KINETICS OF FREE RADICAL BULK POLYMERIZATION OF METHYL METHACRYLATE

by

E.ELİF GÜREL HAMURCU

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APPROVED BY:

Prof.Dr.Bahattin BAYSAL B. Baysal

(Thesis Supervisor)

Doç.Dr.Ivet BAHAR

Prof.Dr.Burak ERMAN Burak Erman

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To My Dearest...

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ABSTRACT

In this work, the free radical bulk polymerization of methyl methacrylate was studied at 22.5^{o}C.

Polymerization reactions were initiated by thermal decomposition of 2,2'-azobisisobutyronitrile (AIBN). Full range of conversion up to glassy state was investigated. The reaction temperature was choosen as 22.5^{o}C for comparison with the experimental results of photo-initiated free radical polymerization of methyl methacrylate.

The conversion-time dependence in polymerization of methyl methacrylate was investigated and the qualitative behaviour of rate and rate constants was discussed over the whole range of reaction.

For the initial stages of polymerization, k_t/k_p^2 and $C_{tr,m}$ values were evaluated and found, to be 303 and $5.6x10^{-5}$ respectively. Efficiency of the initiator was also determined and calculated as about 0.47 for a single low conversion value.

Number average degree of polymerization, P_n, remained constant at the beginning and at the end of the polymerization reaction.

ÖZET

Bu çalışmada, metil metakrilatin 22.5°C deki serbest radikal blok polimerizasyonu incelenmiştir. Polimerizasyon reaksiyonları, 2,2'-Azobisizobutironitril (AIBN)'in termal bozunması yolu ile başlatılmıştır. Camsı bölgeye kadar bütün dönüşüm aralığı araştırılmıştır. Reaksiyon sıcaklığı, aynı sıcaklıktaki fotopolimerizasyonla başlatılan polimerizasyon deneylerinin sonuçları ile karşılaştırmak için 22.5°C olarak seçilmiştir.

Çalışmada dönüşüm-zaman bağımlılığı araştırılmış ve polimerizasyon hızının ve hız sabitlerinin nitel değerleri, tüm dönüşüm aralıklarında tartışılmıştır. Düşük polimerizasyon dönüşümleri için (%15 dönüşümlere kadar) k_t/k_p^2 oranı ve $C_{tr,m}$ monomere zincir transferi sabiti hesaplanmış ve sırasıyla 303 ve $5.6x10^{-5}$ olarak bulunmuştur. Ayrıca, başlatıcının etkinlik katsayısı da araştırılmış ve yaklaşık 0.47 olarak hesaplanmıştır.

Poli(metil metakrilat) polimerlerinin ortalama molekül ağırlıkları düşük ve yüksek dönüşümlerde sabit kalmaktadır.

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A : Slope of the monoradical line (mol^{-1} s.L)

A' : The ratio of $2k_{td} + k_{tc}/k_p^2$ (mol.s.L^{-1})

A'' : The ratio of $k_{tc} + k_{td}/k_p^2$ (mol.s.L^{-1})

a : A measure of polymer-solvent interaction

c : Concentration (g/dl)

C : A constant for viscometer

C_M : Chain transfer constant to monomer

C_I : Chain transfer constant to initiator

C_S : Chain transfer constant to solvent

$C_{tr,cat}$: Chain transfer constant to catalyst

$[cat]$: Catalyst concentration (mol L^{-1})

d : Density

E : A constant for viscometer

e : A parameter related to solvent power

f : Efficiency factor of initiator

$[I]$: Initiator concentration (mol L^{-1})

I : Initiator

k_d : Rate constant for decay of initiator (s^{-1})

k_p : Rate constant of propagation (mol^{-1}.L.s^{-1})

k_t : Rate constant of termination ($mol^{-1}.L.s^{-1}$)

k_{td} : Rate constant of termination by disproportionation ($mol^{-1}.L.s^{-1}$)

k_{tc} : Rate constant of termination by combination ($mol^{-1}.L.s^{-1}$)

K : Overall rate constant ($mol^{-1/2}.L^{1/2}.s$)

k' : Huggins constant

k" : Kraemer constant

[M] : Monomer concentration ($mol\ L^{-1}$)

$[M]_x$: Monomer concentration at any conversion x ($mol\ L^{-1}$)

$[M]_o$: Initial monomer concentration molecular weight ($mol\ L^{-1}$)

M : Monomer

M_w : Weight average molecular weight

M_n : Number average molecular weight

M_v : Viscosity average molecular weight

M_{GPC} : GPC-average molecular weight

N : Number of molecular

P_n : Number average degree of polymerization

P : Polymer

R_p : Rate of propagation ($mol\ L^{-1}s^{-1}$)

R_i : Rate of initiation ($mol\ L^{-1}s^{-1}$)

R.[RM.] : Free radical

r : End to end distance of the segments of the chain

s : Radius of gyration

t : Time

t_0 : Efflux time for the solvent

V_r : Retention volume

V_0 : Mobile phase volume

V_h : Hydrodynamic volume (ml)

W : Mass of the sample in atomic mass units

α : Expansion factor

δ : The ratio of $2k_{td} + k_{tc}/k_p^2$ (mol.s.L^{-1})

ξ : A parameter depending on solvent power

$[\eta]$: Intrinsic viscosity (dl/g)

η_r : Relative viscosity

η_{sp} : Specific viscosity

η_{inh} : Inherent viscosity (dl/g)

η_{red} : Reduced viscosity (dl/g)

κ : The constant of Mark-Houwink-Sakurada equation (dl/g)

ϑ : Kinetic chain length

τ_s : Life time of active center (s)

Φ : Universal constant

CHAPTER 1

INTRODUCTION

The kinetic mechanism of vinyl polymerization by free radicals has been studied extensively and there is vast literature on this subject. Most of the work in the past, however, has been restricted to the so-called ideal region of low conversion and to the determination of the ratio k_p^2/k_t and other parameters available from steady-state experiments.

More recently attention has been directed to theoretical and experimental studies in the more advanced stages of the polymerization process, and it is started to obtain a more reasonable description of the Trommsdorff or gel effect of the reaction mixture by the measurement of absolute rate constants of propagation and termination, k_p and k_t respectively.

The determination of absolute rate constants is a delicate experimental task. Only a limited amount of published data is available and it is mostly restricted to the low conversion range.

Thus it seemed worthwhile or even essential to study the influence of conversion on the propagation and termination rates under non-steady-state conditions in spite of the difficulties to be expected.

The experiments had to be done on a polymer which was well characterized and preferably had a low transfer coefficient, for these reasons methyl methacrylate was chosen as the test monomer.

In order to get low rates of polymerization and negligible thermally initiated polymerization, the experiments were carried out in bulk at 22.5^{0}C using 2,2$'$-azobisisobutyronitrile (AIBN) as the initiator, which decomposes thermally at this temperature.

The low-temperature polymerizations have the advantage of providing well-defined initiation of the kinetic chains and a relatively easy method of determining the k_p^2/k_t ratio. In addition, at this temperature it is still possible to measure the number and weight-average degrees of polymerization by using dilute-solution viscosity method.

In this study, conversion-time dependence in polymerization of methyl methacrylate was investigated and the qualitative behavior of rate and rate constants of the reaction was discussed. For the initial stages of polymerization the quantity k_t/k_p^2, and chain transfer constant to monomer C_M, were found as 303 and 5.6x10^{-5} respectively.

CHAPTER II

KINETICS OF FREE RADICAL POLYMERIZATION

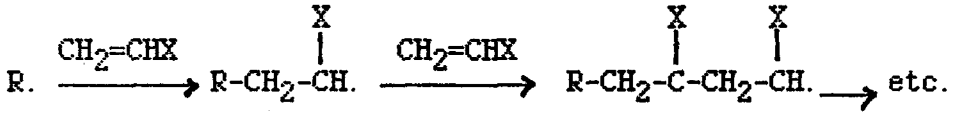
2.1. GENERAL NATURE OF VINYL TYPE POLYMERIZATION

The vinyl monomers may be regarded as monosubstituted derivatives of ethylene, of the structure CH_2=CHX. The following general structures will be referred to as vinyl type monomers and their conversion to a polymer as vinyl polymerization.

(1) CH_2=CHX	Vinyl monomers
(2) CH_2=CXY	1,2 Disubstituted ethylenes and vinylidene monomers
(3) CHX=CHY	1,2 Disubstituted ethylene
(4) CF_2=CXY	Tetrofluoroethylene derivatives
(5) CH_2=CH-CH=CH_2	Butadiene and butadiene derivatives

The theoretical aspect of the free radical polymerization is established very well and there are many fundamental books to describe the essential features of this process. [1-5]

Vinyl polymerization is a chain reaction. This is borne out by the fact that very small traces of initiator may exert a very marked catalytic effect. Many hundreds of molecules of monomer will polymerize for every molecule of initiator. Vinyl type polymerization may be propagated by a free radical chain mechanism a carbonium ion chain mechanism, or a carbanion chain mechanism, depending on the catalyst employed. Although there are some monomers such as isobutylene and propylene which cannot be polymerized by free radical producing catalyst but by cationic catalyst, free radical mechanism is most widely used and most important one. [1] The following free radical chain mechanism, first suggested by Taylor and Bates to explain the polymerization of ethylene induced by free radicals in the gas phase and independently proposed by Staudinger for liquid phase polymerizations, offers an explanation for the general characteristics of vinyl polymerizations.



$$R. \xrightarrow{CH_2=CHX} R-CH_2-\overset{X}{\overset{|}{CH}}. \xrightarrow{CH_2=CHX} R-CH_2-\overset{X}{\overset{|}{C}}-CH_2-\overset{X}{\overset{|}{CH}}. \rightarrow \text{etc.} \qquad (2.1)$$

where x is a substituent which may be C_6H_5, Cl, Br, $OCOCH_3$, $COOCH_3$ or H. Disubstituted monomers such as vinylidene chloride or methyl methacrylate are also included.

R.represents a free radical arising from the homolytic cleavage of the initiator. The dot represents the odd electron of the free radical.

$$\text{Initiator} \longrightarrow 2R.$$

The chain propagation steps consist essentially of free radical attack at one of the double bonded carbon atoms of the monomer. The driving force of the reaction between the odd electron on the initiator fragment and electrons (unsaturation electrons) of the double bond in the monomer is the tendency for two electrons of opposite spin to couple and form a covalent bond. The remaining electron of the double bond shifts to the other carbon atom, which then becomes a free radical. In this way the active center shifts uniquely to the newly added monomer, which is thereby rendered capable of adding another monomer etc. [2] The above driving force is responsible for the continued growth of polymer chain.

Vinyl monomers can be polymerized by heat alone or by ultraviolet radiation. These polymerizations are referred to as thermal polymerization and photopolymerization. These polymerizations proceed via the above mentioned free radical mechanism. Among the substances which initiates and accelerates the polymerization of vinyl monomers via a radical mechanism are first and foremost preoxides, also azo-compounds, persulfates and disulfides. Free radicals can be generated in a number of ways, such as thermal decomposition, photolytic decomposition of covalently bonded compounds (photoinitiation), dissosication of covalent bonds by high energy radiation, oxidation-reductions and electrochemical initiation. [5] Two reactions commonly used to produce radicals for polymerization are the thermal and photochemical decomposition of benzoyl peroxide and azobisbutyronitrile. These initiators decompose cleanly into fragments with the elimination of nitrogen. [6]

$$R - N = N - R' \longrightarrow R'. + R'. + N_2$$

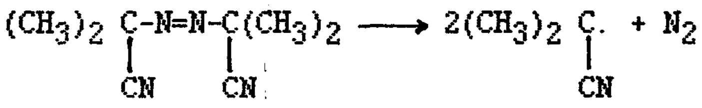
2.2. MECHANISM OF VINYL RADICAL POLYMERIZATION

Vinyl radical polymerization proceeds by three steps: Initiation, propagation and termination. [7]

INITIATION : The process of chain initiation may be considered to involve two steps, the first being the decomposition of the initiator, I (e.g. benzoyl peroxide or azo-bis nitrile) to yield of a pair of free radicals R.

$$I \xrightarrow{k_d} 2\,R. \qquad (2.2)$$

In this study, 2,2'-azobisisobutyronitrile was used as an initiator. The decomposition of this initiator can be given in the following reaction.



$$(CH_3)_2\underset{\displaystyle CN}{C}-N=N-\underset{\displaystyle CN}{C}(CH_3)_2 \longrightarrow 2(CH_3)_2\underset{\displaystyle CN}{C}. + N_2 \qquad (2.3)$$

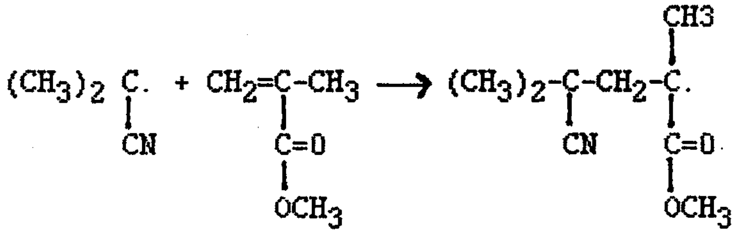
And the second the addition of a monomer M to a primary radical R. to yield a chain radical.

$$R\cdot + M \xrightarrow{k_i} RM_1\cdot \qquad (2.4)$$

The adduct, $R\text{-}CH_2\underset{\substack{|\\ X}}{CH}\cdot$, formed from a vinyl monomer is here represented by M_1.

Since the free radicals have odd numbers of electrons they will be formed in pairs, either or both of which may initiate polymerization according to reaction (2.4). Not all of the radicals released in step (2.2) necessarily yield chain radicals according to (2.4) but some of them may be lost through side reactions. [2]

Addition of MMA (methyl methacrylate) to primary azo radical can be shown in the following reaction.



$$(CH_3)_2\underset{\substack{|\\ CN}}{C}\cdot + CH_2{=}\underset{\substack{|\\ C=0\\ |\\ OCH_3}}{C}{-}CH_3 \longrightarrow (CH_3)_2{-}\underset{\substack{|\\ CN}}{C}{-}CH_2{-}\overset{\substack{CH3\\ |}}{\underset{\substack{|\\ C=0\\ |\\ OCH_3}}{C}}\cdot \qquad (2.5)$$

Azo radical MMA Chain radical

PROPAGATION : The chain radical formed in the initiation step is capable of adding successive monomers to propagate the chain. [1]

The growth of polymer molecules by successive addition of monomers according to reaction (2.1) to the radicals $M_1\cdot$ and to their successors may be represented by

$$\mathrm{RM_1 + M \xrightarrow{k_p} RM_2\cdot}$$

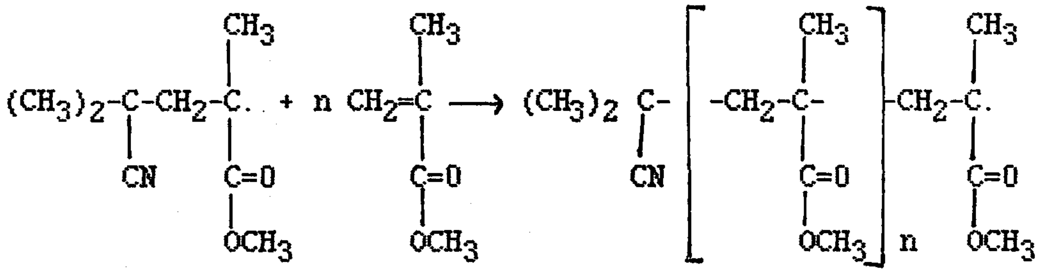
$$\mathrm{RM_2\cdot + M \xrightarrow{k_p} RM_3\cdot}$$

$$\text{-------------------}$$

$$\mathrm{RM_n + M \xrightarrow{k_p} RM_{n+1}\cdot} \qquad (2.6)$$

The same reaction rate constant k_p is written for each propagation step under the assumption that radical reactivity is independent of chain length.

