POLYMETHYL METHACRYLATE: A STUDY OF ITS FORMATION AND MOLECULAR WEIGHT DISTRIBUTION.

BY

OLUFUNMILAYO IRENE MOSAKU (MRS.)
(NEE ADEOYE)

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DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE,
AHMADU BELLO UNIVERSITY,
ZARIA - NIGERIA.

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DECLARATION

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

Mrs. O. I. Mosaku
(nee Adeoye)

Date:----------

DEDICATION

To Soji (my understanding husband),
Kemi and Iyiola (my enduring children),
and Kike Folu and Bisi who were all
denied of my care and attention during
the preparation of this thesis.

AND

To my loving Mother
Care and Glory of God

ACKNOWLEDGEMENTS

Sometimes preparing a thesis such as this affords one the opportunity to realise that there are those who care and feel concerned about one's welfare and progress. I have come to realise this fact during the preparation of this thesis and I therefore want to place on record my appreciation for the care, concern, and help afforded me by the many persons I now know have my interest at heart.

My deep appreciation goes first to my supervisor Dr. J.Y. Olayemi whose constant presence in the laboratory during the course of the experiment prompted me not only to be present but also to be punctual. I am also grateful for the thoroughness with which he read and corrected the scripts even in the face of acute shortage of time. My timely submission of the thesis has been largely due to this special efforts and dedication.

I should also register my profound gratitude and thanks to the Head of Department Dr. H.T. Bozimo, and to Dr. J.O. Amupitan, Dr. E.G. Kolawole, and Mr. A.F. Smith for coming to my aid during the course of the experiment when I ran into trouble of 'almighty' NEPA inconsistency, the experimental set-up, and the supply of essential needs.

Other staff members whose names I have not mentioned should not feel bad that I have probably not recognised their contributions in one way or the other. I should like

to say that even their occasional jokes had served as tonic to my sometimes dejected and unwilling heart. You all have been tremendously helpful and I say thank you.

Finally, I want to thank my husband Soji, my in-laws Sesi, and Femi, my sister Kike, my colleague Margaret and Messrs Adanu and Adeleke for their special cooperation while I was preparing this thesis.

May God help you all.

Mrs. O. I. Mosaku,
(nee Adeoye).

Abstract

The kinetics of the emulsion polymerisation of methylmethacrylate using potassium persulphate as initiator and sodium lauryl sulphate (SLS) as emulsifier has been studied at two different temperatures, with four different emulsifier concentrations, and two different initiator concentrations.

Sigmoid shaped conversion - time curves were obtained, the steep parts of which are linear. The slopes of these were taken as a measure of the rate of polymerisation, and increase with emulsifier and initiator concentrations and with temperature.

The intrinsic viscosity and hence molecular weight of the polymer samples were determined from dilute solution viscosity measurement and found to be considerably high for the polymethylmethacrylate c"7^{1co} obtained while polymerising below the critical micelles concentration of the emulsifier. Molecular weight increased with increase in emulsifier concentration particularly at lower initiator concentration. Molecular weight also increased with increase in temperature. Futhermore molecular weight per unit conversion increased with emulsifier concentration, decreased with initiator concentration and increase in temperature. Huggins constant also suggested a ipoor PMMA acetone interaction*

The polymer samples were characterised by the fractional precipitation method. Two distinct fractions were obtained for each polymer sample produced while polymerising (MMA) below the cmc of (SLS). The molecular weight distribution curve is sigmoidal and indicates polydispersity in the polymer molecular weight. The degree of polydispersity increased with increases in percentage conversion, emulsifier concentration, initiator concentration and temperature of polymerisation of the monomer.

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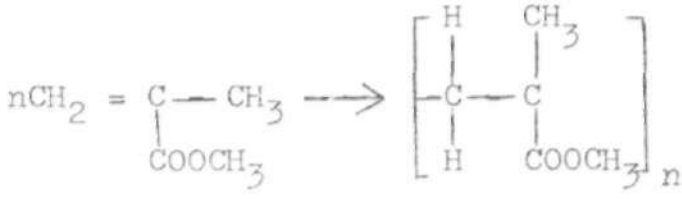
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CHAPTER ONE

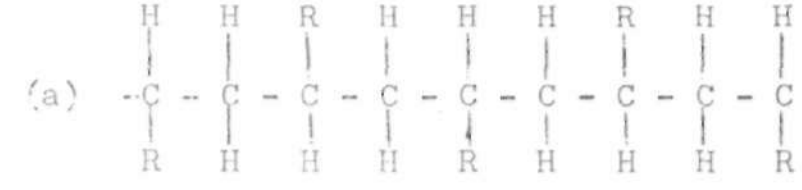
1.0 INTRODUCTION

The series of reactions by which methylmethacrylate (MMA) is converted into its polymer have been studied extensively. The polymerisation reaction may be represented by the general equation

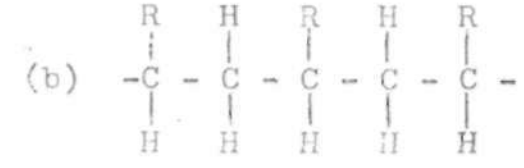


(1 - 1)

Under different reaction conditions and mechanism of polymerisation the tertiary carbon atom present may lead to polymer of different stereoisomers (1). Hence:



(a) Syndiotactic



(b) Isotactic



(c) Atactic

This is the situation whereby polymer obtained from the same monomer may give or exhibit different properties on the basis of structural differences.

1.1 Properties of Methylmethacrylate Monomer:

Methylmethacrylate monomer is a liquid at room temperature and comparatively non-toxic. It has the tendency of self-polymerising at ambient temperature except if treated with an inhibitor like hydroquinone which keeps it stable at this temperature.

1.2 Properties and General Application of PMMA (Polymethylmethacrylate)

Polymethylmethacrylate is a linear thermoplastic, and generally about 70 - 75% syndiotactic (2). Because of this incomplete stereoregularity and its bulky side groups, the polymer is amorphous. Polymethylmethacrylate is highly resistant to many aqueous inorganic reagents including dilute alkalis and acids. These properties widen the application of the polymer in many industries. Its optical properties (3) coupled with a good outdoor weathering make it highly useful in all applications where light transmission is important. Polymethylmethacrylate has been found to have tremendous applications in automotive industry in making tail and signal light lenses, dials and medallions. It is used in moulded form for brush backs, jewelleries and lenses. Cast rods can also be made from the polymer for use in modern architecture (4). The numerous applications of polymethylmethacrylate are closely associated with the high-tensile strength and the good thermal properties of the polymer as well as its fabricability.

However, polymethylmethacrylate has not been found to be a substitute for glass particularly where abrasion may occur as a result of poor scratch resistance.

It is known however, that most of the good properties of polymethyl methacrylate and other polymers, in general, are dictated to a very large extent by the molecular weight distribution pattern of the bulk polymer whenever it is made. The conditions of polymerising the monomer are very important factors that affect the molecular weight distribution in a polymer sample. Hence narrow and broad molecular weight distributions are known in the study of polymer molecular weight.

1.3 Polymerisation of Methylmethacrylate.

Polymerisation of methylmethacrylate in its liquid phase will occur readily in the absence of an inhibitor such as oxygen and hydroquinone but more readily in the presence of an initiator and in an inert (nitrogen) atmosphere. Polymerisations of methylmethacrylate and other vinyl monomers occur in general via chain reaction mechanism which are classified into free radical, anionic and cationic polymerisation, depending upon the type of initiator used.

1.3.1 Free radical polymerisation.

Free radical polymerisation is very important in the polymerisation of vinyl monomers. It is a free radical initiated type of polymerisation. Free radicals are intermediates possessing an odd number of electrons and consequently an unpaired electron. A free radical can be generated in the following ways:-

(a) Photolytic decomposition of covalently bonded compounds as in photo-polymerisation of methylmethacrylate (5) using hydrogen peroxide as photo-initiator.

(b) Thermal decomposition of organic peroxide as in benzoyl peroxide.

$$(C_6H_5COO)_2 \dashrightarrow 2C_6H_5COO \longrightarrow 2C_6H_5 + 2CO_2$$

(c) Dissociation of covalent bonds by high energy radiation. This method was used by Sasuga T et al (6) to polymerise methylmethacrylate at high temperature.

Staudinger Frost (7) and Flory (8) described the steps involved in the polymerisation of vinyl monomers as initiation, propagation and termination stages.

The initiation stage in the presence of an initiator (I) may be considered in two steps. These are:

(i) the production of free radicals as described in (b) above which yields a pair of primary radicals (R)

$$I \xrightarrow{kd} 2R^{\cdot} \qquad (1 - 2)$$

(where kd is initiator dissociation constant)

This is the rate determining step for the decomposition of the initiator into free radicals.

(ii) the second stage involves the addition of the primary radicals to the first monomer molecule (M) to produce the chain initiating species

$$R^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot} \qquad (1 - 3)$$

(where k_i is the initiation rate constant).

The propagation step consists of the growth of (M_i) by successive additions of large numbers of monomer molecules

$$M_1^{\cdot} + M \xrightarrow{(k_p)} M_2^{\cdot} \qquad (1 - 4)$$

$$M_x^{\cdot} + M \xrightarrow{(k_p)} M_{x+1}^{\cdot} \qquad (1 - 5)$$

((k_p) is the propagation rate constant).

Each addition creates a new radical which is larger by one monomer unit. At the same point the propagating polymer chain terminates. Termination can occur by

bimolecular reaction between radicals. The two radicals react either by combination

$$M_x^{\bullet} + M_y^{\bullet} \xrightarrow{k_{tc}} M_{(x+y)} \quad \text{(dead polymer)} \qquad (1-6)$$

or more readily by disproportionation i.e. a hydrogen radical is transferred to another radical centre

$$M_x^{\bullet} + M_y^{\bullet} \xrightarrow{k_{td}} M_x + M_y \quad \text{(dead polymers)} \qquad (1-7)$$

Where one is a saturated molecule while the other is unsaturated molecule. k_{tc} and k_{td} are rate constants for termination by combination and disproportionation respectively. Conclusively, monomer disappears only by initiation reaction (rate = R_i) and propagation reaction (rate = R_p). Therefore the rate of monomer disappearance is the rate of polymerisation given by:

$$\frac{-d[M]}{dt} = (R_i) + (R_p) \qquad (1-8)$$

Since a much greater number of monomer molecules reacts in the propagation step, to a close approximation, (R_i) is regarded to be negligible. Hence rate of propagation (R_p) is the rate of polymerisation.

$$(R_p) = k_p [M^{\bullet}] [M] \qquad (1-9)$$

$[M]$ is the monomer concentration, $[M^{\cdot}]$ is the total concentration of chain radicals.

From steady state assumption, that is rate of initiation is equal to rate of termination ($R_i = R_t$), rate of polymerisation can be rewritten as

$$(R_p) = (k_p)[M]\left(\frac{R_i}{2(k_t)}\right)^{\frac{1}{2}} \qquad (1 - 10)$$

The fourth type of radical displacement reactions in free radical polymerisation are termed chain transfer reactions (9). These reactions terminate the reaction of a radical while simultaneously generating a new radical. That is there is the premature termination of a growing polymer chain by transfer of a hydrogen or other atom or species to it from some compound (e.g. X_A) present in the system. This may be the solvent, monomer or initiator or any other added compound. The reaction is depicted as

$$M_X^{\cdot} + X_A \xrightarrow{k_{tr}} M_A - X + A^{\cdot} \qquad (1 - 11)$$

k_{tr} is the chain transfer rate constant, X_A is the chain transfer agent, X is the species transferred and A is the new radical which then reinitiates polymerisation

$$\text{i.e.} \quad A^{\cdot} + M \xrightarrow{(k_a)} M^{\cdot} \qquad (1 - 12)$$

(k_a) is the reinitiation rate constant

The effect of chain transfer is in decreasing the average size of the polymer. Thus chain transfer agents are used to regulate chain length. The effect of chain transfer agents on the rate of polymerisation depends upon whether or not the rate of reinitiation is comparable with the original rate of propagation. If this is less, there is a decrease in the rate of polymerisation and if it is the same then there is no change in the rate of polymerisation reactions. The rate of chain transfer reaction is therefore given as:

$$(R_{tr}) = (k_{tr}) [M^{\cdot}][X_A] \qquad (1 - 13)$$

Chain transfer also results in branching of the polymer chain

1.3.2 Characteristics of Free Radical Polymerisation:

Free radical polymerisations are known (10) to exhibit the following characteristics

(i) Once initiation occurs the polymer chain forms very quickly (i.e. 10^{-1} to 10^{-6} sec.) and monomer concentration decreases steadily throughout the reaction.

(ii) The concentration of 'active species' is very low. Hence the polymerisation mixture consists primarily of newly formed polymer and unreacted monomer.

(iii) High molecular weight polymer is formed quickly while polymer molecular weight changes only slightly throughout the reaction.

1.4 Polymerisation Techniques:

1.4.1 Bulk Polymerisation:-

This technique involves addition of an initiator to the monomer at an elevated temperature in the absence of a diluent or dispersing agent. The reaction proceeds so rapidly as the free radicals are generated. As a result of this fast reaction, the reaction mixture becomes viscous and polymer formed dissolves more readily in the monomer. Heat transfer and dissipation is poor, hence explosion may result due to excessive heat of polymerisation (11).

This technique is not used extensively for radical chain polymerisation of vinyl monomers for the following reasons

(i) Difficulty in removing polymer from the reactor or dilatometer.

(ii) Branching in the polymer and

(iii) The separation of the polymer from the monomer is often difficult.

1.4.2 Solution Polymerisation:-

Here polymerisation is carried out in a solvent with which the monomer is miscible and the initiator is soluble. The solvent therefore allows easy dissipation of heat and removal of polymer is less cumbersome than in bulk polymerisation. The solvent also acts as a diluent which lowers the viscosity of the medium. Solution polymerisation suffers the following disadvantages:

(i) Difficulty in removing solvent from the polymer at the end of polymerisation.

(ii) Solvent acting as a chain transfer agent. This may decrease the rate of polymerisation (12) and also influence the molecular weight of the polymer produced (13).

1.4.3 Suspension Polymerisation:-

The monomer is suspended in aqueous phase as droplets, this being maintained by agitation and addition of stabilisers as polymer globules and monomer droplets tend to agglomerate. Polymerisation is effected in each globule and a spherical pearl of high molecular weight is obtained. Heat removal is easy because of aqueous suspension medium. Hence it was described by

Holenstein et al (14) and Trommsdorff (15) as water cooled polymerisation. The disadvantages include

(i) Polymer contamination with stabiliser

(ii) It requires continuous agitation which according to Hoff et al (16, 17) controls the particle size during polymerisation.

1.4.4 Emulsion Polymerisation:-

This technique is a unique process and a multi-phase system which makes it of greatest commercial interest apart from its numerous advantage, which include;

(i) Product of high molecular weight

(ii) Low viscosity throughout the polymerisation.

(iii) High rate of conversion. Virtually 100% conversion may be attained reasonably quickly.

(iv) Easy thermal control due to presence of large quantity of water (18).

(v) Emulsion that can be obtained in suitable form for direct application (i.e. no need to isolate the solid polymer).

However emulsion polymerisation suffers the following disadvantages:-

(i) Emulsifiers surfactants and modifiers are difficult to remove. This renders the product impure unless additional cost is incurred for purification and processing.

(ii) High residual level of impurity may also lower the properties of the polymer.

1.4.4.1 General Characteristics of Emulsion Polymerisation:-

An ideal emulsion polymerisation system consists essentially of water (a diluent), water in-soluble monomer (which is finally dispersed in diluent), an emulsifying agent and a free radical initiator. Polymerisation is believed to occur in emulsifying micelles region containing solubilised monomer as discovered by Fiskentscher (19). It is when the emulsifier concentration exceeds a certain value called the critical micelle concentration (c.m.c) that micelles are formed by aggregation of emulsifier molecules. The greater the number of micelles the higher the number of particles formed. The presence of micelles and their number are important factors that affect the macromolecular structures and properties of the polymer formed. Below the critical micelle (i.e. in the absence of micelles) the mechanism of polymer particle formation differs (20). However the number of particles formed in the absence of micelles is also expected to be

less than that formed above the c.m.c. This is because particle formation depends upon the number of micelles.

Although the initiating free radical is generated in the water phase, polymerisation inside the micelles proceeds rapidly and the latex particles grow rapidly from within. It is on the surface of the growing latex particles that the emulsifier is adsorbed thus functioning as a protective colloids. This reduces the concentration of the dissolved emulsifier in the aqueous phase. Also the surface tension of the growing latex particles increases.

The growing latex particles are continuosly being supplied with monomer by diffusion through the aqueous phase from the monomer droplets. Hence the monomer gradually decreases in quantity as the polymerisation proceeds until it finally disappears. Polymerisation rate will gradually fall off after the disappearance of the monomer.

1.5 Brief account of previous work of emulsion polymerisation of MMA.

Many researchers in the past have carried out emulsion polymerisation of MMA with certain specific objectives or to confirm certain theoretical ascertions.

