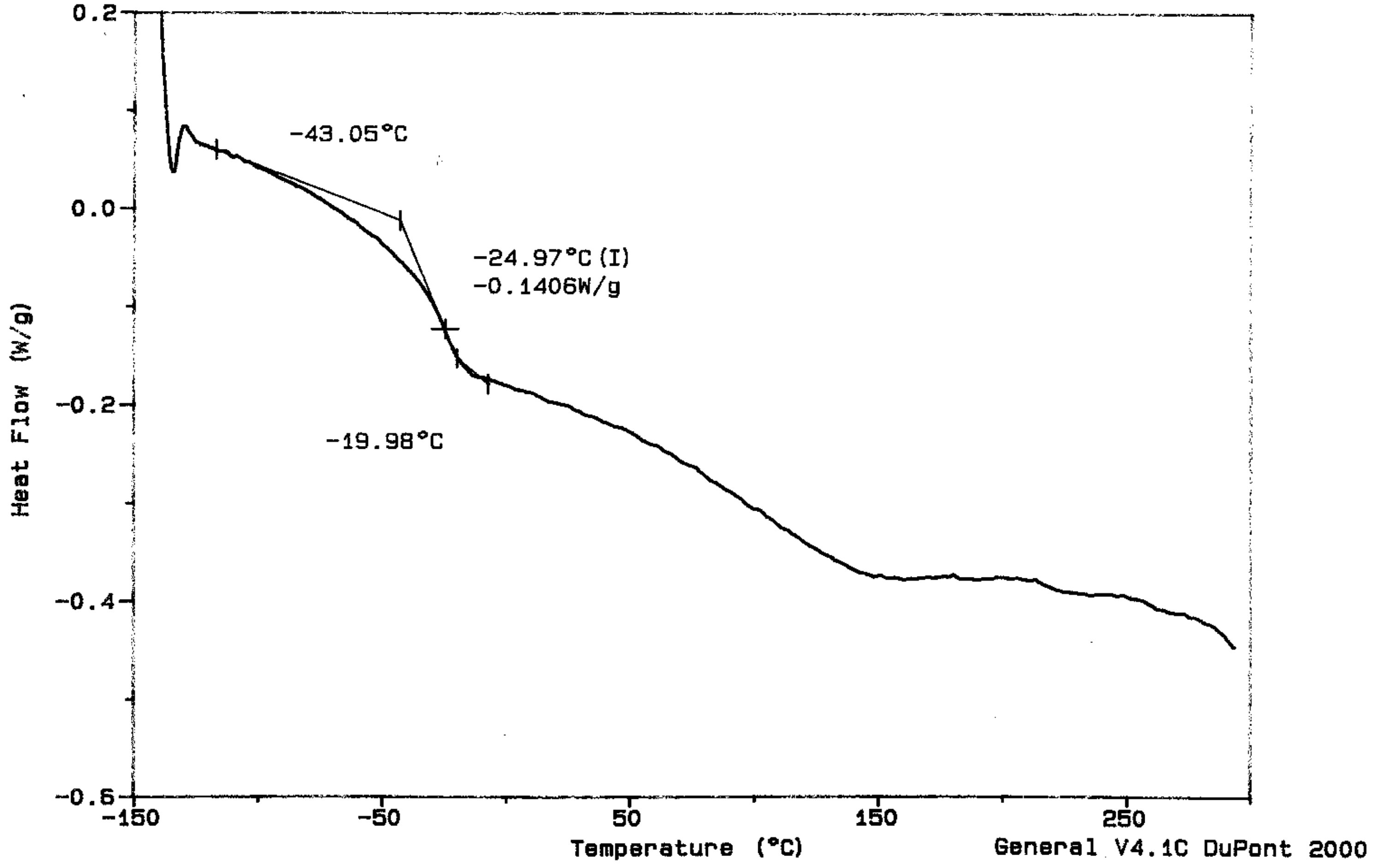


Figure 3.22 **DSC Thermogram of PHEA.ATRP. 4.0 at 90°C**

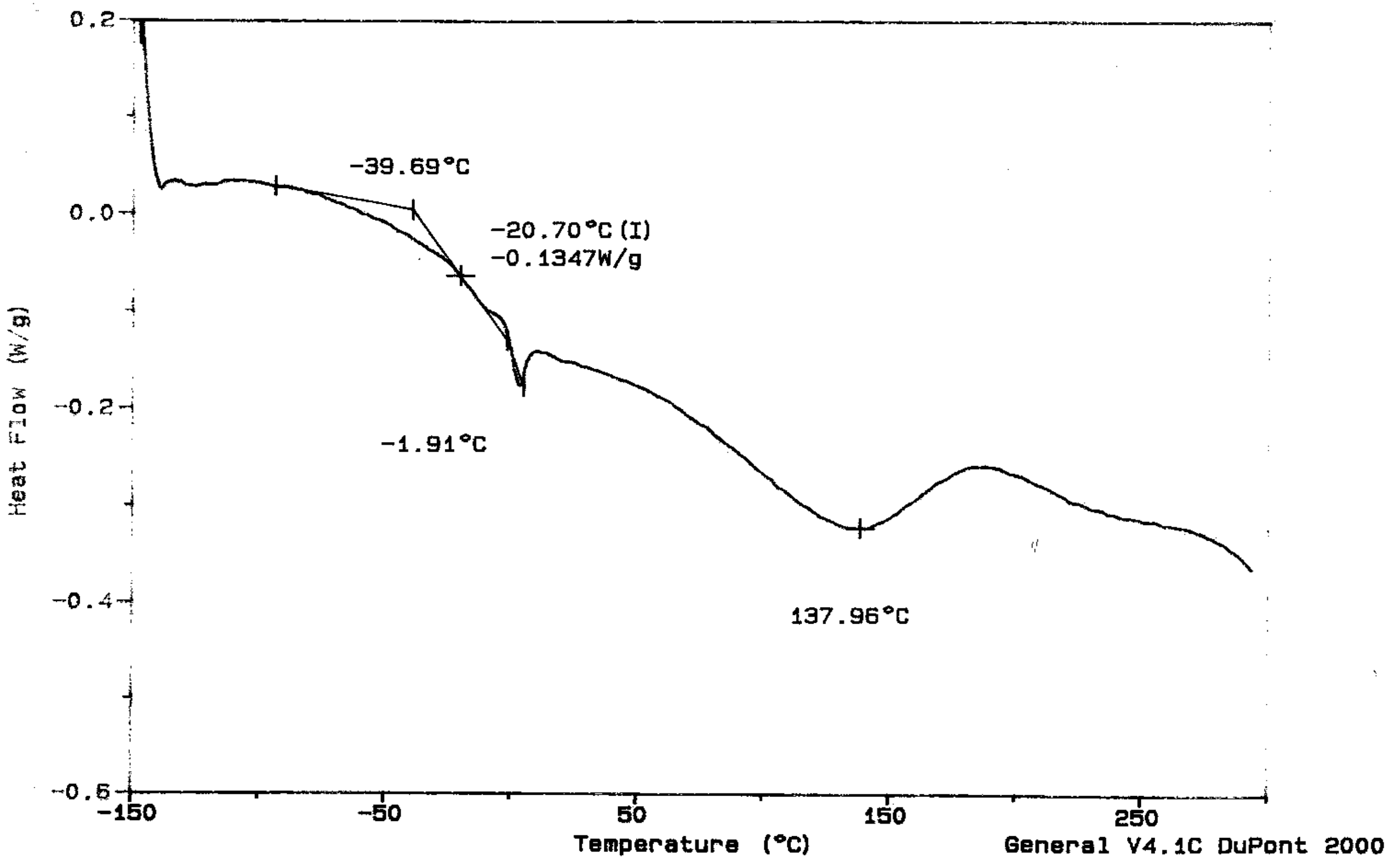


Figure 3.23 **DSC Thermogram of PHEA.ATRP. 4.15 at 90°C**

3.2 TGA CHARACTERIZATION OF PHEA

The thermal stability of PHEA samples were also characterized by means of TGA from 30°C to 600°C in N_2 atmosphere as illustrated in Figure 3.24, 3.25 and 3.26. From the TGA thermograms in Figure 3.24 and 3.25, two measured weight losses were seen for bulk PHEA's in which gamma and BPO were used as initiator. The thermograms are typical for acrylate polymers that thermal degredation is in the form of depolymerization. The small peak at 402 $^\circ$C for polymerization by radical initiator (Figure 3.24) and a similar broad peak for polymer obtained by γ-radiation (Figure 3.25) show the degradation of oligomers and/or residual monomer that may exist in crosslinked polymer. This peak is not observed for polymer obtained by solution polymerization (Figure 3.26). The main decomposition peak is much sharper and appears at lower temperature for the polymer obtained in solution. The broad peaks and higher temperature in first two figures show higher molecular weights and crosslinking or larger dispersive index of polymers.