In the polymerization of MMA (methyl methacrylate) the propagation step of reaction can be given as follows:



$$\mathrm{(CH_3)_2\underset{CN}{C}-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\cdot + n\,CH_2=\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}} \longrightarrow (CH_3)_2\underset{CN}{C}-\left[-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-\right]_n-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\cdot}$$

(2.7)

TERMINATION : Propagation would continue until the supply of monomer was exhausted. Bimolecular reaction between a pair of chain radicals accounts for annihilation of active centers. The termination step can take place in two ways: combination of coupling:

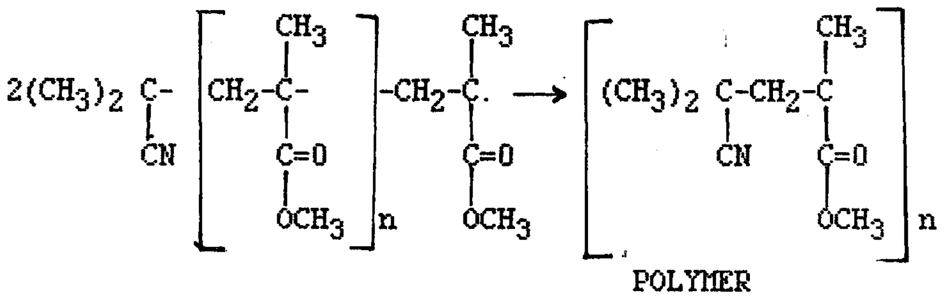
$$RM_n\cdot + RM_m\cdot \xrightarrow{k_{tc}} RM_{n+m}\,R \qquad (2.8)$$

Disproportionation

$$RM_n\cdot + RM_m\cdot \xrightarrow{k_{td}} RM_{n+}\,RM_m \qquad (2.9)$$

in which hydrogen transfer results in the formation of two molecules with one satured and one unsaturated end group. Each type of termination is known. Studies of the number of initiator fragments per molecule show that polystyrene terminates predominantly by combination, whereas polymethyl methacrylates terminates entirely by disproportionation at polymerization temperatures above 60°C and partly by each mechanism at lower temperatures. [5]

Overall termination step of polymethylmethacrylate:



$$2(CH_3)_2\underset{\displaystyle CN}{C}-\left[CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{\displaystyle C=O}{OCH_3}}{C}}-\right]_n-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{\displaystyle C=O}{OCH_3}}{C}}\cdot \longrightarrow \left[(CH_3)_2\underset{\displaystyle CN}{C}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{\displaystyle C=O}{OCH_3}}{C}}\right]_n \tag{2.10}$$

POLYMER

Chain Transfer : It was recognized by Flory (1937) that the reactivity of a radical could be transferred to another species, which would usually be capable of continuing the chain reaction. 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. [2,3]. The mechanism of a chain transfer process in free radical polymerization is described by the following equations:

$$RM_n\cdot + S \xrightarrow{k_{tr(s)}} RM_n + S\cdot \tag{2.11}$$

$$RM_n\cdot + M \xrightarrow{k_{tr(m)}} RM_n + M\cdot \tag{2.12}$$

$$RM_n\cdot + I \xrightarrow{k_{tr(i)}} RM_n + I\cdot \tag{2.13}$$

$$RM_n\cdot + P \xrightarrow{k_{tr(p)}} RM_n + P\cdot \tag{2.14}$$

S,M,I,P indicates the solvent, monomer, initiator and the polymer respectively.

The detailed kinetic consequences of the transfer reaction depend on the reactivity of chain transfer radical (S.,M.,I.,P.) If it has a reactivity at least comparable to that of the propagating radical then it rapidly reinitiates polymerization, through the addition of monomer regenerating the propagating species and maintaining the rate of polymerization. In such cases, S,M,I,P are conventional transfer agents. If reinitiation by S.M.,I.P. are relatively slow the concentration of chain transfer radical in the stationary state will be relatively high and these radicals will take part in the termination reactions, either with themselves or with propagating radicals. The consequence of this is a reduction in the concentration of reactive radicals compared with the corresponding polymerization in the absence of transfer agent and hence, the rate of polymerization is decreased by the presence of the substrate.

2.3. RATE OF VINYL RADICAL POLYMERIZATION

The rates of three steps of polymerization, initiation, propagation and termination may be written in terms of concentrations (in brackets) of the species involved and the rate constants.

The rate of initiation is

$$R_i = \left(\frac{d[M.]}{dt}\right)_i = 2f\ k_d\ [I] \qquad (2.15)$$

where the factor f represents the fraction of the radicals formed by Eq.(2.2) which is successful in initiating chains by Eq.(2.4) The rate of termination is

$$R_t = -\left(\frac{d[M.]}{dt}\right)_t = 2\,k_t\,[RM.]^2 \qquad (2.16)$$

For many cases of interest the concentration of free radicals [RM.] becomes essentially constant very early in the reaction, as radicals formed and destroyed at identical rates. In this steady-state condition $R_i = R_t$ and Eqs. 2.15 and 2.16 may be equated to solve for [RM.]

$$[RM.] = \left(\frac{fk_d[I]}{k_t}\right)^{1/2} \qquad (2.17)$$

The rate of propagation is essentially the same as the overall rate of disapperance of monomer, since the number of monomers used in Eq. (2.4) must be small compared to that used in (Eq.2.6) if polymer is obtained.

Then $$R_p = -\frac{d[M]}{dt} = k_p\,[RM.][M] \qquad (2.18)$$

or, substituting from Eq.(2.17)

$$R_p = k_p \left(\frac{fk_d[I]}{k_t}\right)^{1/2} [M] \qquad (2.19)$$

Thus the overall rate of polymerization should, in early stages of the reaction, be proportional to the square root of initiator concentration and if f is independent of [M], to the first power of the monomer concentration. This is true if the initiator efficiency is high. With very low efficiency, f may be proportional to [M], making R_p proportional to $[M]^{3/2}$.

2.4. ABSOLUTE VALUES OF THE RATE CONSTANTS FOR INDIVIDUAL STEPS

If the rate constant for initiator decomposition and the initiator efficiency are known, the ratio of rate constants k_p^2/k_t can be evaluated from the overall polymerization rate from Eq. (2.15) and (2.19)

$$\frac{k_p^2}{k_t} = \frac{2\,Rp^2}{R_i[M]^2} \qquad (2.20)$$

This ratio is often defined as characteristic ratio and also given by the following equation

$$\frac{fk_p^2}{k_t} = \frac{Rp^2}{[M]^2}\,\frac{1}{2k_d[I]} \qquad (2.21)$$

It is, in fact, quite impossible to arrive at a complete resolution of the rate constants for the individual steps by measuring only rates of polymerization under steady-state conditions and degree of polymerization. These rate constants can be separated only by the non steady-state methods. However determination of absolute rate constants from either steady-state or non-steady state kinetics is not possible, since the former only yields the parameter k_p^2/k_t and the latter k_p/k_t. Separation of k_p and k_t from steady-state measurements alone requires an additional measurement of a suitable independent parameter. This parameter is the average "life time" τ_s of an active center i.e. the average time from the creation, or initiation of a radical chain to its ultimate annihilation, disregarding possible intervening transfer processes. [2]

The average life time of free radicals is given by the following relations:

$$\tau_s = \frac{[RM.]}{2k_t[RM.]^2} = \frac{1}{2k_t[RM.]} \qquad (2.22)$$

or from Eq.(2.18)

$$\tau_s = \frac{k_p[M]}{2k_tR_p} \qquad (2.23)$$

If τ_s were somehow determined at the polymerization rate R_p, the ratio k_p/k_t could be calculated from Eq.(2.23) Having previously obtained k_p^2/k_t it becomes possible at once to solve these ratios for the individual velocity constants.

2.5. DEGREE OF POLYMERIZATION AND KINETIC CHAIN LENGTH

The kinetic chain length ϑ is defined as the number of monomer units consumed per active center it is therefore given by R_p/R_i or R_p/R_t.

$$\vartheta = \frac{k_p[M]}{2k_t[RM.]} \qquad (2.24)$$

Eliminating radical concentration by means of Eq. 2.18

$$\vartheta = \frac{k_p^2[M]^2}{2k_tR_p} \qquad (2.25)$$

For initiated polymerization, use of Eq. 2.17 leads to

$$\vartheta = \frac{k_p}{2(fk_dk_t)^{1/2}} \quad \frac{[M]}{[I]^{1/2}} \qquad (2.26)$$

The average degree of polymerization is directly related to the kinetic chain length, ϑ. Assuming termination by combination of radicals as is indicated by experiments previously cited, each polymer molecule formed in a monoradical-initiated polymerization would consist of two kinetic chains grown from two otherwise unrelated primary radicals and the number average degree of polymerization P_n should equal 2 ϑ. If termination were to occur in part by disproportionation, P_n would still be proportional to ϑ but the constant of proportionality would lie between one and two, its exact value depending on the fraction of termination which occurs by combination.

If we consider chain transfer reactions to monomer, solvent as well as to the initiator, the number average degree of polymerization of the polymer chains can be written as follows.

$$P_n = \frac{R_p}{fk_d[I] + k_{tr,m}[M][RM.] + k_{tr,s}[S][RM.] + k_{tr,i}[I][RM.]} \tag{2.27}$$

where the terms in the denominator represent termination by combination and transfer to monomer, solvent and initiator respectively. If termination is by disproportionation the first term becomes $2fk_d[I]$. If transfer constants are defined as

$$C_M = \frac{k_{tr,m}}{k_p} \quad C_S = \frac{k_{tr,s}}{k_p} \quad C_I = \frac{k_{tr,i}}{k_p} \tag{2.28}$$

then (assuming termination by combination)

$$\frac{1}{P_n} = \frac{k_{tr}}{k_p^2} \frac{R_p}{[M]^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_t}{k_p} \frac{R_p^2}{[M]^3} \qquad (2.29)$$

In the case of bulk polymerization, the third term in 2.29 is missing. If in addition the chain transfer C_I is negligibly small one obtains

$$\frac{1}{P_n} = C_M + AR_p \text{ (monoradical line)} \qquad (2.30)$$

$$\text{where } A = \frac{k_t}{k_p^2[M]^2} \qquad (2.31)$$

In other words, for monoradical producing catalysts showing no transfer with the growing radicals, a plot of $1/P_n$ versus R_p should give a straight line; which is termed the monoradical line. [3,9]

2.6. THE STUDIES ON THE KINETICS OF THE POLYMERIZATION OF METHYL METHACRYLATE

2.6.1. Low Conversion Polymerization

Most of the work in the kinetic mechanism of vinyl polymerization by free radicals has been restricted to the so-called ideal region of low conversion and to the determination of the ratio k_p^2/kt and other parameters available from steady-state experiments. B.Baysal and A.V.Tobolsky [3,9] presented a fairly comprehensive study of the bulk polymerization of methyl methacrylate at 60^oC using various initiators. These studies permitted a comparison of the rates of initiation in styrene and methyl methacrylate produced by catalysts 2-azobisisobutyronitrile benzoyl peroxide, tert-butyl hydroperoxide and cumene hydroperoxide. [10] For polymerization of methyl methacrylate, chain transfer constants to monomer and catalyst and catalyst efficiencies were determined.

The following relations were given for the number average degree of polymerization and the intrinsic viscosities of the unfractionated polymethylmethacrylate samples. [11,12]

$$\log \bar{P}_n = 3.261 + 1.256 \log[\eta] \qquad (2.32a)$$

(unfractionated samples, chloroform, 20^oC)

$$\log \bar{P}_n = 3.420 + 1.13 \log[\eta] \qquad (2.32b)$$

(unfractionated samples, benzene, 20^oC)

$$\log \bar{P}_n = 3.2485 + 1.250 \log[\eta] \qquad (2.33)$$

(unfractionated samples, chloroform, 30^oC)

The following kinetic equations were used for the low conversion bulk polymerization of methyl methacrylate [1,3,9]

$$\frac{1}{P_n} = C_{tr,m}+C_{tr,cat}\frac{[I]}{[M]} + C_{tr,s}\frac{[S]}{[M]} + \frac{A'R_p}{[M]^2} \qquad (2.34)$$

$$A= k_t/k_p{}^2\ [M]^2 \qquad (2.31)$$

$$A'= 2k_{td} + k_{tc}/\ k_p{}^2 \qquad (2.35a)$$

$$S^2 = 2k_{td} + k_{tc}/k_p{}^2 \qquad (2.35b)$$

$$A''= k_{tc} + k_{td}/k_p{}^2 \qquad (2.36)$$

$$R_i= (2k_{tc} + k_{td})\ [RM.]^2 \qquad (2.37)$$

$$Rp^2 = [M]^2/2A''\ R_i \qquad (2.38)$$

$$K = -\frac{R_p}{[I]_0{}^{1/2}[M]_0} \qquad (2.39)$$

$$R_i/[I]= 2A''K^2 \qquad (2.40)$$

The values of A', K, $R_i/[I]$ were calculated and tabulated for methyl methacrylate at various temperatures for several initiators.

The following equations were obtained for the values of A' and $C_{tr,m}$ depending on temperature. [19]

$$A' = 2.59 \times 10^{-5} \exp(9.78 \text{ kcal/RT}) \qquad (2.41)$$

The same equation for $C_{tr,m}$ was derived from the values in the Polymer Handbook (J.Brandrup and E.H. Immerqut) by B.Baysal.

$$C_M = 6.29 \times 10^{-4} \exp(-2.15/RT) \qquad (2.42)$$

The values of A' and $C_{tr,m}$ were all obtained from the plots of $1/P_n$ versus R_p using initiator systems which gave straight lines.

2.6.2. High Conversion Polymerization

In many bulk polymerizations, the reaction mixture passes through a viscous stage and finally to a solid. It is particularly difficult to follow the rates of reaction in these high conversion regions by dilatometric or precipitation techniques. Experimental difficulties accompanying operations with "gelled" systems make sampling and the usual kinetic measurements extremely troublesome.