Notable research works in this area are the work of Smith-Ewart (21), Gardon et al (22, 23, 24, 25), Vanderhoff (26), Bond et al (27), Gershberg et al (28), Brodnyan et al (29), Zimmit (30), Lee et al (31) Howard et al (32) and Arai et al (33).

Smith and Ewart were among the first group of people to work on Emulsion polymerisations in general. They have shown from their studies of the kinetics of styrene emulsion polymerisation that the rate of polymerisation (R_p) and the number average degree of polymerisation ($\bar{X}_n$) are directly proportional to the number of growing particles (N), which in turn is proportional to the initiator and emulsifier concentrations. That is

$$(R_p) = \frac{(N)(k_p)}{2}[M] \qquad (1 - 14)$$

$$(\bar{X}_n) = \frac{(N)(k_p)}{R_i}[M] \qquad (1 - 15)$$

$$(N) \alpha [I]^{2/5} \qquad (1 - 16)$$

$$(N) \alpha [E]^{3/5} \qquad (1 - 17)$$

where (k_p) is the propagation rate constant
(R_i) is the rate of initiation while, $[M]$, $[I]$ and $[E]$ are monomer, initiator and emulsifier concentrations respectively.

These equations were found to be approximately applicable for emulsion polymerisation of water-insoluble monomers e.g. styrene and methylmeltacrylate. In equations (1 - 16) and (1 - 17) the proportionality constant in their theory is not defined in terms of independent parameters. One possible limitation of Smith - Ewart theory is that the basic assumptions are not applicable to all monomers and to all experimental conditions.

It was on the basis of Smith-Ewart theory that Gardon (22) proposed his own theory based on theoretical calculations. On the basis of his research he found out that it is possible to distinguish three intervals in single-charge emulsion homopolymerisation (of methyl methacrylate for instance). These he designated intervals I, II and III. He concluded that all particles are formed in interval I, and in the absence of aggregation, the number of particles is constant in intervals II and III. Furthermore in intervals I and II, the reaction mixture consists of three phases, monomer-swollen latex particles, droplets of monomer, and the aqueous phase. When the concentration has proceeded far enough, the monomer droplets disappear, and the reaction mixture becomes a two phase system of monomer-swollen latex particles and aqueous phase in interval III.

In other words Gardon believed that the particle number increases and monomer droplets are present in interval I, the particle number is constant and monomer droplets are present in interval II, whilst in interval III, although the particle number is constant, there are no monomer droplets present.

On the basis of his experimental results for the emulsion polymerisation of MMA and styrene using sodium lauryl sulphate as emulsifier and potassium persulphate as initiator, Gardon (22, 23) was able to predict that rate of polymerisation is proportional to emulsifier concentration raised to power 0.6 and to initiator concentration raised to power 0.4 was observed. The theoretical predictions for the rate are in good agreement with this experimental results obtained for MMA and styrene. Gardon believed that Smith-Ewart theory only provided a complete description of interval I and II. In his experimental findings he concluded that in interval I, the particles are nucleated and there monomer is present in excess of that needed to saturate latex particles and water. Also particles size varies with conversion of MMA (23) while number of growing particles depends on temperature, soap and initiator concentrations. But Vanderhoff et al (26) found that, with increasing temperature number of growing particles is increased at

potassium persulphate initiation and decreased at initiation by irradiation. While in interval II, Gardon (23) found that for low particle size systems at low initiation rates, the conversion in this interval was found to be linear with time and the rate per particle was found to be independent on number of growing particles. It means that if both interval I and interval II models are correct, the interval II rate should be proportional to $[E]^{0.6}$ and $[I]^{0.4}$. Soap and initiator concentrations and temperature also affect rate in interval II. While in interval III the conversion proceeds far enough so that unconverted monomer present is only dissolved in latex particles and in water. In addition, the molecular weight obtained in interval II was higher than the theoretical molecular weight while the molecular weight in interval III is lower. The reason for high molecular weight in interval II is slow termination and the reason for low molecular weight in interval III is that monomer concentration in the particle is low resulting in slow propagation rates. But in interval I the molecular weight is about the same as the theoretical predictions.

Although Smith-Ewart assumed that termination rate within the particles is instantaneous Gardon (24, 25) discovered this to be untrue, but rather, rate of termination

is slow and takes place solely within the particles and proceeds at a finite rate. Also conversion time curves describing molecule conversion process is generally of sigmoid shape. Other predictions made included;

(a) the interval II conversion time curve is convex to the time axis.

(b) Even if the conversion time curve appears to be linear, the conversion rate is not proportional to the particle number.

(c) When initiation is post-added during interval II, the conversion rate increases.

(d) The molecular weight in interval II increases with conversion.

(e) The particle size distribution broadens with increasing conversion.

Bond et al (27) also reported emulsion polymerisation of methylmethacrylate. Cupric sulphate-hydrazine-Oxygen system was used as an initiator and sodium dodecyl sulphate was used as emulsifier. They found rate of polymerisation to depend on emulsifier concentration and on initiator concentration.

Furthermore on the basis of Smith Ewart theory of emulsion polymerisation, Gershberg studied (28) the behaviour of monomers possessing a degree of water solubility. He found that for monomers with a water solubility greater than 0.04% to 0.07% deviation from the Smith-Ewart theory occur. He proposed an emperical expression that $R_p \alpha [E]^{x \pm 0.07} [I]^{0.45 \pm 0.05} P^o$ where P^o is the phase ratio.

Gershberg claimed that $[x]$ varies with changing water solubility and for monomers whose water solubility is less than 0.04% to 0.07%, (x) is 0.6 as predicted by Smith-Ewart theory. For methylmethacrylate, Gershberg quoted (x) to be 0.3 to 0.4. Brodnyan et al (29) concluded that the water solubility of the monomer is relatively unimportant rather, it is the particle size that is important. They found (x) to be 0.5 for both methyl and n-butylmethacrylate, where methylmethacrylate is an example of an insoluble monomer whilst n-butylmetha orylate is sparingly soluble. In contrast to this Gershberg concluded that the value of (x) Brodnyan et al obtained in the kinetic part of their study was in accordance with his own theory.

Zimmit (30) also concluded from a particle size study that the emulsion polymerisation of methylmethacrylate follows Smith-Ewart kinetics. On the basis of uncertainty that exists as to whether the water solubility of the

monomer affects the value of x or not, Lee et al (31) too studied the emulsion polymerisation of methylmethacrylate in an attempt to clarify the situation. The study included the use of sodium dodecylsulphate as emulsifier and using four similar initiators. He proposed that dependence of rate of polymerisation of emulsion polymerisation on soap concentration is not simply a function of the solubility of the monomer in water as suggested by Gershberg (28). Lee et al therefore found that the rate dependence on soap concentration was different for each initiator. The extent of this variable was found to be $(R_p) \propto [\text{soap}]^{0.18 - 0.55}$.

In addition Howard et al (32) too studied emulsion polymerisation of methylmethacrylate and styrene using potassium persulphate as initiator, potassium hydroxide, water. Emuphogene BC-840 and sodium lauryl sulphate as emulsifiers. Among the results obtained are smooth and continuous rate curves indicating the presence of three distinct stages in the polymerisation rates. These agreed with that obtained by Gardon (22). Constant rate period too was observed for both polystyrene and polymethyl methacrylate in interval II which was the area of their study. They observed an increase in molecular weight with conversion.

Arai et al (33) studied the rate of soapless emulsion polymerisation of methylmethacrylate with potassium

persulphate as initiator and water. The concluded that soapless emulsion polymerisation of MMA gave different time conversion and time - average molecular weight curves from those of bulk and emulsion polymerisations. Overall rate was found to be proportional to two factors, the number of polymer particles and the average intrinsic rate per particle.

1.6 Characterisation of a Polymer.

After the preparation of polymer it is important to study its physical properties and molecular weight structure and distribution which otherwise is called characterisation of the polymer.

The scope of characterisation can be relatively narrow or extremely broad. This depends upon the degree of scientific and commercial interests. But characterisation of polymer can be considered under two broad categories - molecular structure and physical properties.

Characterising polymer on the basis of its molecular structure and physical properties is necessary because the end-use of any polymer depends greatly upon these properties.

1.6.1 Variety of Molecular Weight Distributions:

Characterising a polymer involves specifying the three dimentional arrangements of atoms that constitute

a molecule in its most complete sense (34). This includes the study of the molecular weight and its distribution, crystallinity, melt viscosity, elemental analysis, spectroscopy etc. Unlike in simple compounds, however, there are often great difficulties in characterising a polymer this way. This is chiefly due to the inhomogeneity of the molecular weight and its degree of crystallinity. These problems result from the large size and isomeric complexity of the polymer. The latter is as a result of the origin of the polymers via the repetition of the kinetic chain length particularly in the propagation step. Thus the molecular weight assigned to a polymer in general refers to an average molecular weight of the individual chains in the polymer mixtures. This average may become equal to the molecular weight of each of the individual molecule when the polymer preparation is monodispersed.

Depending on the method of molecular weight measurement, different types of average molecular weights proposed by Lansing and Kraemer (35) can be described for a polymer. The averages are distinguished by whether the contribution of each molecule to the measured property is proportional to the number of molecules or to a power of the weight of molecules present (36). The former category leads to a number average molecular weight ($\bar{M}_n$),

while the latter leads to the weight average molecular weight ($\bar{M}_w$).

$\bar{M}_n$ is defined as

$$\bar{M}_n = \frac{\text{Total weight of molecules}}{\text{Total number of molecules}} = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad (1 - 18)$$

where (N_i) is the number of molecules of molecular weight (M_i) of every species i. OR

$\bar{M}_n = \Sigma N_i M_i$ where (N_i) is the number of fraction of molecular weight (M_i).

Simply, the weight average molecular weight is given by

$$\bar{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \Sigma w_i M_i \qquad (1 - 19)$$

where (w_i) is the weight fraction of each species. of molecular weight (M_i).

The third type of the average molecular weight commonly measured is the viscosity average molecular weight ($\bar{M}_v$) which was recognised by Staudinger 1930 (37). The viscosity average molecular weight affects the viscosity of a solution.

For polymer having homogeneous molecular size, all the averages mentioned will be equal but the greater the

inhomogeneity the greater the disparity among them. Thus the distribution of molecular weights for typical heterogeneous or poly-dispersed system is as follows:

$$\bar{M}_w > \bar{M}_v > \bar{M}_n, \quad (38)$$

This is shown graphically in illustration (one) which depicts the typical molecular weight distribution of a polymer sample.

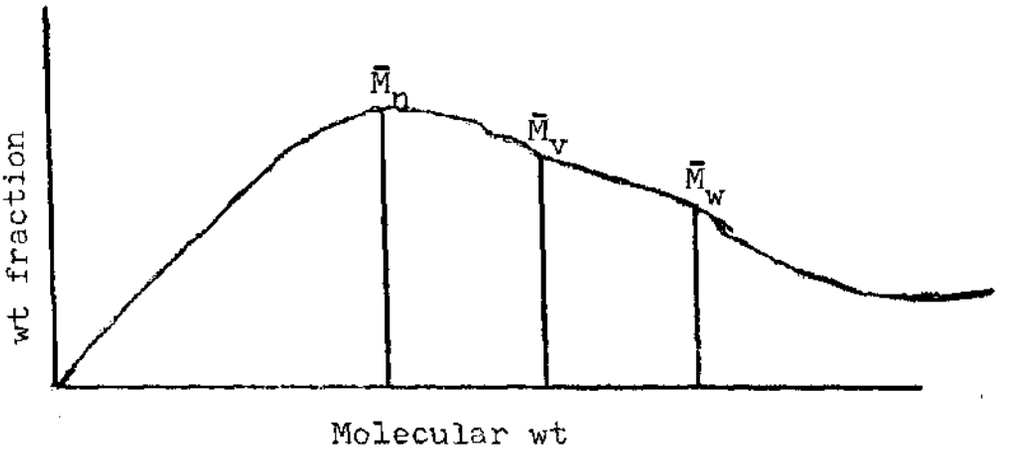


Illustration 1: Distribution of Molecular weight in a polymer sample.

But in nearly monodispersed sample all the average molecular weights are expected to become close. That is $\bar{M}_n \simeq \bar{M}_v \simeq \bar{M}_w$. The shape of the molecular weight distribution will differ from one shown above. This would be a simple sigmoid, which becomes steeper the closer these averages are to themselves.

The characterisation of a polymer by molecular structure is very important. Also, knowledge about molecular weight distribution in a polymer helps in the understanding of the mechanism of the polymerisation reaction. In addition, it supplies information about the breadth of the spectrum of the chain lengths that constitute the polymer molecules. For instance, one information that can be readily obtained is the degree of inhomogeneity in the polymer. This is given by the ratio $\bar{M}_w/\bar{M}_n$. When this ratio is unity, the polymer is monodispersed, but if greater than 1, the polymer is polydispersed. $\bar{M}_n$ and $\bar{M}_w$ of the whole polymer can theoretically be obtained using equations (1 - 18) and (1 - 19) respectively.

In addition to the different average molecular weights of a polymer sample, it is sometimes necessary to know the exact distribution of molecular weights, especially that the narrowness or otherwise of the distribution will affect the property and subsequent end use of the polymer. Molecular weight distribution of a polymer sample can be achieved by using any of fractionation methods. The molecular weight of each fraction is determined and plotted as the molecular weight distribution.

1.6.2 Fractionation of a polymer.

The separation of a polymer is based upon a primary property of the individual polymer molecule, namely its size (39). Such properties as diffusion and sedimentation, solubility and volatility are related to the molecular weight, hence fractionation may be achieved in several ways.

Essentially fractionation can be defined as the separation of polymer mixture into a number of fractions according to their molecular weights. There are eight well established methods of fractionation, the selection of any of the methods will depend upon the specific properties of the system being studied and the objectives which the method intended to achieve.

The fundamental methods of fractionation are:

Methods	Principle of fractionation
(1) Thermal diffusion	The ratio between diffusion and thermal diffusion co-efficients is a function of the molecular weight.
(2) Turbidimetric titration	The precipitation threshold is a function of the molecular weight and of the concentration of polymer solution
(3) Sedimentation in the ultracentrifuge	The sedimentation velocity increases with increasing molecular weight.
(4) Ultrafilteration	The 'sieve' effect. This separates on the basis of particle size.

Methods	Principle of fractionation
(5) Chromatographic adsorption	The large molecules are more strongly adsorbed.
(6) Distribution between inmislible liquids	The distribution coefficient is a function of the molecular weight.
(7) Fractional dissolution	The solubility and the diffusion rate decrease with increase in molecular weight.
(a) Varying temperature	
(b) By the rate of diffusion	
(8) Fractional precipitation	The solubility decreases with increasing molecular weight.
(a) Addition of precipitant	
(b) Evaporation of solvent	
(c) Lowing of temperature	

In a case where the polymerisation reaction mechanism is to be studied, it is enough to apply one of the first three mentioned methods which permits the determination of the molecular weight distribution function without fractionating, i.e. by purely analytical method. But where it is intended to study the dependence of mechanical, chemical and other properties on the molecular weight and the degree of polydispersity, any one of the last five methods listed could be employed in order to obtain a number of narrow polymer fractions.

For simplicity, availability of apparatus and chemicals, certain obvious advantages coupled with the relevance to the objectives of this research, fractional precipitation method has been employed.

1.6.3 Fractional Precipitation Method:-

This is the most widely employed method and was already applied in polydispersity characterisation in the early studies of Staudinger (40). The fractional precipitation method gives reproducible results and in most cases yields fractions with sufficiently narrow distribution.

The basic principle of fractionation being in the decreasing solubility with increasing polymer molecular weight. Also the fractional precipitation method amounts to the isolation of the larger high molecular weight particles through changes in dynamic equilibrium of the system solid/solution. This is done by gradually changing the composition of the solution by addition of a precipitant at a constant temperature or by lowering the temperature.

In fractional precipitation, a precipitant or a non-solvent is slowly added to a dilute solution of the polymer. The polymer gradually precipitates out to give

fractions of different molecular weights. The higher molecular weight macromolecules usually separate out first. The lowest molecular weight fractions separate out last and only with added large quantities of non-solvent.

The success of any fractionation depends upon the properties of the polymer, the solvent and the precipitant on the one hand and upon the concentration of the solution (41) on the other hand. It is therefore important to select the solvent - precipitant (non-solvent) system properly so as to obtain clearly separated fractions with narrow distribution. Since solubility of polymer products produced from monomer of members of a homologous series in a specific solvent decreases as the molecular weight increases, the change in solubility parameter of a solvent system may be used to an advantage for the fractionation of discrete molecular range (42). That is solvent with solubility parameter close to that of the polymer will likely dissolve the polymer. Whilst liquids with solubility parameter different from that of the solvent and polymer will likely precipitate the polymer from the solution. Also in this technique the addition of small quantity of miscible non-solvent results in the precipitation of the polymer in the sequential order - that is polymer with higher molecular weight first.

