

POLYMERIZATION AND CHARACTERIZATION  
OF  
METHYLMETHACRYLATE BY ATOM TRANSFER RADICAL  
POLYMERIZATION

A THESIS SUBMITTED TO  
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES  
OF  
MIDDLE EAST TECHNICAL UNIVERSITY

BY

BENGIİ ARAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE  
IN  
POLYMER SCIENCE AND TECHNOLOGY

MAY 2004

Approval of the Graduates School of Natural and Applied Sciences

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## **ABSTRACT**

### **POLYMERIZATION AND CHARACTERIZATION OF METHYL METHACRYLATE BY ATOM TRANSFER RADICAL POLYMERIZATION**

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May 2004, 83 pages

In this work, methylmethacrylate, MMA was polymerized by ATRP method to obtain low molecular weight living polymers. The initiator was p-toluenesulfonylchloride and catalyst ligand complex system were CuCl-4,4' dimethyl 2,2'bipyridine. Polymers with controlled molecular weight were obtained.

The polymer chains were shown by NMR investigation to be mostly syndiotactic. The molecular weight and molecular weight distribution of some

polymer samples were measured by GPC method. The K and  $\alpha$  constants in  $[\eta]=K M^\alpha$  equation were measured as  $9.13 \times 10^{-5}$  and 0.74, respectively. FT-IR and X-Ray results showed regularity in polymer chains. The molecular weight-Tg relations were verified from results of molecular weight-DSC results.

Key words: controlled living polymerization, ATRP, methyl methacrylate, GPC, monodispersed polymer.

## ÖZ

### METİLMETAKRİLATIN ATRP METODU İLE POLİMERLESTİRİLMESİ VE KARAKTERİZASYONU

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Mayıs 2004, 83 sayfa

Bu çalışmada, düşük molekül ağırlıklı polimerler elde edebilmek için metilmetakrilat, MMA, atom transfer radikal polimerleştirme (ATRP) metodu ile polimerleştirildi. Başlatıcı olarak p-toluensulfoniklorit ve katalizör-ligand sistemi olarak CuCl-4,4' dimetil 2,2'bipiridin kullanıldı.

Kontrollü molekül ağırlığına sahip polimerler elde edildi. NMR sonuçlarına göre polimer zincirlerinin genellikle sindiotaktik olduğu anlaşıldı. Bazı polimer örneklerinin molekül ağırlığı ve molekül ağırlık dağılımı GPC methodu ile belirlendi.  $[\eta]=K M^\alpha$  denklemindeki K ve  $\alpha$  sabitleri sırası ile  $9.13 \times 10^{-5}$  ve 0.74 olarak hesaplandı. FT-IR ve NMR sonuçlarına göre polimer zincirlerinde düzenlilik gözlemlendi. Molekül ağırlık- Tg ilişkileri molekül ağırlık-DSC sonuçları ile belirlendi.

Anahtar kelimeler: kontrollü aktif polimerleşme, ATRP, metilmetakrilat, GPC, düzgün dağılımlı polimer.

## **ACKNOWLEDGEMENT**

I would to thank most sincerely to Prof.Dr.Ali Usanmaz for his excellent supervision, continued interest and help throughout this work.

I am grateful to Miss Elif Vargün for supporting me morally throughout the thesis and for many stimulating discussions and critical suggestions.

I would also like to thank Miss Elif Anaçoglu for her help and understanding throughout the thesis, without her help this work would not have been possible.

Thanks go to Metin Yank for his help on glass materials.

Lastly, I wish to express my deep appreciation to my mother and brother for the encouragement, support and comprehension, and I would like to thank my father; I feel proud and lucky to have a father like him and I would also like to thank him for making me feel his presence around me all the time.

*To the memory of my father,*



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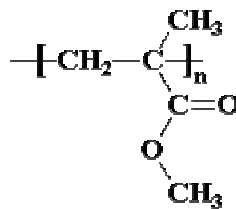
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# CHAPTER 1

## INTRODUCTION

### 1.1 POLYMETHYLMETHACRYLATE

Poly (methyl methacrylate), PMMA (Figure 1.1) is one of the most important commercial polymers which is known as Lucite and Plexiglas in America; Perpex and Plexiglas in Europe. The polymer possesses a remarkable combination of useful properties, including versatility in forming, excellent clarity, color stability to light and heating, and moderately high softening temperature, which makes it the best synthetic glass-like plastics, for most applications.<sup>1</sup>



**Figure 1.1** Structure of PMMA

### 1.1.1 HISTORY

In 1843, Redtenbacher oxidized acrolein with aqueous slurry of silver oxide and isolated acrylic acid. During the 1860's, Beilstein obtained acrylic acid from the distillation of the salts of hydracrylic acid, and Frankland and Duppa<sup>2</sup> dehydrated ethyl  $\alpha$ -hydroxyisobutyrate with phosphorus trichloride to form ethyl methacrylate, which was hydrolyzed to methacrylic acid.

In 1873 methyl, ethyl and allyl acrylate were prepared, and only the last one was observed to polymerize. However, Kahlbaum<sup>1</sup> reported the polymerization of methyl acrylate in 1880. Fittig and Engelhorn<sup>1</sup> found that methacrylic acid and some of its derivatives polymerize readily. Ethyl acrylate was prepared in 1891.

The name of the German chemist Röhm<sup>1</sup> has been associated with acrylic ester polymers for nearly half a century, beginning with his doctoral dissertation in 1901. Polymers from acrylic esters of lower alcohols are all soft at ordinary temperatures, and Röhm contemplated their use as rubber substitutes. In 1914, an early U.S. patent he sought to vulcanize polyacrylic esters with sulfur and at the same time disclosed that acrylic esters can be derived from lactic acid.

In 1927, Röhm and Haas<sup>1</sup> 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 & Haas A. -G. in Germany, and by Imperial Chemical Industries Ltd. in England.<sup>1</sup>

## 1.2 PROPERTIES OF METHYLMETHACRYLATE AND POLYMETHYLMETHACRYLATE

Physical properties of MMA monomer are given in Table 1.1.

**Table 1.1** Physical properties of MMA monomer

Boiling point, °C	100,6
Melting point, °C	-48
Specific gravity	0,940
Flash point, °C	8
Specific heat, J/gr/°C	2,05
Heat of polymerization, kJ/mole	53,97

MMA is miscible with most common organic solvents. It is only slightly soluble in glycerin and in ethylene glycol. The monomer readily dissolves MMA polymers except when the latter are crosslinked or of extremely high degree of polymerization.<sup>1</sup>

Acrylic and methacrylic polymers have characteristics of brilliance, optical clarity, high transparency, mechanical properties, adhesion and chemical stability. The photostability of aliphatic acrylic and methacrylic polymers is generally very high. The carbonyl ester group in the polymer units is not directly photochemically active, and the general content of trace impurities, which could initiate the photo-induced degradation, is inferred to be very low. The acrylate units were found to be more reactive towards oxidation, in comparison with the methacrylates.<sup>1</sup>



Among the synthetic plastics, MMA polymers are outstanding in stability and in optical properties, particularly in clarity and light transmission. Light conducting instruments from unplasticized MMA polymer have found wide applications in surgery. In addition to dentures, teeth, contact lenses and artificial eyes, acrylic plastics have been used for splints, braces and many other prosthetic and orthopedic devices.<sup>1</sup>

In specific gravity and strength properties, MMA plastics have outstanding advantages over glass. Perhaps the most serious limitation of MMA plastics is pure abrasion compared to glass. The strength characteristics of MMA polymers are little affected by moisture or low temperatures.<sup>1</sup>

Another failure of PMMA leading to impaired light transmission is crazing. Contact with organic solvents or severe mechanical treatment such as flexing, causes a network of very small cracks to form, beginning at the surface.<sup>1</sup>

PMMA's when free of crosslinking are soluble in acetone, ethyl acetate, ethylene dichloride, carbon tetrachloride, toluene, acetic acid and related solvents. They are softened by ethanol and by some aliphatic hydrocarbons. PMMA's are resistant to many aqueous inorganic reagents at room temperature including hydrochloric acid, nitric acid and ammonium hydroxide. Of the lower alkyl methacrylate polymers, only MMA polymer is said to dissolve in formic acid at 25°C.<sup>1</sup>

The depolymerization of MMA polymer on heating is believed to proceed by a free-radical-chain mechanism, and the nature of the end groups appears to influence the stability towards thermal breakdown.<sup>1</sup>

### 1.3 LIVING RADICAL POLYMERIZATION

The radical polymerization is very common and the mechanism is known in detail. However, its major limitation is the uncontrolled structure and broad polydispersity of the resulting polymers. This limitation is mainly due to the termination process that occurs from the very beginning of the polymerization. Some chain polymerizations may be performed in such a way that all molecules grow under identical conditions and are consequently quite monodisperse. These polymerizations are called “living”. For a long time, synthetic procedures were searched for a way that would allow also the radical polymerization to proceed as a living one while maintaining its versatility. Several procedures of this type were developed recently.<sup>3</sup>

In a perfect living polymerization all polymer chains would be initiated at the same time, grow at the same rate until all the monomer is exhausted, and then would stay alive (capable of resuming their growth) until deliberately terminated. This scenario implies the absence of chain termination during the growth process. In addition, the rate of polymerization must be kept slow enough so that the exothermic polymerization reaction does not get out of control. In classical radical polymerization, the rate control is provided by the continuous chain termination that keeps the number of growing chains sufficiently small at all times. In a living polymerization the number of simultaneously growing chains is necessarily, very large-it is equal to the final number of polymer molecules. Thus, the rate of growth of individual chains has to be reduced. Even more importantly, the recombination of growing radicals (that are now present in much larger concentration than in classical polymerization) must be prevented or at least very substantially repressed.<sup>3</sup>

New methods were developed in the mid-1990s based on the idea of reducing of the growth rate and suppression of the termination that are achieved

by keeping the growing chain in a dormant state for most of the time. Three approaches were the most successful.<sup>4</sup>

1. Control via a reversible homolytic cleavage of a weak covalent bond leading to a propagating radical and a stable free radical. The latter should only react with the propagating radical and can be a nitroxide, an N-based radical, or an organometallic species. 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).

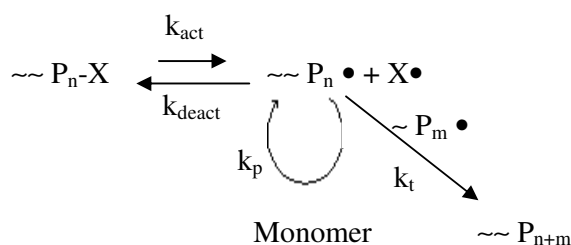
3. Degenerative chain transfer with alkyl iodides or dithioesters (RAFT or MADIX).

While these three systems possess different components, the general similarities between the living radical polymerization processes are in the use of initiators, radical mediators (i.e., persistent radicals or transfer agents), and in some cases, catalysts. It is important to note that while SFRP/NMP and ATRP are subject to the Persistent Radical Effect (PRE) the degenerative processes, such as RAFT, do not conform to the PRE model due to the transfer dominated nature of the reaction.<sup>4</sup>

### **1.3.1 Stable Free Radical Polymerization and Nitroxide Mediated Polymerization (SFRP and NMP)**

In 1993, Georges et al. reported on the controlled radical polymerization of styrene initiated by benzoyl peroxide and mediated by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a stable nitroxide radical. TEMPO was able to bond reversibly to the polystyryl chain end and provide polystyrenes with predetermined molecular weights and low polydispersities. Nitroxides used

earlier to control radical polymerizations were less successful. Figure 1.2 illustrates the mechanism of the Stable Free Radical Polymerization. Although several types of nitroxides had been synthesized and their ability to trap radicals reversibly was known, this was the first open literature report on using TEMPO to moderate a polymerization successfully. Unfortunately, TEMPO can only be used for the polymerization of styrene-based monomers at relatively high temperatures ( $>120^{\circ}\text{C}$ ). With most other monomers, the bond formed is too stable and TEMPO acts as an inhibitor in the polymerization, preventing chain growth. With methacrylates,  $\beta$ -hydrogen abstraction results in a stable hydroxylamine and unsaturated chain ends.<sup>4</sup>

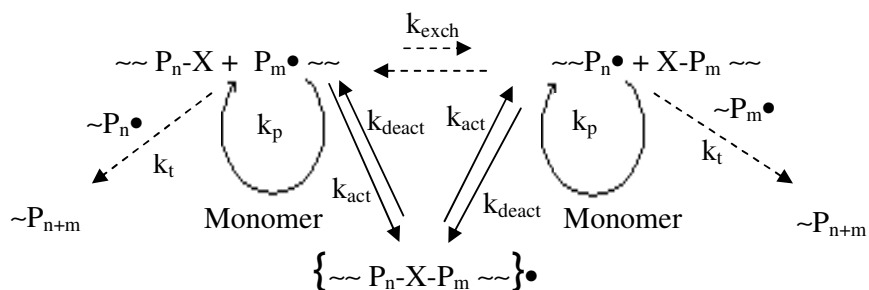


**Figure 1.2** The mechanism of SFRP and NMP polymerization.

Since TEMPO is only a regulator, not an initiator, radicals must be generated from another source; the required amount of TEMPO depends on the initiator efficiency. Application of alkoxyamines (i.e., unimolecular initiator) allows for stoichiometric amounts of the initiating and mediating species to be incorporated and enables the use of multifunctional initiators, growing chains in several directions.<sup>4</sup>

### 1.3.2 Degenerative Chain Transfer Including RAFT

This technique for controlling radical polymerizations is based on one of the oldest techniques, that of chain transfer, and has often been used in telomerization. Similar to the concept of degenerative transfer with alkyl iodides, reversible addition fragmentation chain transfer with dithioesters (RAFT) is successful because the rate constant of chain transfer is faster than the rate constant of propagation. Analogous to both nitroxide-mediated and ATRP reactions, the polymer chains spend the majority of the reaction time in the dormant state and are only activated for a short period of time. Like iniferters, the RAFT agents are stabilized dithio compounds, which contain a small molecule capable of initiating a polymer chain. After homolytic cleavage to release the initiator, the RAFT agent can reversibly deactivate the polymer chains, resulting in a level of control over the polymerization not obtained with other chain transfer agents. Figure 1.3 illustrates the concept of RAFT polymerization.<sup>4</sup>

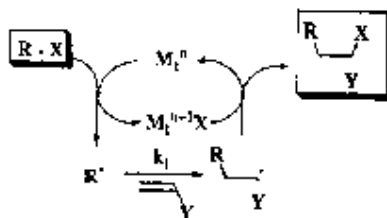


**Figure 1.3** The mechanism of RAFT polymerization

### 1.3.3. Atom Transfer Radical Polymerization (ATRP)

The name atom transfer radical polymerization originates from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP has its roots in atom transfer radical addition (ATRA), which targets the formation of 1:1 adducts of alkyl halides and alkenes, also catalyzed by transition metal complexes. ATRA is a modification of Kharasch addition reaction, which usually occurs in the presence of light or conventional radical initiators. Because of the involvement of transition metals in the activation and deactivation steps, chemo-, regio-, and stereoselectivities in ATRA and Kharasch addition may be different.<sup>5</sup>

In ATRA, a copper (I) complex undergoes a one-electron oxidation with concomitant abstraction of a halogen atom from a starting compound. This reaction generates an organic radical and a copper (II) complex, and substituents on the organic halide can facilitate the reaction by stabilizing the resulting radical. The organic radical can then add to an unsaturated group in an inter- or intramolecular fashion and then reabstract a halogen atom from the copper (II) complex to re-form the original copper (I) complex and to form the product (Figure 1.4). Compounds derived from the self-reaction of radicals (i.e., termination) comprise very little of the product, because the copper (II) complex acts as a persistent radical and controls the concentration of the intermediate radicals. Substrates for this reaction are typically chosen such that if addition occurs, then the newly formed radical is much less stabilized than the initial radical and will essentially react irreversibly with the copper (II) complex to form an inactive alkyl halide product ( $k_{\text{act}} \gg k'_{\text{act}}$ ). Thus, in ATRA, usually only one addition step occurs; however, if starting and product alkyl halides possess similar reactivities toward atom transfer, then it should be possible to repeat the catalytic cycle and add multiple unsaturated groups as in a polymerization reaction.<sup>6</sup>

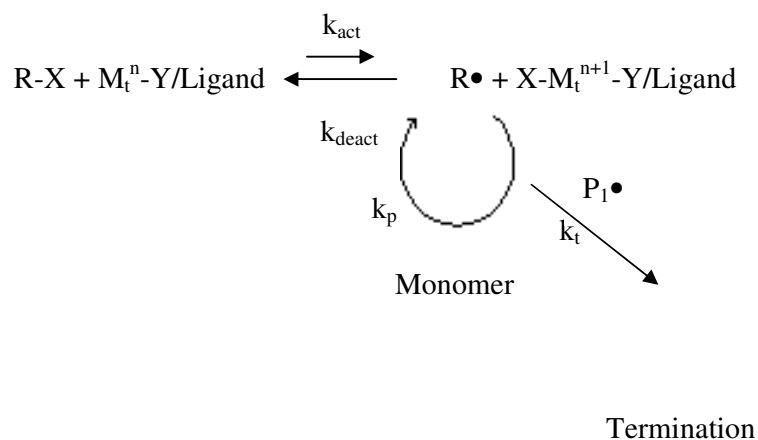


**Figure 1.4** The mechanism of ATRP

ATRP has roots in the transition metal catalyzed telomerization reactions. These reactions, however, do not proceed with efficient exchange, which results in a nonlinear evolution of the molecular weights with conversions and polymers with high polydispersities. ATRP also has connections to the transition metal initiated redox processes as well as inhibition with transition metal compounds. These two techniques allow for either activation or deactivation process, however, without efficient reversibility. ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the polymerization conditions such that the molecular weights increased linearly with conversion and polydispersities were typical of a living process. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers.<sup>5</sup>

A general mechanism for ATRP is shown in Figure 1.5. The radicals, or the active species, are generated through a reversible redox process catalyzed by a transition metal complex ( $M_t^n - Y/\text{Ligand}$ , where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, R-X.