In 1952 M.A.Naylor and F.W Billmeyer [14] described a new apparatus for following the rate of a reaction and presented certain data in the study of photocatalyzed polymerization of methyl methacrylate. Their apparatus has been termed an oblique-line refractometer and it has proved operable over the range of 0 to 100 % conversion with methyl methacrylate. Polymerizations were carried out using benzoin or 2,2'-azobisisobutyronitrile as photacatalysts with light primarily in the 3600 A^0 region. The kinetics in such a system were identical with those of polymerization employing thermal catalysts except for differences which can be attributed to the method of forming chain initating radicals. These latter differences resulted in several interesting effects, which, however were in agreement with generally accepted mechanism of vinyl polymerization.

In the above mentioned study, Naylor and Billmeyer obtained several rate curves [14]. These are given in Fig.(2.1) They illustrate the normal shape of the rate curve for bulk polymerization of methyl methacrylate.

The curve for a first-order dependence of rate upon monomer concentration was calculated from the initial portion of the observed rate curve at 20^0. The following equation was found to explain the results obtained to a first approximation.

$$\frac{-d[M]}{dt} = k_2[M] \left(\frac{k_1[cat]I}{k_3}\right)^{1/2} \qquad (2.43)$$

where [M] = monomer concentration

k_1 = rate constant for chain initiation

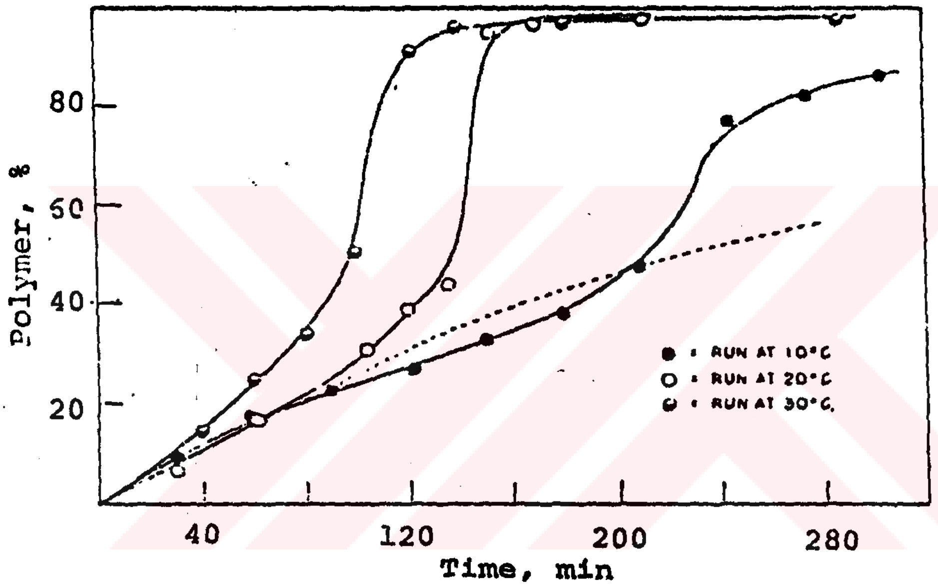


Fig. 2.1 Effect of temperature on rate of photopolymerization of MMA (0.2% benzoin). The dotted curve is the theoretical first-order curve using the initial observed rate constant for the run at 20°. [14]

k_2 = rate constant for chain propagation

k_3 = rate constant for chain termination

[cat] = catalyst concentration

I = light intensity

Significant deviation from the first-order rate curve in Fig (2.1) was noted at about 25 % conversion isothermal conditions were maintained, the hypothesis that the increase in rate is caused by a decrease in chain termination seems most likely. Naylor and Billmeyer also investigated the effect of temperature, catalyst concentration and light intensity on rate of polymerization. They found that the molecular weight increased as the temperature was raised over the range from -27^{o} to $+92^{o}$ other variables held constant as shown in Fig (2.2). They demonstrated the dependence of rate upon the square root of the light intensity for the initial stages of bulk polymerization (up to 30% conversion). The influence of catalyst concentration on rate was quite comparable with the effect of light intensity.

The effect of increasing viscosity on the course of polymerization reactions has been studied for some time. The cause of the acceleration of the polymerization rate often observed has been shown to be due to the decrease in the rate at which polymeric radicals react with each other.

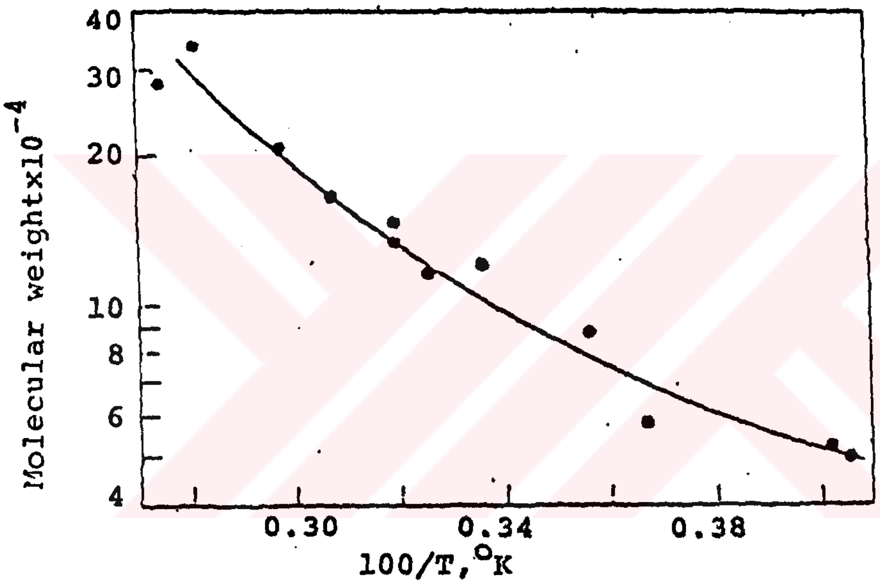


Fig.2.2 Effect of Temperature on Molecular Weight of Photopolymerized MMA. [14]

P.Hayden and Sir Harry Melville [15] dealt with the whole range of polymerization of methyl methacrylate. The apparatus used was similar to that described by Bengough and Melville. [16] The principle was to measure the increase in temperature as a function of time as an exothermic reaction proceeds under adiabatic conditions. The rise in temperature was measured using a copper-constantan thermocouple sealed into a soft glass dilatometer. The signals from the thermocouple were amplified and displayed on a pen-recorder.

Hayden and Melville [15] measured the rate of polymerization and corresponding lifetime in the early stages of the conversion by recording the non stationary state of the polymerization reaction. These measurements were made at 22.5^{o}C. According to experimental results of Hayden and Melville, the rate of polymerization of methyl methacrylate and the lifetime of the kinetic chain gradually increase as the conversion proceeds.

As the conversion proceeds, the physical nature of reaction medium changes from a very viscous fluid to a soft solid. Both the polymerization rate and the lifetime increase as the conversion proceeds. Meanwhile the intensity exponent of the rate decreases from 0.5 to about 0.3. The calculated values of energies of activation of propagation and termination reactions both increase with the extent of conversion. During the later stages of the conversion, i.e. at about 50% monomer consumption, the polymerization rate passes through a maximum and subsequently gradually decreases to zero. The lifetime of the kinetic chain increases as the conversion proceeds, but simultaneously it becomes less dependent on the intensity of the irradiation.

A new study on the free radical polymerization of methyl methacrylate in bulk was performed by R.Sack, G.V.Schulz and G.Meyerhoff. [17] The free radical polymerization of methyl methacrylate in bulk at 0^oC initiated by photochemical decay of azobis (cyclohexanenitrile) (ACN) was tested over the full range of conversion up to the glassy state. Rate constants of propagation, k_p, and termination, k_t, are evaluated by rotating sector technique and after effects. Instantaneous degree of polymerization and efficiencies f, were given for all conversions.

The non-steady state experiments were evaluated together with classical steady-state polymerizations yielding fk_p^2/k_t. For the determination of the ratio k_p/k_t in the low conversion range, intermittent illumination of the reaction by a rotating sector was used. For the more advanced and high conversion regimes the post effect was measured as the decrease of polymerization rate after illumination had been stopped and thus generation of ACN radicals had been stopped.

They used the following relations to calculate R_p and the characteristic ratio fk_p^2/k_t.

$$R_p = \left(\frac{2fk_d k_p^2}{k_t}\right)^{1/2} [I]^{1/2}[M]_x \qquad (2.19)$$

$$\frac{fk_p^2}{k_t} = \frac{R_p^2}{[M]^2_x} \cdot \frac{1}{2k_d[I]} \qquad (2.21)$$

The evaluation of gel chromatographic and light-scattering experiments resulted in cumulative number-and weight-average degrees of polymerization P_n and P_w.

The efficiency f was determined from P_n and $U=P_w/P_n-1$. The number average degree of polymerization P_n and the nonuniformity U were obtained from size-exclusion chromatography (GPC or SEC) on styrene gel (waters and TSK) and controlled pore glass (Rhône-Poulenc) columns in tetrahydrofuran at 25°C using refractive index and U-V absorption detectors to measure the concentration.

The reaction mixtures were sealed in poly(ethylene terephtalate) (PET) bags and placed in osmometer like device consisting of two quartz windows joined to a capillary which was filled with a water-methanol mixture. The fall of meniscus in the capillary allowed the evaluation of the polymerization rate R_p.

These are the first experiments of absolute rate measurements for radical polymerizations proceeding to very high conversion since Hayden and Melvilles who evaluated k_p and k_t for methyl methacrylate at 22.5°C from measurements of the heat of polymerization. The rate constants of Hayden and Melville show similar behaviour, namely, the rate constant of propagation first runs through a minimum, then through a maximum and finally decreases with increasing steepness. Hayden and Melville did not attempt to determine the efficiencies. Therefore their k_p actually corresponds to fk_p. In the study of Sack, Schulz and Meyerhoff, the fk_p values of Hayden and Melville were used for comparison. The curvatures for the plots of fk_p versus conversion (Fig.2.3) for the two different determination methods are qualitatively the same although the minimum and maximum at 22.5°C are more pronounced than for 0°C experiments.

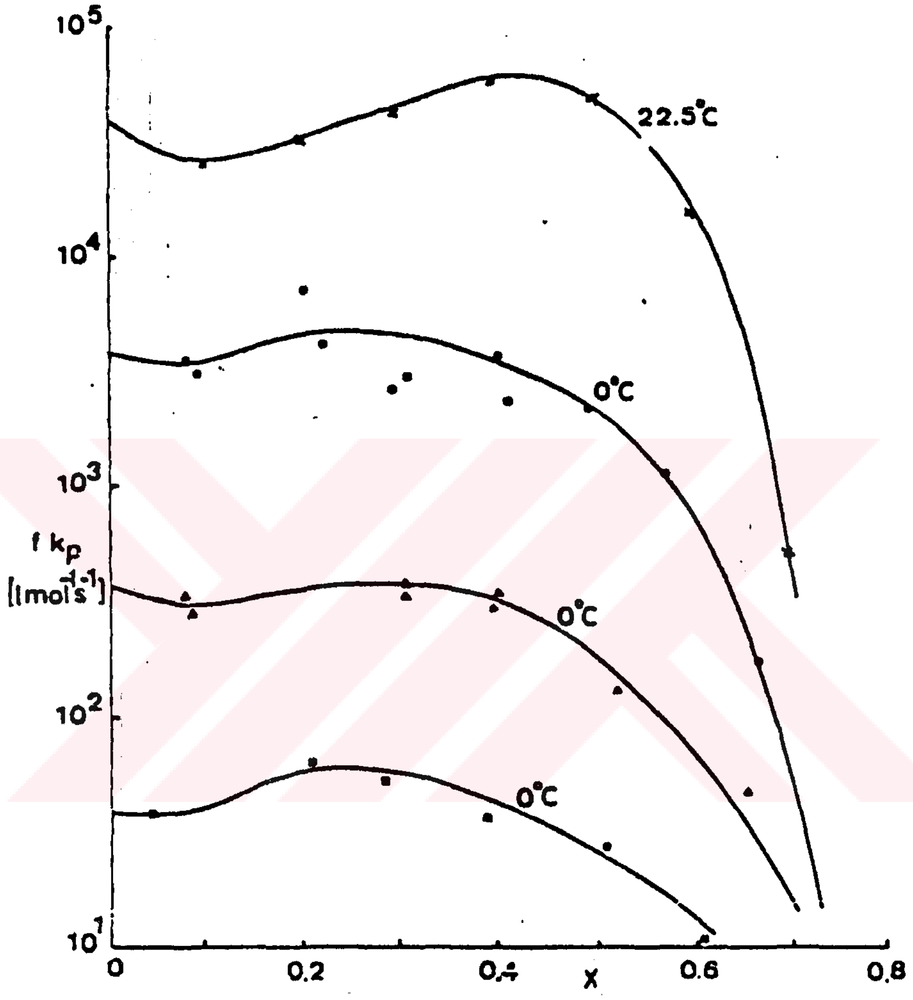


Fig. 2.3 Products fk_p from Hayden and Melville for poly(methyl methacrylate) at 22.5^{0}C and from the work at 0^{0}C with initiation rates: 22.5^{0}C (x), R_i=2.8x10^{-8} mol $L^{-1}s^{-1}$, 0^{0}C (o) R_i=1.0x10^{-8}, (Δ)2.1x10^{-9}, (□)3.5x10^{-10} mol $L^{-1}s^{-1}$.[17].