Therefore to obtain a sharp distribution, it is necessary that the volume of the solution mixture be very large relative to that of the precipitant (non-solvent), and that the solvent used to dissolve the polymer is somewhat a poor solvent for the polymer.

Fractional precipitation technique can be carried out in three ways. These are by addition of precipitant, evaporation of solvent and lowering of temperature.

(i) Fractional precipitation by addition of precipitant is the most widely used of the three methods. The technique is carried out by addition of the non-solvent to a dilute solution of the polymer until a slight turbidity develops at the temperature of fractionation. This turbid solution is then warmed until it is homogeneous to establish equilibrium, allowed to cool back to room temperature which should be maintained. The precipitated phase is allowed to settle to a coherent layer, and the supernatant phase is removed. A further addition of the precipitant to the supernatant solution is done and the process repeated. This method of precipitation gives reproducible results and other advantages as earlier mentioned. However it has the disadvantage involving the use of large volume of solvent and non-solvent.

(ii) Fractional precipitation by evaporation of solvent is not popular with the fractionation of polymers. This is because fractionation takes place at high temperature when it is possible for polymer of interest to start degrading or crosslinking. These situations will change the structural properties of the polymer thereby affecting the end-use. The larger particles separate out first.

(iii) Fractional precipitation by decreasing temperature of solution is where polymer is dissolved in its solvent, allowed to precipitate out and the temperature of the thermostat is gradually decreased. The higher molecular weight fractions precipitate out first since the longer chains are less mobile.

The advantage of this method is that the work is carried out at constant volume. However the low molecular weight fractions cannot always be separated by cooling alone. In such cases more precipitant (non-solvent) must be added after removing the higher molecular fractions. Methods (ii) and (iii) are known to be generally less accurate and reliable.

1.6.3.1 Possible factors affecting fractional precipitation methods.

The following factors have been found to affect the fractional precipitation method.

(i) Chemical type:- The solubility of polymers is determined primarily by their chemical composition, molecular weight is only a secondary variable. Therefore if chemical composition differences exist among the polymer species in a sample, fractions are likely to occur primarily as a result of these differences and thus yielding information on them rather than on the distribution of molecular weights.

(ii) Chain branching:- Chain branching decreases the solubility of high polymers. Thus at any given stage in a solubility based fractionation process, the branched polymer being separated will consist of mixture of species of low branching low molecular weight and others of more branching but with compensating higher molecular weights, all having the same solubility. As a result additional information is needed to characterise such a system in terms of branching and molecular weight.

1.6.4. Determination of Molecular Weight of a Polymer:-

Solution viscosity method is the most widely used of the various methods of determining the molecular weight of either the bulk or fractionated polymer. This is because of its speed, relative freedom from experimental complications, fairly accurate and requires only simple apparatus. However this method of determining molecular weight is not an absolute method.

Molecular weight determination by viscosity method started from the realisation that viscosity of a solution depends upon the molecular weight of the dissolved solute (43). Thus the size or extension in space of polymer molecules are measured by solution viscosity. The higher the molecular weight within a given series of linear polymer homologs, the greater the increase in viscosity produced by a given weight concentration of polymer. That is the intrinsic viscosity, which represents the capacity of a polymer to enhance the viscosity increases with M, hence viscosity measurements afford a measure of molecular weight.

Therefore the specific viscosity of the solution η_{sp} is obtained by determining the relative viscosity of the solution η_r, which is the ratio of the efflux time of solution t, to that of solvent (t_o). This is given by:-

$$\eta/\eta_o = \frac{t}{t_o} = \eta_r \qquad (1 - 20)$$

$$\text{and } \eta_{sp} = \eta_r - 1 = \frac{t - t_o}{t_o} \qquad (1 - 21)$$

η = viscosity of solution, η_o = viscosity of solvent, t = viscometer efflux time of the solution t_o = viscometer efflux time of the solvent.

Since viscosity of a polymer solution also depends upon its concentration, the reduced viscosity (η_{red}) can be defined as the specific viscosity per unit concentration

$$\text{i.e. } \frac{\eta_{sp}}{c} = \frac{\eta - \eta_o}{(\eta_o)c} \qquad (1 - 22)$$

η_{sp} is the specific viscosity and

$\frac{\eta_{sp}}{c}$ is the viscosity number.

$$\text{and } \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad (1 - 23)$$

Equation (1 - 23) is known as Flory-Huggins equation (44) where (k') is the Huggins constant. A graph of ($\frac{\eta_{sp}}{c}$) versus c is linear (for $\eta_r < 2$) and should permit extrapolation to infinite dilution for linear polymer. The intercept $[\eta]$ is then related to the molecular weight of the polymer by the emperical Mark-Houwink-Sakarada equation (45) given as

$$[\eta] = k\bar{M}_v^{\alpha} \qquad (1 - 24)$$

where (k) and (α) are constants for a given polymer-solvent system at a constant temperature.

Though viscosity method provides a simple and convenient way of determining molecular weights, it suffers certain limitations. For example it is a relative method and requires calibration for each polymer and solvent

type when absolute molecular weight is needed (46). Furthermore, according to Flory, intrinsic viscosity depends on molecular weight instead of mass (47). Thus only if there is a unique relationship between size and mass can Mark-Houwink's equation be expected to hold strictly. This requires that the polymer be linear and unbranched; that the polymer solution be measured in the same solvent and at the same temperature for which (k) and (α) are determined, and that the polymer be of the same chemical type as that used in determining (k) and (α). It should also be noted that since the intrinsic viscosity is temperature and solvent dependent, its specification is incomplete unless those quantities are given as well as the units (48).

1.7 Objectives.

The present study has been aimed at finding out the effect of conditions of emulsion polymerisation of methyl methacrylate on the molecular weight distribution pattern of the bulk polymer. While some information are available on molecular weight distribution in PMMA obtained by emulsion polymerisation of the monomer using emulsifier concentrations above the cmc of the soap, and at least the work of Arai et al (33) discusses the soapless polymerisation of MMA and the theoretical molecular weight

distribution in the polymer, virtually no information exists on studies between these extremes concentrations of the soap. The main objective of this study, therefore, is to fill this gap, i.e. to study

(i) the kinetics of emulsion polymerisation of MMA using sodium lauryl sulphate concentration below its cmc and

(ii) molecular weight distribution in the bulk polymers obtained under selected experimental conditions.

The hope is to establish some form of relationship between

(i) the kinetics, and possibly mechanism of the polymerisation and

(ii) the molecular weight distribution pattern of PMMA produced below the cmc of (SLS), with variables such as temperature, emulsifier and initiator concentration

CHAPTER TWO

2.0 EXPERIMENTAL AND MATERIALS

2.1 Materials:

(i) Methylmethacrylate Monomer.

Hydroquinone stabilised methylmethacrylate monomer of commerical grade supplied by the British Drug House (BDH) Poole England was used. This was purified by distillation under vacuum. The purity of the distillate was ascertained by treatment of a small quantity of the purified monomer with aqueous NaOH in a separating funnel to obtain yellow coloration, if any, in the aqueous layer. Presence of such yellow colour was indicative of presence of some inhibitor as impurity. Whenever this was observed, distillation was repeated until satisfactory result was obtained, giving pure monomer sample. The purified monomer was stored in a brown bottle in a refrigerator.

(ii) Initiator and Emulsifier:

The initiator (Potassium persulphate - $K_2S_2O_8$) and emulsifier (sodium lauryl sulphate - $C_{12}H_{25}OSO_3Na$) were all also from (BDH) British Drug House Ltd but only the initiator was of analytical grade whilst the emulsifier was the reagent grade.

(iii) Nitrogen Gas:

Pure nitrogen gas was required to create inert atmosphere for polymerisation. Two methods of purification

of nitrogen gas were tried i.e. alkaline pyrogallol (49) and Fieser solution (50). To obtain complete oxygen removal from the nitrogen (N_2) gas supplied, Fieser solution method was preferred and used. This solution was changed from time to time to avoid its exhaustion.

(iv) Other Reagents:

These were chloroform, methanol and acetone which were also supplied by the (BDH). They were purified through simple distillation.

(v) Apparatus:

Water bath, thermostat, thermometer, reaction vessel, beakers, pipettefillers, pipettes, stop watch, viscometer, magnetic stirrer, burrete, electric stirrer, vacuum pump, vacuum oven, condensers, and distillation apparatus were needed.

2.2 Design of Experiment.

In order to accomplish the objectives of this work as set out in the introduction, the experiment was divided into four distinct phases viz:-

(i) Emulsion polymerisation
(ii) Recovery of polymer
(iii) Fractionation
(iv) Viscosity measurement.

2.2.1 Emulsion Polymerisation of methylmethacrylate.

The polymerisations were carried out in a constant temperature bath at two different temperatures viz $50^{\circ}C \pm 0.05^{\circ}C$ and $55^{\circ}C \pm 0.05^{\circ}C$. One litre capacity reaction kettle was used. The polymerisations were carried out using different emulsifer concentrations, different initiator concentrations, different volumes of water, and the same monomer concentration (1.133M/l).

Two sets of emulsion polymerisations were carried out. The recipes for the first set are shown in tables 2.1 and 2.2, whilst the recipes for the second set are shown in tables 2.3 and 2.4. Whereas the first set is for kinetic study, the second set is for molecular weight distribution study. The total volume of reaction mixture was $250cm^3$ in each case of polymerisation.

In carrying out the polymerisation the water bath was heated up to the required temperature ($50^{\circ}C$ or $55^{\circ}C$). The polymerisation reaction kettle containing a solution of specific concentration of water, initiator, and emulsifier was kept inside the water bath to attain bath temperature as it was being stirred. Nitrogen gas was passed through the Fieser solution to remove oxygen, then through lead acetate solution to remove any trace of hydrogen sulphide gas, through concentrated sulphuric

TABLE 2.1

Recipes for methylmethacrylate polymerisation at 50°C for kinetic study.

Sample Number	Distilled water M/l	Initiator concentration x 10^3 M/l	Emulsifier concentration x 10^3 M/l
A_1	48.33	3.70	1.63
A_2	47.78	3.70	3.25
A_3	46.67	3.70	6.49
A_4	44.44	3.70	12.97
A_5	48.33	4.44	1.63
A_6	47.78	4.44	3.25
A_7	46.67	4.44	6.49
A_8	44.44	4.44	12.97

TABLE 2.2

Recipes for methylmethacrylate polymerisation at 55°C for kinetic study.

Sample Number	Distilled water M/l	Initiator concentration x 10^3 M/l	Emulsifier concentration x 10^3 M/l
B_1	48.33	4.44	1.63
B_2	47.78	4.44	3.25
B_3	46.67	4.44	6.49
B_4	44.44	4.44	12.97

TABLE 2.3

Recipes for methlmethacrylate polymerisation at 50°C for molecular weight distribution Study.

Sample Number	Distilled water M/l	Intiator concentration x 10^3 M/l	Emulsifier concentration x 10^3 M/l	Time % polymirisation
C_1	48.33	3.70	1.63	140
C_2	48.33	3.70	1.63	180
C_3	47.78	3.70	3.25	120
C_4	47.78	3.70	3.25	150
C_5	46.67	3.70	6.49	110
C_6	46.67	3.70	6.49	130
C_7	44.44	3.70	12.97	80
C_8	44.44	3.70	12.97	100
C_9	48.33	4.44	1.63	100
C_{10}	48.33	4.44	1.63	130
C_{11}	47.78	4.44	3.25	90
C_{12}	47.78	4.44	3.25	110
C_{13}	46.67	4.44	6.49	70
C_{14}	46.67	4.44	6.49	90
C_{15}	44.44	4.44	12.97	50
C_{16}	44.44	4.44	12.97	70

TABLE 2.4

Recipes for methylmethacrylate polymerisation at 55°C for molecular weight distribution study.

Sample Number	Distilled water M/l	Initiator concentration x 10^3 M/l	Emulsifier concentration x 10^3 M/l	Time % polymerisation in minutes
D_1	46.67	4.44	6.49	30
D_2	46.67	4.44	6.49	40
D_3	44.44	4.44	12.97	25
D_4	44.44	4.44	12.97	30

acid to remove water, and finally through sodium hydroxide pelletes to remove any acidic moisture, into the reaction kettle. After fifteen minutes of degassing, 30cm^3 (1.133M/l) of purified methylmethacrylate (MMA) was introduced over 15 secs. and stirring continued till the end of polymerisation. In the first set of polymerisation, 25cm^3 of aliquot was pipetted out at suitable time intervals from the reaction mixture (during the course of the reaction) and was poured into pure ice-cold methanol, stirred briskly and allowed to settle. In the second set of polymerisation the reaction was stopped at a predetermined time by the introduction of an inhibitor (hydroquinone) and the total reaction mixture was poured out of the reaction kettle into pure ice-cold methanol stirred and also allowed to settle.

2.2.2 Recovery of polymer:

The settled polymer in methanol was filtered through a sunction pump, washed thoroughly during filtration with distilled water to remove traces of emulsifier and other water soluble impurities. Each filtrate (polymer) was dried in vacuum oven at 35^{o}C to a constant weight. The percentage conversion from the monomer was calculated for each sample.

2.2.3 Fractionation Experiment:

About 1g. of polymethylmethacrylate (PMMA) obtained from the emulsion polymerisation experiment as described earlier was accurately weighed into a beaker. 50cm^3 of chloroform was added to the sample which was allowed to dissolve undisturbed at room temperature. 50cm^3 burette was filled with a non-solvent (methanol). This was introduced into the polymer solution dropwise and stirred briskly with a magnetic stirrer until the polymer solution became slightly turbid. The turbid solution was covered with aluminium foil paper and was further stirred with magnetic stirrer for sufficient time, about 5hrs. Slow dropwise addition of methanol was continued until the solution turned milky. The milky solution was then warmed up in hot water until it became clear signifying that the polymer had dissolved. The solution thus obtained was stirred gently until it had cooled down to ambient temperature. This was then left undisturbed for the precipitate to form and settle. The solid was separated by decantation. It was filtered and dried to a constant weight in a vacuum oven at 35^{o}C. The procedure was repeated on the supernantant solution to obtain subsequent polymer fractions. The dried fractions obtained from each sample were weighed and the molecular weights were determined by viscosity measurement.

2.2.4 Viscosity Measurements and Molecular.weight determination of the PMMA.

The apparatus required were the Ubbelohde dilution type viscometer, a constant temperature bath and a stop watch.

The viscometer was first cleaned by filling it with chromic acid for twenty four hours. It was then washed thoroughly with distilled water and then left to dry properly. About 0.15g of each dried polymer sample was weighed accurately and dissolved to make $50cm^3$ solution in purified acetone. A thermostat bath was set up, heated to $30 \pm 0.05^{\circ}C$. The stock polymer solution and the pure solvent (acetone) all in separate volumetric flasks were kept inside the bath for sufficient time for them to attain thermal equilibrium before measurements were made. The viscometer was clamped inside the bath, and $10cm^3$ of purified acetone was pipetted into the viscometer. The efflux time of acetone was determined repeatedly until very close reproducible values were obtained. The viscometer was emptied and the solvent allowed to evaporate.

$10cm^3$ of the stock PMMA solution, already at bath temperature, in acetone (containing accurately weighed about about $0.15g/50cm^3$ of polymer) was measured into the

viscometer. The efflux time for the solution was determined as for pure acetone. Stepwise dilutions ($3cm^3$ of acetone at a time) of the polymethylmethacrylate (PMMA) solution in the viscometer were made and the efflux time determined after each addition of $3cm^3$ of acetone. In all, five stepwise dilutions were made.

From the values of efflux time, the specific (ηsp) and the relative (η_r) viscosity values were calculated. The linear plot of ($\eta sp/c$) versus concentration of PMMA (in g./dl) was made to obtain the limiting viscosity by extrapolation to zero solution concentration. Least square calculations were made in each case to obtain the best straight line through the experimental points. The viscosity average molecular weight of the PMMA samples were obtained from the limiting viscosity values using Mark-Houwink Sakarada equation where at $30^{\circ}C$ for acetone as solvent for PMMA,

$$k = 42.8 \times 10^{-3} cm^3 g^{-1}$$

and $$\alpha = 0.64 \quad (51)$$

The slope of the $\eta sp/c$ against concentration (giving k^1) in Huggins equation (1 - 20) was determined to obtain k^1 (Huggins constant).

CHAPTER THREE

3.0 RESULTS AND DISCUSSIONS

3.1 Kinetic study of emulsion polymerisation of methylmethacrylate.

Methylmethacrylate was polymerised for different lengths of time and with different concentrations of sodium laurylsulphate (SLS) in the presence of potassium persulphate below the critical micelle concentration (cmc) of the emulsifier. The results obtained are shown graphically in figure 3.1. The curves obtained have sigmoid shape similar to those obtained by Gardon (24) and Howard et al (32) when methylmethacrylate was polymerised above the cmc of (SLS). Each curve depicts an increase in the rate of polymerisation with time of polymerisation. Each graph can be divided into three intervals I, II and III according to Gardon (22). The intervals were also observed by Howard (32). In figure 3.1 the interval I corresponds to range of conversion below 35%. This interval was described by Gardon (22) to be particle forming period. As soon as these are formed, monomer will then begin to diffuse to the respective radicals. The reaction mixture has three phases viz monomer-swollen polymer particle, droplets of monomer and the aqueous phase. The rate of polymerisation also increases in interval I steadily. The increase in rate is not constant, consequently the interval is non-linear.