This process occurs with a rate constant of activation,  $k_{\text{act}}$ , and deactivation  $k_{\text{deact}}$ . Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation  $k_p$ . Termination reactions ( $k_t$ ) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes,  $X-M_t^{n+1}$ , as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.<sup>5</sup>



**Figure 1.5** The mechanism of ATRP



A variety of monomers such as styrenes, (meth) acrylates, (meth) acrylamides, and acrylonitrile have been successfully polymerized using ATRP.<sup>7-16</sup> Ring opening polymerization has been also successful. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ( $K_{eq}=k_{act}/k_{deact}$ ) determines the polymerization rate. ATRP will not occur or occur very slowly if the equilibrium constant is too small. In contrast, too large an equilibrium constant will lead to a large amount of deactivating higher oxidation state metal complex; which will shift the equilibrium toward dormant species and may result in the apparently slower polymerization. Each monomer possesses its own intrinsic radical propagation rate. Thus, for a specific monomer, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain polymerization control. However, since ATRP is a catalytic process, the overall position of the equilibrium not only depends on the radical (monomer) and the dormant species, but also can be adjusted by the amount and reactivity of the transition-metal catalyst added.<sup>5</sup>

The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increase reciprocally with the initial concentration of initiator in a living polymerization.<sup>5</sup>

$$DP = \frac{[M]_0}{[initiator]_0} \times conversion \quad (1)$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is the best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of styrene in ruthenium- and rhenium-based ATRP. Fluorine is not used because the C-F bond is too strong to undergo homolytic cleavage. A variety of initiators has been used successfully in ATRP. Many different types of halogenated compounds are potential initiators. Such as; halogenated alkanes, benzylic halides,  $\alpha$ -haloesters,  $\alpha$ -haloketones,  $\alpha$ -halonitriles and sulfonyl halides.<sup>5</sup>

The most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere round the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth, the ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system.<sup>5</sup>

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, acetone, and many others, have been used for different monomers. A solvent is sometimes necessary, especially when the obtained polymer is insoluble in its monomer (e.g., polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition,

interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, should be minimized. The possibility that the structure of the catalyst may change in different solvents should also be taken into consideration.<sup>5</sup>

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher  $k_p/k_t$  ratios and better control (“livingness”) may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures. In general, the solubility of the catalyst decomposition may also occur with the temperature increase. The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight.<sup>5</sup>

At high monomer conversions, the rate of propagation slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent. Prolonged reaction times leading to nearly complete monomer conversion may not increase the polydispersity of the final polymer but will induce loss of end groups. Thus, to obtain polymers with high end-group functionality or to subsequently synthesize block copolymers, conversion must not exceed 95% to avoid end-group loss.<sup>5</sup>

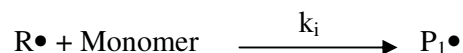
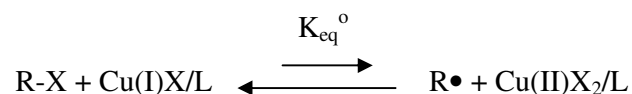
Additives are sometimes essential for a successful ATRP. For example, a Lewis acid, such as aluminum and other metal alkoxides, is needed for the controlled polymerization of MMA catalyzed by  $\text{RuCl}_2 \cdot (\text{PPh}_3)_3$  or other systems. No or very slow polymerization was observed in the absence of the Lewis acid activator. Presumably, the aluminum compound can activate and stabilize the catalyst in the higher oxidation state. Polymerization in the presence

of very polar solvents such as water can be accelerated. The presence of strong nucleophiles such as phosphines may sometimes terminate the process.<sup>5</sup>

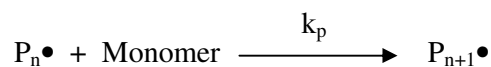
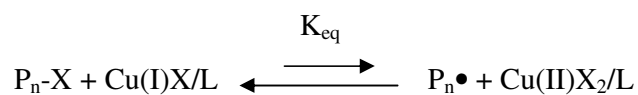
### 1.3.3.1 Kinetics

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.

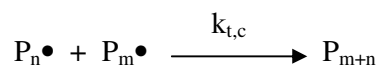
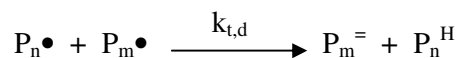
Initiation:



Propagation:



Termination:

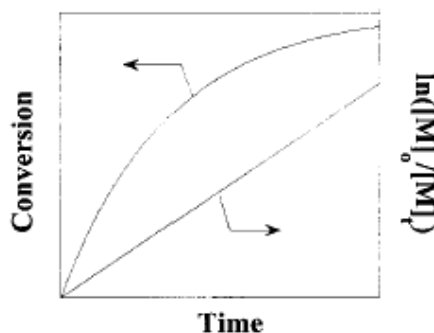


The propagation rate will be as follows:

$$R_p = k_{app} [M] = k_p [P_n g][M] = k_p K_{eq} [In] \frac{[Cu^I]}{[Cu^{II} X]} [M] \quad (2)$$

Integration gives;

$$\ln \left\{ \frac{[M]_0}{[M]} \right\} = k_p K_{eq} [In] \frac{[Cu^I]}{[Cu^{II}]} t = K_{app} t \quad (3)$$



**Figure 1.6** Schematic representation of the dependence of the conversion on time in linear and semilogarithmic coordinates.

Figure 1.6 shows a typical linear variation of conversion with time in semilogarithmic coordinates. Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. However, since termination occurs continuously, the concentration of the Cu (II) species increases and deviation from linearity may be observed.<sup>5</sup>

For a well-controlled ATRP, initiation should be fast and quantitative. The apparent initiation rate constant; ( $k_i^{\text{app}} = k_i K_0$ , where  $k_i$  is the absolute rate constants of addition of the initiating radical to the alkene and  $K_0$  is the atom transfer equilibrium constant for the initiating species.) should be at least comparable to the apparent propagation rate constant ( $k_p^{\text{app}} = k_p \times K_{\text{eq}}$ , where  $k_p$  is the absolute rate constant of propagation and  $K_{\text{eq}}$  is the atom transfer equilibrium constant for the propagating species). If  $k_i^{\text{app}} \ll k_p^{\text{app}}$ , polymers with higher molecular weights than the theoretical values and higher polydispersities will be obtained. This behavior is based on the assumption that the system is equilibrated or there was deactivator added initially. This situation is more complex when the amount of the deactivator is small and the rate-determining step of initiation is only activation. If initiation is too fast and a lot of radicals are generated during the initiation step, irreversible radical termination will reduce the initiator efficiency and slow the polymerization. A general guideline for choosing a suitable ATRP initiator is that the initiator should have a chemical structure similar to the dormant polymer species.<sup>5</sup>

Results from kinetic studies of ATRP for styrene, MA and MMA under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator and Cu (I) complex concentrations. These observations are all consistent with the derived rate law. The kinetically optimum ratio of ligand to copper in the polymerization of both styrene and MA was determined to be 2:1. Below this ratio the polymerization rate was usually slower, and above this ratio, the polymerization rate remained constant. It should be noted that the optimum ratio could vary with regard to changes in the monomer, counterion, ligand, temperature, and other factors.<sup>5</sup>

### 1.3.3.2. Mechanism

The radical nature of the reactive or propagating species in ATRP requires very careful examination. The direct detection of growing radicals by EPR is often impossible due to the overwhelming presence of transition metals in the reaction. The g-values of the Cu (II) species and the propagating free radicals are too close to enable the direct detection of the radicals when they are present in minute amounts.

The existence of free radical has been proposed in Cu-mediated ATRP based on several experimental observations.<sup>5</sup>

1. The ATRP equilibrium has been approached from both sides:  $RX/M_t^n$  and radicals/ $X-M_t^{n+1}$  species (reverse ATRP). Thus, successful polymerizations have been carried out using conventional free radical initiators, such as AIBN and BPO, as well as organic halides.

2. Chemoselectivity is similar to that for conventional radical polymerizations. Typical radical inhibitors, such as galvinoxyl and TEMPO, inhibit the polymerization and the polymerization is retarded by the presence of a small amount of oxygen.

3. Stereoselectivity are similar to and do not exceed that for a conventional radical polymerization. All the polymers formed by ATRP have regular head-to-tail structures with the dormant species of the typical secondary/tertiary alkyl halide structures, as evidenced by NMR. In addition, polymers have the same tacticity as those prepared by conventional radical polymerization.

4. EPR studies have revealed the presence of X-Cu (II) species resulting from the persistent radical effect. Additionally, the doubling of the molecular

weight or crosslinking in multifunctional initiator systems as a result of radical-radical termination has been observed.

5. Cross-exchange between different halogens and different polymerization systems (thermal and ATRP or nitroxide mediated and ATRP) demonstrate that they have the same intermediates and supports the radical mechanism.

6. Propagating free radicals were directly observed by EPR in ATRP of dimethacrylates catalyzed by CuBr/HMTETA. This has been possible due to the reduction of the termination coefficients resulting from the radicals trapping in the crosslinked matrix of the formed polymer.

#### **1.4. COMPARISON OF DIFFERENT LIVING POLYMERIZATION METHODS**

Each of the explained three methods (ATRP, RAFT and SFRP and NMP) for controlling the radical polymerization of vinyl monomers has its strengths and weaknesses. For example, the rates in ATRP can be easily adjusted through both the amount and activity of the transition metal complexes (both activator and deactivator). Faster rates in RAFT require larger amounts of initiators, i.e., more uncontrolled chains, while faster NMP requires less persistent radicals, which may result in more termination higher polydispersities. At the same time, transition metal complexes, although not attached to the polymer chains, require removal and can potentially be recycled.



Many ATRP initiators, including multifunctional systems, are either commercially available or very simple to make. Alkoxyamines and RAFT reagents are usually prepared from the corresponding alkyl halides. ATRP, however, requires the aforementioned catalysts, although they can be used in much less than equimolar amounts. The terminal halogens produced in ATRP can be easily converted to much useful functionality, e.g., by nucleophilic substitution. Displacement of nitroxides and dithioesters is more difficult.

The range of polymerizable monomers is the largest for RAFT, but control requires adjustment of the dithioester structure and may be accompanied by retardation when targeting polymers with lower molecular weights. NMP cannot yet be successfully applied to methacrylates. ATRP can be used to polymerize many monomers and, by using the halogen exchange, can be used for very efficient cross-propagation from acrylates to methacrylates, which is impossible to achieve by other methods.<sup>4</sup>

## **1.5. AIM OF THIS STUDY**

In this study, methyl methacrylate is polymerized by ATRP method. Even though several studies have been reported, there are still many questions to be answered. The nature of structure of polymer obtained has not been studied. Therefore, in this work, in addition to kinetic of polymerization, the structure and possible stereoregularity of polymer is investigated. The molecular weight distribution, thermal properties and structure of polymer are studied by FTIR, NMR, DSC, GPC and X-Ray.

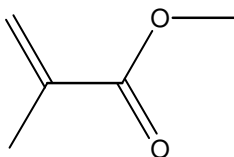
## CHAPTER 2

### EXPERIMENTAL

#### 2.1 MATERIALS

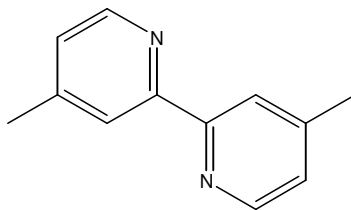
##### 2.1.1 Monomer

Methyl Methacrylate (Merck) was used as monomer without further purification.



##### 2.1.2 Ligand

4,4'-Dimethyl 2,2'-bipyridine (Fluka) was used as ligand for atom transfer radical polymerization without further purification.



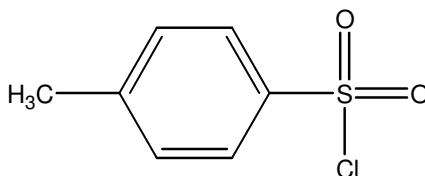
### 2.1.3 Catalyst

Copper(I)chloride (Riedel-De-Haen) was used as catalyst for atom transfer radical polymerization without further purification.



### 2.1.4 Initiator

p-toluenesulfonylchloride (Aldrich) was used as initiator for atom transfer radical polymerization without further purification.



### 2.1.5 Solvents

Methanol and toluene (Merck) 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.

### **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 hour 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  $1.5 \times 10^{-2}$  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 Viscometer**

Viscosities of different concentrations of polymer solutions were measured with toluene as a solvent at 25 °C 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

## **2.2.4 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.

## **2.2.5 Differential Scanning Calorimetry**

The thermal analyses of the samples were recorded by TA-DSC 910S differential scanning calorimeter. Heating rate was 10°C/ min. from -20°C to 350°C under nitrogen gas atmosphere.

### **2.2.6 Nuclear Magnetic Resonance**

The molecular structure of PMMA was determined by using Magnetic Resonance Spectrometer, Ultrashield 400 MHz Digital NMR Bruker, with  $^1\text{H}$  and  $^{13}\text{C}$  Spectrometers.

### **2.2.7 Gel Permeation Chromatography**

For the molecular weight calculation of polymers, it was necessary to know the values of “a” and “K” constants in the Mark-Houwink equation. Therefore, the molecular weights of several polymer samples were measured by GPC using Agilent HP GPC. For the calibration; PS was used as a standard and the mobile phase was THF.

### **2.2.8 X-Ray Powder Diffractometer**

X-Ray powder diffraction patterns (XRD) were taken by using Rigaku Miniflex with Cu ( $K\alpha$  30 kV, 15 mA,  $\lambda=1.54178\text{\AA}$ ) radiation.

## 2.3 EXPERIMENTAL PROCEDURE

### 2.3.1 Atom Transfer Radical Polymerization of MMA

ATRP employs a Cu (I) halide, which is complexed with ligands 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, 0.0037 g 4-4'-dimethyl-2-2'-bipyridine, 0.0010 g CuCl, 0.0038 g p-toluene sulfonyl chloride and 2 mL of MMA were placed and degassed via several 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. The contents were first dissolved in toluene, then polymer precipitated in methanol. The polymers were transferred into a crucible and they were put into the drying oven at 50°C under vacuum until constant weight. The conversions were calculated gravimetrically.

$$\%Conversion = \frac{(Mass\ of\ polymer)}{(Mass\ of\ monomer)} \times 100 \quad (4)$$

The experiments were repeated for modifying amount of each reaction components.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 ATOM TRANSFER RADICAL POLYMERIZATION OF MMA

MMA was polymerized in an oil bath at 90°C using CuCl/4,4' dimethyl 2,2' bipyridine as a catalyst system and p-toluenesulfonylchloride as the initiator and % conversions are calculated. The amount of each material used in each experiments are given in Table 3.1.