CHAPTER III

MOLECULAR CHARACTERIZATION OF POLYMER CHAINS

3.1. MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

Polymerization reactions are a compilation of certain random processes. As a result of this behaviour polymeric materials have a molecular weight distribution. A typical situation is shown in Fig (3.1). This figure shows also the approximate positions of the several important average molecular weights yielded by the various experiments. It is important to note the significance of the absolute and relative values of the various average molecular weights in relation to polymer properties. First, the properties of strength, toughness and low sensitivity to chemical attack characteristic of polymers as a class of materials are not well developed until a molecular weight level of around 10,000 is reached. Second, it is possible to obtain information on the breadth of the molecular-weight distribution from the relative values of two different averages. Because of their accessibility, the ratio of the weight molecular weight, M_w, to the number

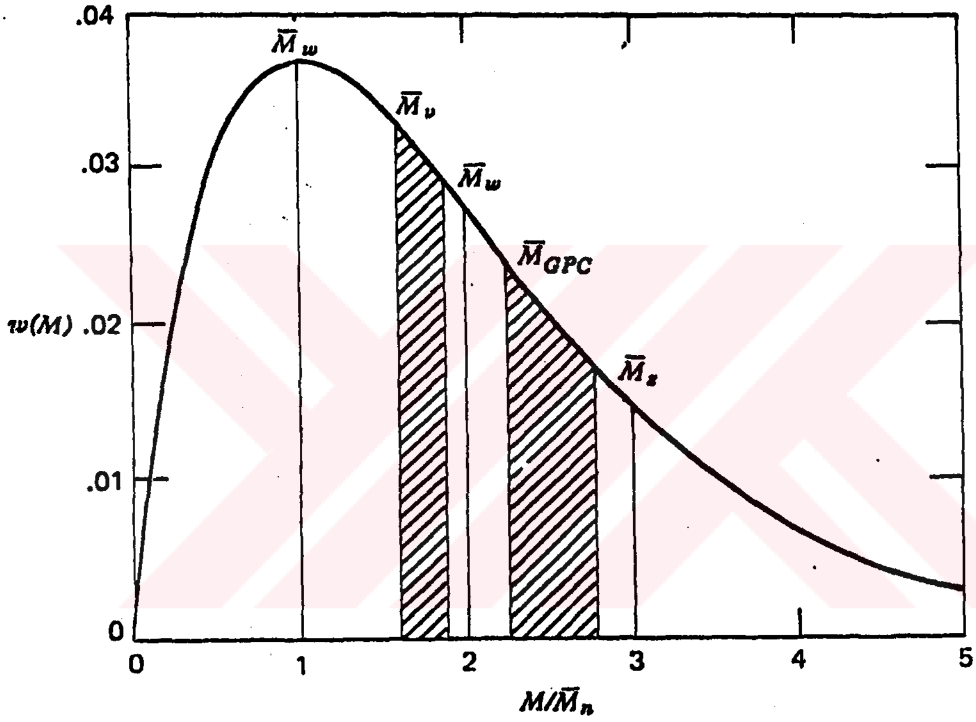


Fig. 3.1 Distribution of Molecular Weights in a Typical Polymer. Showing the Positions of Important Averages. [6]

average, molecular weight, M_n is usually used.

3.1.1. Number-Average Molecular Weight

The number average molecular weight, M_n is the simple counting average in which the mass of the sample, expressed in atomic mass units or daltons, is divided by the number of molecules it contains: $M_n=W/N$. Expressing N as the sum over all species of the number N_i of the molecules of the i th kind, and w similarly as ΣW_i where $W_i=N_iM_i$, the defining equation for the number-average molecular weight is usually written [4]

$$M_n = \Sigma N_iM_i/\Sigma N_i \tag{3.1}$$

Methods for the determination of the number-average molecular weight fall in two categories: chemical or physical methods based on end- group analysis; and those based in measurement of one of the colligative properties, vapor pressure lowering, freezing point depression (cryoscopy), boiling-point elevation (ebulliometry) and the osmotic pressure.

3.1.2. Weight-Average Molecular Weight

The weight average molecular weight defined as

$$M_w = \Sigma N_iM_i^2/\Sigma N_iM_i \tag{3.2}$$

Light scattering and equilibrium ultracentrifugation experiments are the methods to obtain the weight-average molecular weight. In the light scattering experiment, measurement is made of the difference in scattered-light intensity between a polymer solution and its solvent. This scattered intensity depends upon both concentration and the angle between the incident and scattered light beams. The second requirement sets the major design features of light-scattering photometers. [4]

3.2. MOLECULAR SIZE

As a result of the random-coil nature of most synthetic high polymers, the concept of the size of the molecule differs significantly from that of its mass. The use of the term size, is restricted to the description of the amount of space taken up by the molecule, expressed either as a linear dimension or a volume. Since the size, so defined, of a single molecular coil varies with time as a result of conformational changes due to Brownian motion and similarly the molecular size varies from molecule to molecule of identical mass and structure, size can be described only in terms of average properties. Two such average size parameters describing linear dimensions of polymers are the root-mean-square end-to-end distance $(r^2)^{1/2}$ and the radius of gyration $(S^2)^{1/2}$. The former is self-explanatory, and the latter is defined as the root-mean-square distance of the segments of the chain from its center of gravity. When polymer solutions are referred to, the common volume parameter is the hydrodynamic volume, the volume that

the chain appears to occupy based on a specific property, such as the viscosity increase it imparts to the solution. For linear polymers, all these quantities are uniquely related. [4]
For example $r^2 = 6\ s^2$

3.2.1. Dilute-Solution Viscosity Method

Dilute-solution viscosity experiment is a characterization method based on measurement of molecular size. Staudinger (1930) was the first to cite the viscosity of polymer solutions as evidence for their long chain, high molecular-weight character.

Nomenclature of solution viscosity is shown in the Table (3.1). Relative viscosity, n_r is given by the ratio of efflux time for the solution, t, to that of the solvent t_0 strictly, $n_r = \eta/\eta_0$., where the viscosities of the solution and solvent are related to the corresponding efflux times by

$$\eta = ctd - Ed/t^2 \ ; \quad \eta_0 = ct_0 d_0 - Ed_0/t_0^2 \qquad (3.3)$$

where d is the density and C and E are constants for the particular viscometer used. For dilute solutions, d and d_0 are substantially equal, and viscometers are designed so that, for efflux times greater than 100 sec or so, the second terms are negligible.

The specific viscosity can be seen to be the relative increment in viscosity of the solution over that of the solvent,

Table 3.1. Nomenclature of Solution Viscosity

Common Name	Recommended Name	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_0 \cong t/t_0$
Specific viscosity	---	$\eta_{sp} = \eta_r - 1 = (\eta - \eta_0)/\eta_0 \cong (t - t_0)/t_0$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/c)_{c=0} = [(\ln \eta_r)/c]_{c=0}$

and the reduced viscosity is this quantity taken per unit concentration. This is still dependent upon C, however, so extrapolation to c=0 is required. It is convenient to extrapolate not only the reduced viscosity but also the inherent viscosity to c=0. By expanding the logarithm in the defining equation for n_{inh} and observing the behaviour as c——o. It is easy to demonstrate that both quantities extrapolate to the same intercept, denoted the intrinsic viscosity $[\eta]$(always written with square brackets). The unit of η_{red}, η_{inh}, and $[\eta]$ can be seen to be reciprocal to those of concentration, and are dl/g, since η_r and η_{sp} are dimensionless ratios.

The families of straight lines obtained in these extrapolations, for a series of polymer samples differing only in molecular size have slopes which are not constant but vary in a regular way, increasing as $[\eta]$ increases. They are described by no theory, but by several sets of purely empirical equations of which are used only those due to Huggins (1942).

$$\eta_{sp/c} = [\eta] + k'[\eta]^2 c \qquad (3.4)$$

and Kraemer (1938)

$$(\ln \eta_r)/c = [\eta]+k''[\eta]^2c \qquad (3.5)$$

where k' and k" are known as the Huggins and Kraemer constants, respectively. For all but unusual cases, k" is negative, and often $k'-k''\cong 0.5$ Staudinger's equation implies that the reduced viscosity is independent of concentration, which is known to be in error. He wrotes, $\eta_{sp}=KcM$, where K is a constant which he could evaluate from measurements on oligomers of known molecular weight. Later work has demonstrated that Staudinger's equation must be modified by raising M to a power a, usually between 0.5 and 0.8, yielding the equation

$$[\eta] = \kappa M_v^a \qquad (3.6)$$

which is usually attributed to Mark, Houwink and Sakurada. Schaefgen and Flory [25] gave the viscosity average molecular weight by the following equation [4,6]

$$\bar{M}_v = [\Sigma N_i M_i^{1+a}/\Sigma N_i M_i]^{1/a} \qquad (3.7)$$

It can be seen that the value of this average and its relation to others depend on a, a measure of polymer solvent interactions. Since M_v is not available from other experiments one often substitutes M_w for it, as the nearest directly measurable average of course for a monodisperse polymer all averages would be identical, allowing κ and a to be determined with ease; but such samples are not usually available. Extensive tables of κ and a are available (for example Kurata 1966 [23]) but caution is required in using these sources since they are not selective, though reasonably comprehensive.

The empirical correlation between $[\eta]$ and molecular weight is subject to several restrictions, which become understandable in the light of the fundamental dependence of the intrinsic viscosity on molecular size instead of mass. Only if there is a unique relationship between size and mass Eq.(3.6) can be expected to hold. This requires the polymer be linear, not branched; that the polymer solutions be measured in the same solvent and at the same temperature for which κ and a were determined; and that the polymer be of the same chemical type as that used in determining κ and a. It should be noted that, since $[\eta]$ depends upon the solvent and temperature, its specification is incomplete unless these quantities are given as well as units.

The most useful theory relating the intrinsic viscosity to molecular size is that of Flory [20,21,22] The most important relation is

$$[\eta]\, M = \Phi_0 \; V_h = \Phi_0\, \xi^3\, (\bar{S}^2)^{3/2} \qquad (3.8)$$

where V_h is the hydrodynamic volume, Φ_0 is a universal constant with the value $2.8\mathrm{x}10^{21}$ if V_h is expressed ml and $[\eta]$ in dl/g.

In order to relate the product $[\eta]M$ to a more familiar size parameter such as the radius of gyration $(S^2)^{1/2}$, another parameter, ξ, which depends upon solvent power, should be introduced. Perhaps the greatest value of Flory's viscosity theory lies in its interrelations with his theories of the configuration of real polymer chains and the thermodynamics of polymer solutions. The dimensions of the polymer chains are determined both by short-range interactions, which can be predicted by calculation, and by long-range interactions. The latter contributions depend upon the polymer-solvent interactions and described by an expansion factor α, the ratio of the chain dimension in a given solvent and at a specified temperature to its value in the absence of such interactions (unperturbed dimensions): $\alpha=(S^2/S_0{}^2)^{1/2}$, for example. The unperturbed dimensions of polymers vary in a known way with molecular weight, such that quantities of the type $S_0{}^2/M$ depend only on chain structure (chemical type) and not on solvent or temperature.

Use can be made of these facts by replacing S^2 by $\alpha^2 S_0{}^2$ and isolating the term in $S_0{}^2/M$

$$[\eta] = \Phi_0 (S_0{}^2/M)^{3/2} M^{1/2} \xi^3 \alpha^3 = KM^{1/2} \xi^3 \alpha^3 \qquad (3.9)$$

where $K = \Phi_0(S^2/M)^{3/2}$ is a constant for a given polymer, independent of solvent, temperature, and molecular weight. The dependence of ξ on solvent power is given by Ptitsyn [24] as

$$\xi^3 = \xi_0^{\,3}\ (1-2.63e + 2.86\ e^2), \tag{3.10}$$

where e is a parameter which can be related to other measures of solvent power, for example the exponent a in Eq.(3.6): e=(2a-1)/3. The value of ξ_0, referring to the unperturbed state of the chain, is independent of solvent power and can be incorporated into K.

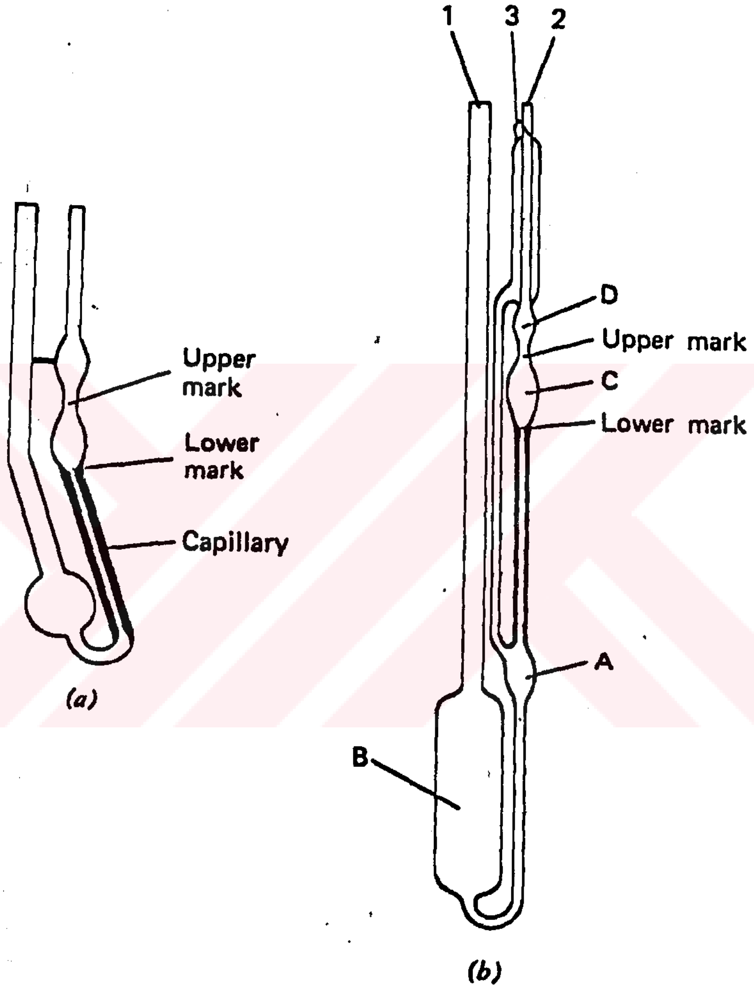
Several limititations to the empirical correlation of [η] with M instead of molecular size were mentioned above. In addition, it should be noted that the viscosity of polymer solutions is dependent upon shear rate in the viscometer.

In contrast to other characterization methods, viscometry requires only the simplest apparatus: one or more glass capillary viscometers, a constant-temperature bath, and a timer good temperature control is essential; variations of solution temperature during the experiment must be kept below 0.01-0.02^{o}C. In most instances, the measurement of efflux times is carried out by visiual observation of the passage of the liquid meniscus past two lines marked on the viscometer at which times a stop watch or electric timer is started and stopped. There are automatic timers and systems which automatically prepare dilutions from a stock solution, clean and fill a viscometer, and obtain the efflux times. They are considerably more precise but are expensive and have the disadvantage that they provide timing for only one viscometer at any moment.

There are two types of viscometer in wide use, shown in Fig(3.2) The simplier Cannon-Fenske viscometer is a constant-volume device, whereas in the Ubbelohde instrument, the effluent from the capillary flows into a bulb separate from the main liquid reservoir so that the viscometer operates independent of the total volume of liquid present. This allows the convenience of preparing and measuring solutions having a range of concentrations without the need of transferring them. [4]

3.3. MOLECULAR WEIGHT DISTRIBUTION: GEL PERMEATION CHROMATOGRAPHY (GPC)

To obtain information about the molecular-weight distribution, other than through comparison of two or more average molecular weights, it is necessary to separate the molecular species in a sample by some sort of fractionation process, and to determine the amounts and molecular weights of all the fraction. From these data, the distribution curve (like that of Fig.3.1) can be plotted and the various average molecular weights calculated. The separation and determination steps may be carried out independently, or be combined, as in a chromatographic process with



(a)

(b)

Fig.3.2 Capillary Viscometers Commonly Used for Measurement Used for Measurement of Dilute-Solution Viscosity: (a) Cannon-Fenske; (b)Ubbelohde. [6]

suitable calibration such as gel permeation chromatography or in the ultracentrifuge.

Chromatographic processes may be defined as those in which the solute is transferred between two phases, one of which is stationary and the other moving, often traversing along tube called a column.