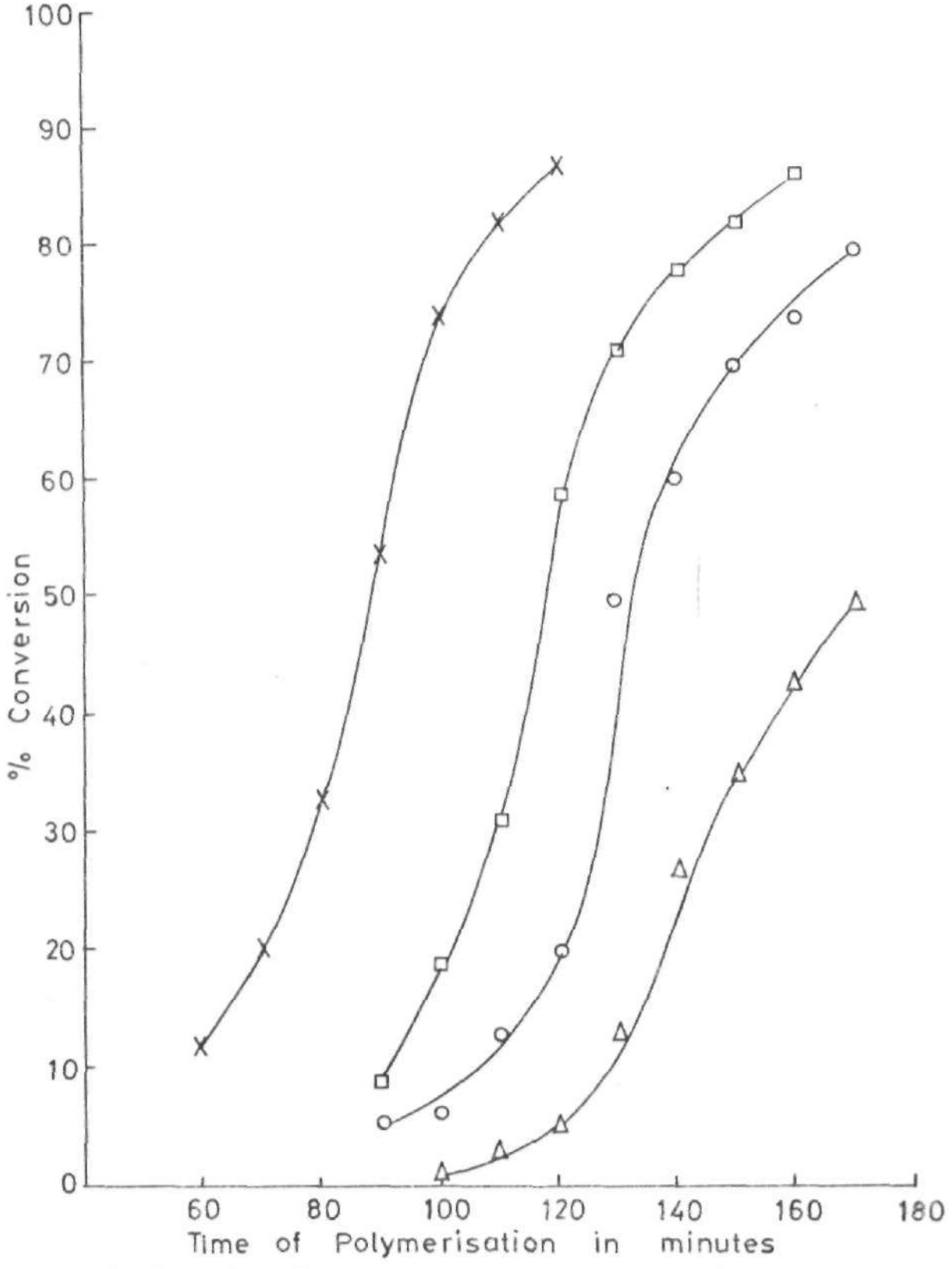


FIG. 3·1: KINETIC OF THE POLYMERISATION OF 1·13 M/L MMA AT 50°C, $3 \cdot 70 \times 10^{-3}$ M/L ($K_2 S_2 O_8$)
EMULSIFIER CONCENTRATION (Δ) $1 \cdot 63 \times 10^{-3}$ M/L
(o) $3 \cdot 25 \times 10^{-3}$ M/L (o) $6 \cdot 49 \times 10^{-3}$ M/L (X) $12 \cdot 97 \times 10^{-3}$ M/L

Interval II represents the special polymerisation period. According to Gardon (22) the number of particles is constant in the absence of aggregation in interval II. The major event taking place at this interval is mainly diffusion of monomer to the growing chains. This trend in polymerisation of methylmethacrylate could have occurred as a result of chain reaction polymerisation and growth by radical addition of monomer to a small number of active centres. The linear part of each curve varies from one curve to the other but in general it represents a range of conversion between 35 - 70%. Gardon (22) also concluded that the reaction mixture also has three phases as in interval I.

In interval III, the rate of polymerisation is no longer constant but begins to slow down to a minimum. This region is non-linear with concave shape, when termination is expected to set in gradually and finally at 100% conversion. This is in agreement with what was obtained by Gardon (25) but differs from what is anticipated on the basis of Smith - Ewart's (21) assumption, that termination is instataneous. It is believed that monomer concentration in the reaction mixture must have reduced greatly leading to its disappearance. Thus the reaction mixture becomes a two phase system of monomer-swollen particles and aqueous phase in interval III. In addition the conversion is

believed to have proceeded far enough so that the unconverted (MMA) was present as solvent for the polymer particles.

Figures 3.2 and 3.3 also show variation in percentage conversion with time of polymerisation as in figure 3.1. Although the conditions of polymerisation in Figures 3.2 and 3.3 differ from those of figure 3.1 the trends of the curves are essentially the same. The three intervals can also be recognised on each of the curves.

3.1.1 Induction period:

During the course of polymerisation a period was observed when apparently no polymerisation took place. This period is called the induction period. It is the period of apparently zero rate of polymerisation.

Induction period could be caused by the presence of an inhibitor such as oxygen in the system. However the design of the experiment ensured the complete removal of an inhibitor from the system. For example purified monomer was used, and purified nitrogen was used to displace any oxygen that might be contained in the reaction kettle before monomer was introduced. The initiator used was also of analytical grade. However another reason that might be adduced for this elapsed

period is the fact that the molecules of monomer, initiator, emulsifier and water had to be rearranged or readjusted for polymerisation to take place. This requires some time.

Induction period was observed for every polymerisation carried out. The observed period could be estimated from figures 3.1, 3.2 and 3.3 obtained under different conditions of polymerisation. It can be observed from these figures that induction period is dependent upon emulsifier concentration [E], initiator concentration [I] and also upon the temperature of polymerisation. The period increases with decrease in [E], [I] and temperature of polymerisation.

3.1.2 Features of polymer obtained:

Under the conditions of polymerisation of methylmethacrylate (MMA) monomer as previously described, the polymer obtained exhibited certain physical features. The colour was white and the polymer was powdery. As [E] increased the polymer obtained became more powdery.

3.1.3 Effects of emulsifier concentration on the kinetic of polymerisation:

Emulsifier concentration [E] affects the kinetics of polymerisation of methylmethacrylate. The effect can be seen in figures 3.1, 3.2 and 3.3. From these graphs the percentage conversion is dependent upon [E] .

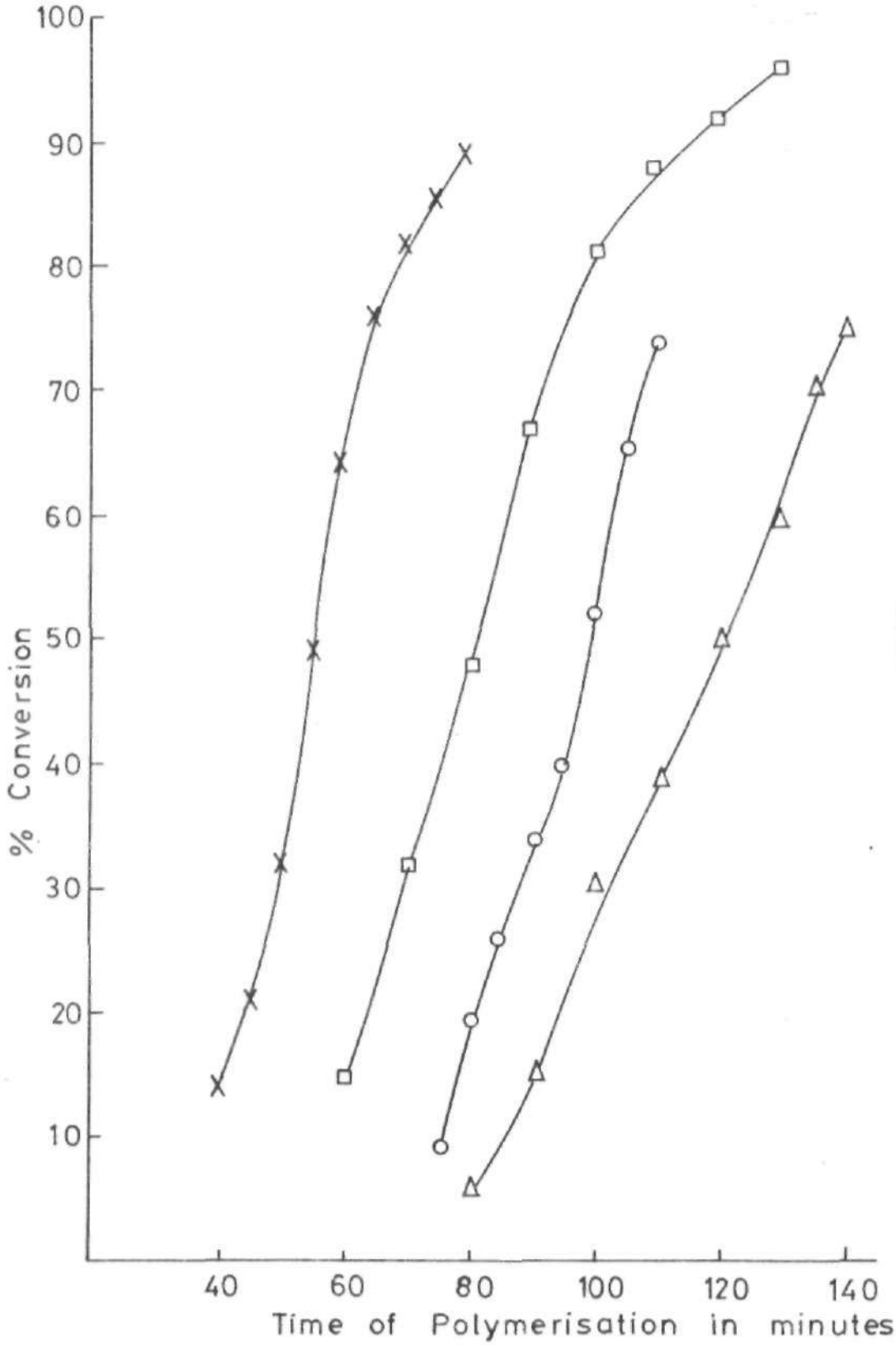


FIG. 3·2: KINETIC OF THE POLYMERISATION OF 1·13 M/L (MMA) AT 50°C, $4 \cdot 44 \times 10^{-3}$ M/L ($K_2S_2O_8$) EMULSIFIER CONCENTRATION (Δ) $1 \cdot 63 \times 10^{-3}$ M/L (o) $3 \cdot 25 \times 10^{-3}$ M/L (□) $6 \cdot 49 \times 10^{-3}$ M/L (X) $12 \cdot 97 \times 10^{-3}$ M/L

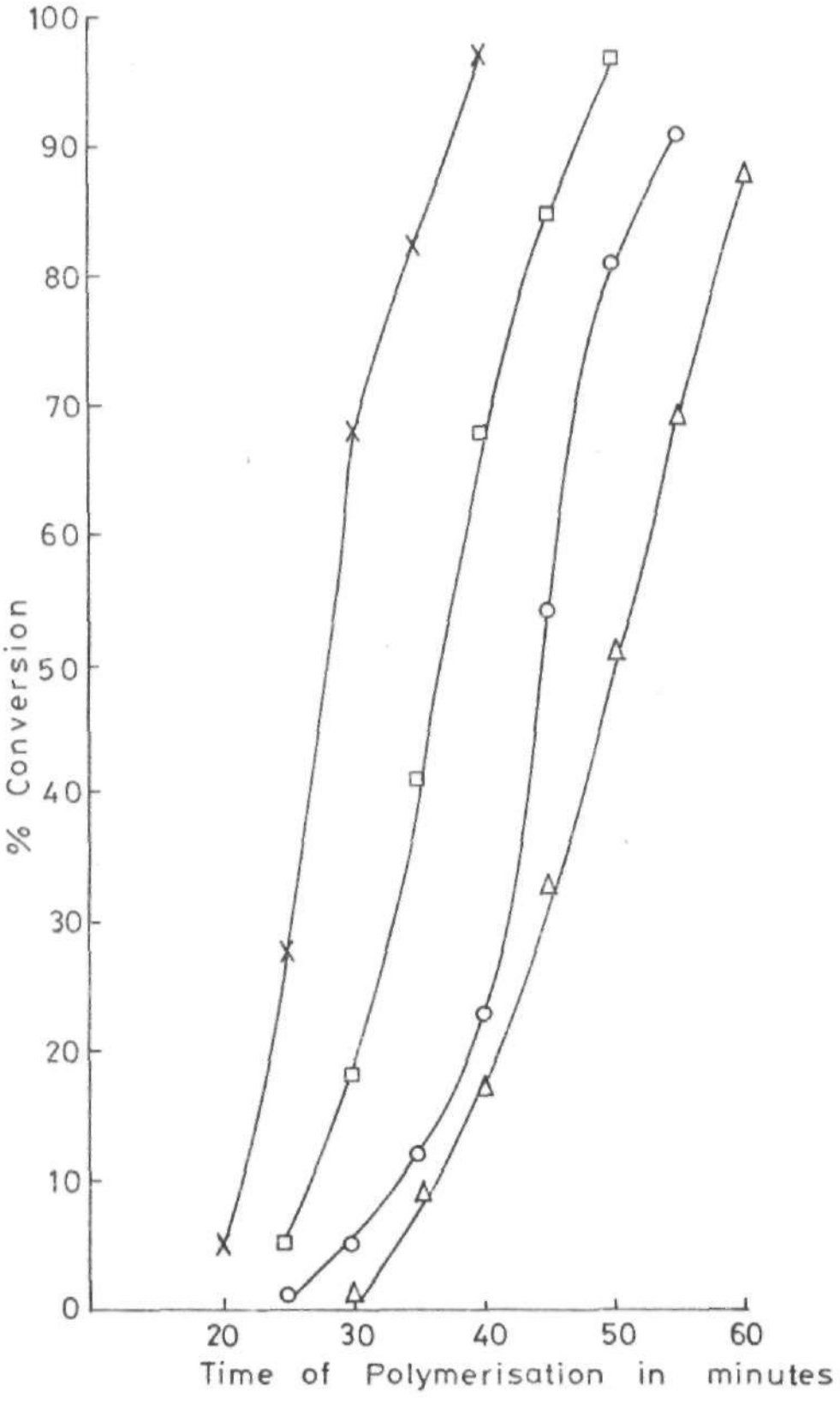


FIG. 3·3: KINETIC OF THE POLYMERISATION OF 1·13 M/L (MMA) AT 55°C. $4·44 \times 10^{-3}$ M/L ($K_2S_2O_8$), EMULSIFIER CONCENTRATION (Δ) $1·13 \times 10^{-3}$ M/L (o) $3·25 \times 10^{-3}$ M/L (□) $6·49 \times 10^{-3}$ M/L (X) $12·97 \times 10^{-3}$ M/L

The polymer yield increased with time of polymerisation as well as increase in $[E]$ for figures 3.1, 3.2 and 3.3. It means therefore that polymer particles increased with $[E]$.

Figure 3.4 also shows a plot of percentage conversion versus emulsifier concentration $[E]$ for 30, 35, 45 and 50 minutes of polymerisation respectively. The four curves confirm that appreciable amounts of polymer were formed below the critical micelle concentration (cmc) of (SLS). Since there were no micelles below the (cmc) of (SLS), the result can be explained by assuming that emulsifier still plays a substantial role in the emulsion polymerisation of water insoluble monomer (MMA). This was further proved by the variation of conversion with emulsifier concentration $[E]$ in which percentage conversion increase, with $[E]$ below the (cmc), i.e. from 1.63×10^{-3} M/l of (SLS) to that above the (cmc), 12.97×10^{-3} M/l of (SLS).