**Table 3.1** Different material combination used in polymerization

# of sets	mL of MMA	mol of Ligand ( $10^{-5}$ )	mol of CuCl ( $10^{-5}$ )	mol of pTsCl ( $10^{-5}$ )
1	2	2.01	1.01	$4.98 \times 10^{-6}$
2	2	2.01	1.01	$6.61 \times 10^{-6}$
3	2	2.01	1.01	$9.97 \times 10^{-6}$
4	2	2.01	1.01	1.99
5	2	2.01	1.01	3.99
6	0.5	2.01	1.01	1.99
7	0.67	2.01	1.01	1.99
8	1	2.01	1.01	1.99
9	4	2.01	1.01	1.99

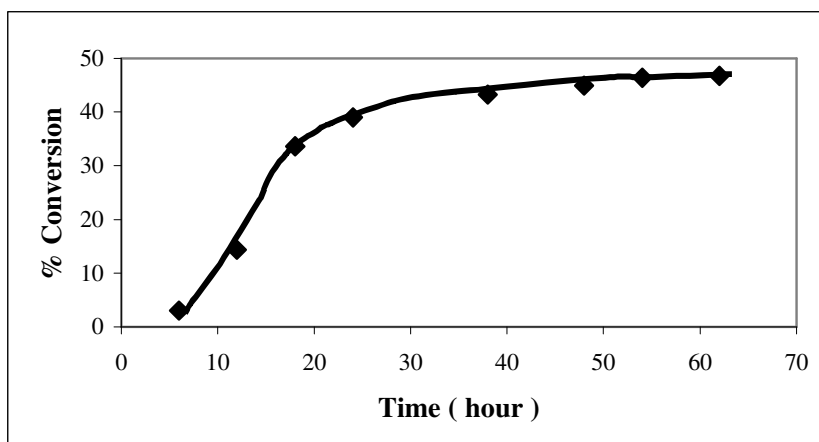


The polymerization reaction is highly exothermic and the heat of polymerization could not be dissipated readily from the viscous medium.

The percent conversion versus time for ATRP of monomer for the first set is given in Table 3.2 and the percent conversions are plotted against time in Figure 3.1.

**Table 3.2** The percent conversion vs. time for the first set.

Time ( hour )	% Conversion
6	3.0
12	14.4
18	33.6
24	39.0
38	43.3
48	45.0
54	46.4
62	46.8

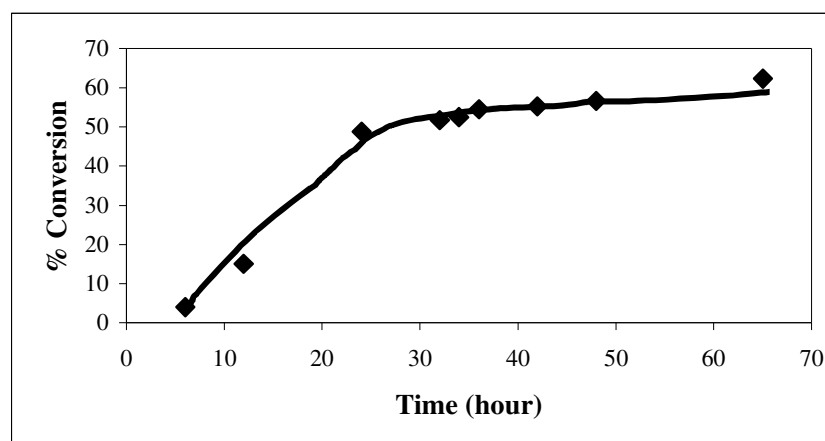


**Figure 3.1** % Conversion vs. Time graph for the first set

The percent conversion versus time for ATRP of monomer for the second set is given in Table 3.3 and the percent conversions are plotted against time in Figure 3.2.

**Table 3.3** The percent conversion vs. time for the second set.

Time ( hour )	% Conversion
6	4.0
12	15.0
24	48.8
32	51.8
34	52.5
36	54.5
42	55.3
48	56.7
65	62.3

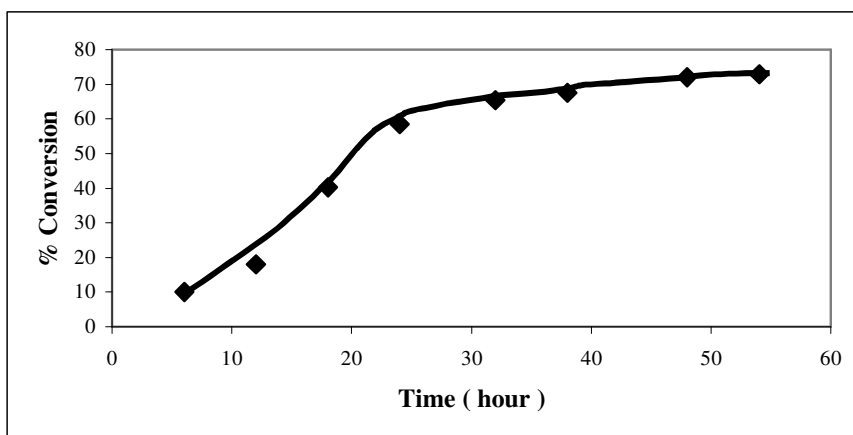


**Figure 3.2** % Conversion vs. Time graph for the second set

The percent conversion versus time for ATRP of monomer for the third set is given in Table 3.4 and the percent conversions are plotted against time in Figure 3.3.

**Table 3.4** The percent conversion vs. time for the third set.

<b>Time ( hour )</b>	<b>% Conversion</b>
6	10.0
12	18.0
18	40.2
24	58.4
32	65.5
38	67.5
48	72.0
54	72.9

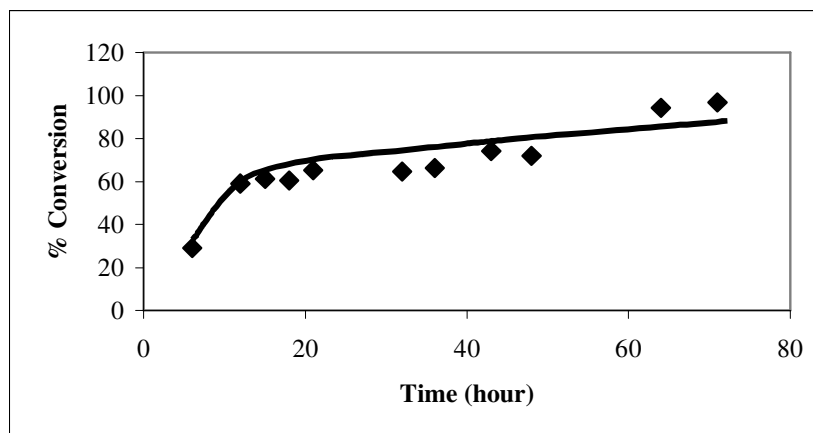


**Figure 3.3** % Conversion vs. Time graph for the third set

The percent conversion versus time for ATRP of monomer for the fourth set is given in Table 3.5 and the percent conversions are plotted against time in Figure 3.4.

**Table 3.5** The percent conversion vs. time for the fourth set.

Time ( hour )	% Conversion
6	29.0
12	59.1
15	61.2
18	60.3
21	65.3
32	64.7
36	66.4
43	74.0
48	72.0
64	94.2
71	96.9

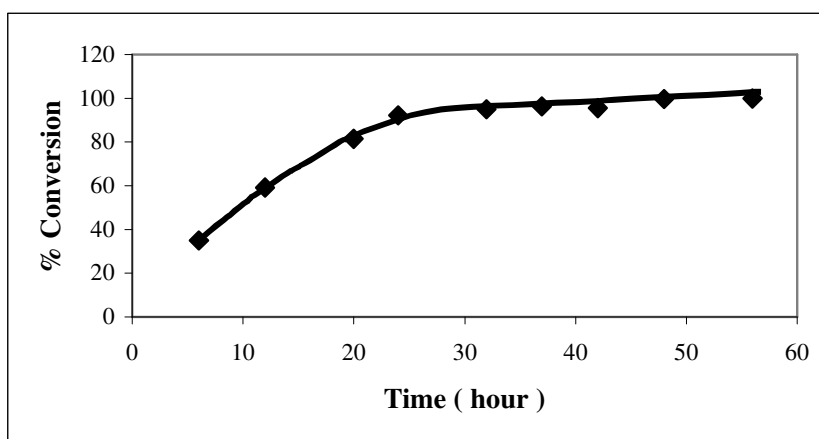


**Figure 3.4** % Conversion vs. Time graph for the fourth set

The percent conversion versus time for ATRP of monomer for the fifth set is given in Table 3.6 and the percent conversions are plotted against time in Figure 3.5.

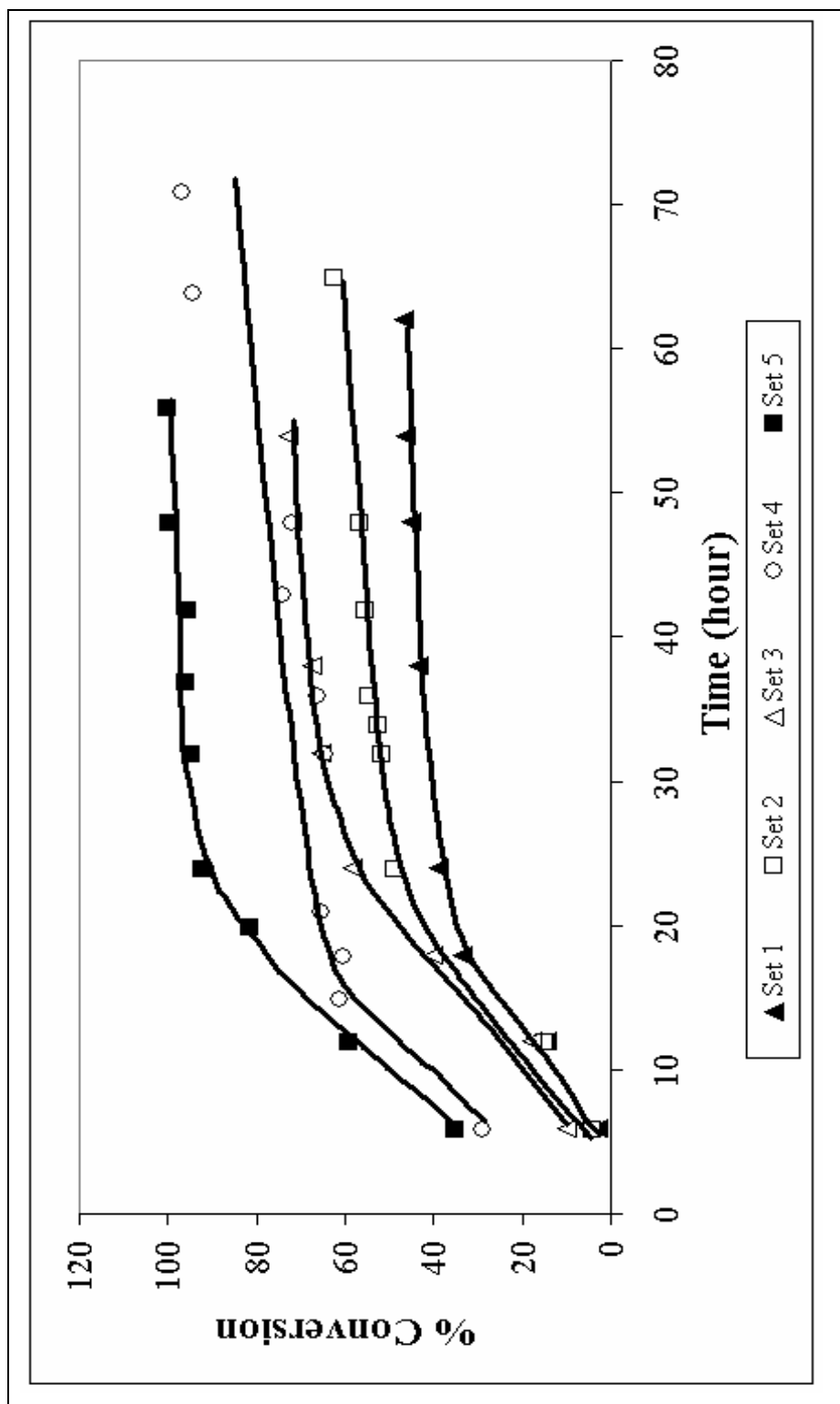
**Table 3.6** The percent conversion vs. time for the fifth set.

<b>Time ( hour )</b>	<b>% Conversion</b>
6	35.0
12	59.1
20	81.4
24	92.3
32	94.9
37	96.2
42	95.6
48	99.6
56	100



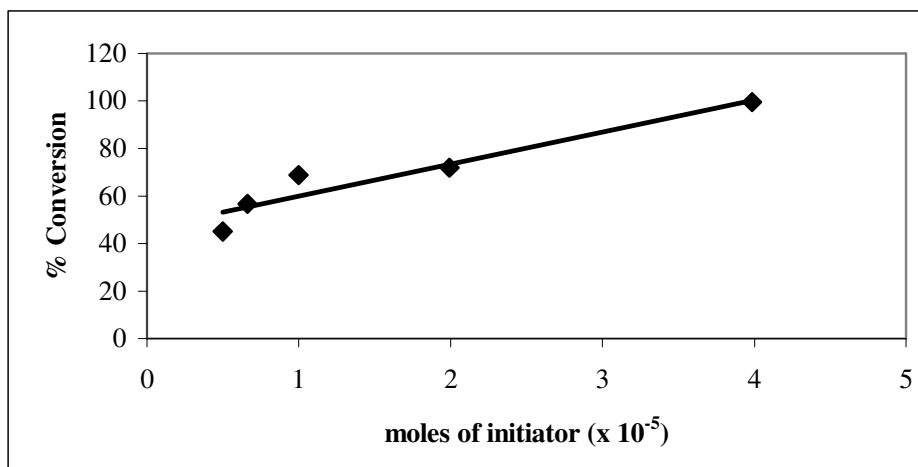
**Figure 3.5** % Conversion vs. Time graph for the fifth set

From all of the kinetic figures; it is seen that the polymerization of MMA exhibits two-stage propagation rate. In the first stage, rate of polymerization is high, then in the second stage rate decreases. The percent conversion changes almost linearly with time in each stage. In these sets, all of the amounts of the used materials except the initiator was kept constant. The amounts of initiator have been changed to understand the effect of it to the polymerization mechanism. In order to observe the differences of ATRP of MMA with different amounts of initiator, the percent conversions vs. time graph are combined in Figure 3.6.



**Figure 3.6** Comparison of the percent conversion vs. time graphs of ATRP of MMA for different sets.

It can be seen from Figure 3.6 that as the amount of initiator increases, the % conversions also increase due to the increased concentration of active species. As the concentration of radicals increase, the time required for achievement of the high conversion decreases. The fifth set which has the highest amount of initiator, shows the highest conversion. In order to have a better understanding of change of conversion with initiator concentration, the conversion at 48 hour for each experimental sets of 1 to 5 are plotted against moles of initiator in Figure 3.7. the percent conversion increases linearly with initiator concentration.



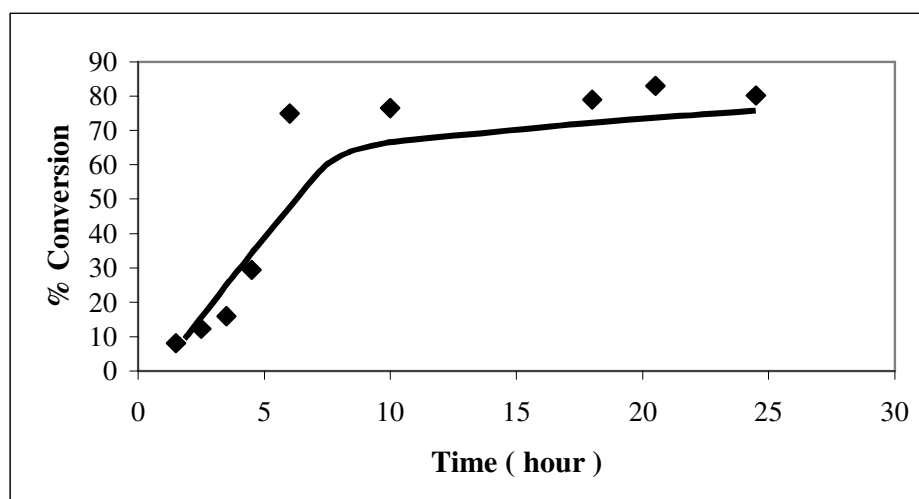
**Figure 3.7** % Conversion vs number of mol of initiator graph



The percent conversion versus time for ATRP of monomer for the sixth set is given in Table 3.7 and the percent conversions are plotted against time in Figure 3.8.