Polymer molecules are separated by size in the GPC experiment because of their ability to penetrate part of the internal volume of the gel particles, that is, stationary phase. As the sample moves along the column with the mobile phase, the largest molecules are almost entirely excluded from the stationary phase, while the smallest (with a properly chosen gel) find almost all the stationary phase accessible.

The smaller the molecule, the more of the stationary-phase volume is accessible to it, and the longer it stays in that phase. Small molecules thus fall behind larger ones, and are eluted from the column later. For large molecules completely excluded from the gel, the retention volume V_r is equal to the mobile phase volume V_0, whereas for very small molecules, for which the entire stationary phase is accessible, $V_r=V_0+V_i$, where V_i is the internal pore volume of the gel, that is, the stationary-phase volume.

Little use is made of this theory in the practice of GPC, however since V_r cannot yet be predicted from molecular parameters.

Instead, calibration curves are prepared by running standards of known molecular weight and narrow molecular weight distribution, and preparing a plot of log molecular weight versus retention volume. By experience, it is found that this plot is often nearly linear over a range of molecular weights which, depending upon the selection of the gels used, can be quite wide.

A new and different molecular weight, which is called the "GPC-average" is defined by this process.

$$\bar{M}_{GPC} = \sum_{i=1}^{\infty} W_i M_i^{1+a} \;/\; \sum_{i=1}^{\infty} W_i M_i \qquad (3.11)$$

The GPC-average molecular weight is equal to M_z if a=1 and is somewhat greater than M_w if a=0.5

$$\bar{M}_z = \sum_{i=1}^{\infty} N_i M_i^3 \;/\; \sum_{i=1}^{\infty} N_i M_i^2 = \sum_{i=1}^{\infty} W_i M_i^2 \;/\; \sum_{i=1}^{\infty} W_i M_i \qquad (3.12)$$

Many of the limitations of GPC method stem from the fact that separation is based upon molecular size, not the molecular weight. For linear homopolymers, this leads to difficulties in absolute calibration techniques, which are partially overcome by making the calibration in terms of hydrodynamic volume. The problem of branched polymer can be simplified by use of the universal calibration technique, but no complete interpretation in terms of molecular-weight distribution is possible. [2,4]

CHAPTER 4

EXPERIMENTAL WORK

4.1. MATERIALS

4.1.1. Methyl methacrylate (MMA)

Methyl methacrylate was obtained from Fluka Chemika Company of Switzerland. It was purified by several washings with 5% aqueous sodium hydroxide, followed by many washings with distilled water to remove basic solution. Subsequent to drying with anhydrous calcium chloride, the material was distilled at vacuum (100 mmHg and 40^{0}C) It was stored +4^{0}C during the experiments.

4.1.2 2,2'-Azobisisobutyronitrile,

AIBN, was obtained from Fluka Chemika Company of Switzerland. It was recrystallized twice from chloroform and methanol, then dried in a vacuum oven at room temperature for two days. It had the melting point of 102-104^{0}C.

4.1.3. Chloroform

Chloroform, from Fluka Chemika Company of Switzerland was analytical reagent of boiling point 61.2°C. It was used as a solvent of poly(methylmethacrylate) during the experiment and viscosity measurements.

4.1.4. Methanol

Commercially supplied methanol was used in the precipitation of the polymer. It had a boiling point of 62-63.5°C and used without further purification.

4.2. EXPERIMENTAL SET-UP

The experimental set-up used for this study consisted of two constant temperature baths controlled by thermoregulators. A vacuum distillation apparatus, an Ubbelohde type viscometer, a vacuum oven, Nitrogen gas cylinder with pressure regulators and other auxilary equipment such as syringe needles, stop watches, erlenmayer flasks, rubber caps, sintered glass-filters and various thermometers.

4.2.1 Constant Temperature Water Baths

The polymerization reactions and the viscosity measurements were performed in constant temperature water baths. The temperatures of these thermostats were controlled ±0.5^{o}C by means of electronic regulators.

4.2.2 Vacuum Distillation Apparatus

Vacuum distillation was used in the purification of monomeric methyl methacrylate. The operation pressure was about 100 mm Hg and the boiling point of MMA at this pressure was 39-40^{o}C. The diagram of distillation apparatus is shown in Fig 4.1

4.2.3. Drying apparatus: Vacuum Oven

Removal of solvent in the polymer samples were carried out in the vacuum oven from Dedeoğlu A.Ş. There were a temperature control system and manometer on the oven. The pump to provide vacuum in the oven was from Germany.

4.2.4. Ubbelohde Viscometer

Intrinsic viscosities were determined by using an Ubbelohde type viscometer (Cannon 75 D 88). It is shown in Fig (3.2) Ubbelohde viscometer used during the experiments was independent of total volume of solution therefore it had the advantage of being useful as dilution viscometer, namely solutions prepared at different concentrations were measured in situ.

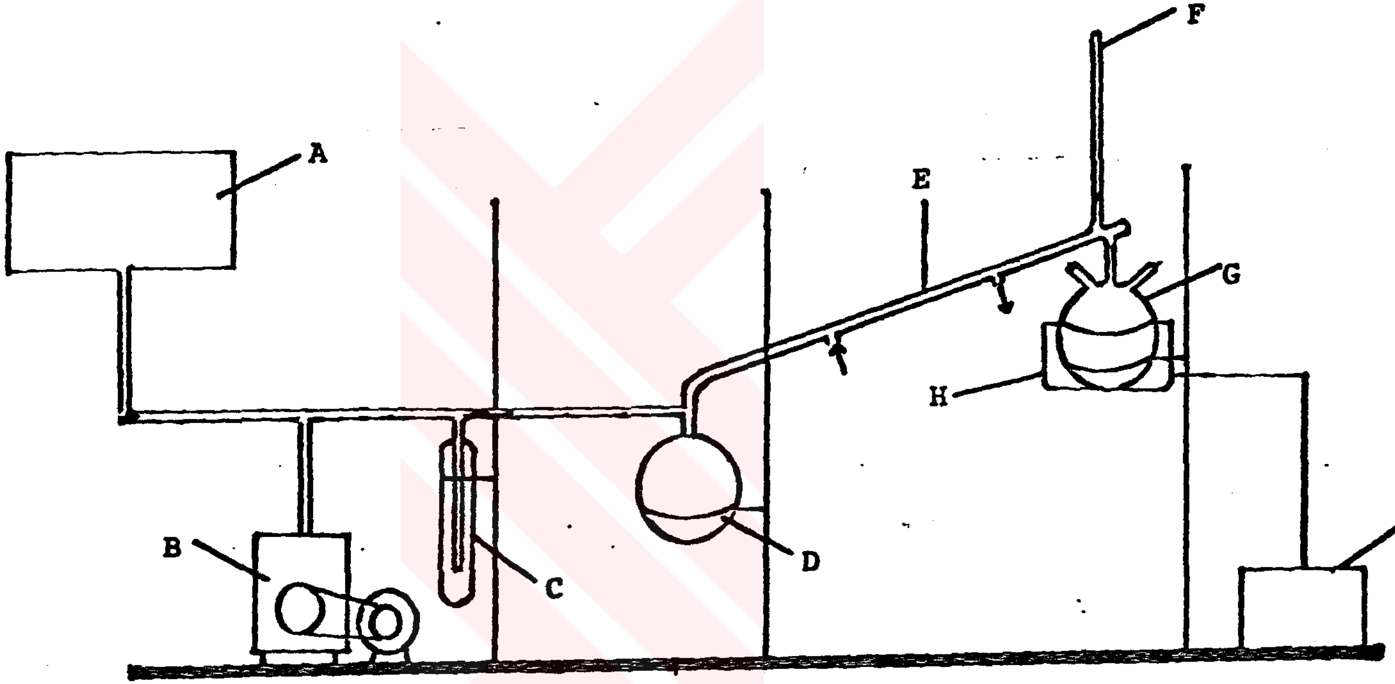


Fig.4.1 Sketch of the Components of the Vacuum Distillation Apparatus.
A:Manostat pressure regulator
B:Vacuum pump
C:Cold trap
D:Sample collector
E:Condenser
F:Thermometer
G:Distillation flask
H:Heating mantle
I:Heater

4.2.5. Nitrogen gas cylinder

Nitrogen gas was used as an inert gas in the polymerization reactions. Air is flushed out by purging through syringe needles and filling the flasks with an inert nitrogen gas.

4.3. EXPERIMENTAL PROCEDURE

4.3.1. Purification of Monomer

Methyl methacrylate was purified by washing with 5% aqueous sodium hydroxide solution. The inhibitor, such as hydroquinone or t-butylpyrocatechol, was removed by this procedure. The monomer was then washed with distilled water three times.

Anhydrous calcium chloride was used as the drying agent. It was added into the purified monomer. After the above mentioned purification step, methyl methacrylate was distilled in vacuum. The operating pressure and temperature 100 mmHg and 39-40^{0}C in the vacuum apparatus. The monomer was stored at +4^{0}C during the experiments.

4.3.2 Recrystallization of Initiator,

2,2'-Azobisisobutyronitrile, AIBN, was dissolved in chloroform and methanol by heating slightly and cooled in refrigerator. The procedure was repeated twice. AIBN was then dried in vacuum oven at room temperature for two days. The melting point of AIBN was 102-104 °C. It was then stored in refrigerator.

4.3.3 Polymerization of Methyl Methacrylate

The free-radical polymerization of methyl methacrylate was initiated by 2-2' azobisisobutyronitrile. Conversions at various time intervals were determined. The experimental procedure is as follows: The initiator, AIBN, was weighed in a clean, dry erlenmayer flask, and certain amount of MMA was then added. The concentration of monomer was 9.369 mol/lt at 22.5°C. Polymerization was carried out in 25 ml erlenmayer flask sealed with a rubber cap. Air was flushed out by purging with an inert nitrogen gas through syringe needles. This is shown in Fig.(4.2)

Then the flask, was transferred to a constant temperature water bath regulated at 22.5 ±0.5°C. After the proper reaction time, the polymerization flasks were removed from the bath and cooled, with water. The content of the flask was diluted with toluene or chloroform, for the samples containing high amounts of polymer, solution procedure took several days.

The dissolved polymer was then precipitated in methanol. The precipitated polymer was collected on sintered-glass filters and dried in the vacuum oven at 60-65°C for 1 or 2 days. Then it was weighed to determine the conversion of monomer into polymer. The weighed polymer was stored for viscosity measurements to determine

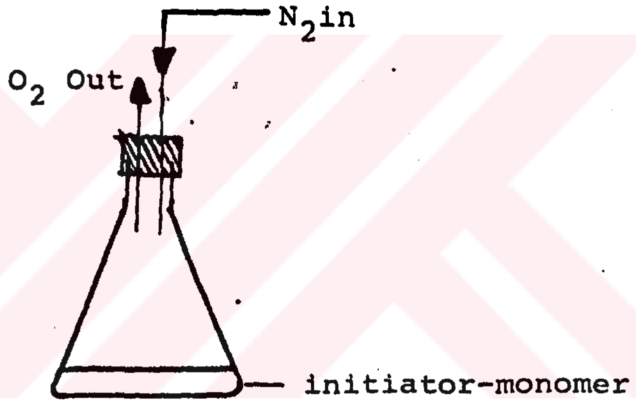


Fig 4.2 Polymerization Flask Filling with N_2

the intrinsic viscosity. The above procedure was repeated for different reaction times.

4.4. CONVERSION CALCULATIONS

The conversion of monomer to polymer was given by the following equation:

$$X = \frac{[M]_0 - [M]}{[M]_0} \qquad (4.1)$$

In this equation $[M]_0$ and $[M]$ are the concentrations of monomer at the beginning and at any reaction time, respectively. The unit of concentration is expressed as mol/liter.

If the dimensional analysis of both numerator and the denominator are made the following equations can be obtained

$$X = \frac{[M]_0(\text{mol/L}) - [M]\ (\text{mol/L})}{[M]_0\ (\text{mol/L})} = \frac{[M]_0(\text{mol}) - [M](\text{mol/L})}{[M]\ (\text{mol/L})}$$

If both numerator and denominator are multiplied by M_0, molecular weight of the monomer, the ratio is not changed. Hence,

$$X = \frac{[M]_0(\text{mol}) x\ m_0\ (\text{g/mol}) - [M](\text{mol}) x\ m_0(\text{g/mol})}{[M]\ (\text{mol}) x\ m_0\ (\text{g/mol})}$$

Here, $[M]_0 x\ m_0$ = Initial mass of monomer (grams)

$[M] x\ m_0$ = Mass of monomer at any time of reaction (grams)

So, the difference between initial mass of monomer and the mass of monomer at any time will give the amount of polymer which is obtained. Therefore the equation can be used in the following simile form:

$$X = \frac{\text{Polymer obtained (g)}}{\text{Initial monomer load (g)}}$$

4.5. INTRINSIC VISCOSITY AND MOLECULAR WEIGHT DETERMINATIONS

The molecular weights of the polymer samples at each conversion were determined by using dilute solution viscosity method. An Ubbelohde type viscometer at constant temperature water bath regulated at 25°C was used, shown in Fig.3.2. Firstly, the dilute solutions 0.5 g polymer /100 ml $CHCl_3$ solution) of samples were prepared. The efflux times of the solutions at 25°C in this type of viscometer were determined. The several dilutions of the solutions were carried out in the viscometer, hence the several efflux times of the different concentrations would be measured. Specific viscosities of each concentration were determined from the following relation:

$$\eta_{sp} = \frac{t-t_0}{t_0} \qquad (4.2)$$

Here, t and to are the efflux times of the solution and the solvent (chloroform) respectively.

η_{sp} values of each concentrations were used to calculate μ_{sp}/c values and from the graph of μ_{sp}/c vs concentration (c) the intercept, $[\eta]$ intrinsic viscosity was determined. These graphs can be seen in Fig.A1, Fig.A2, Fig.A3, Fig.A4 given in the appendix, for some of the polymeric samples obtained at different conversions.

$$\text{limit } (c \rightarrow o)\ \eta_{sp}/c = [\eta]$$

The following equations were used to calculate the molecular weight of the poly(methylmethacrylate) dissolved in chloroform at 25^{o}C. [7,9,12]

ii) $\log P_n = 3.261 + 1.256 \log [\eta]$ (2.32a)

i) $\log P_n = 3.2485 + 1.250 \log [\eta]$ (2.33)

iii) $M = M_0 \times P_n$ (4.3)

where P_n is the number average degree of polymerization, M_0 is the molecular weight of the monomer and M is the molecular weight of the polymer.

CHAPTER 5

RESULTS AND DISCUSSION

In this work, the free radical bulk polymerization of methyl methacrylate was studied at 22.5°C. Polymerization reactions were initiated by thermal decomposition of 2,2'-azobisisobutyronitrile. The reactions were carried out over the full range of conversion up to glassy state.