Emulsifier concentration $[E]$ also affects the rate of polymerisation below the cmc of (SLS) as depicted in figure 3.5. From the Smith-Ewart's theory (21) of emulsion polymerisation $(R_p) \alpha [E]^{0.6}$ and $(R_p) \alpha (N)$. This is expected to apply strictly to water insoluble monomers such as styrene when they are individually

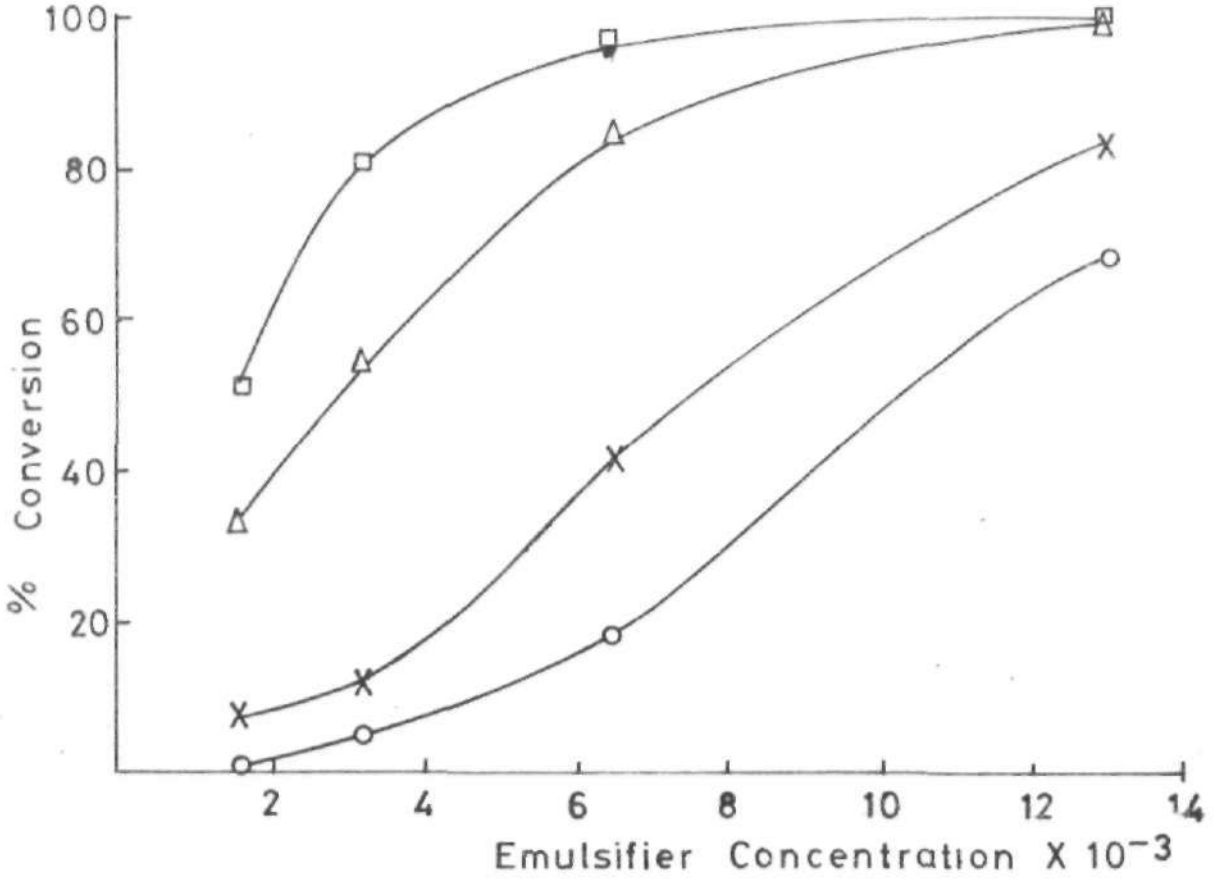


FIG 3·4: EFFECT OF EMULSIFIER CONCENTRATION ON THE KINETICS OF POLYMERISATION OF 1·13 M/L (MMA) AT 55°C, 4·44 X 10^{-3} M/L ($K_2 S_2 O_8$), (o) 30 Minutes, (X) 35 Minutes, (Δ) 45 Minutes, (□) 50 Minutes.

polymerised below the cmc and methylmethacrylate. The portion of the conversion - time curve over which the rate of polymerisation was constant was used to obtain (R_p), the rate of polymerisation. The logarithm of (R_p) was plotted against logarithm of $[E]$ in figures 3.5, 3.6 and 3.8. The plots are approximately linear.

From equation

$$(R_p) \alpha [E]^a \qquad (3 - 1)$$

$$(R_p) = k [E]^a \qquad (3 - 2)$$

$$\ln(R_p) = \ln k + a \ln [E] \qquad (3 - 3)$$

Hence the plot of $\ln(R_p)$ vs $\ln[E]$ has a slope of (a) and intercept of lnk.

From the plots, the following results were obtained

(i) $(R_p) \alpha [E]^{0.44}$ with 3.70×10^{-3} M/l $[I]$ at 50°C

(ii) $(R_p) \alpha [E]^{0.50}$ with 4.44×10^{-3} M/l $[I]$ at 50°C

and (iii) $(R_p) \alpha [E]^{0.60}$ with 4.44×10^{-3} M/l $[I]$ at 55°C

The results obtained compare with Medvecley-Sheinkner (20) and Brednyan (29) relationship where

$$(R_p) \alpha [E]^{0.50}$$

whilst only that obtained at 55°C, 4.44M/l of $[I]$ agrees with what should be expected on Smith-Ewart arguments. It therefore appears that the exponent (a) depends greatly on the concentrations of emulsifier, initiator and on temperature for a fixed (monomer)/(water) ratio.

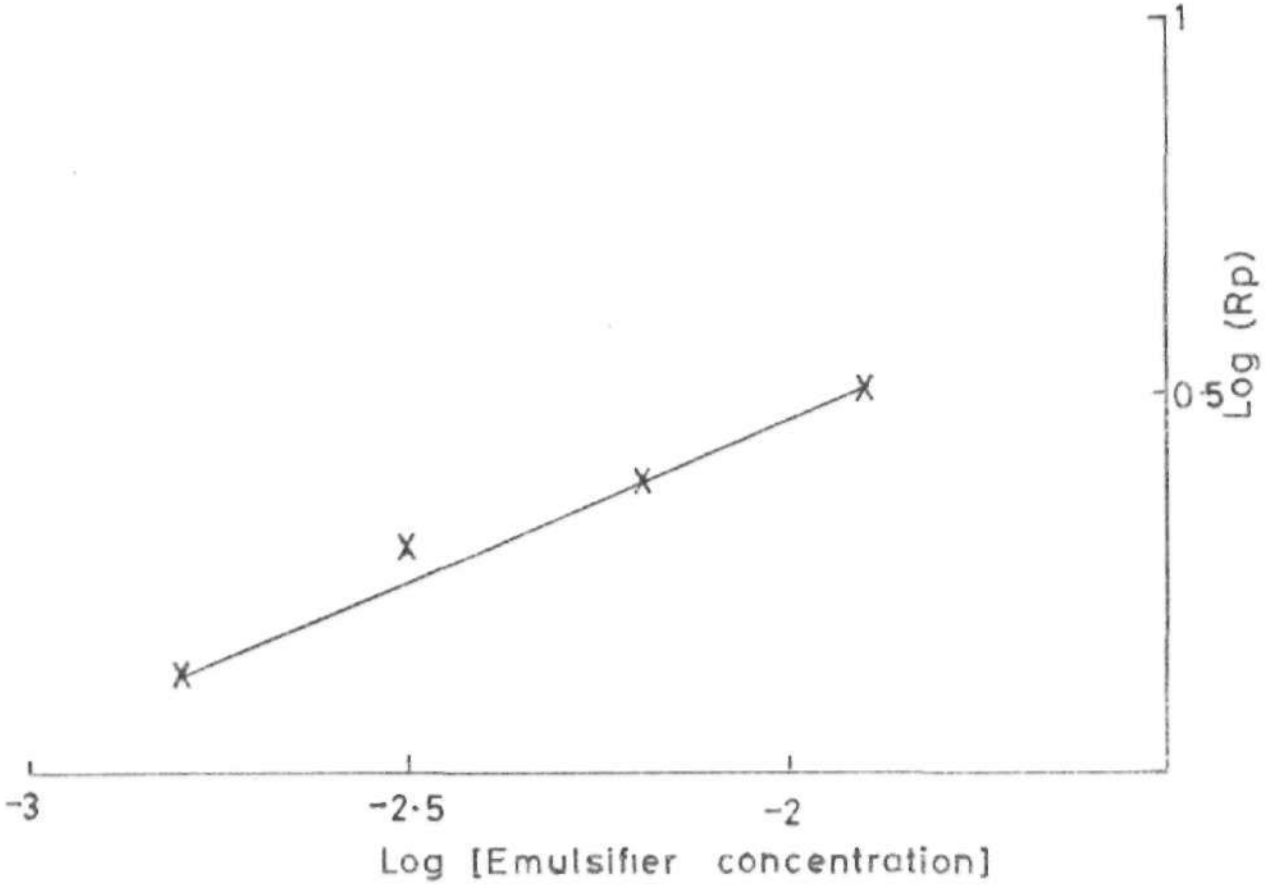


FIG. 3·5: EFFECT OF EMULSIFIER CONCENTRATION ON THE RATE OF POLYMERISATION OF 1·13M/L (MMA) AT 50°C WITH $4{\cdot}44 \times 10^{-3}$ M/L ($K_2S_2O_8$) SLOPE = 0·50

3.1.4 Effect of initiator concentration on the rate of polymerisation.

Figures 3.1 and 3.2 were obtained on polymerising (MMA) with different initiator concentrations. When the two graphs are compared it can be seen that percentage conversion increases with initiator concentration $[I]$ for a set of experimental conditions. This is to be expected because as the concentration of initiator increases, the number of initiator decomposing into primary radicals also increases thereby increasing the number of growing particles hence the increase in percentage monomer conversion.

Figure 3.6 also illustrates the plot of log rate of polymerisation against log of $[E]$ for two initiator concentrations. Although the plots are linear, the slopes differ from one another thus confirming futher that initiator concentration has an effect on the rate of polymerisation.

The slopes obtained are

$$0.44 \text{ for } 3.70 \times 10^{-3} \text{M/l of } [I]$$

$$0.50 \text{ for } 4.44 \times 10^{-3} \text{M/l of } [I]$$

Using equation (3 - 1) rate of polymerisation can be written as

$$(R_p) \propto [E]^{0.44} \text{ with } 3.70 \times 10^{-3} \text{M/l of } [I]$$

$$\text{and} \quad (R_p) \propto [E]^{0.50} \text{ with } 4.44 \times 10^{-3} \text{M/l of } [I]$$

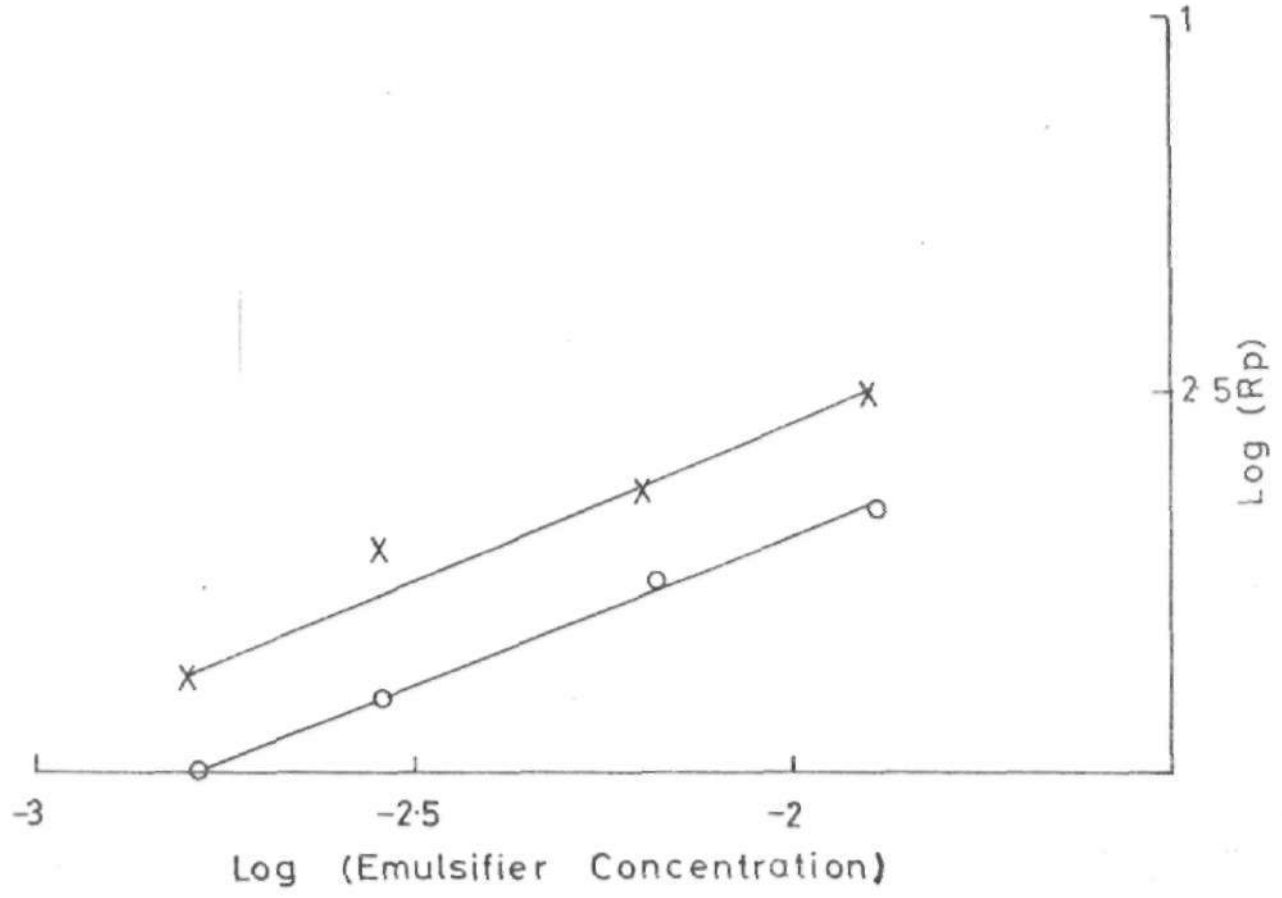


FIG. 3·6: EFFECT OF EMULSIFIER CONCENTRATION ON THE RATE OF POLYMERISATION FOR TWO INITIATOR ($K_2S_2O_8$) CONCENTRATION (o) $3{\cdot}70 \times 10^{-3}$ M/L AND (X) $4{\cdot}44 \times 10^{-3}$ M/L AT 50° WITH 1·13 M/L (MMA).

It therefore implies that the bigger the slope the higher the rate of polymerisation and this also means that [I] affects the power to which [E] is raised.

3.1.5 Effect of temperature variation on polymerisation of methylmethacrylate (MMA).

Figure 3.7 illustrates the effect of temperature on the kinetics of emulsion polymerisation of (MMA). As the temperature increases, the rate of polymerisation also increases and hence the percentage conversion at a given time of polymerisation prior to 100% of the former. This situation will occur because as temperature increases the rate of radical dissociation will increase. Also increase in temperature accelerates the rate of monomer diffusion of growing polymer chain. This implies therefore that (k_i) and (k_p) will increase with increase in temperature. If the assumption of steady state holds, (k_i) is regarded to be negligible and therefore rate of polymerisation is equal to (k_p). In addition, the result obtained is similar to that obtained by Venderhoff et al (26) in which he observed an increase in the number of growing particles as temperature is increased when potassium persulphate was used as an initiator for the polymerisation of methylmethacrylate.