**Table 3.7** The percent conversion vs. time for the sixth set.

<b>Time ( hour )</b>	<b>% Conversion</b>
1.5	8.0
2.5	12.2
3.5	16.0
4.5	29.4
6	75.0
10	76.6
18	79.0
20.5	83.0
24.5	80.2

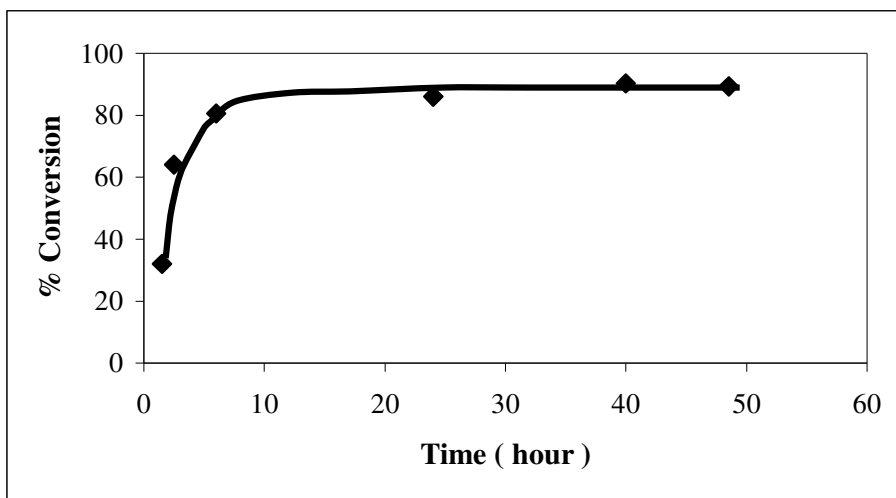


**Figure 3.8** % Conversion vs. Time graph for the sixth set

The percent conversion versus time for ATRP of monomer for the seventh set is given in Table 3.8 and the percent conversions are plotted against time in Figure 3.9.

**Table 3.8** The percent conversion vs. time for the seventh set.

<b>Time ( hour )</b>	<b>% Conversion</b>
1.5	32.0
2.5	64.0
6	80.6
24	86.0
40	90.2
48.5	89.4

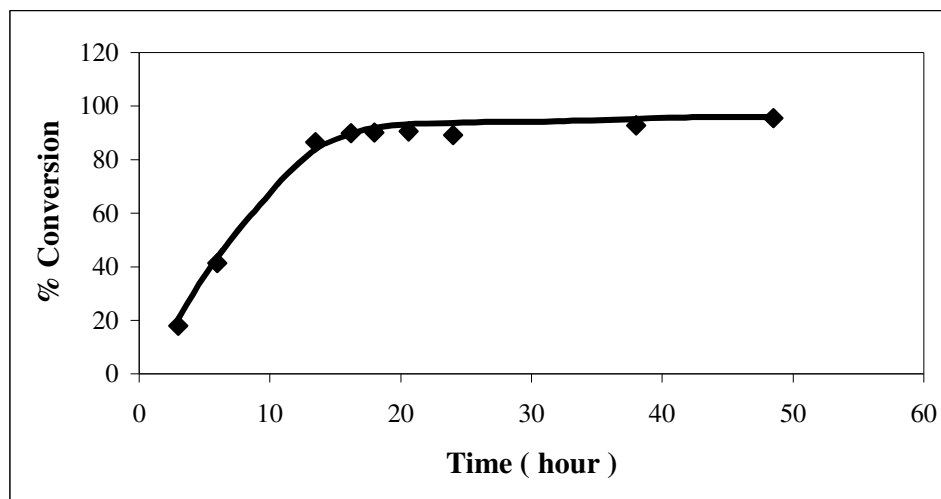


**Figure 3.9** % Conversion vs. Time graph for the seventh set

The percent conversion versus time for ATRP of monomer for the eighth set is given in Table 3.9 and the percent conversions are plotted against time in Figure 3.10.

**Table 3.9** The percent conversion vs. time for the eighth set.

Time ( hour )	% Conversion
3	18.0
6	41.4
13.5	86.6
16	90.0
18	90.2
20.5	90.6
24	89.2
38	92.7
48.5	95.6

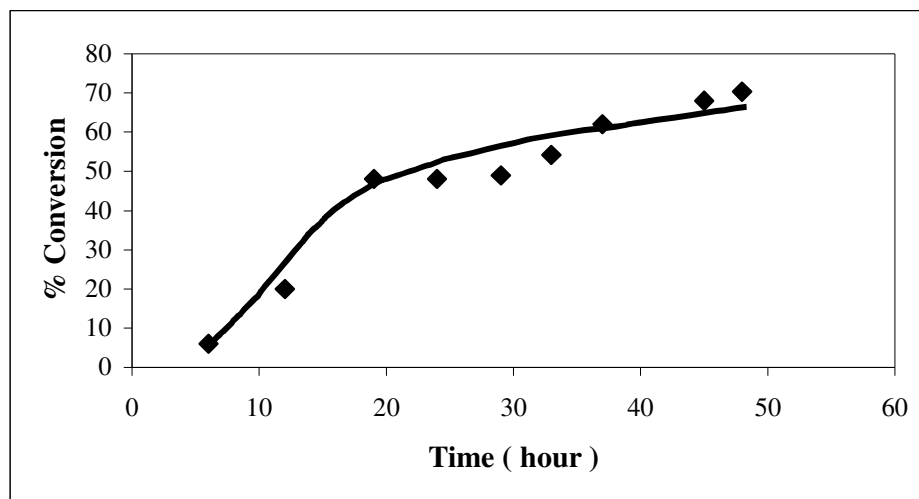


**Figure 3.10** % Conversion vs. Time graph for the eighth set

The percent conversion versus time for ATRP of monomer for the ninth set is given in Table 3.10 and the percent conversions are plotted against time in Figure 3.11 .

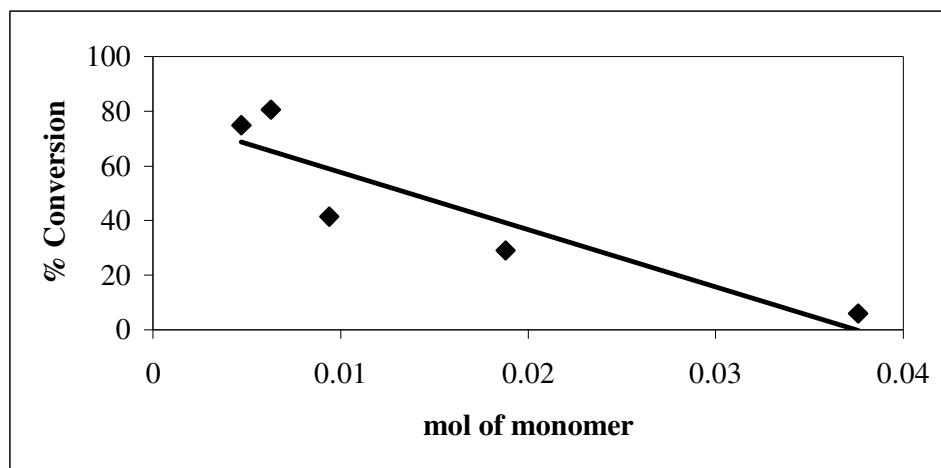
**Table 3.10** The percent conversion vs. time for the ninth set.

Time ( hour )	% Conversion
6	6.0
12	20.0
19	48.0
24	48.0
29	49.0
33	54.2
37	62.0
45	68.0
48	70.4

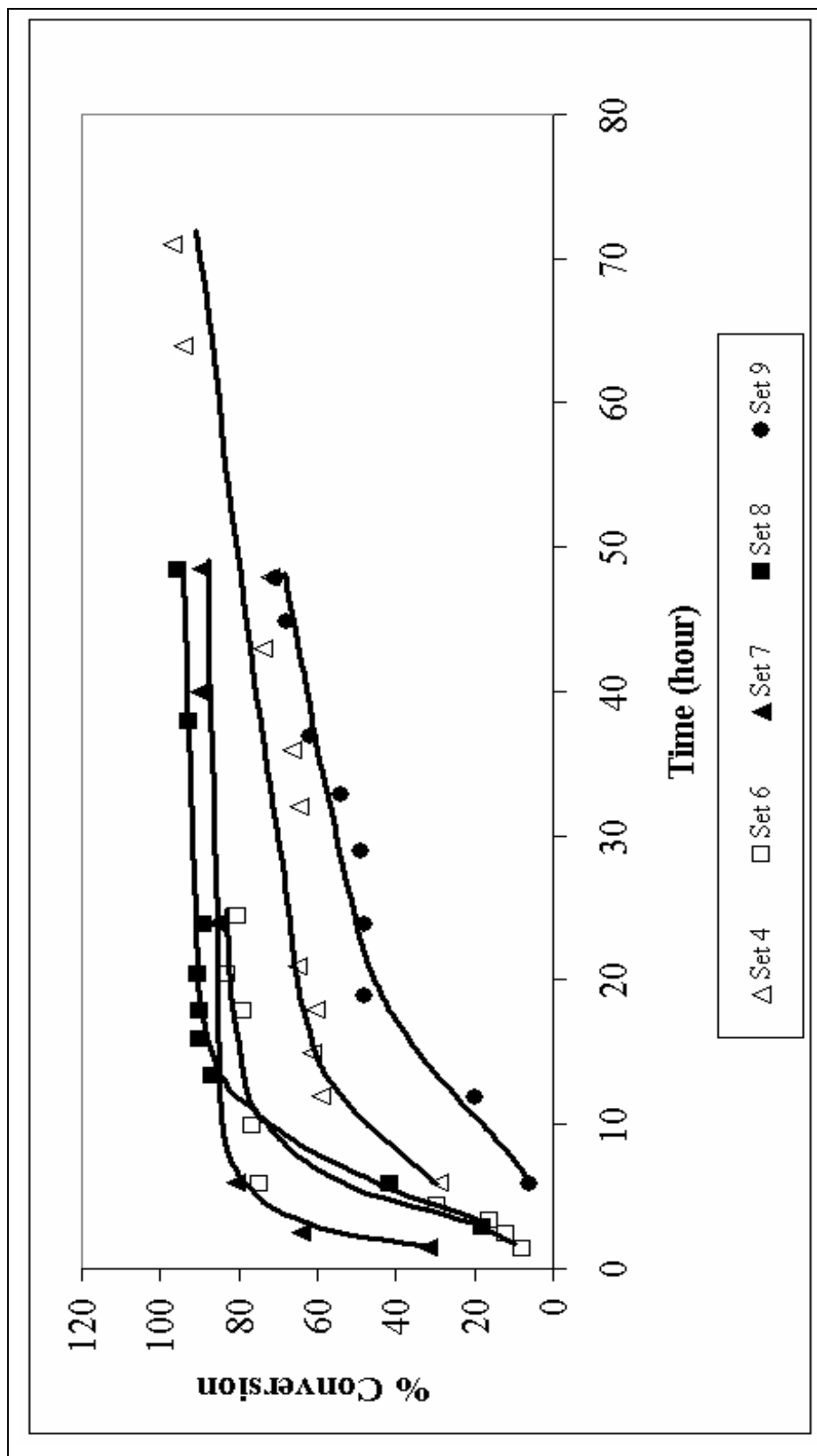


**Figure 3.11** % Conversion vs. Time graph for the ninth set

It has been proposed that termination rate coefficients are chain length dependent and decrease during the polymerization to result in a steady rate of polymerization. This helps to form well-defined polymers at higher conversions. However, when the monomer concentration becomes very low, propagation slows down but termination and other side reactions may still occur with the usual rate. Thus, there is a certain window of concentration and conversions where the polymerization is well controlled.<sup>5</sup> In these sets, all of the amounts of the used materials except the monomer was kept constant. The amounts of monomer have been changed to understand the effect of it to the polymerization mechanism. In order to observe the differences of ATRP of MMA with different amounts of monomer, the percent conversions vs. time graph is shown in Figure 3.13. In order to have a better understanding of change of conversion with monomer concentration, the conversion at 6 hour for each experimental sets of 6 to 9 and set 4 are plotted against moles of monomer in Figure 3.12. The percent conversion decreases linearly with monomer concentration.



**Figure 3.12** % Conversion vs number of mol of monomer graph



**Figure 3.13** Comparison of the percent conversion vs. time graphs of ATRP of MMA for different sets.

### 3.2 GEL PERMEATION CHROMATOGRAPHY MEASUREMENTS

Gel permeation chromatography (GPC), also referred to as Size Exclusion Chromatography (SEC) is a liquid chromatography in which the components of a mixture are separated on the basis of size. In GPC, large molecules elute from the column first, followed by smaller molecules. It is an important tool for the analysis of polymers. The essential results are molecular weight data and molecular weight distribution curves that are needed to characterize a polymer with regard to differences in properties. GPC is mainly used for samples with a molecular weight above 2000 although it is also in use for oligomer separations. There is no upper limit in the molecular weight; even polymer analyses with molecular weights of several millions are possible. Demands on the instrumentation are very stringent due to a special calibration procedure using a linear elution volume on the x-axis versus a logarithmic molecular weight on the y-axis.

Since for some polymers no molecular weight standards are available, very early possibilities were studied to convert existing calibrations for use with other types of polymers. This method developed by Benoit is based on the assumption, that the property that determines the elution behavior in GPC is hydrodynamic volume,  $V_h$ , of the polymer under investigation. Since  $V_h$  should be proportional to the product of intrinsic viscosity,  $[\eta]$ , and molecular weight,  $M$ , it follows for two polymers eluting at the same elution volume.

Instead of viscosity measurements the polymer standards with known weight average molecular weight ( $M_w$ ) are characterized by GPC.  $V_p$  is determined and  $[\eta]M(V_p)$  is calculated from the calibration curve of a polymer, whose Mark-Houwink constants are known. Thus, it is possible to determine intrinsic viscosities of polymers by GPC.<sup>17</sup>

From the GPC measurements of PMMA's; the Mark-Houwink coefficients were determined and knowing these constants, the viscosity average molecular weight of the polymers were calculated by using Ubbelohde viscometer method. The results are obtained by using styrene as the standard polymer for universal calibration and given in Table 3.11.

**Table 3.11** Results obtained from the GPC measurements with polystyrene (K=0.01363 mL/g, a=0.714 in THF at 25°C)

Sample	$M_w$	$M_z$	$M_v$	$M_n$	D	$[\eta]$	$V_p$	$M_p$
Set4 time	(g/mol)	(g/mol)	(g/mol)	(g/mol)		(mL/g)	mL	(g/mol)
12(hour)	1.0878e5	2.4334e5	9.6373e4	5.4527e4	1.99	4.9322e1	8.2655	5.5443e4
15(hour)	7.5058e4	2.2619e5	6.3243e4	3.0439e4	2.46	3.6511e1	8.4527	3.1738e4
18(hour)	1.3930e5	3.1300e5	1.2068e5	5.6145e4	2.48	5.7914e1	8.2943	5.0801e4
21(hour)	1.8363e5	3.5729e5	1.6081e5	5.5901e4	3.28	7.1089e1	8.2078	6.6055e4

$M_w$ = Weight average molecular weight,

$M_z$ = Z-average molecular weight,

$M_v$ = Viscosity average molecular weight,

$M_n$ = Number average molecular weight,

D= Polydispersity ( $M_w/M_n$ )

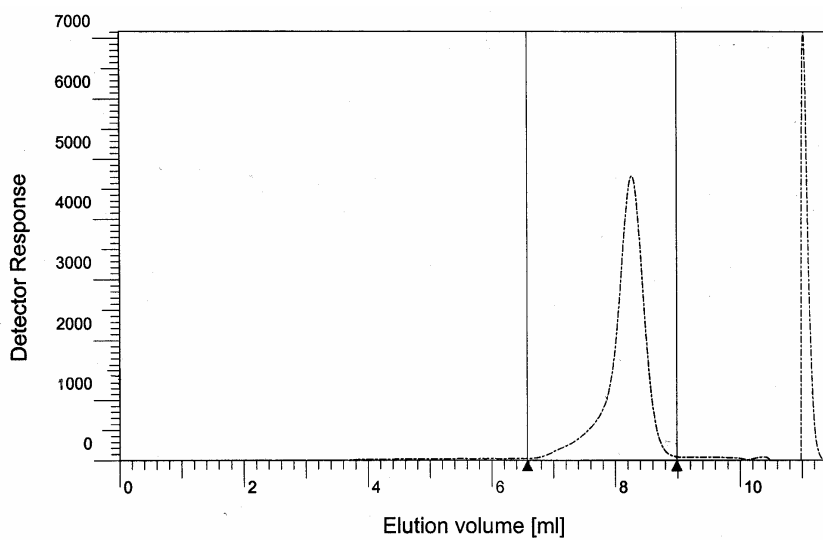
$[\eta]$ = Intrinsic viscosity calc. Using Mark-Houwink coefficient of calibration curve,

$V_p$ = Volume at the peak maximum of the elugram,

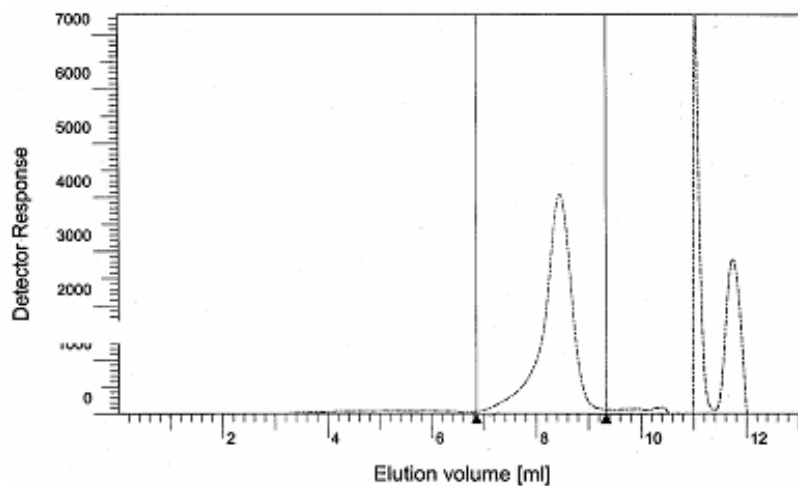
$M_p$ = Molecular weight at peak maximum of the elugram.