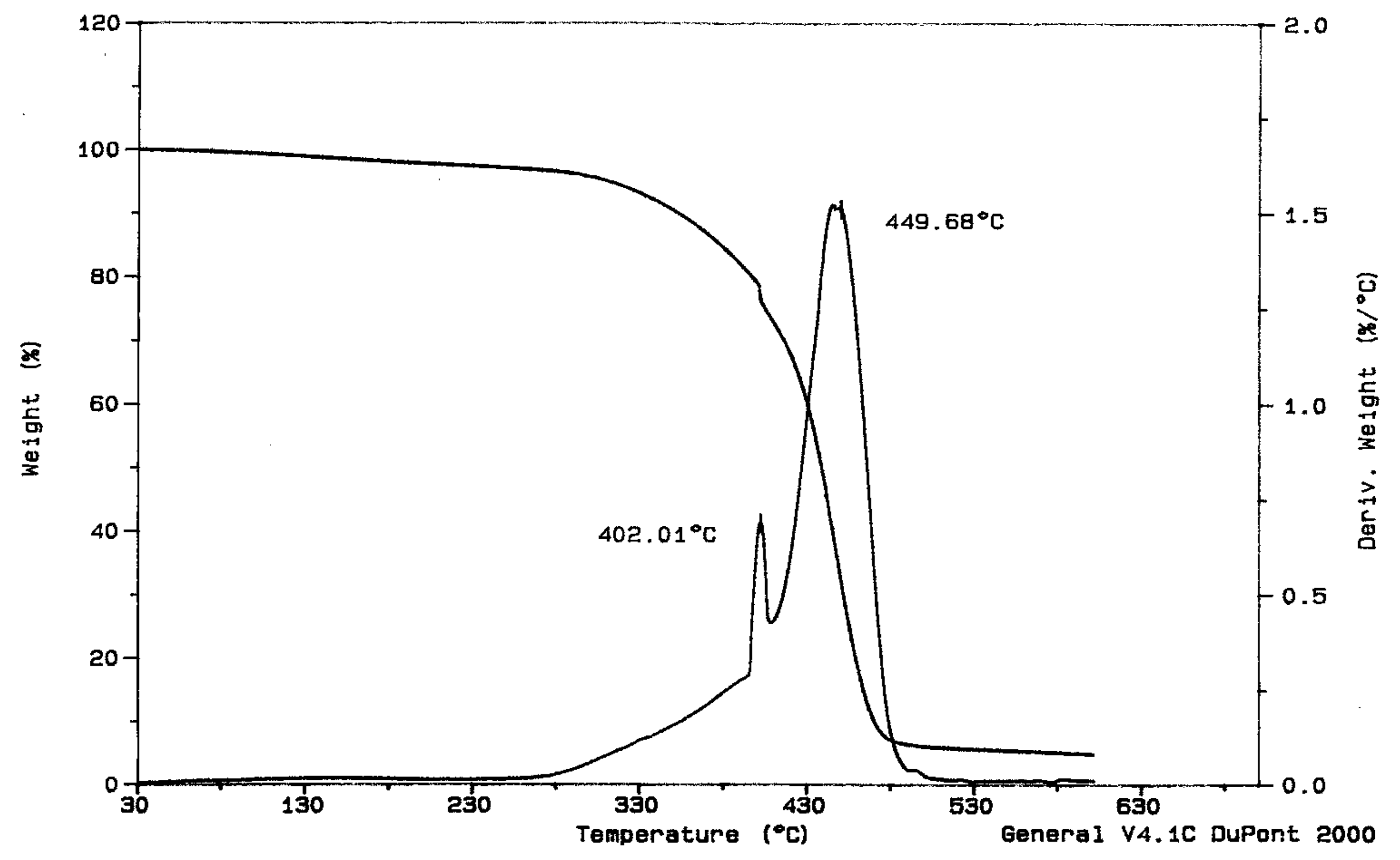


Figure 3.24 **TGA Thermogram of BULK PHEA.BPO initiator**

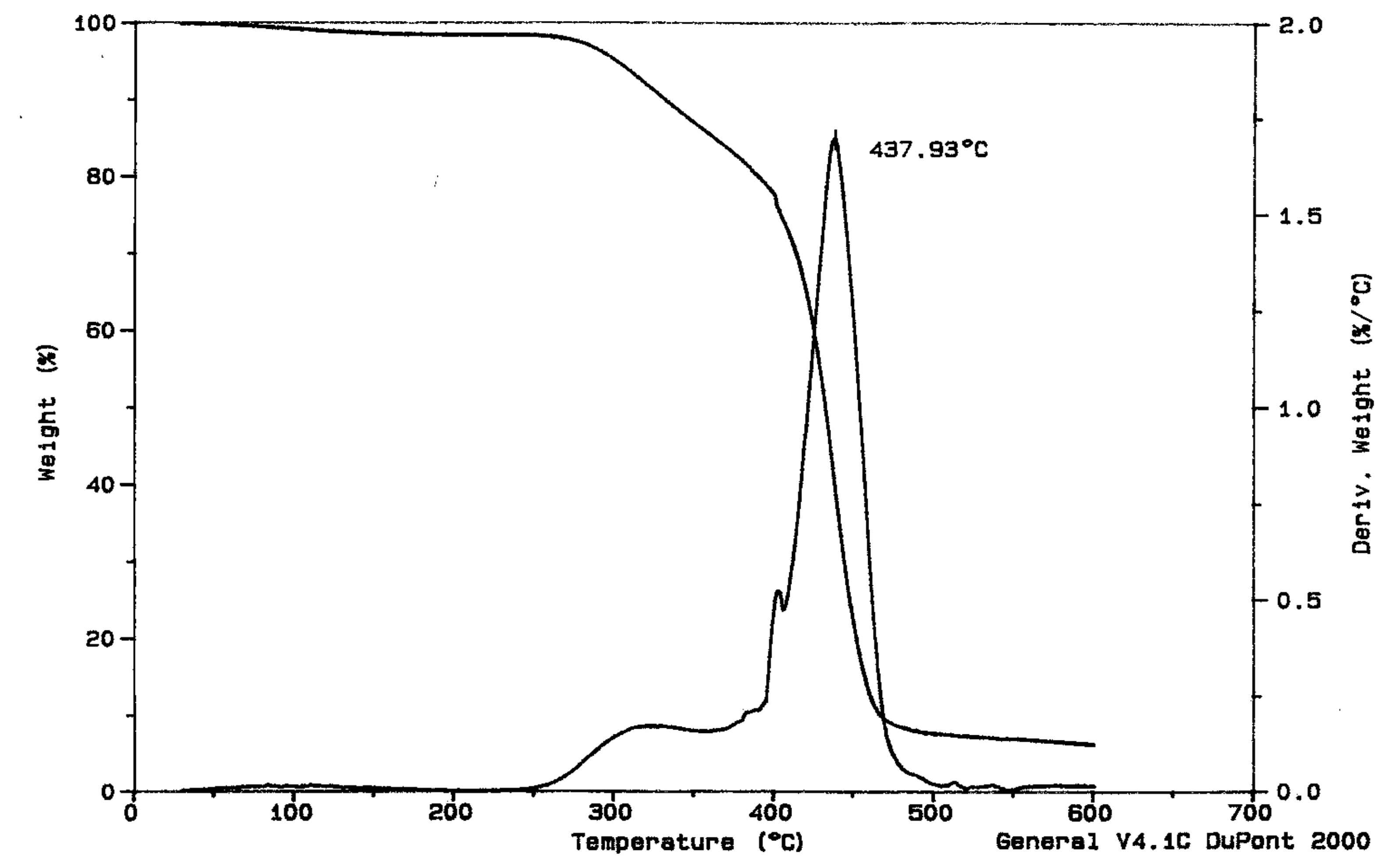


Figure 3.25 **TGA Thermogram of BULK PHEA.GAMMA**

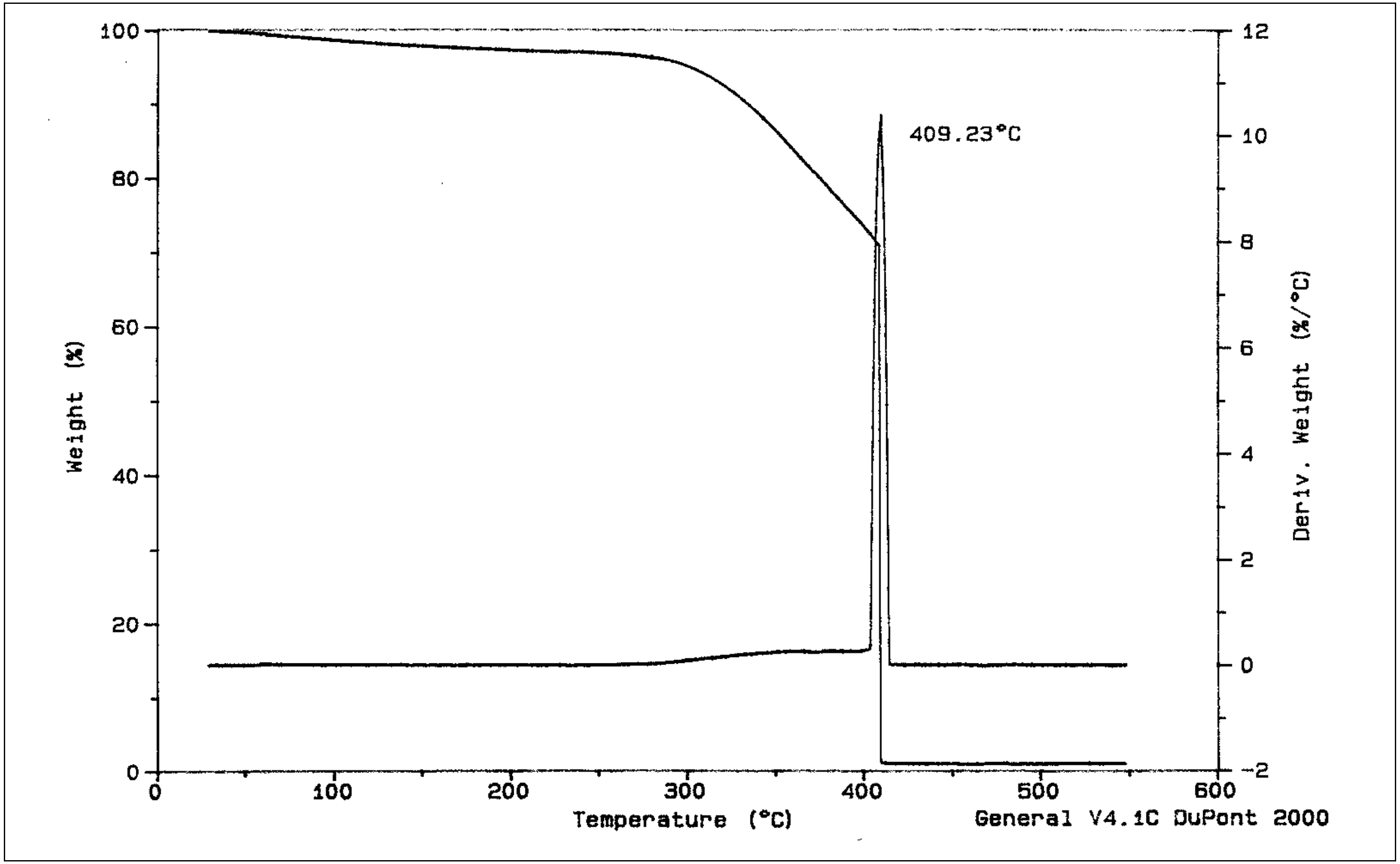


Figure 3.26 **TGA Thermogram of SOLUTION PHEA (10%)**

3.8 TENSILE TEST RESULTS FOR PHEA

Tensile tests results for polymer samples in average are given in Table 3.9 in Figure 3.27.

Table 3.12 Stress-strain properties of PHEA

Young's modulus (MPa)	Tensile strength (MPa)	Stress at yield (Mpa)	% Strain at yield	Stress at break (Mpa)	% Strain at break
86.26	0.79	0.62	24.07	0.75	71.35

PHEA samples have rubber properties and they are not hard and brittle as other acrylates or methacrylates. Modulus of PHEA is low and percent strain is moderate due to it's hydrogel properties.

Figure3.27 Stress vs % Strain

CHAPTER 4

CONCLUSION

From the results of this experimental investigation the following conclusions can be mentioned:

1. In bulk polymerization of HEA by free radical mechanism, the rate of polymerization and the molecular weight of polymers obtained are very high. The control of molecular weight is not possible. Polymers obtained are insoluble in common solvents.

2. The polymerization curves showed and autoacceleration mechanism.

3. Oxygen acts as an inhibitor and gives an induction period of polymerization.

4. Solution polymerization in CCl_4 decreases the rate of polymerization and molecular weight of polymer by radical transfer to solvent. But in the case of solution polymerization the molecular weight of polymers are still very high.

5. IR and NMR results showed that polymerization takes place by opening of carbon-carbon double bond.

6. The DSC thermograms showed that molecular weight for most samples are smaller than the limiting value that gives Tg^{∞}.

7. The TGA thermograms showed that degradation is by depolymerization. The polymer obtained from solution has much lower dispersive index.

8. Tensile tests show that PHEA hydrogel has low tensile strength due to the gel characteristic. Mechanical properties of PHEA can be enhanced by crosslinking.

9. ATRP polymerization results are preliminary work and detailes of this method and copolymerization will be carried out in future research.

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