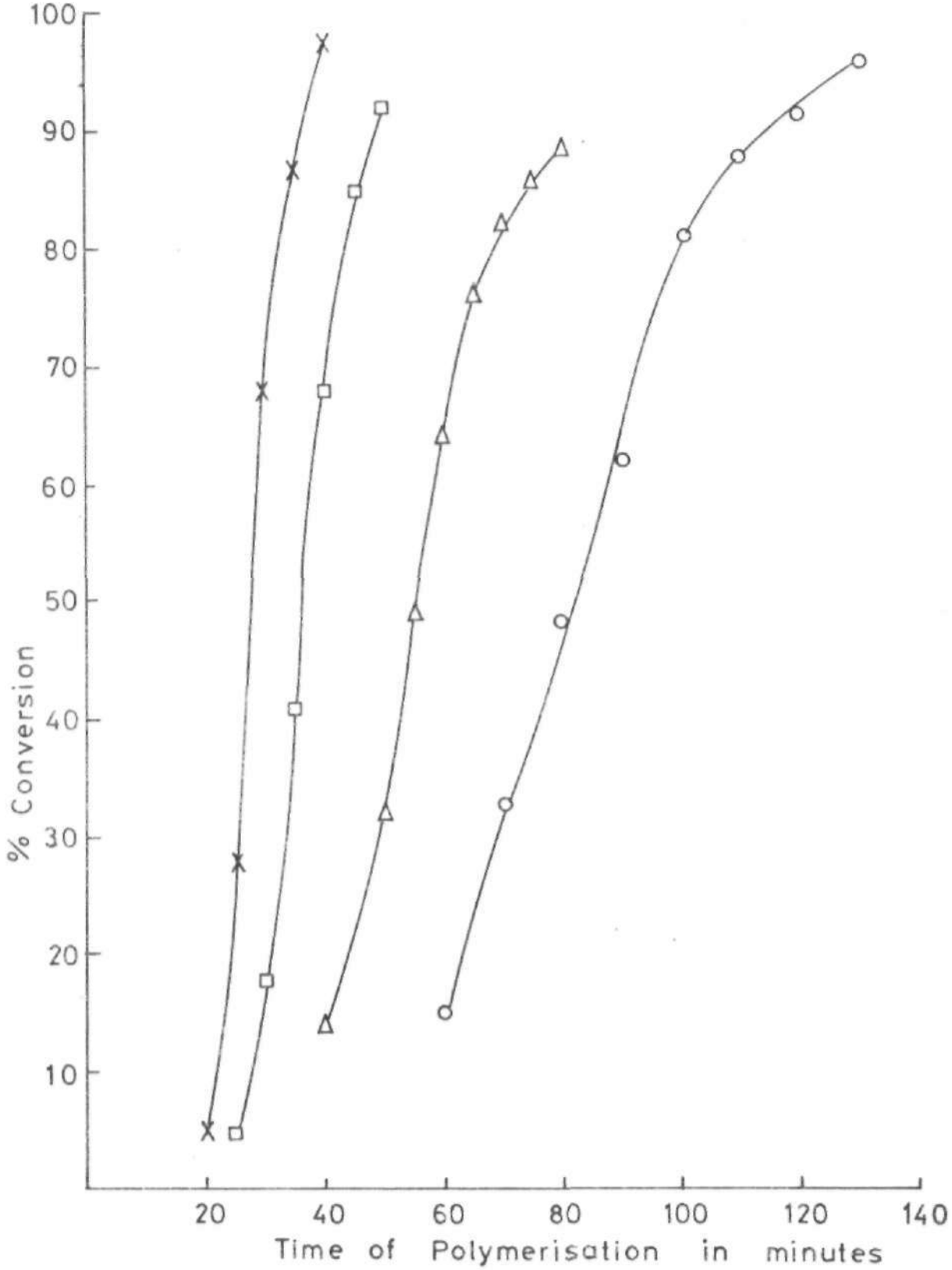


FIG. 3·7: EFFECT OF TEMPERATURE ON THE KINETIC OF POLYMERISATION OF 1·13 M/L MMA AND $4·44 \times 10^{-3}$ M/L ($K_2 S_2 O_8$), FOR TWO EMULSIFIER CONCENTRATIONS (o) 50°C $6·49 \times 10^{-3}$ M/L (S L S) (□) 55°C $6·49 \times 10^{-3}$ M/L (S L S) (Δ) 50°C $12·97 \times 10^{-3}$ M/L (S L S) (X) 55°C $12·97 \times 10^{-3}$ M/L (SLS)

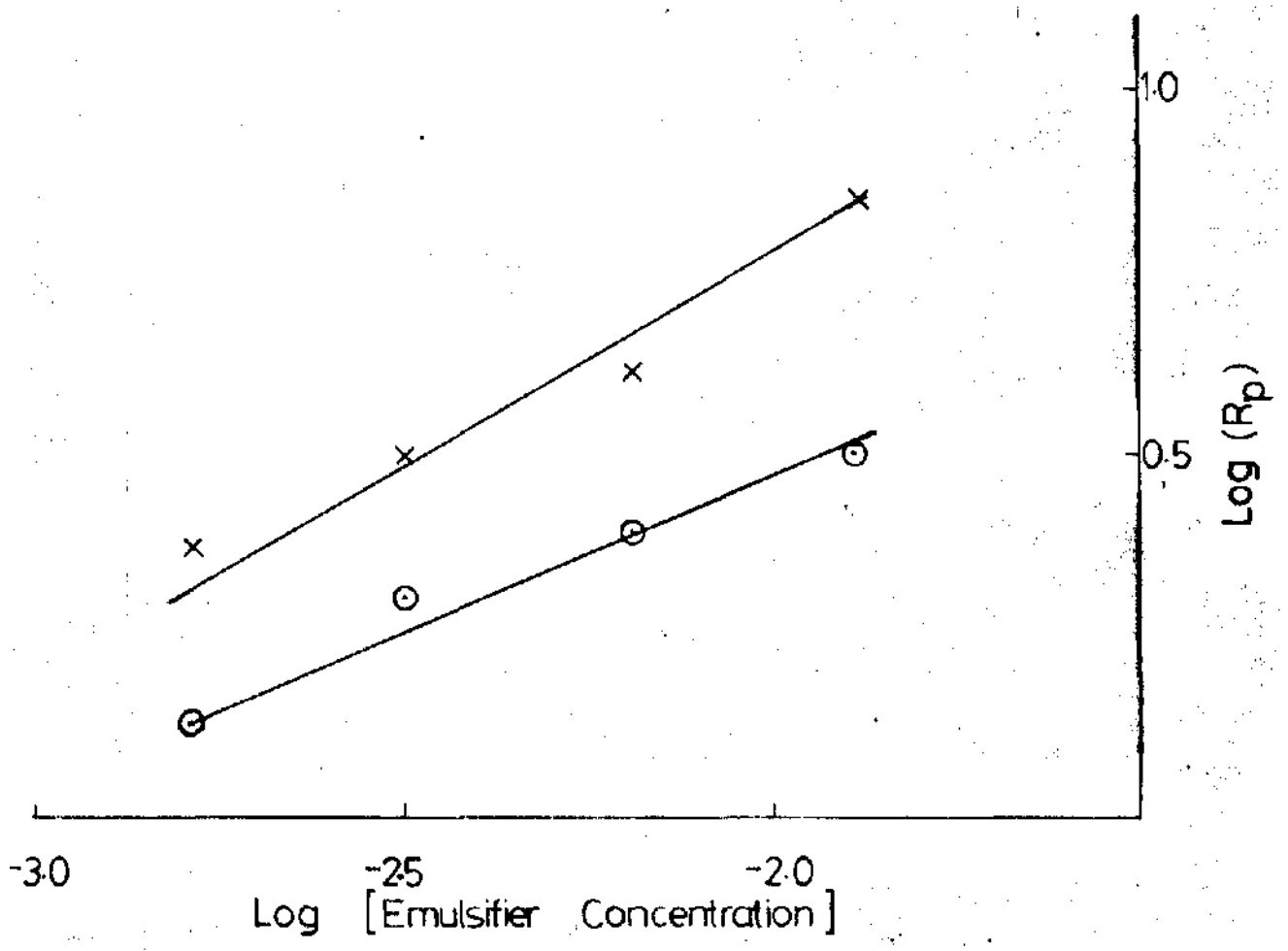


FIG 3.8: EFFECT OF THE RATE OF POLYMERISATION OF 1.13M/L (MMA) ON EMULSIFIER CONCENTRATION AT(⊙) 50°C, (X) 55°C WITH 4.44×10^{-3} M/L ($K_2S_2O_8$).

Figure 3.8 which is also the plot of logarithm of rate of polymerisation against the logarithm of emulsifier concentration $[E]$, illustrates how rate of polymerisation depends upon temperature of polymerisation. This effect is reflected in the values of the slopes obtained. These are

$$0.50 \text{ at } 50^{\circ}C$$

$$0.60 \text{ at } 60^{\circ}C$$

$$\text{and hence } (R_p) \alpha [E]^{0.50} \text{ at } 50^{\circ}C$$

$$\text{and } (R_p) \alpha [E]^{0.60}$$

From the above therefore the power to which $[E]$ is raised is dependent upon temperature variation.

Also the difference in the rate of polymerisation at different temperatures may be due to increased mobility of molecules in the polymerisation system. Increase in mobility of molecules is due to increase in their kinetic energy during the course of reactions such as radical dissociation, propagation, and termination in the system.

3.2 Molecular Weight Distribution Study.

3.2.1 Molecular weight of unfractionated polymer samples:

The viscosity average molecular weights ($\bar{M}_v$) of the unfractionated polymer samples were determined and the results are shown in tables 3.1, 3.2 and 3.3 respectively.

TABLE 3.1

Molecular weight of unfractionated polymer samples on polymerising 1.13M/l of (MMA), in different emulsifier concentration and water at 50°C with 3.70×10^{-3} M/l ($K_2S_2O_8$)

Samples	$[E] \times 10^{3}$ M/l	Conversion %	$[\eta]$ (g/dl)	$\bar{M}_v \times 10^{-6}$	$\bar{M}_v$/ conversion	Huggins constan
C_1	1.63	21.21	5.30	2.48		0.48
C_2	1.63	51.62	5.50	2.63	6322	0.44
C_3	3.25	34.15	6.70	2.58		0.51
C_4	3.25	77.72	7.10	3.92	7800	0.51
C_5	6.49	37.80	7.20	4.04		0.71
C_6	6.49	94.75	7.60	4.39	6250	0.75
C_7	12.97	44.93	8.00	4.73		1.22
C_8	12.97	90.25	8.30	5.01	6180	1.48

TABLE 3.2

Molecular weight of unfractionated polymer samples on polymerising 1.13M/l of (MMA) in different emulsifier concentration and water at 50°C with 4.44×10^{-3} M/l ($K_2S_2O_8$)

Samples	$[E] \times 10^{5}$ M/l	Conversion %	$[\eta]$ (g/dl)	$\bar{M}_v \times 10^{-6}$	$\bar{M}_v$/ conversion	Huggins constant.
C_9	1.63	25.59	5.10	2.34		0.52
C_{10}	1.63	66.92	5.34	2.51	4210	0.61
C_{11}	3.25	37.25	6.80	3.67		0.68
C_{12}	3.25	90.18	7.20	4.01	6461	0.73
C_{13}	6.49	36.10	5.90	2.94		0.87
C_{14}	6.49	88.38	6.30	3.26	6060	0.83
C_{15}	12.97	28.25	5.60	2.71		0.41
C_{16}	12.97	85.56	6.00	3.02	5322	0.60

TABLE 3.3

Molecular weight of unfractionated polymer samples on polymerising 1.13M/l (MMA) in different emulsifier concentration and water at 55°C with 4.44×10^{-3} M/l ($K_2S_2O_8$)

Samples	$[E] \times 10^3$ M/l	Conversion %	$[\eta]$ (g/dl)	$\bar{M}_v \times 10^{-6}$	$\bar{M}_v$/conversion	Huggins constant
D_1	6.49	40.85	6.40	3.33		
D_2	6.49	83.01	6.60	3.56	3910	
D_3	12.97	21.63	6.50	3.42		
D_4	12.97	76.21	6.70	3.58	3040	

On the basis of the various molecular weights, one general comment can be made. That is below the cmc of (SLS), polymer obtained has molecular weight in millions. This result, therefore, does not support the idea that polymerisation below the cmc of the emulsifier involves the precipitation of mainly oligomers (20) and formation of only low molecular weight polymer.

It can be seen in table 3.1 that for a substantial increase in the percentage conversion of monomer-to-polymer there is just a slight increase in the molecular weight of polymer formed. The result agrees with the observation of Arai et al (33) that the molecular weight remains almost constant to their initial values over almost the complete course of reaction in the emulsion polymerisation of (MMA) above the cmc of (SLS). In the experiment the molecular weight remains almost constant to the initial values over the range of conversion studied under the polymerisation conditions. Even under different conditions of polymerisation as revealed in tables 3.2 and 3.3, the same trend of slight increase in ($\bar{M}_v$) over a wide percentage conversion is observed.

The effect of emulsifier concentration [E] on the molecular weights of the bulk polymer samples can also

be recognised in tables 3.1, 3.2 and 3.3. In tables 3.1 and 3.3 it could be seen that low molecular weights vary with emulsifier concentration [E]. It implies that in polymerising 1.13M/l of (MMA) with 3.70 x 10^{-3}m/l of ($K_2S_2O_8$) in different [E] at 50°C and 4.44 x 10^{-3}m/l of ($K_2S_2O_8$) at 50°C and 55°C temperatures, molecular weight will increase slightly with increase in [E] below the cmc of (SLS). Brodnyan (29) however observed little or no increase in the molecular weight of PMMA produced by the emulsion polymerisation of (MMA) above the cmc of the emulsifier. In this result the molecular weight increased relatively with increase in [E] below the cmc of (SLS) as shown in table 3.1. In addition table 3.2 shows molecular weight of polymer with different [E] for a different [I] from that used in table 3.1. From table 3.2 variation in [E] affects viscosity average molecular weight in which less values were obtained at higher [I] than at lower [I] values. The ($\bar{M}_v$) is smaller with those on table 3.1 which means that the higher the [I] for the same [E] the lower the ($\bar{M}_v$).

By comparing the molecular weights in tables 3.1 and 3.2 it will be seen that the lower the initiator concentration [I] the higher the average molecular weight of the polymer obtained under a set conditions of polymerisation. This result is similar to the observations of Olayemi et al (52) that molecular weight of PMMA

decreases with increase in initiator concentration [I] used in the polymerisation. The reason that may be adduced for this is that as the amount of initiator increases more radicals are likely to be produced. Hence the growing polymer particles is not likely to grow extensively before termination sets in, and most likely by the mode of combination (10).

Temperature affects the molecular weight of a polymer during its production . The effect of temperature on the molecular weight is demonstrated by the results in tables 3.2 and 3.3. Comparing these two tables, it can be seen that molecular weight increases with temperature but ($\bar{M}_v$/conversion) decreases. This implies that as the temperature of polymerisation increases, rate of particle formation is increased as well as the rate of monomer diffusion and addition to the growing particle chain thereby increasing the molecular weight of polymer under study. The rate of termination might also be increased slightly so as to control the rate of the variation of ($\bar{M}_v$/conversion) accordingly.

During polymerisation, number of monomer unit added per unit conversion ($\bar{M}_v$/unit conversion) varies. Tables 3.1, 3.2 and 3.3 convey this general information although

only two corresponding values of viscosity average molecular weight of the samples have been studied for the temperatures. In calculating the ratio ($\bar{M}_v$/conversion) it was assumed that over a reasonable spread of monomer conversion, the growth of the polymer chain was at reasonable linear rate, that is ($\bar{M}_v$) varies linearly with monomer conversion. That this might not necessarily be an over-assumption is supported by the work of Gardon (24). From the result obtained the number of monomer unit added per minute or unit conversion, varies with $[E]$, $[I]$, and temperature of polymerisation. The trend is that monomer unit addition per unit conversion (i) decreases with increase in $[E]$, except at 3.25×10^{-3} M/l of $[E]$ that there is increase, (ii) decreases with $[I]$ and with temperature of polymerisation. It means that as the $[E]$ increases, the number of polymer particles increases thus reducing the number of monomer added per unit conversion. This is justified by the values on the table 3.1 where 12.97×10^{-3} M/l $[E]$ above the cmc of (SLS) has the smallest value compared with 1.63×10^{-3} M/l $[E]$ below the cmc. Whilst with low initiator concentration $[I]$, the number of particles are less, more monomer can join the growing polymer particles thus increasing the number of monomer addition per unit conversion before termination sets in. But as temperature increases, the monomer

addition too decreases. This is because at high temperature molecules are more mobile, more radicals will be formed and termination will set in earlier than when a lower temperature is used.

Using equation (1 - 23) which is the

$$\left(\frac{sp}{c}\right) = [\eta] + k'[\eta]^2_c$$

Flory-Huggins equation (44) (k') is Huggins constant determined.

The values of (k') are shown in the last column of tables 3.1, 3.2 and 3.3. It has been reported (53) that the normal range of (k') for good polymer-solvent interactions is about 0.2 - 0.4. Huggins constant for each polymer-solvent sample differs, and it was found to be outside of the range quoted for good polymer-solvent interaction for most of the polymer samples studied. The results shows generally that the higher the molecular weight of the polymethylmethacrylate sample, the lower the polymer-solvent interaction and the higher the values of (k'). It also suggests that the polymer produced might exist in the form of coils, especially if the temperature of the viscosity study was far below the theta temperature for the system. Huggins constant of PMMA-acetone

system is also affected by $[I]$, $[E]$ and temperature of polymerisation. The constant was found to (i) increase in $[E]$, (ii) decrease with in increase in $[I]$ and temperature. Since all these factors affect molecular weight of the polymer samples, their effects on the values of (k^1) are therefore not surprising.