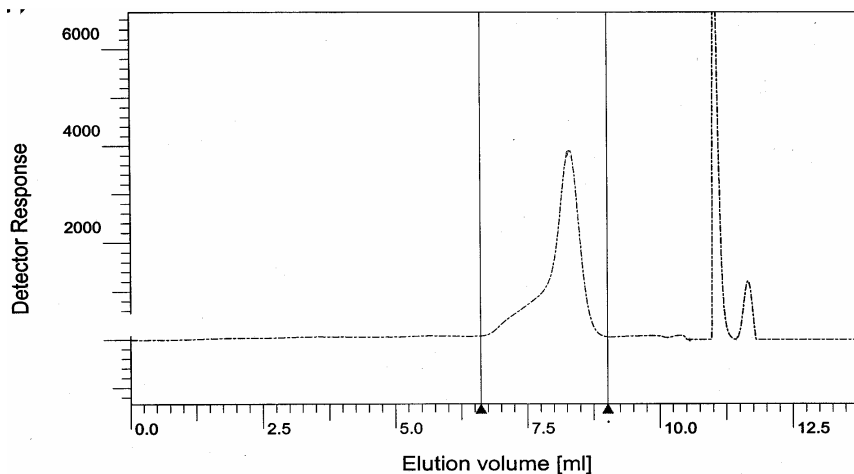
The Figures 3.14, 3.15, 3.16 and 3.17 are the elugrams of the samples (set 4, time(hour); 12, 15, 18 and 21 respectively).



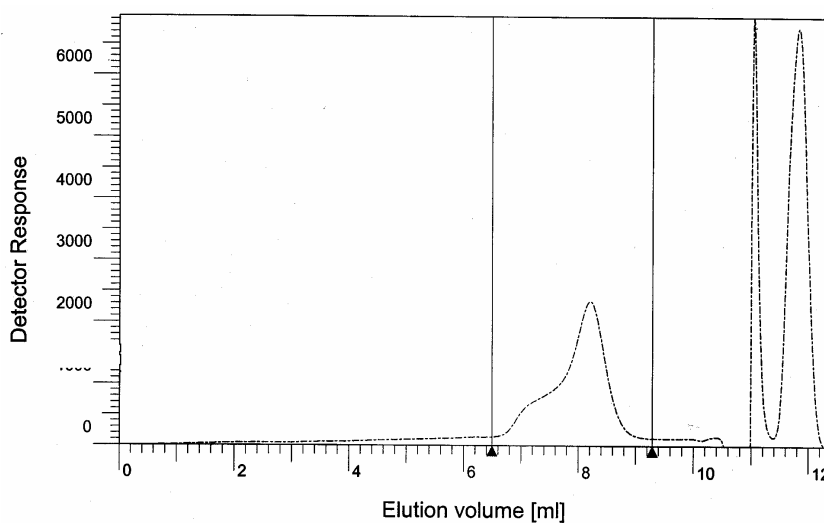
**Figure 3.14** GPC elugram for the set 4 (12 hour)



**Figure 3.15** GPC elugram for the set 4 (15 hour)



**Figure 3.16** GPC elugram for the set 4 (18 hour)



**Figure 3.17** GPC elugram for the set 4 (21 hour)

The plot of  $\log[\eta]$  against  $\log M_w$  (Table 3.11) is given in Figure 3.18, the Mark-Houwink coefficients were calculated from the intercept and the slope and given as  $K=9.13 \times 10^{-5}$  (dL/g) and  $\alpha=0.74$  in toluene at 25°C.

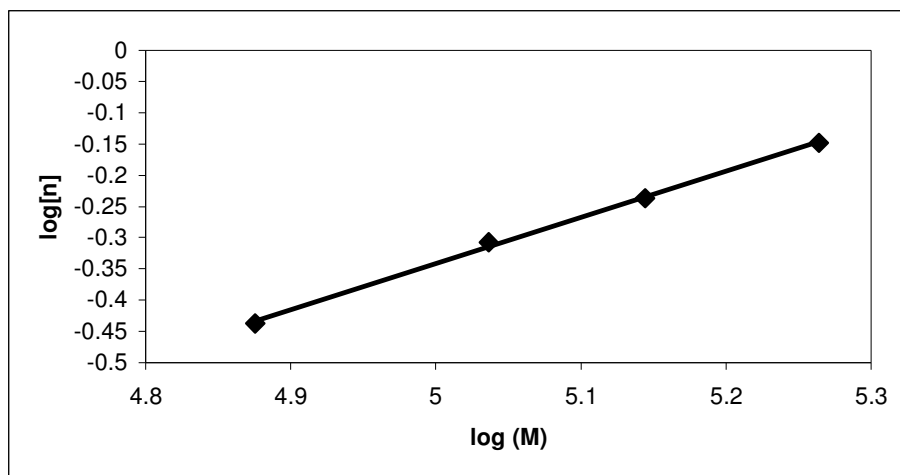
Therefore from the Mark-Houwink equation;

$$[\eta] = KM^\alpha \quad (5)$$

$$\log[\eta] = \alpha \log M_w + \log K \quad (6)$$

The equation becomes;

$$[\eta] = 9.15 \times 10^{-5} M^{0.74} \quad (7)$$



**Figure 3.18** log plot of  $[\eta]$  vs.  $M_w$  for PMMA in GPC

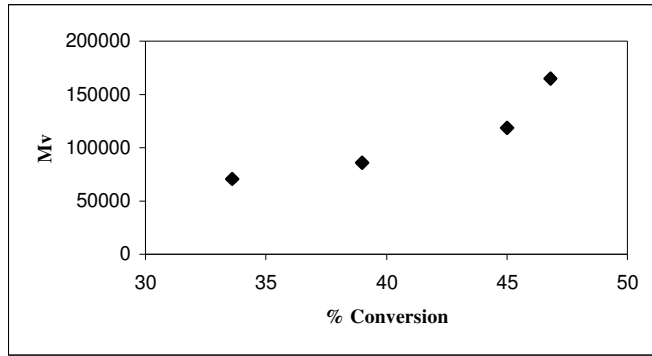
### 3.3 MOLECULAR WEIGHT % CONVERSION RELATION

Since the rate constants of propagation for methacrylates are relatively large, initially, higher polydispersities were observed because several monomer units are added during each activation step. However, with the progress of the reaction, chains become more uniform due to continuous exchange reactions.

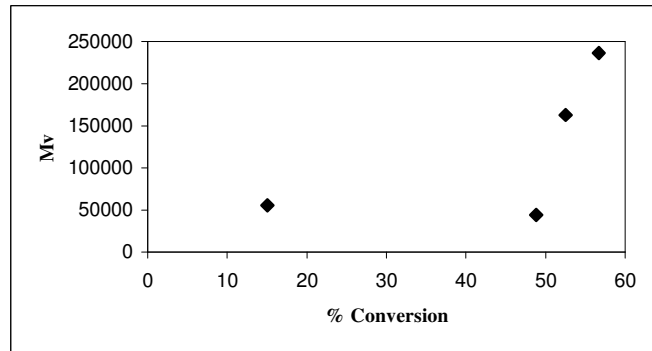
The polydispersities drop with conversion. Polydispersities should decrease with an increasing concentration of deactivator, although at the cost of slower polymerization rates.<sup>5</sup> In Table 3.12, the percent conversion of the polymer sets and their molecular weights are given. Figure 3.19 shows a typical linear increase of the molecular weights with conversion in the ATRP of methyl methacrylate.

**Table 3.12** The Percent Conversion vs. Molecular Weight for the sets

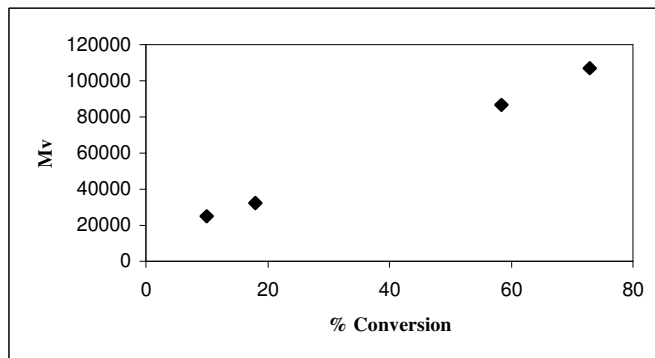
Set 1		Set 2		Set 3	
% Conv.	Mv (g/mol)	% Conv.	Mv (g/mol)	% Conv.	Mv (g/mol)
10	24889	61.2	50376	94.9	19714
18	32304	60.3	78018	96.2	26968
58.4	86665	74	98854	95.6	34345
72.9	107157	96.9	224545	99.6	43727
Set 4		Set 5		Set 6	
% Conv.	Mv (g/mol)	% Conv.	Mv (g/mol)	% Conv.	Mv (g/mol)
33.6	70799	15	55837	16	12497
39	86068	48.8	44037	75	25989
45	118430	52.5	162503	79	84453
46.8	165020	56.7	236247	80.2	247320
Set 7		Set 8		Set 9	
% Conv.	Mv (g/mol)	% Conv.	Mv (g/mol)	% Conv.	Mv (g/mol)
32	33921	18	53615	20	10315
64	43299	86.6	108231	48	11141
80.6	72125	90.6	155903	48.95	12428
89.4	247582	95.6	249977	54.23	14264



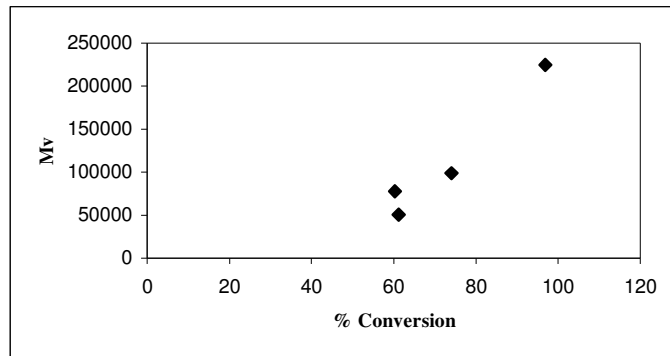
Set 1



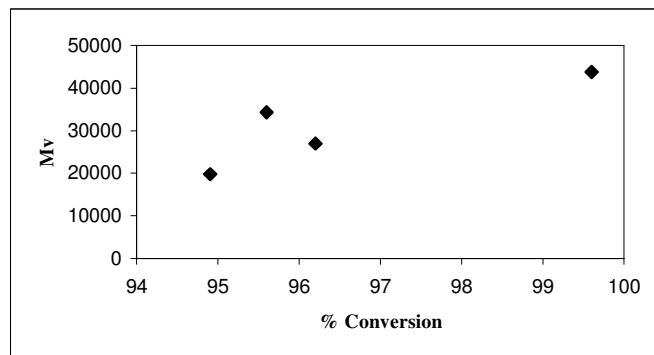
Set 2



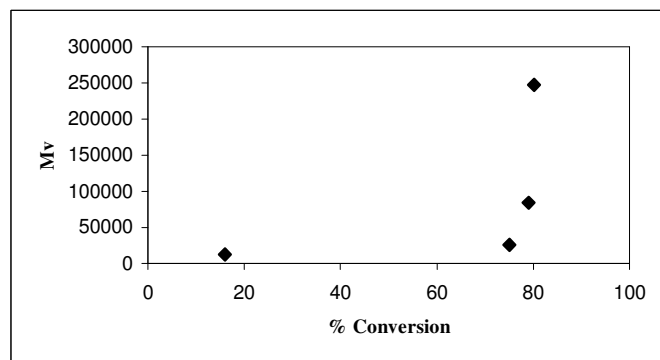
Set 3



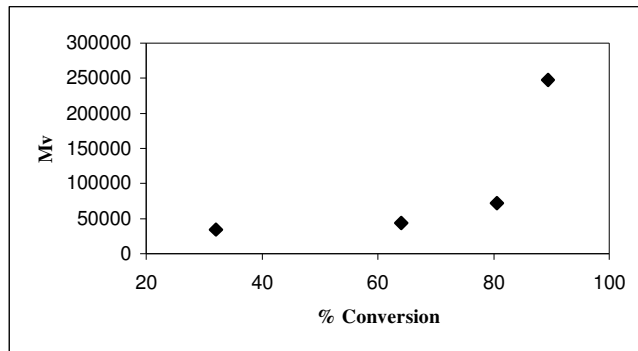
Set 4



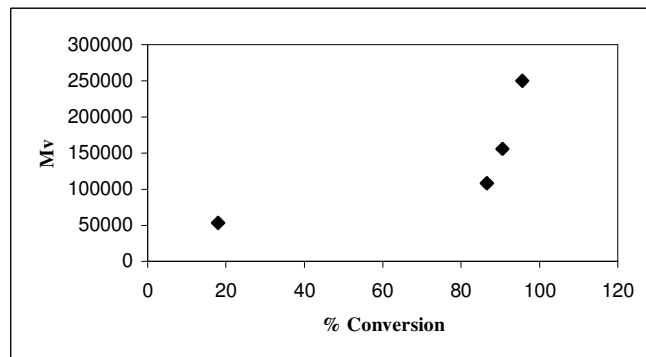
Set 5



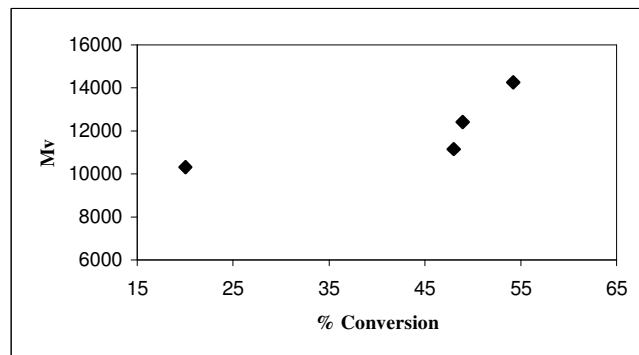
Set 6



Set 7



Set 8



Set 9

**Figure 3.19** Dependence of molecular weights on conversion in ATRP of MMA

### 3.3 DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

Differential scanning calorimetry is one of the most widely used techniques to measure  $T_g$  and  $T_m$ . The measurements were carried out at  $N_2$  atmosphere by heating polymer samples in the temperature range of  $-25^\circ\text{C}$  to  $300^\circ\text{C}$ . Some examples of the thermograms are shown in Figure 3.21, 3.22, 3.23 and 3.24. In the thermograms, there is no melting peak of most polymer samples observed due to the amorphous structure.

The form of dependence of  $T_g$  on molecular weight is approximated by the Fox-Flory equation<sup>18</sup>.

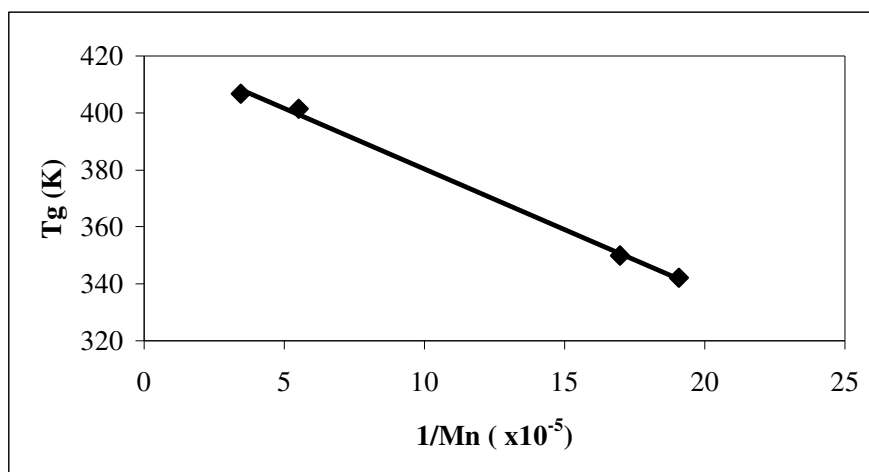
$$T_g = T_g^\infty - \frac{K}{M_n} \quad (8)$$

where  $T_g^\infty$  is the limiting value of the  $T_g$  at high molecular weight (obtained from the intercept of a plot of  $T_g$  versus reciprocal number average molecular weight) and  $K$  is a constant depending on the nature of polymer. The molecular weight were recalculated from the GPC results in terms of  $M_n$ . The results are tabulated in Table 3.13 and the  $T_g$  is plotted against  $1/M_n$  in Figure 3.20. From intercept of the straight line  $T_g^\infty$  is 423 K and from the slope of the line, the  $K$  constant is  $4.3 \times 10^5$ .