The polymerization temperature was choosen as 22.5°C in order to compare experimental results with photo-initiated free radical polymerization reactions. [15]

The overall kinetic characteristics of methyl methacrylate polymerization have been shown to be due to the changes in the kinetics of elemantary reactions involved. The polymerization seemed to fall into three stages. Fig(5.1) represents the increase of percent-conversion, x, with time, t, for the initiator concentration $[I]_0$=0.0569 (mol L^{-1}). The initial stage of the reaction may be considered to hold up to about 15% conversions.

After about 15% conversions, the rate of polymerization is rapid until the conversion reaches to about 70% conversions. After this point the overall rate of polymerization becomes slow, due to the fact that the polymer-monomer mixture has reached to the glassy state. The value of limiting conversion is about 80% at the reaction temperature of 22.5°C.

The value of conversions for the bulk polymerization of methyl methacrylate were calculated from the following equation; (section 4.4)

$$X = \frac{[M]-[M]_0}{[M]_0} \qquad (4.1)$$

For the initial stage of polymerization certain kinetic parameters were determined by using the following relations, (section 2.6.1)

$$A' = 2k_{td} + k_{tc} / k_p^2 \qquad (2.35a)$$

$$C_{tr,m} = k_{tr,m}/k_p \qquad (2.28)$$

$$\frac{1}{P_n} = C_M + \frac{A'}{[M]^2} R_p \qquad (2.30)$$

In order to obtain molecular weight and the number average degree of polymerization, P_n, for unfractional polymeric samples, we carried out dilute-solution viscosity measurements. Intrinsic viscosities (deciliters per gram) were determined in chloroform at 25°C, P_n values were calculated by using the following relations. B.Baysal and A.V.Tobolsky [9]

$$\log \bar{P}_n = 3.261 + 1.256 \log [\eta] \qquad (2.32a)$$

and by T.E.Ferington and A.V.Tobolsky [12]

$$\log \bar{P}_n = 3.2485 + 1.250 \log [\eta] \qquad (2.33)$$

P_n values were obtained taking the arithmetic mean of those values calculated from the above equations, (2.32a) and (2.33)

A plot of $1/P_n$ versus R_p yielded a straight line for initial stage of polymerization, as shown in Fig (5.2) A' value calculated from the slope of this straight line is 303. The intercept of the line is equal to $C_{tr,m}$ and found to be $5.6x10^{-5}$. $C_{tr,m}$ is rather small its experimental determination by this method is not too precise. However both constants, A' and $C_{tr,m}$ evaluated in this study are in the range of the results compiled from various literature sources. In Table (5.1), A' and $C_{tr,m}$ for methyl methacrylate at 20,22.5,25 30°C were tabulated. [12]

Table 5.1. A' and $C_{tr,m}$ Methyl Methacrylate at 20,22.5,25,30°C

T,°C	A'	$C_{tr,m}$	Initiator	Ref.
20	311	$3x10^{-6}$	Azo	[12]
22.5	303	$5.61x10^{-5}$	Azo	This work
22.5	-	$6.26x10^{-5}$	-	(*)
25	292	$1.5x10^{-5}$	Azo	[12]
30	176	$1.2x10^{-5}$	Azo	[12]
30	193	$1.5x10^{-5}$	Azo	[12]

(*) The value of $C_{tr,m}$ was calculated from Eq. (2.42)

Additional kinetic analysis were performed by considering the following relation [17], given in section (2.6.2)

$$R_p = \left(\frac{2fk_d k_p^2}{k_t}\right)^{1/2} [I]^{1/2}[M]_x \qquad (2.43)$$

$$\frac{fk_p^2}{k_t} = \frac{R_p}{[M]_x^2} \cdot \frac{1}{2k_d[I]} \qquad (2.21a)$$

In Fig.(5.3) the ratio $R_p/[M]_x k_d^{1/2}$ is shown as a function of $X[M]_0$ where k_d is the rate constant for the decay of initiator, 2,2'-azobisisobutyronitrile (AIBN), and $[M]_x$ is the monomer concentration at conversion x.

The overall rate expression for decomposition of this azo compound is given by J.P.Van Hook and A.V.Tobolsky [18] The value of k_d was calculated as $2.613x10^{-8}$ sec^{-1} at 22.5°C

$$k_d = 1.58x10^{15} \text{ exp. } (-30.8 \text{ kcal/RT})$$

As can be seen in Fig(5.3), the overall rate of polymerization R_p shows a slight decreases for low conversion as it was observed in photopolymerization of methyl methacrylate at 0°C [17]. This slight decrease in R_p is followed by a slowly accelerating increase, starting at or below the point of entanglement of polymer chains. This is in constrast with the accepted theory that the increase of R_p with conversion, results only from the restriction in mobility of the growing radicals.

The rate of propagation during radical polymerization is chemically determined as long as there are molecules readily available for the radical chain ends of the growing polymers. This will be true for the first stages of polymerization. However, for the second stage of polymerization where the acceleration takes place we have to consider diffusion controlled reactions, in between monomer molecules and growing polymeric radicals.

As mentioned above, with the onset of entanglement a distinct increase of the rate of polymerization is observed resulting from a diffusion hindrance for termination reaction.

Because of the increasing viscosity of the reaction mixture, two radical chain ends need more and more time to come close enough to react. The self-diffusion of the end segments of the polymer radicals should govern this process and results in well-known increase of chain length.

Experimental set up in this work does not permit us to obtain precise data for the second stage of reaction. This can be seen from Fig.5.3.

The ratio of fk_p^2/k_t were also evaluated by using usual steady-state assumption and first order dependence of rate upon monomer concentration, given by equation (2.21a) Figure 5.4 shows the behaviour of this characteristic ratio, fk_p^2/k_t as a function of $X[M]_0$ for a given initiator concentration.

The characteristic ratio, fk_p^2/k_t first runs through a maximum and finally decreases with increasing steepness toward the glass point. Sack, Schulz and Meyerhoff discussed the same qualitative behaviour of k_p as function of conversion at 0^0C for photopolymerized MMA. [17] They reported that this phenomenon has been expected to be connected with the self-diffusion coefficient of translation of monomer. They showed this fact, for the first time, by using experimental k_p values obtained from non-steady state measurements.

As can be seen from Fig.5.4 after passing the maximum fk_p^2/k_t decreases more and more rapidly with conversion and finally approaches to the glassy state where reaction system consists mainly of dead polymer chains, some polymer radicals and some monomer. Fig.5.3. shows that, R_p then becomes extremely slow during last stages of conversion the remaining mobility of monomer should govern chain propagation. This mobility is represented by the self diffusion coefficient of the monomer in the reaction mixture.

The technique used in this study was not capable of evaluating the rate constants, k_p and k_t by a direct measurement. If rotating sector technique or the observation of post effect were used, k_p/k_t ratio would be derived. From k_p/k_t and k_p^2/k_t the single rate constants could be evaluated. However, the qualitative behaviour of k_p and k_t as a function of conversion can be observed from the plot of fk_p^2/k_t as mentioned above.

Fig.5.5 shows the number average degree of polymerization P_n versus conversion x. P_n values of polymeric samples are rather constant at the beginning and at the end of the polymerization process. With the onset of entanglement due to the Trommsdorf effect, the increase of the degree of polymerization becomes very pronounced. For the polymers obtained at the glassy state the number-average degree of polymerization seems to be constant. Since we have not measured the weight average molecular weights we are not in a position to say anything about the degradation of polymeric chains.

Finally, in this study, the efficiency f, the kinetically effective fraction of the initiator radicals formed, calculated from the following equation.

$$f = \frac{A'R_p{}^2}{2[M]^2{}_x[I]k_d} \qquad (2.21b)$$

where $A' = \dfrac{k_t}{k_p{}^2}$

The value of f was calculated for the initial stage of polymerization reaction; and it was found to be 0.472 for A'=303, $R_p{}^2$ = 3.305x10^{-10} (mol/Ls)^2 $[M]_x$ = 8.452 (molL^{-1}) [I]=5.684x10^{-2} (molL^{-1}) and k_d=2.613x10^{-8} sec^{-1}. The other values of f calculated for low conversions were close to unity.

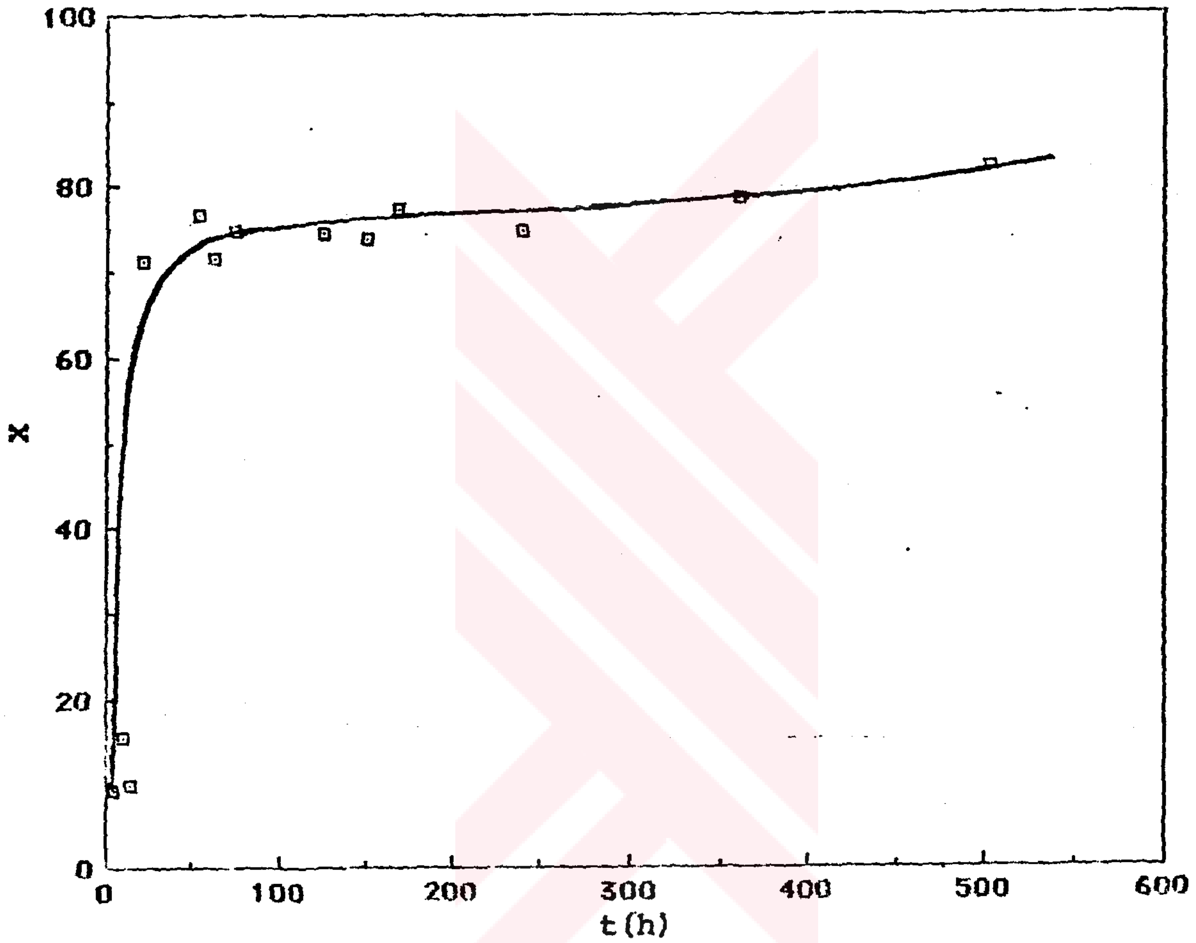


Fig. 5.1 Polymerization of Methyl Methacrylate at 22.5°C. Conversion x versus time for $[I]_0 = 5.69\times10^{-2}$ mol L^{-1}

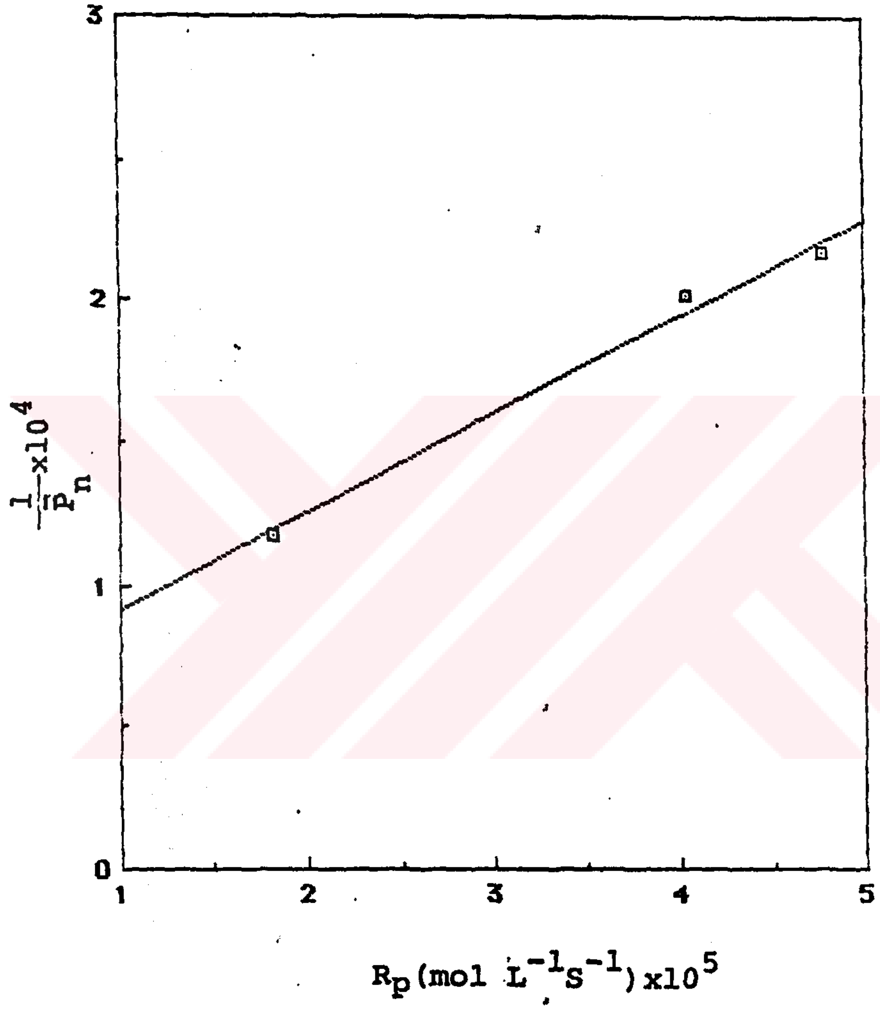


Fig. 5.2 1/P_n versus R_p for Methly Methacrylate Initiated by 2,2'-Azobisisobutyronitrile at 22.5°C