3.2.2 Fractionated samples:

Generally when one gram of each of the bulk polymer samples was fractionated, only two fractions were obtained except for polymer samples obtained at $50^{o}C$ with the highest $[E]$ value 12.97×10^{-3} M/l, which is above the cmc of (SLS) that yielded a very small third fraction. Fractionation was repeated for each bulk polymer sample until at least ten fractions were obtained for the determination of molecular weight distribution curve. This then means that only two distinct fractions could be obtained from PMMA bulk samples by the fractionation method employed irrespective of the emulsifier concentration $[E]$ and the degree of monomer conversion. With this method, the first fractions were found to be bigger than the second fractions.

The dilute solution viscosity for each fraction was carried out and the molecular weight calculated from the determined $[\eta]$. The results of these are shown in table 3.4 - 3.24. Weight fractions were obtained by

dividing the weight of the fractions by total weight used for fractionation. The cummulative weight fractions (54) were calculated using the formular

$$C(M_2) = \tfrac{1}{2}w_i + \sum_{1}^{i-1} w_i \qquad (3 - 2)$$

TABLES 3.4 to 3.23: ILLUSTRATE THE INTRINSIC VISCOSITY, AVERAGE MOLECULAR WT., WT. FRACTION, CUMMULATIVE WT. FRACTION AND HUGGINS CONSTANT 'K' FOR SAMPLES C_1 to C_{16} AND D_1 to D_4.

TABLE 3.4

SAMPLE C_1 $\bar{M}_v = 2.48 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	1.59	0.37	0.08	0.04	0.00
2	1.70	0.42	0.10	0.12	0.00
3	2.55	0.79	0.14	0.24	0.46
4	2.75	0.89	0.18	0.39	0.94
5	5.50	2.30	0.81	0.88	0.32
6	5.18	2.40	0.82	1.70	0.40
7	5.25	2.45	0.78	2.50	0.42
8	5.32	2.49	0.77	3.27	0.44
9	5.62	2.72	0.75	4.03	0.51
10	6.15	3.13	0.70	4.70	0.56

Average 'k' - 0.405

TABLE 3.5

SAMPLE C_2 $\bar{M}_v = 2.63 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	2.45	0.74	0.08	0.04	0.27
2	3.55	1.32	0.10	0.13	0.42
3	3.60	1.36	0.13	0.24	0.72
4	4.39	1.85	0.18	0.39	0.57
5	5.02	2.28	0.85	0.91	0.57
6	5.11	2.34	0.88	1.78	0.40
7	5.44	2.59	0.88	2.66	0.51
8	5.52	2.69	0.76	3.58	0.53
9	5.72	2.80	0.88	4.30	0.49
10	5.89	2.94	0.76	5.12	0.46

Average 'k' = 0.496

TABLE 3.6

SAMPLE C_3 $\bar{M}_v$ = 2.58 x 10^6

FRACTION NO	$[\eta]$ g/dl	M_v x 10^{-6}	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	1.20	0.24	0.08	0.04	0.00
2	2.25	0.65	0.10	0.13	0.32
3	4.05	1.63	0.17	0.26	0.49
4	6.32	3.26	0.18	0.44	0.49
5	6.11	3.59	0.78	0.92	0.63
6	6.83	3.69	0.82	1.72	0.64
7	6.89	3.74	0.81	2.53	0.63
8	6.99	3.82	0.87	3.37	0.65
9	7.41	4.19	0.88	4.25	0.58
10	7.58	4.34	0.79	5.08	0.57

Average 'k' = 0.500

TABLE 3.7

SAMPLE C_4 $\bar{M}_v$ = 3.92 x 10^6

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v$ x 10^{-6}	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	1.72	0.43	0.09	0.05	1.08
2	1.93	0.51	0.16	0.17	0.89
3	2.09	0.58	0.18	0.34	1.49
4	2.25	0.65	0.27	0.56	2.17
5	7.35	4.13	0.79	1.09	0.97
6	7.48	4.25	0.85	1.91	0.60
7	7.52	4.29	0.87	2.76	0.60
8	7.91	4.64	0.87	2.76	0.55
9	8.12	4.83	0.83	4.41	0.01
10	8.65	5.33	0.88	5.27	0.53

Average 'k' = 0.889

TABLE 3.8

SAMPLE C_5 $\bar{M}_v = 4.04 \times 10^5$

FRACTION NO	[n] d/gl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGINS CONTANT 'k'
1	3.15	1.10	0.08	0.04	1.03
2	3.96	1.57	0.11	0.16	0.73
3	4.47	1.90	0.25	0.37	0.67
4	6.87	3.72	0.86	0.92	0.65
5	7.32	4.13	0.68	1.69	0.59
6	7.55	4.32	0.73	2.40	0.58
7	7.65	4.41	0.75	3.14	0.58
8	7.70	4.45	0.80	3.91	0.61
9	7.81	4.55	0.86	4.74	0.60
10	8.19	4.90	0.73	5.30	0.56

Average 'k' = 0.660

TABLE 3.9

SAMPLE C_6 $\bar{M}_v = 4.28 \times 10^6$

FRACTION NO	[n] g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	5.15	2.37	0.08	0.04	0.45
2	6.18	3.16	0.15	0.15	0.43
3	6.45	3.38	0.17	0.31	0.70
4	7.32	4.11	0.18	0.48	0.73
5	7.62	4.38	0.87	1.01	0.53
6	7.64	4.40	0.89	1.89	1.00
7	7.87	4.61	0.89	2.77	0.62
8	8.03	4.75	0.84	3.64	0.60
9	8.43	5.12	0.87	4.49	0.55
10	8.76	5.45	0.83	5.34	0.62

Average 'k' = 0.623

TABLE 3.10

SAMPLE C_7 $\bar{M}_v = 4.73 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	1.52	0.35	0.08	0.04	0.09
2	1.91	0.50	0.08	0.12	0.82
3	2.00	0.54	0.10	0.20	0.75
4	3.92	1.55	0.12	0.36	0.55
5	6.75	3.62	0.89	0.91	0.66
6	7.05	3.88	0.87	1.72	0.60
7	7.22	4.03	0.84	2.65	0.59
8	7.41	4.19	0.85	3.49	0.59
9	7.68	4.13	0.83	4.33	0.89
10	8.25	4.96	0.82	5.16	0.52

Average 'k' = 0.61

TABLE 3.11

SAMPLE C_8 $\bar{M}_v = 5.01 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	3.42	1.25	0.08	0.35	0.30
2	4.28	1.78	0.19	0.85	0.68
3	6.35	3.29	0.23	1.06	0.92
4	7.64	4.40	0.65	1.49	0.73
5	8.18	4.89	0.70	2.16	0.78
6	8.28	4.99	0.74	2.88	0.77
7	8.79	5.47	0.80	3.61	0.72
8	8.89	5.57	0.78	4.43	0.48
9	9.01	5.69	0.81	5.18	0.75
10	9.15	5.83	0.88	6.12	0.77

Average 'k' = 0.69

TABLE 3.12

SAMPLE C_9 $\bar{M}_v = 2.34 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	1.22	0.25	0.08	0.04	3.36
2	3.86	1.51	0.12	0.14	0.34
3	3.95	1.57	0.15	0.28	0.53
4	4.13	1.68	0.18	0.44	0.50
5	4.99	2.25	0.76	0.91	0.49
6	5.70	2.78	0.82	1.70	0.48
7	5.72	2.80	0.86	2.53	0.49
8	5.78	2.84	0.86	3.39	0.56
9	5.89	2.93	0.84	4.24	0.54
10	6.03	3.04	0.79	5.06	0.57

Average 'k' = 0.49

TABLE 3.13

SAMPLE C_{10} $\bar{M}_v = 2.51 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	4.05	1.73	0.08	0.04	0.39
2	4.22	1.74	0.08	0.12	0.36
3	4.65	2.02	0.09	0.20	0.46
4	4.98	2.25	0.76	0.63	0.88
5	6.25	3.21	0.88	1.45	0.60
6	6.25	3.21	0.88	2.33	0.64
7	6.82	3.88	0.86	3.26	0.56
8	6.82	3.68	0.86	4.17	0.56
9	6.92	3.77	0.89	5.04	0.55
10	7.01	3.84	0.82	5.89	0.58

Average 'k' = 0.56

TABLE 3.14

SAMPLE C_{11} $\bar{M}_v = 3.67 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	2.62	0.83	0.10	0.05	0.41
2	2.71	0.87	0.11	0.15	0.61
3	2.92	0.98	0.14	0.27	0.97
4	5.58	2.69	0.16	0.42	0.55
5	7.45	4.23	0.76	0.89	0.59
6	7.60	4.36	0.86	1.70	0.62
7	7.72	4.47	0.75	2.51	0.64
8	7.94	4.67	0.88	3.32	0.60
9	8.25	4.96	0.83	4.18	0.58
10	8.65	5.34	0.88	5.04	0.56

Average 'k' = 0.61

TABLE 15

SAMPLE C_{12} $\bar{M}_v = 4.01 \times 10^6$

FRACTION NO	$[\eta]$ g/dl	$M_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGINS CONSTANT 'k'
1	1.82	0.47	0.08	0.04	0.42
2	2.15	0.61	0.14	0.14	0.38
3	2.24	0.65	0.15	0.29	1.24
4	3.22	1.13	0.18	0.45	0.62
5	3.71	1.42	0.19	0.63	0.54
6	7.79	4.53	0.89	1.17	0.45
7	7.89	4.62	0.85	2.04	0.47
8	7.91	4.64	0.85	2.89	0.54
9	8.25	4.96	0.69	3.66	0.54
10	8.98	5.66	0.76	4.38	0.50

Average 'k' = 0.57

TABLE 3.16

SAMPLE C_{13} $\bar{M}_v = 2.94 \times 10^6$

FRACTION NO	[η] g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	1.18	0.24	0.17	0.09	0.72
2	1.90	0.50	0.08	0.21	0.50
3	2.15	0.61	0.08	0.29	0.58
4	2.18	0.62	0.15	0.35	0.69
5	2.51	0.77	0.16	0.56	0.52
6	4.25	1.76	0.84	1.05	0.69
7	4.88	2.18	0.76	1.85	0.59
8	5.05	2.30	0.83	2.65	0.69
9	5.32	2.50	0.83	3.48	0.71
10	5.82	2.87	0.73	4.26	0.83

Average 'k' = 0.65

TABLE 3.17

SAMPLE C_{14} $\bar{M}_v = 3.26 \times 10^6$

FRACTION NO	[η] g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	1.64	0.40	0.06	0.04	1.49
2	1.92	0.51	0.10	0.13	1.14
3	2.18	0.62	0.15	0.25	1.26
4	3.18	1.12	0.25	0.70	0.65
5	4.45	1.89	0.27	0.70	0.65
6	5.75	2.82	0.73	1.20	0.55
7	5.88	2.92	0.83	1.98	1.63
8	6.15	3.13	0.78	2.28	0.53
9	6.65	3.54	0.84	3.59	0.52
10	6.88	3.73	0.84	4.43	0.49

Average 'k' = 0.93

TABLE 3.18

SAMPLE C_{15} $\bar{M}_v = 2.71 \times 10^6$

FRACTION NO.	[η] g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	CUMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	1.61	0.39	0.18	0.04	0.32
2	1.75	0.44	0.10	0.12	0.36
3	2.23	0.64	0.17	0.26	0.39
4	2.70	0.87	0.08	0.38	0.49
5	2.90	0.97	0.19	0.52	0.44
6	5.02	2.28	0.80	1.02	0.21
7	5.32	2.50	0.80	1.82	0.37
8	5.72	2.80	0.90	2.57	0.35
9	5.85	2.90	0.70	3.37	0.34
10	5.93	2.96	0.86	4.25	0.35

Average 'k' = 0.36

TABLE 3.19

SAMPLE C_{16} $\bar{M}_v = 3.02 \times 10^6$

FRACTION NO	[η] g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	2.00	0.54	0.08	0.04	0.00
2	2.59	0.81	0.15	0.15	0.79
3	5.37	2.53	0.08	0.26	0.21
4	5⅛64	2.74	0.15	0.38	0.25
5	5.84	2.89	0.86	0.88	0.32
6	6.25	2.21	0.75	1.35	0.29
7	6.28	3.24	0.08	1.76	0.30
8	6.32	3.27	0.73	2.40	0.40
9	6.39	3.33	0.81	3.26	0.39
10	6.89	3.74	0.76	4.05	0.39

Average 'k' = 0.33

TABLE 3.20

SAMPLE D_1 $\bar{M}_v = 3.33 \times 10^6$

FRACTION NO.	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	1.61	0.39	0.08	0.04	0,24
2	2.30	0.67	0.16	0.16	0.54
3	2.35	0.70	0.13	0.30	0.23
4	2.42	0.73	0.17	0.45	0.73
5	3.72	1.43	0.39	0.73	0.44
6	5.95	2.98	0.86	1.36	1.32
7	6.30	3.27	0.79	2.21	0.52
8	6.32	3.70	0.75	2.72	0.61
9	6.89	3.85	0.84	3.79	0.51
10	7.42	4.20	0.90	4.61	0.50

Average 'k' = 0.56

TABLE 3.21

SAMPLE D_2 $M_v = 3.56 \times 10^{-6}$

FRACTION NO.	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
11	2.18	0.62	0.08	0.04	0.17
2	3.81	0.92	0.11	0.13	0.31
3	3.37	1.22	0.20	0.28	0.25
4	4.01	1.61	0.11	0.43	0.42
5	4.05	1.63	0.18	0.58	0.61
6	4.96	2.24	0.84	1.08	1.48
7	7.16	3.97	0.85	1.93	0.72
8	7.52	4.29	0.84	2.39	0.68
9	8.32	5.02	0.72	2.79	0.64
10	8.42	5.12	0.81	3.56	0.64

Average 'k' = 0.59

TABLE 3.22

SAMPLE D_3 $\bar{M}_v = 3.42 \times 10^6$

FRACTION NO.	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	2.05	0.56	0.08	0.04	0.51
2	2.18	0.62	0.08	0.12	0.30
3	2.48	0.76	0.10	0.20	0.58
4	4.59	1.98	0.21	0.36	0.48
5	4.73	2.08	0.24	0.58	0.47
6	5.02	2.28	0.73	1.07	0.48
7	5.44	2.59	0.75	1.81	0.48
8	6.02	3.03	0.74	2.56	0.71
9	7.45	4.22	0.84	3.35	0.87
10	7.52	4.29	0.87	4.21	0.86

Average 'k' = 0.57

TABLE 3.23

SAMPLE D_4' $\bar{M}_v = 3.58 \times 10^6$

FRACTION NO.	$[\eta]$ g/dl	$\bar{M}_v \times 10^{-6}$	WEIGHT FRACTION	COMMULATIVE WT. FRACTION	HUGGIN'S CONSTANT 'k'
1	1.20	0.24	0.08	0.04	0.83
2	2.20	0.63	0.12	0.14	0.30
3	2.38	0.71	0.19	0.29	0.33
4	2.78	0.91	0.71	0.73	0.32
5	3.00	1.02	0.70	1.44	0.28
6	5.97	2.99	0.75	2.16	0.59
7	6.33	3.36	0.85	2.96	0.53
8	6.52	3.43	0.85	3.81	0.55
9	6.95	3.79	0.88	4.67	0.52
10	7.63	4.39	0.90	5.56	0.47

Average 'k' = 0.47

3.2.2.1 Molecular weight distribution in polymethyl methacrylate:

When cummulative weight fraction was plotted against viscosity average molecular weight ($\bar{M}_v$) sigmoid shaped graphs were obtained. These are represented in figures 3.9 to 3.28. The sigmoid shaped curves can generally be divided into two sections, viz. low molecular weight range and high molecular weight range. The transition point between these two is called 'end of low molecular weight' (ELM). The (ELM) varies from one polymer sample to the other. The (ELM) values can also be used as a measure of polydispersity. The broader the range of the low molecular weight species before the sharp rise, the more polydispersed the polymer is. The result obtained, show in table 3.24, depicts how (ELM) values vary with percentage monomer conversion, [E], [I] and temperature of polymerisation.

The trend is that (ELM) increases with percentage monomer conversion [E], [I] and temperature of polymerisation.