**Table 3.13** Some of the  $T_g$  values of PMMA

Set/time (hour)	$T_g$ of polymer (°C)	Molecular Weight(g/mol)
7/24	133.66	28869
7/48.5	128.44	18112
5/12	76.99	5894
9/19	69.13	5241



**Figure 3.20** Glass transition temperature versus reciprocal  $M_n$

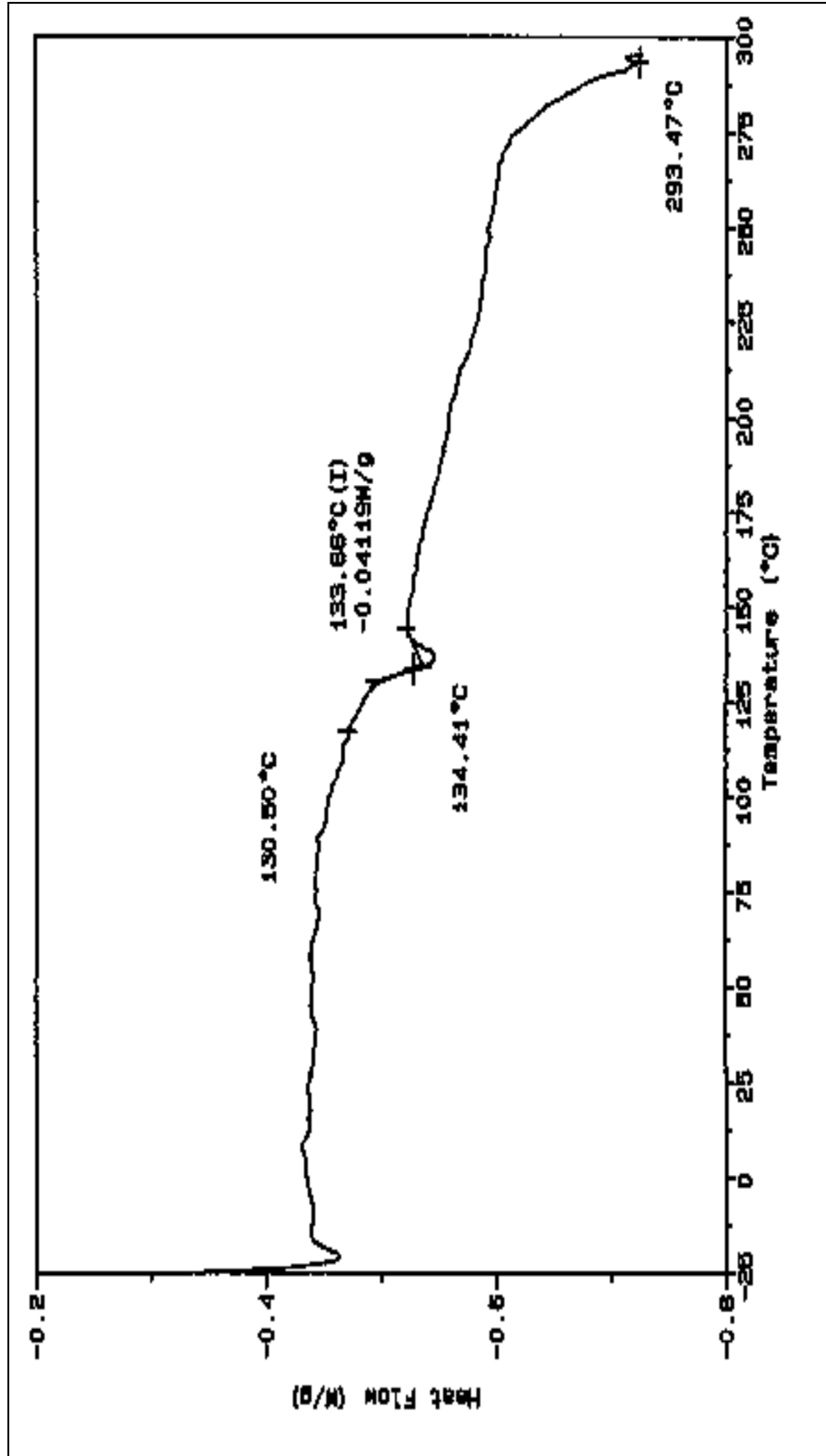


Figure 3.21 DSC thermogram of Set 7 at 24 hour

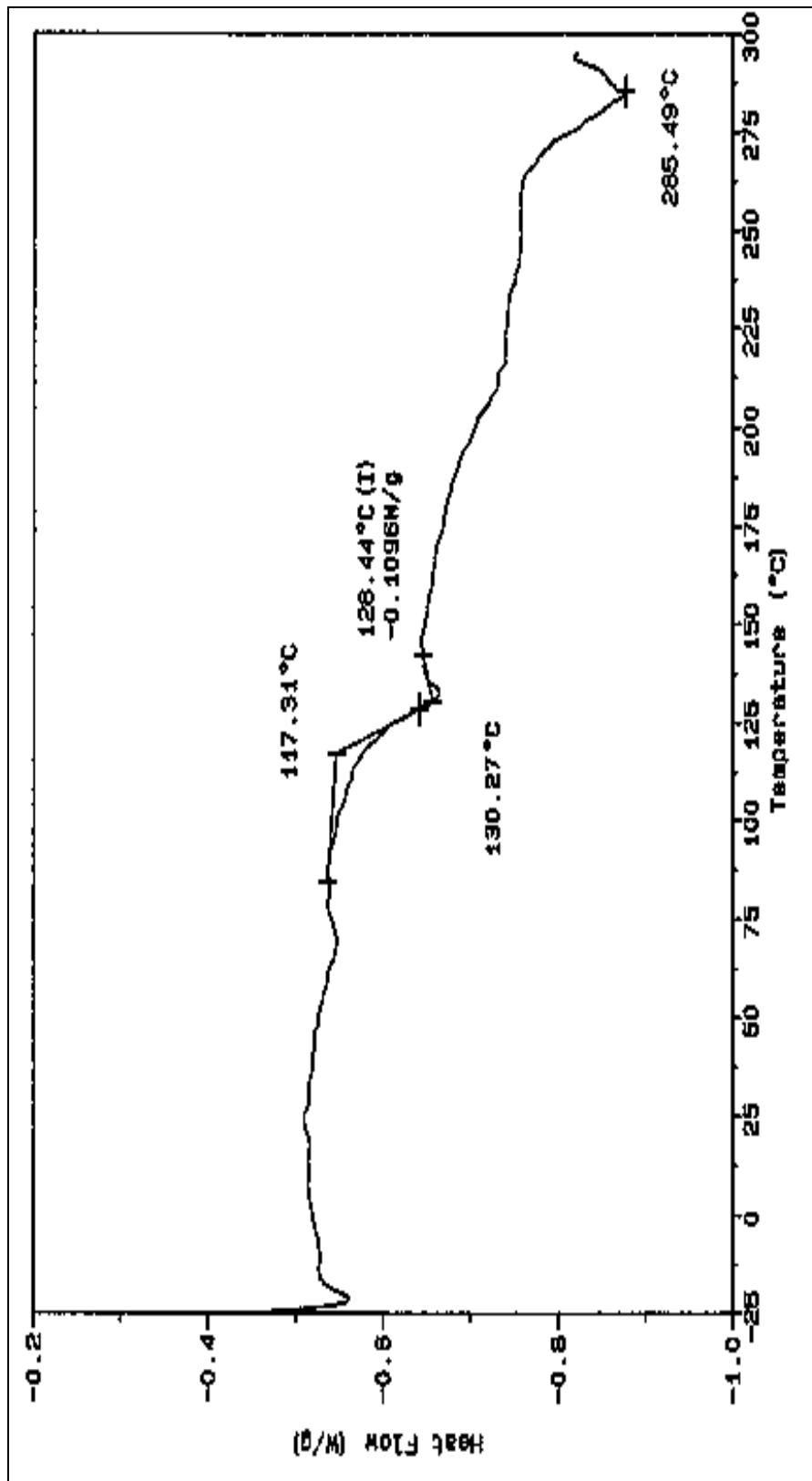


Figure 3.22 DSC thermogram of Set 7 at 48.5 hour

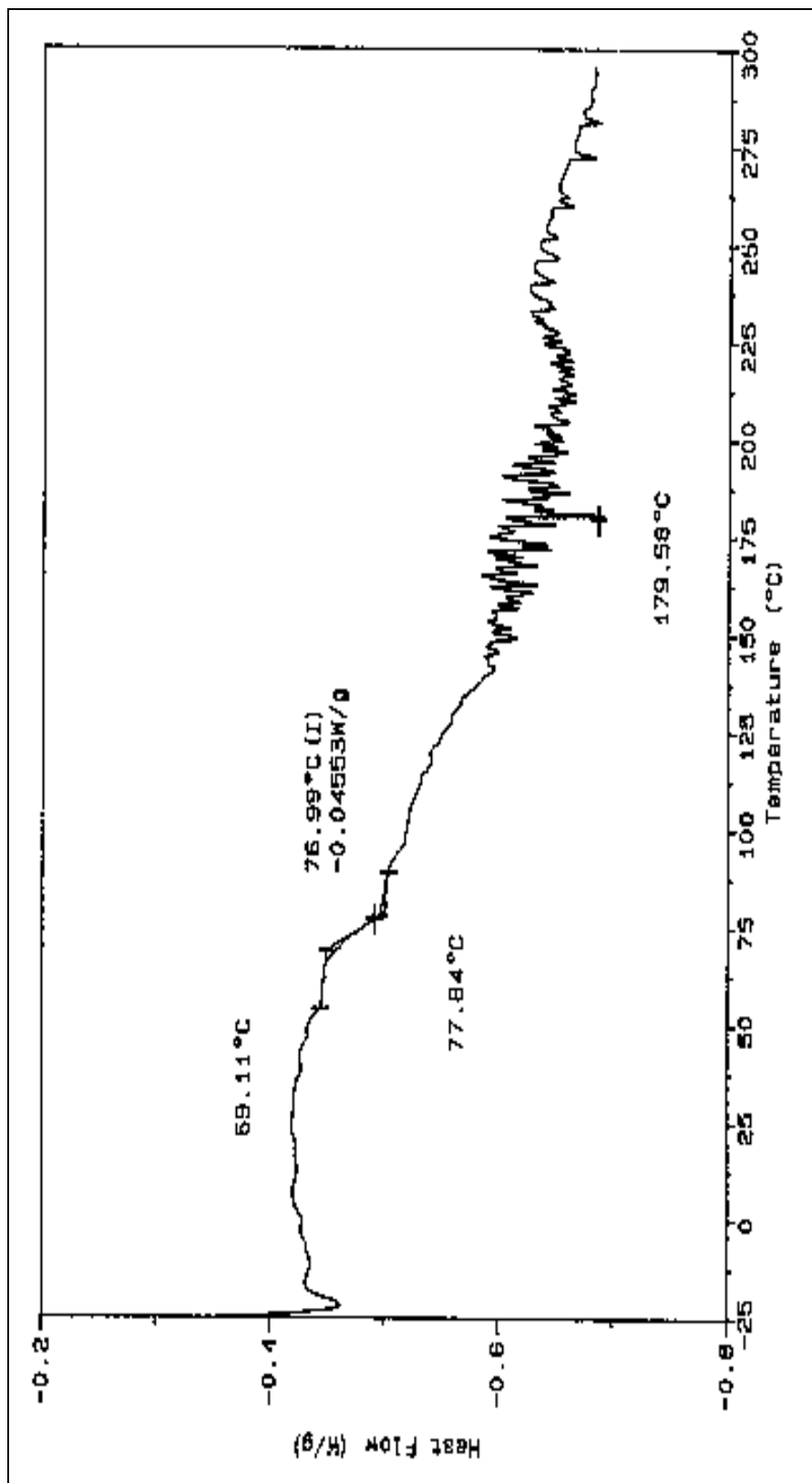


Figure 3.23 DSC thermogram of Set 5 at 12 hour

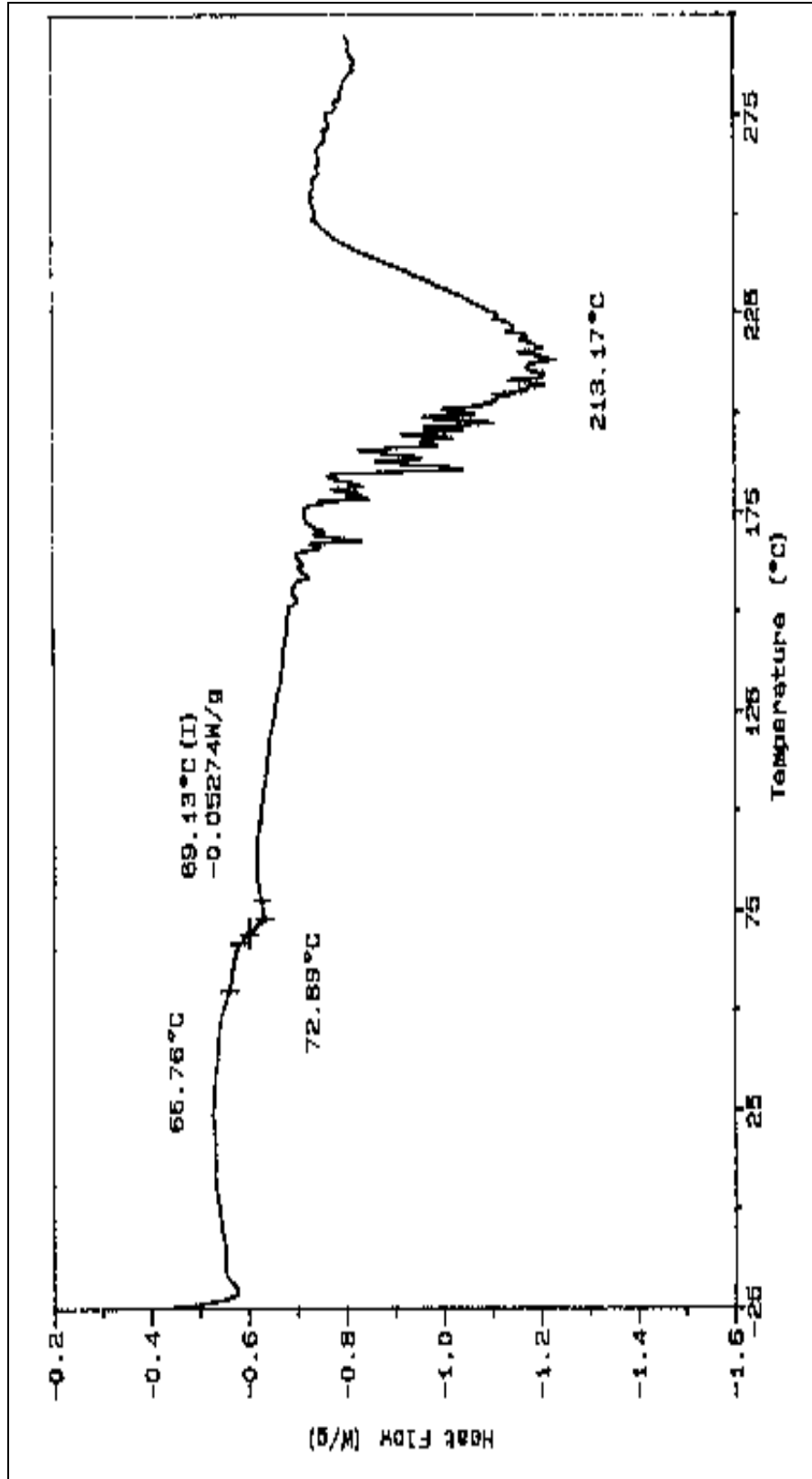


Figure 3.24 DSC thermogram of Set 9 at 19 hour

### 3.4 FT-IR ANALYSIS

The FT-IR spectra obtained for MMA and PMMA are shown in Figure 3.25 and 3.26, respectively.