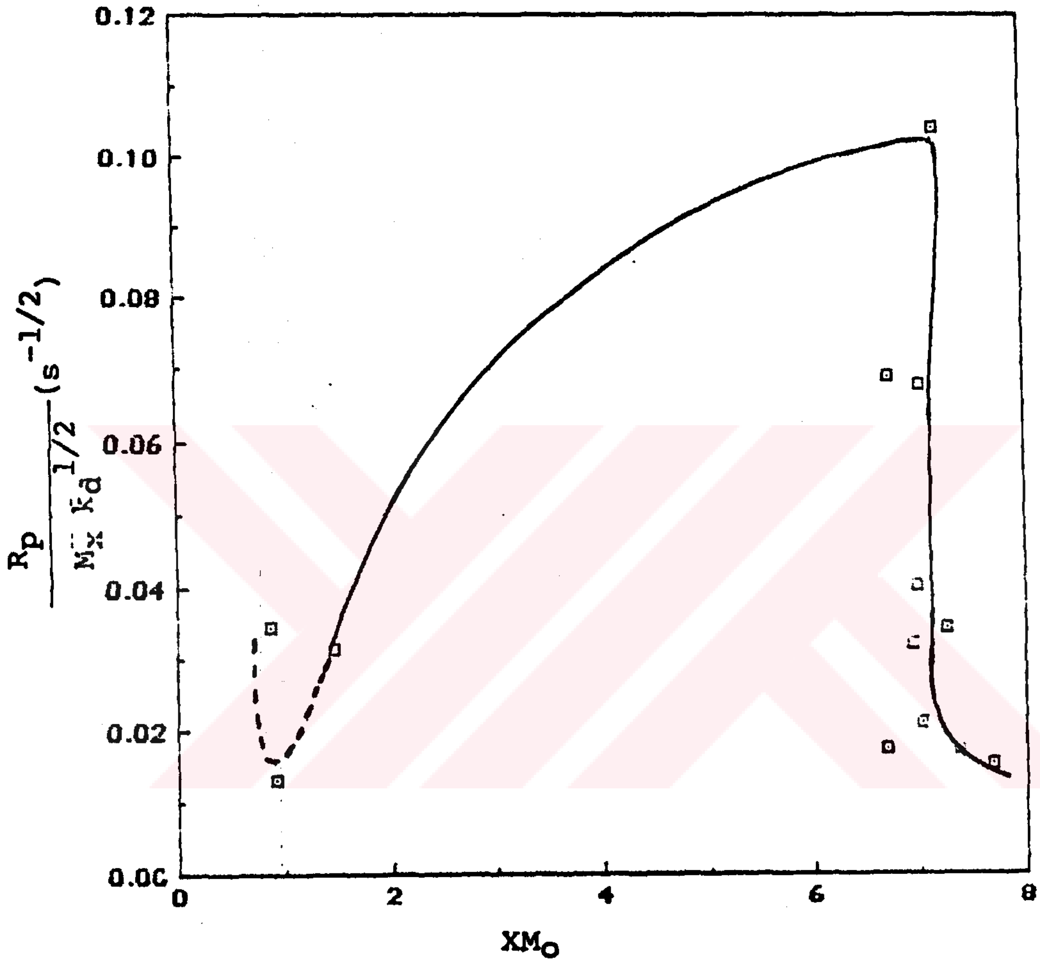


Fig. 5.3 Overall rate of polymerization reduced for consumption of monomer and variation of k_d as a function of conversion.

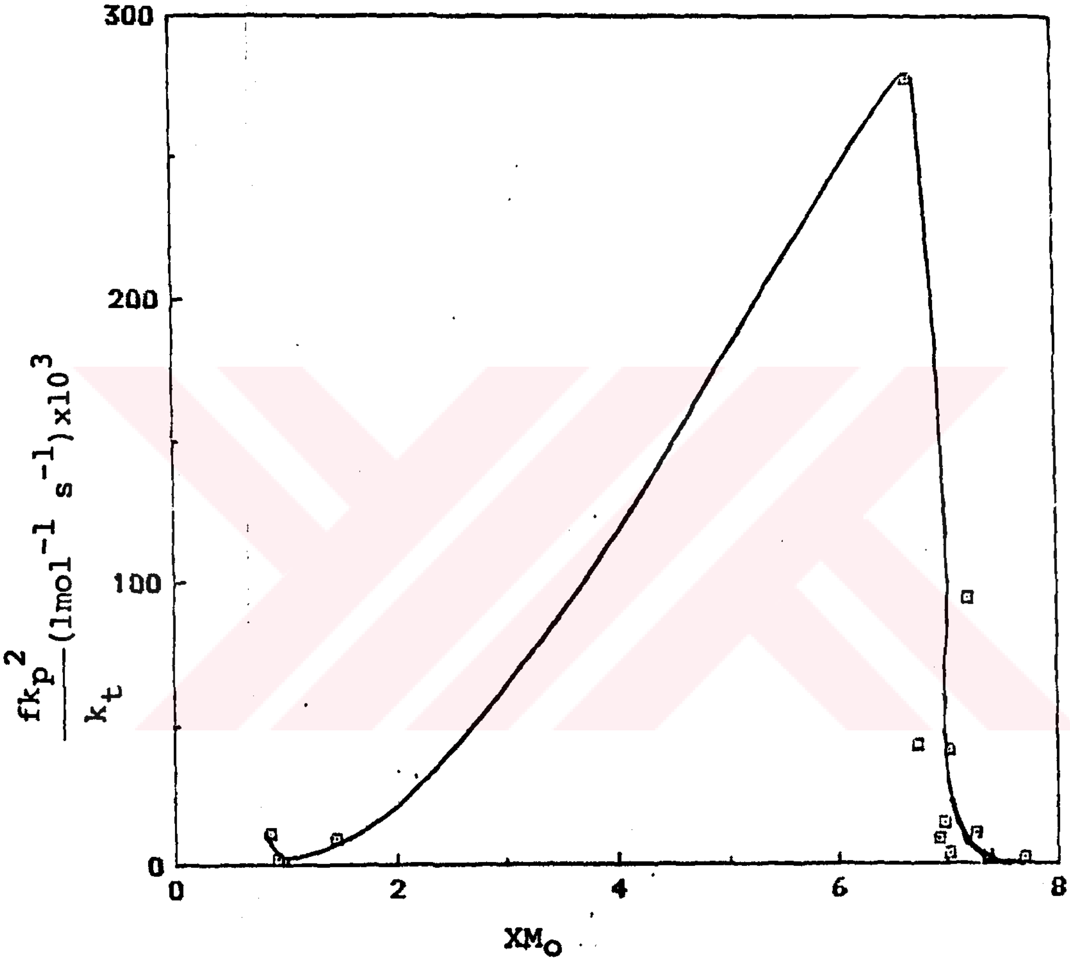


Fig. 5. 4 Characteristic Ratio fk_p^2/k_t as a Function of Conversion

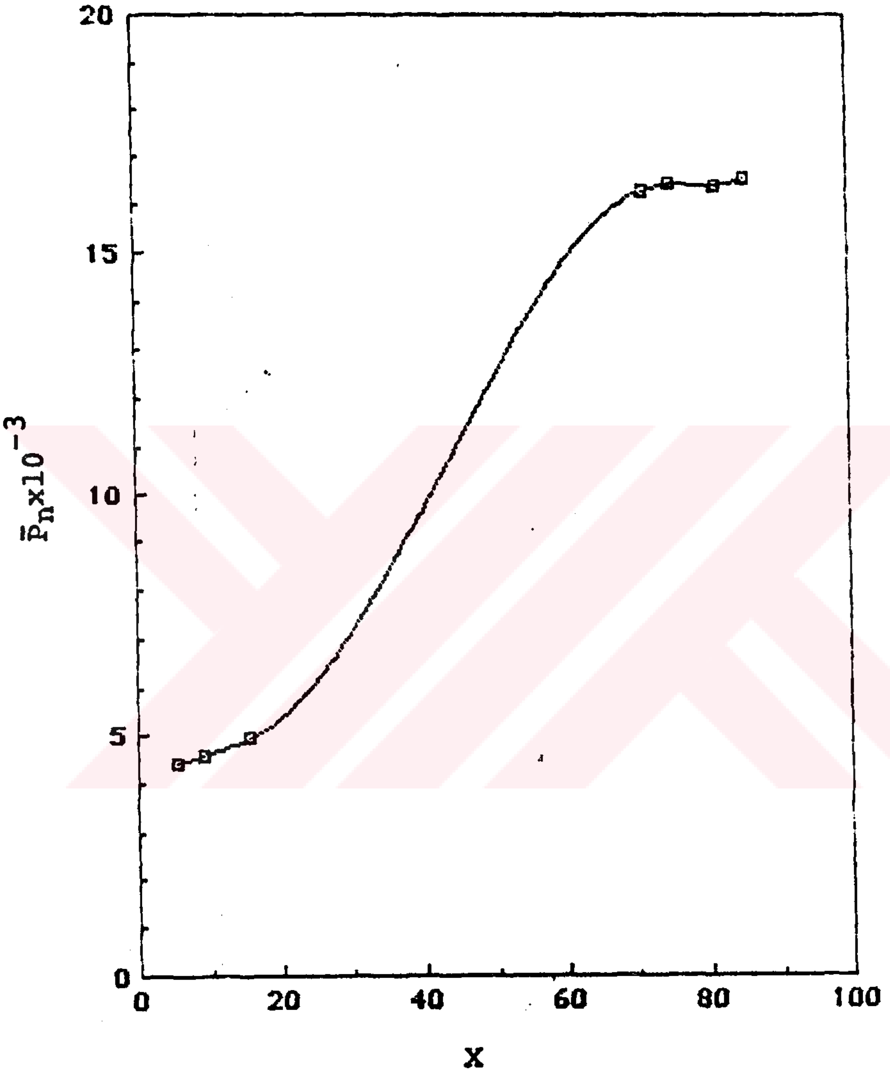


Fig.5.5 Number Average Degree of Polymerization, P_n, as a Function of Conversion x.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1. CONCLUSIONS

The conclusions which can drawn from the experimental findings of this study can be summarized as follows:

The free radical bulk polymerization of methyl methacrylate was studied at 22.5^{0}C and the results were compared with the photopolymerization of the same monomer.

The conversion of methyl methacrylate in bulk at 22.5^{0}C seems to fall into three distinct stages: Initial, intermediate and glassy. The rate of polymerization is rapid after 15% conversion until the conversion reaches to about 70% conversion. As the conversion proceeds, the physical nature of the reaction medium changes from very viscous fluid to a soft solid. At 70% conversion overall rate of polymerization becomes slow and gradually decreases to zero. The maximum conversion of methyl methacrylate to polymer is about 80%.

For the initial stages of polymerization, k_t/k_p^2 and $C_{tr,m}$ constants were evaluated. They were found as 303 and 5.6×10^{-5}, respectively. They are in the range of the values compiled from several literature sources.

Number average degree of polymerization, P_n, remains constant at the beginning and at the end of the polymerization process. Efficiency of the initiator, f, was found to be 0.472 for a single conversion value at the initial stage. The other values determined for low conversions were close to unity.

6.2. RECOMMENDATIONS FOR FUTURE STUDIES

6.2.1 Improvements in the experimental set-up.

In this work, the polymerization of methyl methacrylate was carried out in 25 ml flasks sealed with rubber caps and blanketed with inert nitrogen gas.

Since oxygen must always be carefully excluded to obtain well-controlled polymerization it can be better to use a high vacuum apparatus as shown in Fig.6.1.

During the polymerization process, we faced with some problems to obtain reliable and reproducible data, especially in the intermediate stage of the polymerization, due to the difficulties in the removal of oxygen from the reaction medium.

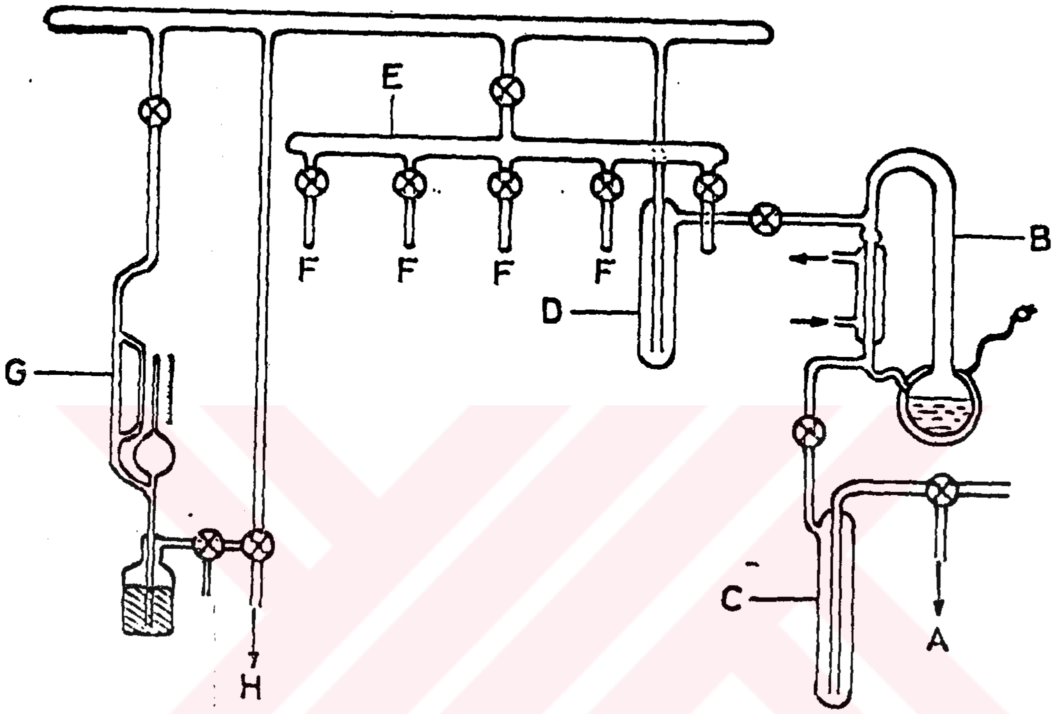


Fig. 6.1 Schematic Diagram of High Vacuum System
A: Connection to the main rotary vacuum pump
B: Diffusion pump
C: Trap
D: Trap
E: Manifold
F: Tube holders
G: McLeod manometer
H: Connection to the second rotary vacuum pump

Therefore we strictly decided that, a high vacuum apparatus will be required to obtain more precise experimental results.

6.2.2 Recommendations for further work

i) The intermediate stage of the free radical, thermally initiated, bulk polymerization of methyl methacrylate have to be investigated. This data is necessary in order to interpret the reaction rates.

ii) The number average degree of polymerization and weight average degree of polymerization have to be determined by using Gel Permeation Chromatography in order to discuss molecular weight distribution of polymeric samples obtained in a similar work.