In the IR spectrum of monomer; a characteristic carbonyl stretch of the ester peak is at  $1727\text{ cm}^{-1}$ . The peaks for the C=C are observed at  $1638\text{ cm}^{-1}$  and at  $940\text{ cm}^{-1}$ . The  $-\text{CH}_2-$  peak is at  $1444\text{ cm}^{-1}$ . The (-O-C-) stretching is seen at  $1199\text{ cm}^{-1}$ . The peak at  $2956\text{ cm}^{-1}$  corresponds to (-O-CH<sub>3</sub>) stretching and the peak at  $1326\text{ cm}^{-1}$  is assigned to (-CH<sub>3</sub>-) stretching.

In the spectrum of PMMA, the carbonyl stretch of the ester is seen at  $1731\text{ cm}^{-1}$ . The peaks at  $1272\text{-}1147\text{ cm}^{-1}$  are made up of contributions from C-C-O, O-C-C and C-C-C stretching vibrations. Peak of double bond observed in the spectrum of monomer at  $1638\text{ cm}^{-1}$  disappeared in the spectrum of PMMA. However, the vinyl group peak observed at  $940\text{ cm}^{-1}$  in the monomer spectrum shifted to  $989\text{ cm}^{-1}$  and did not completely disappear. This is an indication that more chain ends are obtained by disproportionation and also chains are in syndiotactic configuration. The sharpness of FT-IR peaks in polymer spectrum is also an evidence of the stereoregularity of polymer chains.

It can be concluded from IR spectra investigation that polymer was successfully achieved and the polymerization proceeds by carbon-carbon double bond opening. All the other polymer spectra resemble to the one shown in Figure 3.26.

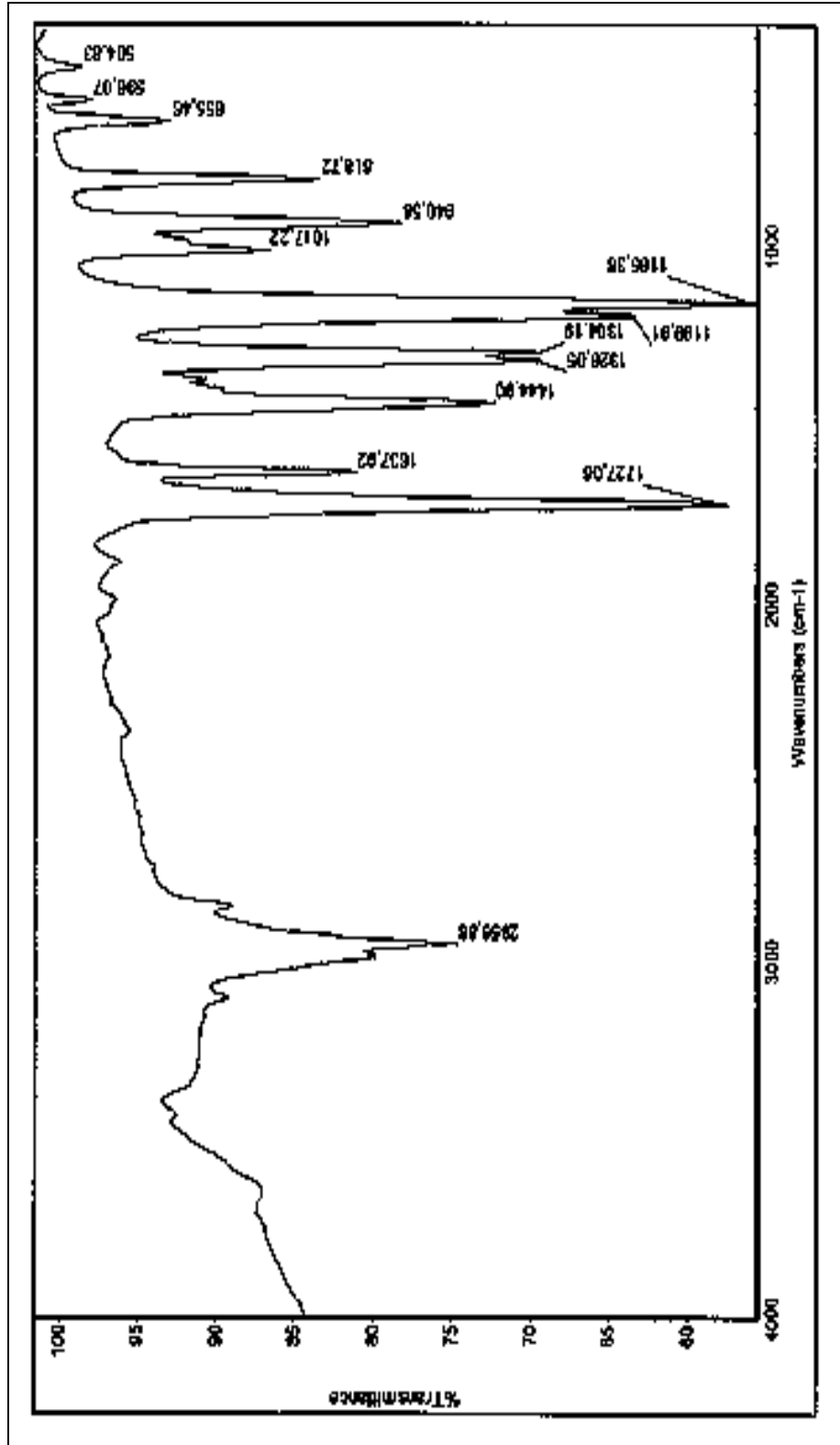


Figure 3.25 IR Spectrum of MMA

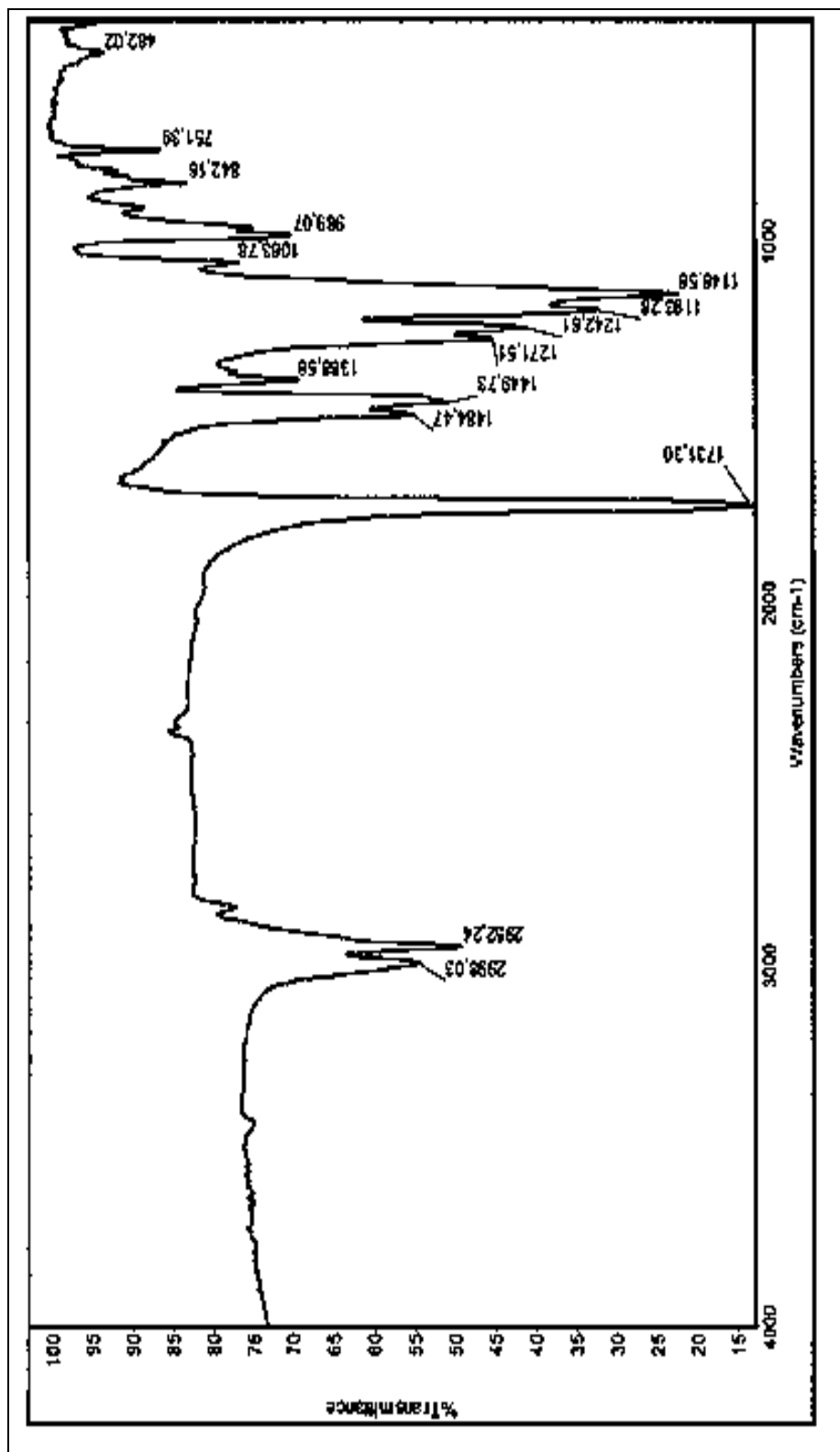


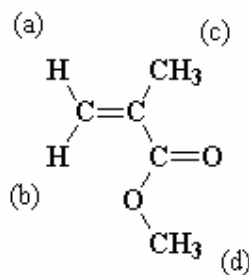
Figure 3.26 IR Spectrum of Set 1/time 24 (hour)



### 3.5 NUCLEAR MAGNETIC RESONANCE ANALYSIS

The monomer and polymers were identified by  $^1\text{H-NMR}$  and the spectra are given in Figure 3.27 and Figure 3.29, 3.30, 3.31, respectively.

In the  $^1\text{H-NMR}$  spectrum of MMA, four different peaks were observed. The assigned protons are shown in formula of molecule and the chemical shifts in Table 3.14.



**Table 3.14** The  $^1\text{H-NMR}$  spectrum of MMA

Proton type	Shift (ppm)	Group
Ha	5.43	Ethylene
Hb	5.97	Ethylene
Hc	1.79	Methyl
Hd	3.62	Ester

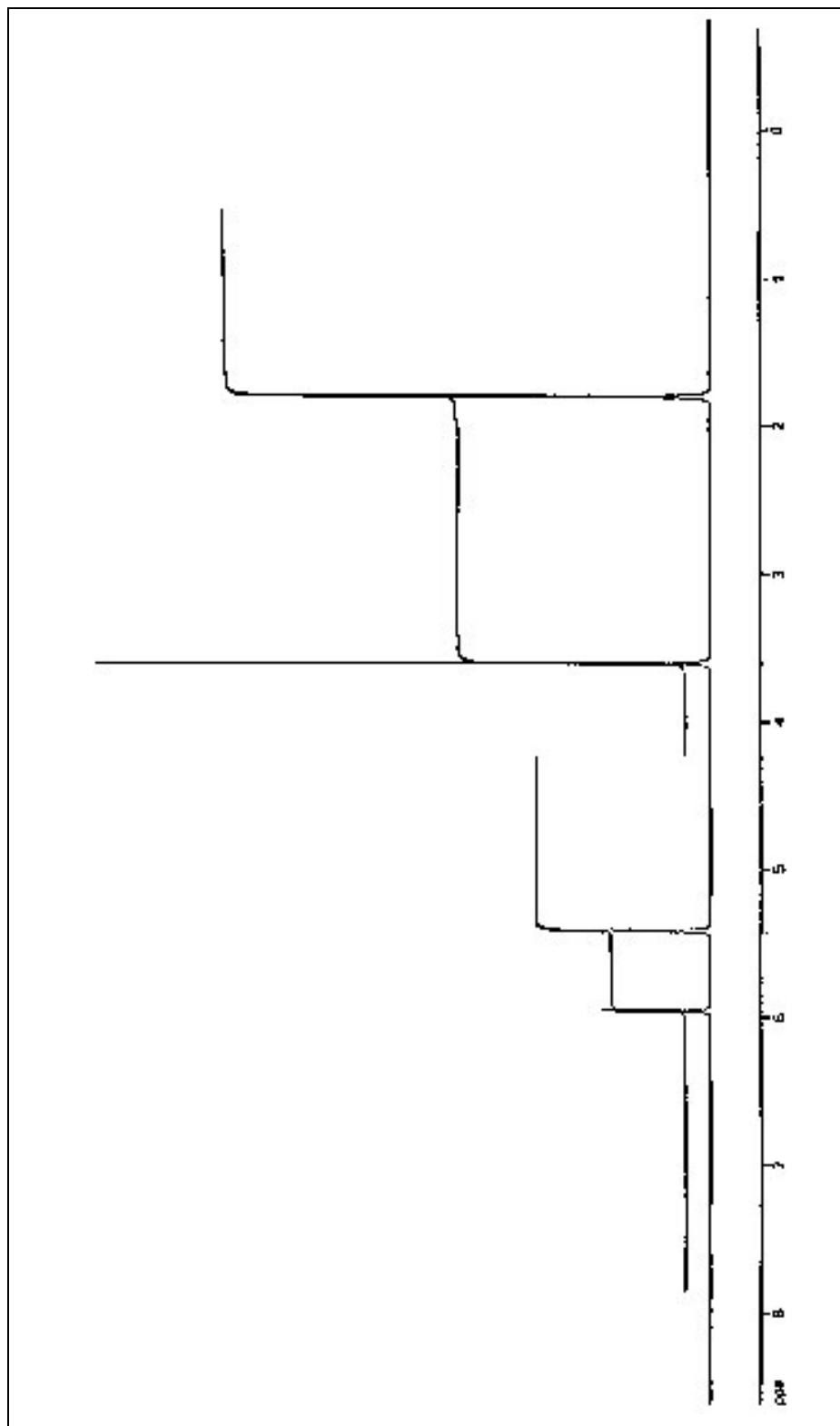
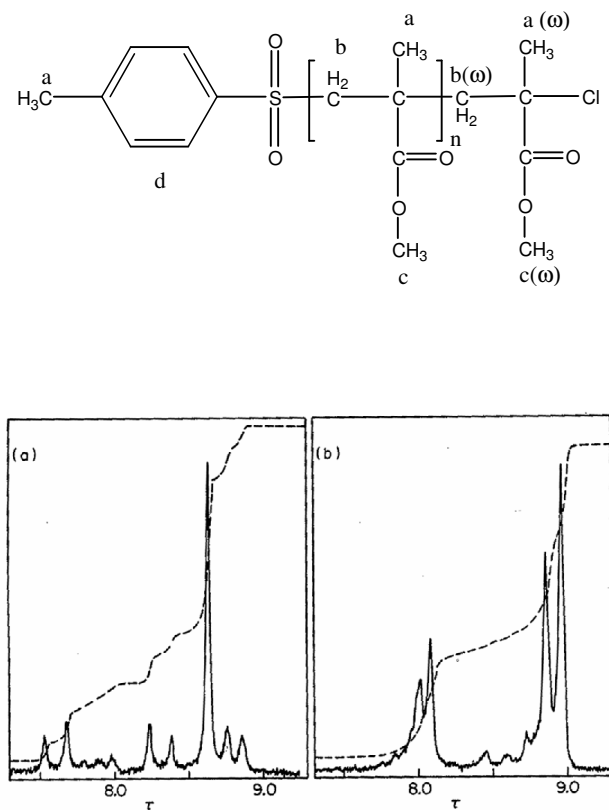


Figure 3.27 <sup>1</sup>H-NMR spectrum of MMA

In the  $^1\text{H-NMR}$  spectrum of PMMA (Figure 3.29), the signals at 0.59-0.95, 1.17-1.77, and 3.14-3.48 ppm are assigned to the protons of methyl groups [peak a] of  $-\text{C}(\text{CH}_3)(\text{COOCH}_3)$ , methylene groups [peak b] of  $-\text{CH}_2-$ , and methoxy groups [peak c]  $-\text{C}(\text{CH}_3)(\text{COOCH}_3)$ , respectively. In particular, the signal at 3.48 ppm [peak c( $\omega$ )] is for the protons of the methoxy group, that at 2.08 ppm [peak b( $\omega$ )] is for the methylene protons, and that at 0.95 ppm [peak a( $\omega$ )] exhibits the characteristic chemical shifts of the terminal MMA unit capped with an  $\omega$ -end chlorine. The assigned peaks explain that all polymers have predominantly syndiotactic structure<sup>19</sup>. Similar spectra were observed for polymers obtained under different conditions.



**Figure 3.28** 100 MHz spectra of two samples of PMMA, illustrating use of integral spectra (dashed lines) to determine relative peak areas; (a) predominantly isotactic and (b) predominantly syndiotactic polymers.<sup>19</sup>

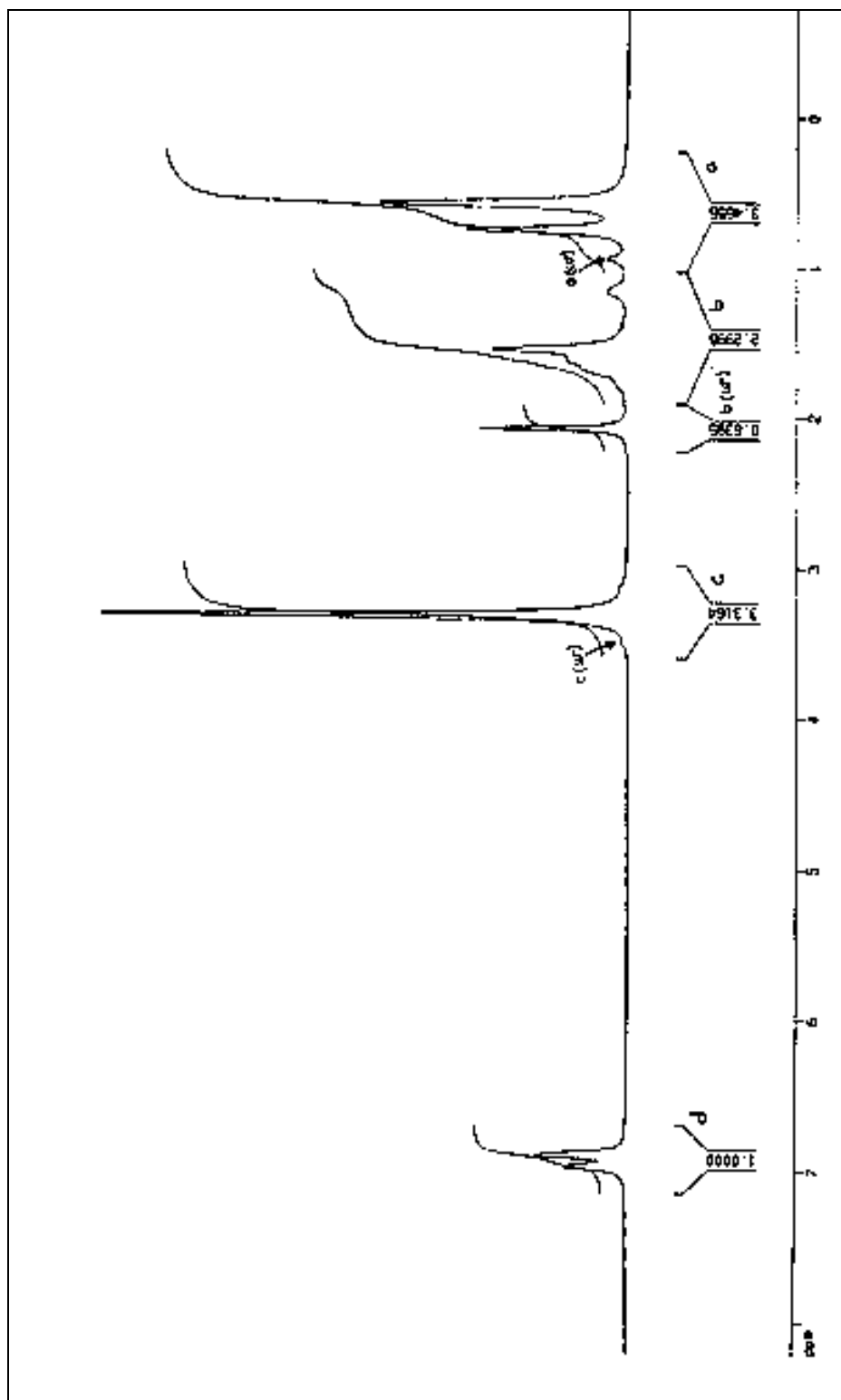
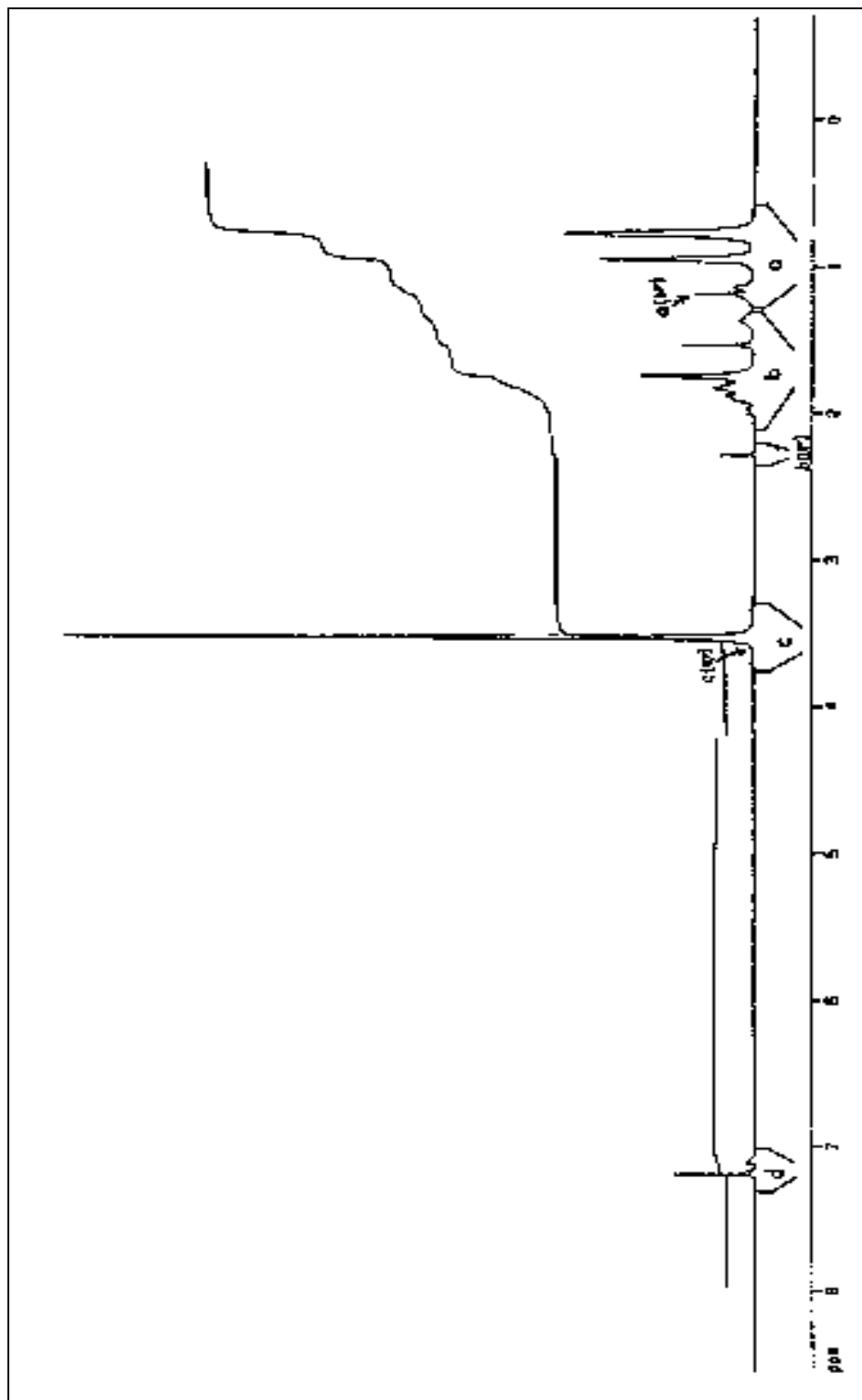
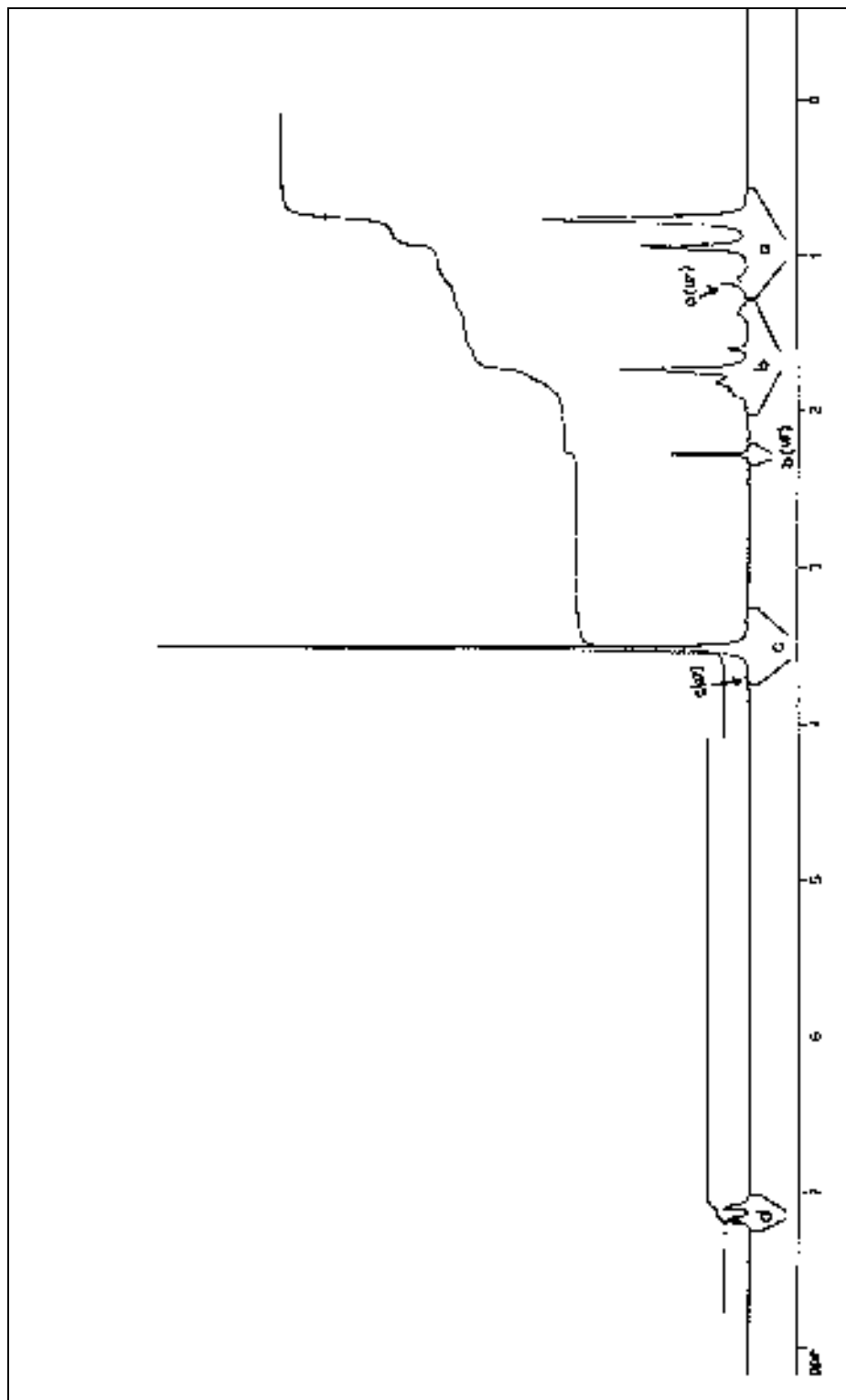


Figure 3.29  $^1\text{H-NMR}$  spectrum of Set 7/time 40 (hour)



**Figure 3.30**  $^1\text{H-NMR}$  spectrum of Set 4/time 21 (hour)



**Figure 3.31**  $^1\text{H-NMR}$  spectrum of Set 6/time 24 (hour)

### 3.6 X-RAY ANALYSIS

The NMR results showed that polymer obtained are mostly syndiotactic and FT-IR results indicate high regularity in polymer chains. However, no proper melting peaks were observed in DSC thermograms of polymers. In order to understand the crystallinity of polymer obtained, the X-Ray powder pattern of polymer was taken (Figure 3.32). The samples could not be powdered properly and therefore particule sizes were large. This will affect the X-Ray powder pattern to give orientations, but not many characteristic X-Ray peak of the sample. Thus, in Figure 3.32, the broad peaks show orientation and chain structure regularity, but not much crystallinity of the sample.

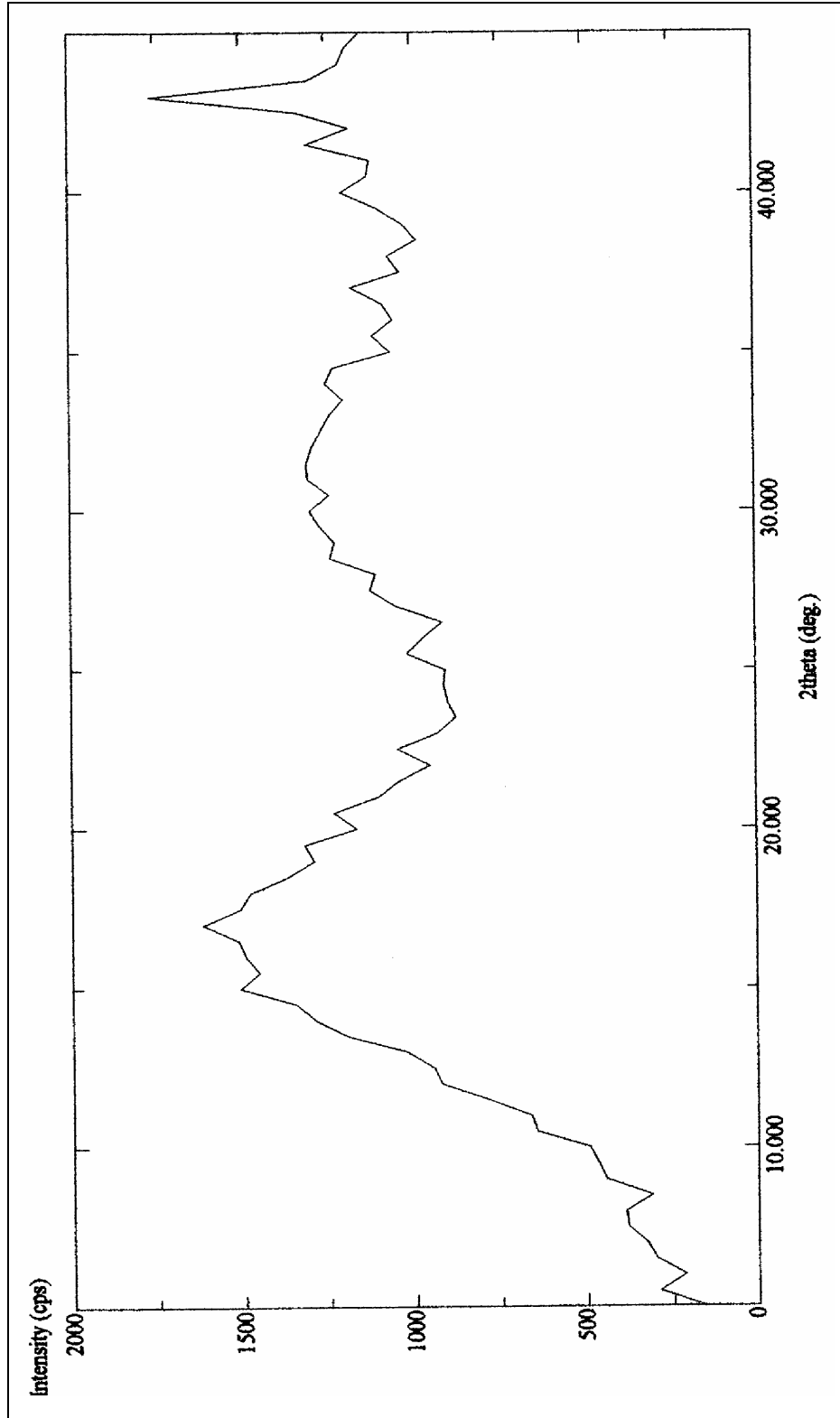


Figure 3.32 X-Ray Spectrum of Set 9/time 48 (hour)



## CHAPTER 4

### CONCLUSIONS

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

1. MMA can be polymerized by ATRP method.
2. The molecular weight control for PMMA by ATRP method can be properly achieved.
3. The constants, K and  $\alpha$  in  $[\eta]=KM^\alpha$  equation are obtained from GPC results.
4. FT-IR and NMR results showed that the polymer obtained have chain structure regularity and is mostly syndiotactic.
5. The relation between Tg and Mn was verified and K constant was determined from the results of DSC.
6. The X-Ray powder pattern showed high orientation of polymer chains, but no crystallization of polymer.

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