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APPENDIX

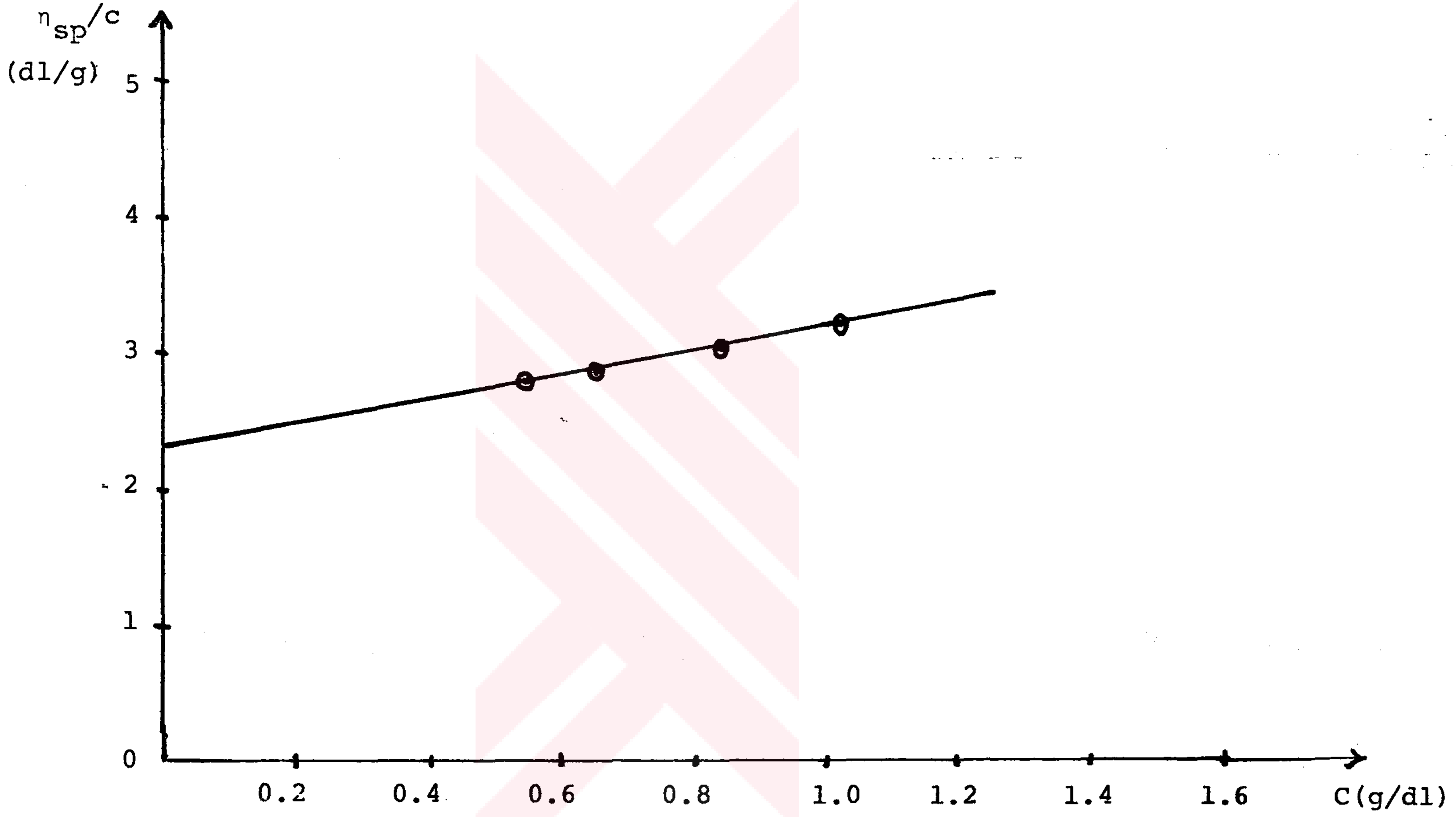

Fig.A.1 η_{sp}/c vs c graph for conversion, 9.17%

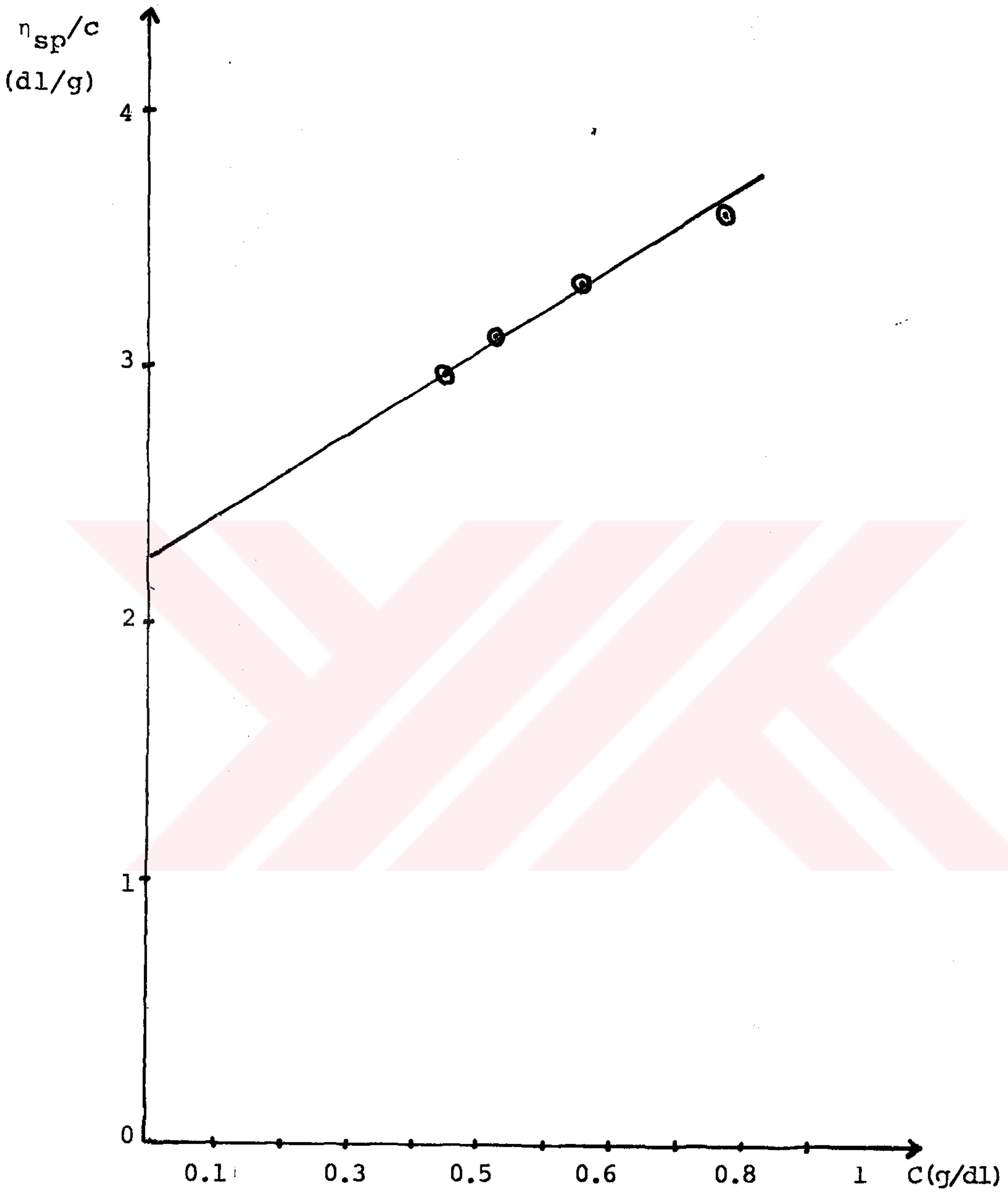

Fig.A.2 η_{sp}/c vs c graph for conversion, 15.5%

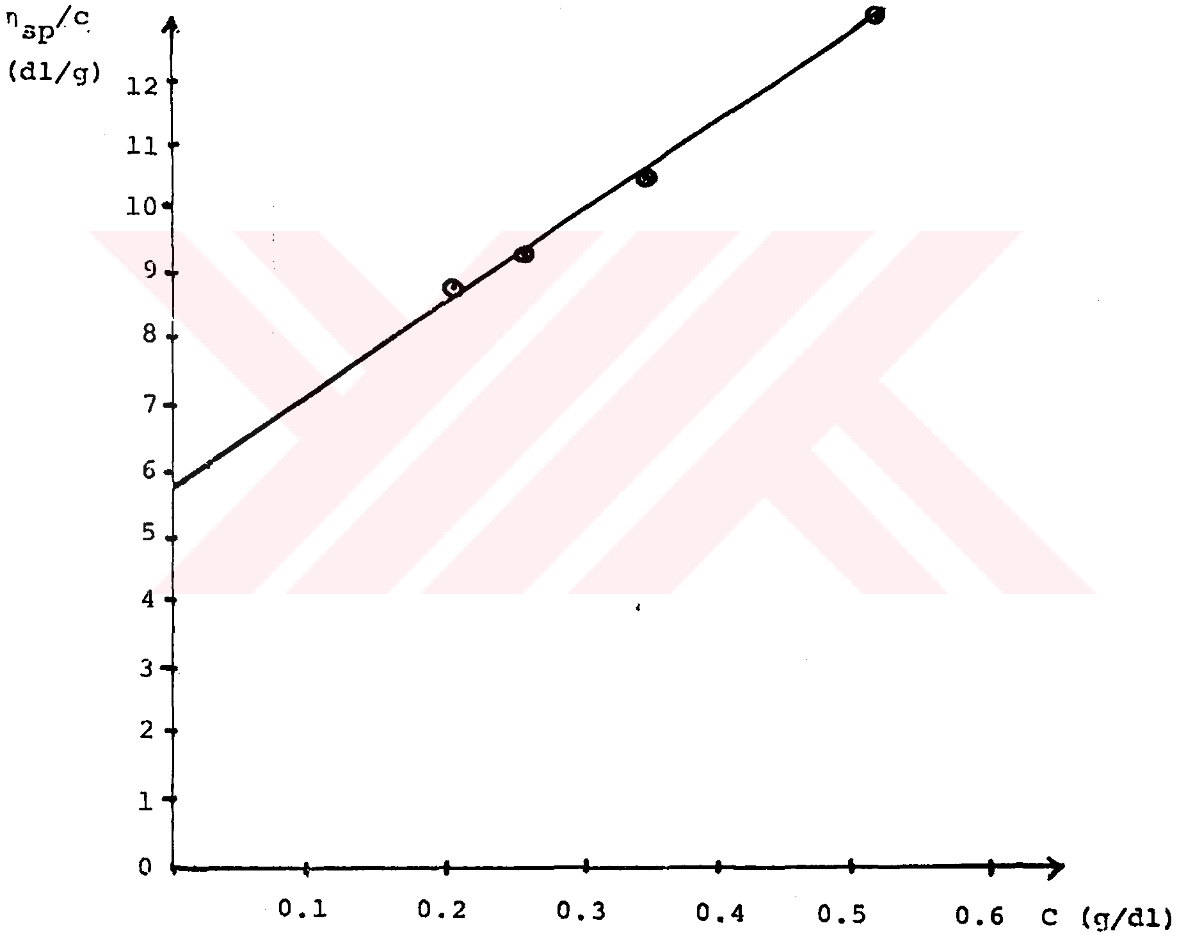

Fig.A.3 η_{sp}/c vs c graph for conversion, 70.7%

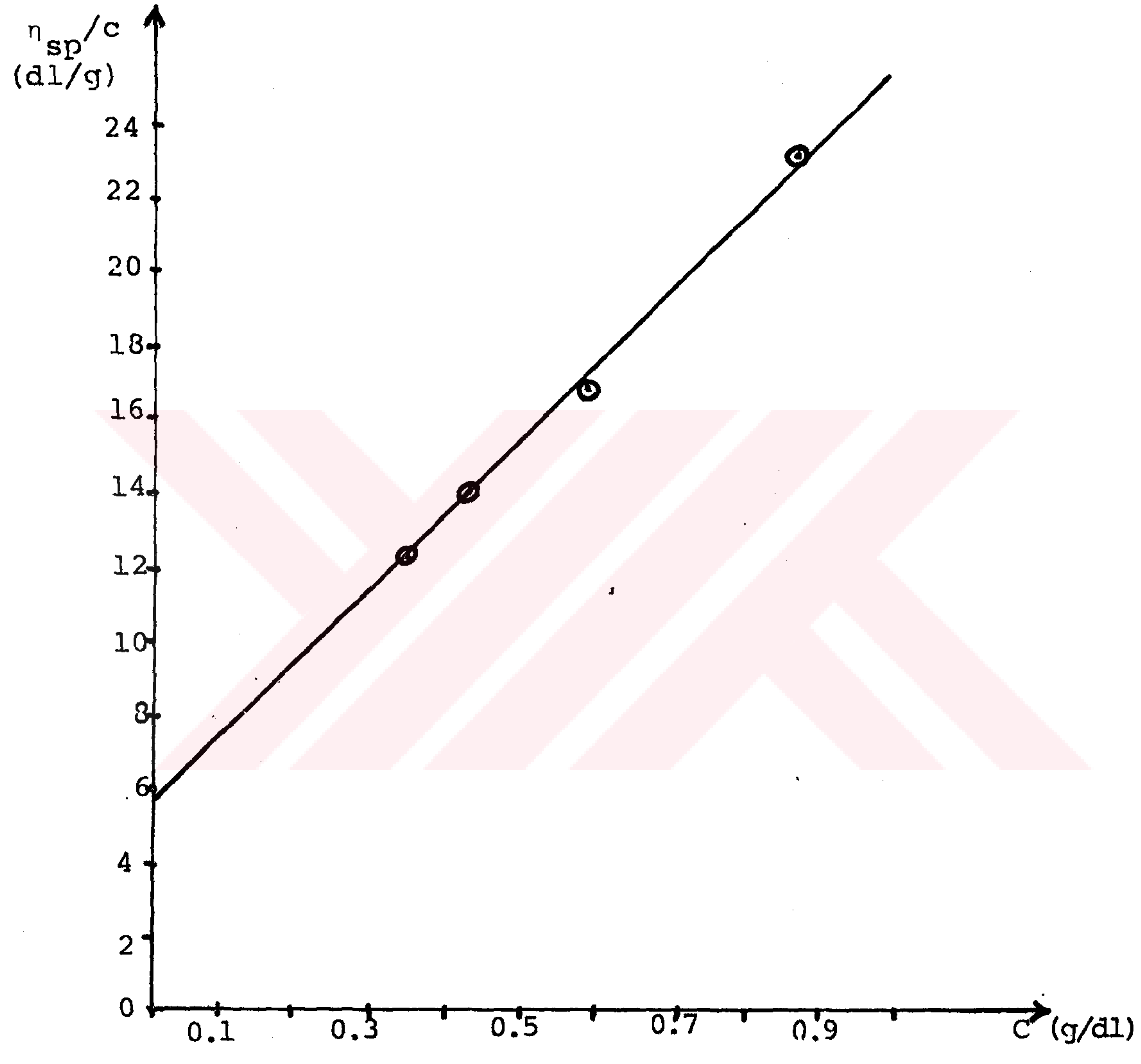

Fig.A.4 - η_{sp}/c vs c graph for conversion, 74.5%