The degree of polydispersity was determined by using the ratio ($\bar{M}_w/\bar{M}_n$), where ($\bar{M}_w$) is weight average molecular weight and ($\bar{M}_n$) is the number average molecular weight. When the ratio is unity, the polymer is monodispersed but if greater than one, the polymer is polydispersed. The extent of the deviation from unity is normally taken as a measure of the polydispersity. ($\bar{M}_n$) and ($\bar{M}_w$) of the polymer were obtained by using equations (1 - 18) and (1 - 19) respectively. The results obtained are seen in table 3.24. The results show low ($\bar{M}_w/\bar{M}_n$) varies with percentage conversion. It would be observed that the lower the percentage conversion, the higher the ($\bar{M}_w/\bar{M}_n$) value, hence the smaller the polydispersity. It implies that polymer produced to lower conversion are more monodispersed than those produced to higher conversion. When ($\bar{M}_w/\bar{M}_n$) ratio for samples C_1 to C_8 are compared, as percentage conversion increases, the value of ($\bar{M}_w/\bar{M}_n$) decreases. The ratio also decreases with increase in emulsifier concentration. It means that as [E] increases from th lowest value, below cmc of (SLS) to high values, above the cmc, polymers produced become more polydispersed. This supports the work of Gardon (25) in which he obtained polydispersed polymer samples with [E] above the cmc of (SLS) when (MMA) was polymerised.

The ratio ($\bar{M}_w/\bar{M}_n$) is also affected by $[I]$. It decreases with increase in initiator concentration. This is particularly true when the values for samples C_1 to C_8 are compered with those of samples C_9 to C_{16} which were produced under different initiator concentrations; 3.70×10^{-3}M/l and 4.44×10^{-3}M/l respectively. This implies that the larger the number of radicals present in the reaction system the greater the number of active sites and consequently the chains growing simultaneously and hence the polydispersity of the molecular weight distribution of the final product.

The ($\bar{M}_w/\bar{M}_n$) ratio is also affected by temperature of polymerisation. According to the study, the faster the reaction the lower the value of ($\bar{M}_w/\bar{M}_n$) hence the higher the polydispersity of molecular weight distribution of the polymer. This is demonstrated by the results of samples D_1 to D_4 compared with those of samples C_{13} to C_{16} which were obtained at different temperatures, 55°C and 50°C respectively.

Furthermore to determine the trend in the molecular weight distribution, the slopes of the steep portions of the distribution curves were estimated and shown in

table 3.24. These slopes might not be a decisive measure of the breadth of the molecular weight distribution in the entire sample, but rather, of the distribution only of those fractions above the (ELM). Thus if only the samples having ($\bar{M}_v$) average above the (ELM) are plotted together, the slope calculated could be regarded as representing the spread of their molecular weight distribution. This implies that ($\bar{M}_v/\bar{M}_n$) envisaged on the bases of the fractions above the (ELM) would likely be different, and much higher than those recorded in table 3.24. Comparing the values of the slopes for the samples, it appears that the lower the percentage conversion, the smaller the slope, particullarly if the former is below 80%, and the narrower the molecular weight distribution The higher [E] is, the wider the molecular weight distributio because the smaller the slope obtained.

When results for samples C_1 to C_8 are compared with those for C_9 to C_{16} obtained for different [I] , the same trend is followed except that the effect of conversion on distribution is smaller. Generally the higher the value of [I], the smaller the slope, thus the wider the molecular weight distribution. This is because the smaller the concentration of the initiator and hence the number of the radicals, the narrower the molecular weight distribution as explained earlier.

The slope of the linear part of the molecular weight distribution curve was taken for polymer samples obtained at 55°C for samples D_1 to D_4. The values of the slopes obtained were much lower than the values obtained for samples C_9 to C_{16} obtained at 50°C. This means that the higher the temperature the smaller the slope, the wider the molecular weight distribution. At a higher temperature, more active sites are formed leading to an increase in the number of growing chains and hence molecules of different molecular weight and consequently broader molecular weight distribution was obtained.

The above deductions can be summarised thus, narrow molecular weight distribution is obtained in the polymer sample produced using low [I], low [E] and lower temperature. Molecular weight distribution in the samples become broader as [I], [E] and temperature increased. Also the polymer obtained above the cmc of (SLS) which is 8.9×10^{-3} M/l tends to be more polydispersed than those below the cmc.

Tables 3.7 to 3.24 include Huggins constant 'k' obtained for the different fractions. Its values range from 0.02 to 1.5. The values of 'k' recorded here suggest that the polymer solvent interaction is generally poor and varied possibly in the pattern of variations on the macromolecular structures i.e. molecular weight and conformations of the polymers. The average value.

TABLE 3.24

Percentage conversion, end of low molecular weight (ELM), $\bar{M}_w/\bar{M}_n$ ratio, slopes of polymer samples for C_1 to C_{16} and samples D_1 to D_4.

Sample	Conversion (%)	$(ELM)_6$ x 10^6	$(\bar{M}_w/\bar{M}_n$ x 10^2	Slope of the steep part of Mwt. Distribution curve.
C_1	28.21	1.55	6.81	10.22
C_2	51.62	1.95	6.56	7.00
C_3	34.15	2.85	7.90	9.00
C_4	77.73	3.80	7.42	4.40
C_5	37.80	2.99	6.80	8.80
C_6	94.75	4.12	6.42	7.50
C_7	44.93	3.10	7.69	6.80
C_8	90.25	3.30	6.86	6.30
C_9	25.59	2.3	7.10	13.00
C_{10}	66.92	2.80	6.67	9.00
C_{11}	37.25	3.50	7.18	7.66
C_{12}	90.18	4.10	7.08	6.60
C_{13}	36.10	1.60	6.76	6.80
C_{14}	88.38	2.05	6.66	3.00
C_{15}	28.25	2.05	6.80	8.00
C_{16}	85.56	2.50	5.27	8.00
D_1	40.85	1.50	7.23	3.00
D_2	83.01	2.40	6.56	1.80
D_3	21.63	2.70	7.87	2.40
D_4	76.21	2.80	6.40	1.58

of 'k' for fractions from the same parent bulk polymer generally tends to increase with (%) conversion, initiator concentration and temperature. An explanation for this observation is yet to be found.

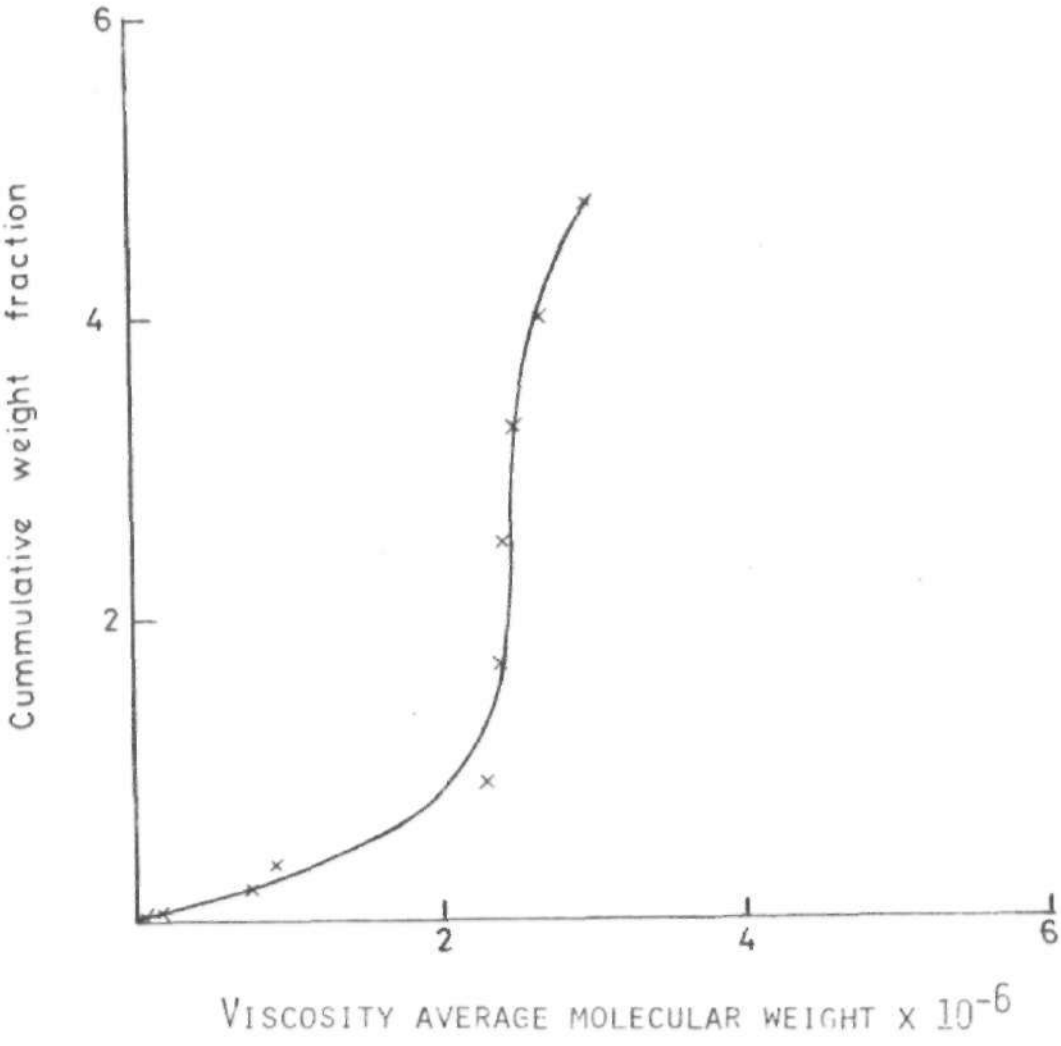


Fig 3.9: Molecular weight distribution of PMMA samples (C_1). Produced under 1.13M/L (MMA), 48.33M/L (H_2O) 3.70×10^{-3}M/L ($K_2S_2O_8$), 1.63×10^{-3}N/L (SLS) to 28.21% Conversion at 50°C.

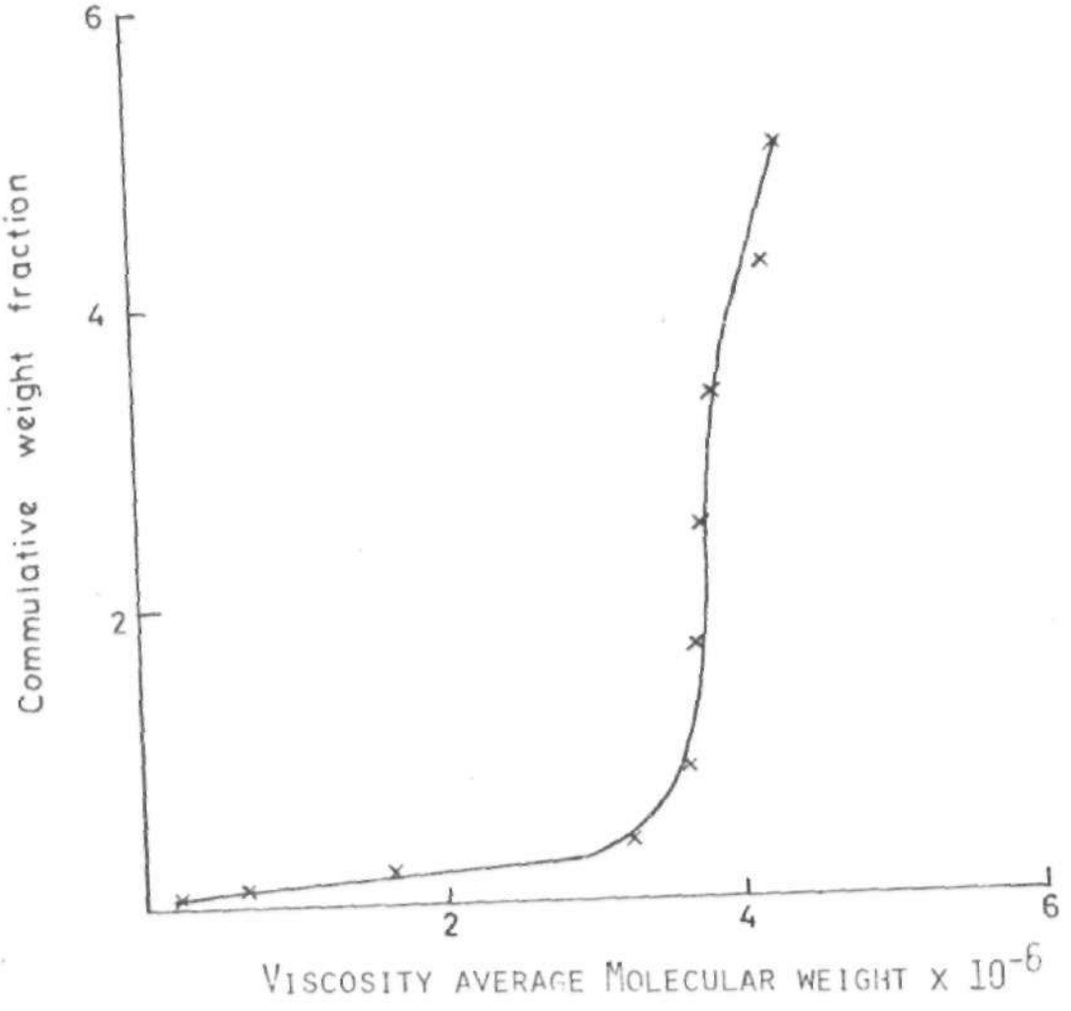


Fig. 3.11: Molecular weight distribution of (PMMA) Samples (C_3), Produced under 1.13M/L (MMA), 47.78M/L (H_2O) 3.70×10^{-3}M/L ($K_2S_2O_8$) 3.25×10^{-3}M/L (SLS) 34.15% conversion at 50°C.

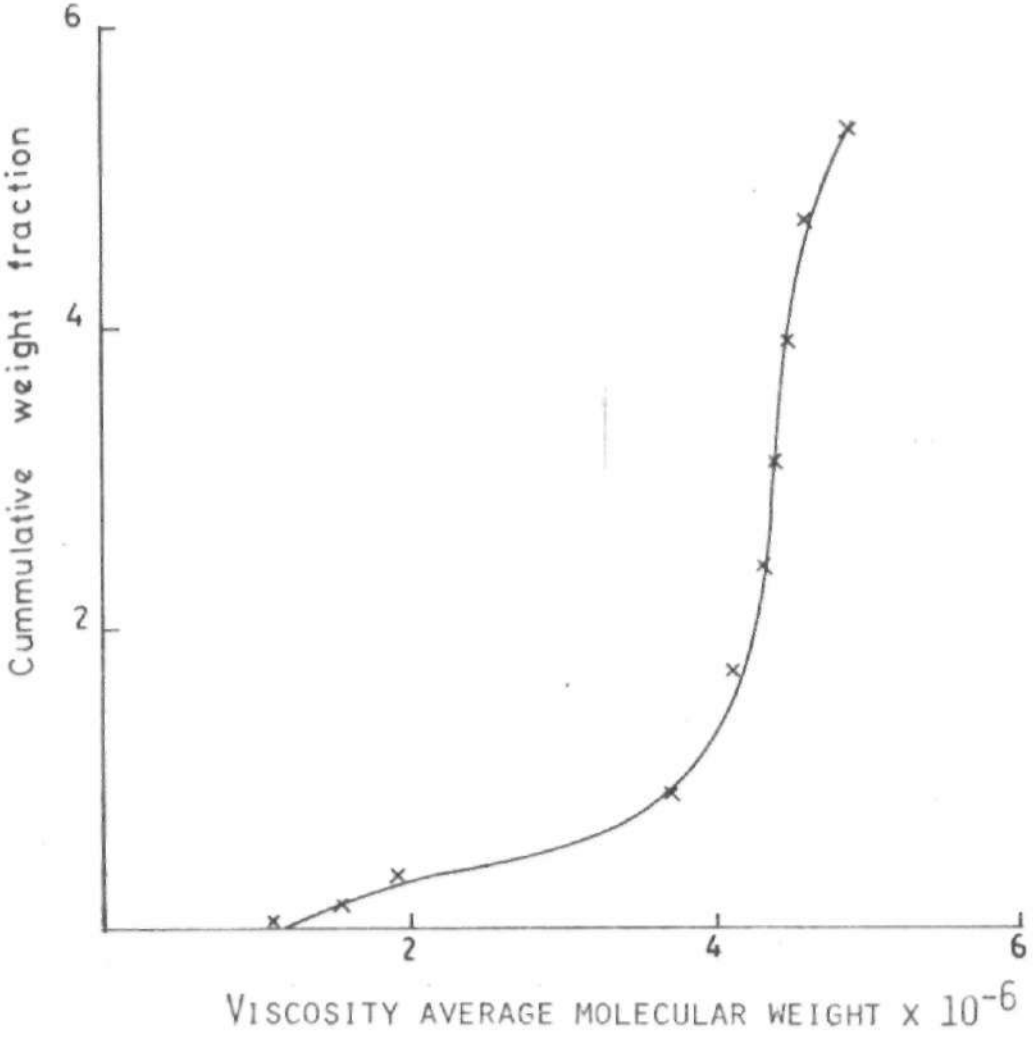


Fig. 3.13: Molecular weight distribution of PMMA Samples (C_5) . Produced under 1.13M/L (MMA), 46.67M/L (H_2O) 3.70×10^{-3} ($K_2S_2O_8$), 6.49×10^{-3}M/L (SLS) to 37.80% conversion at 50°C.

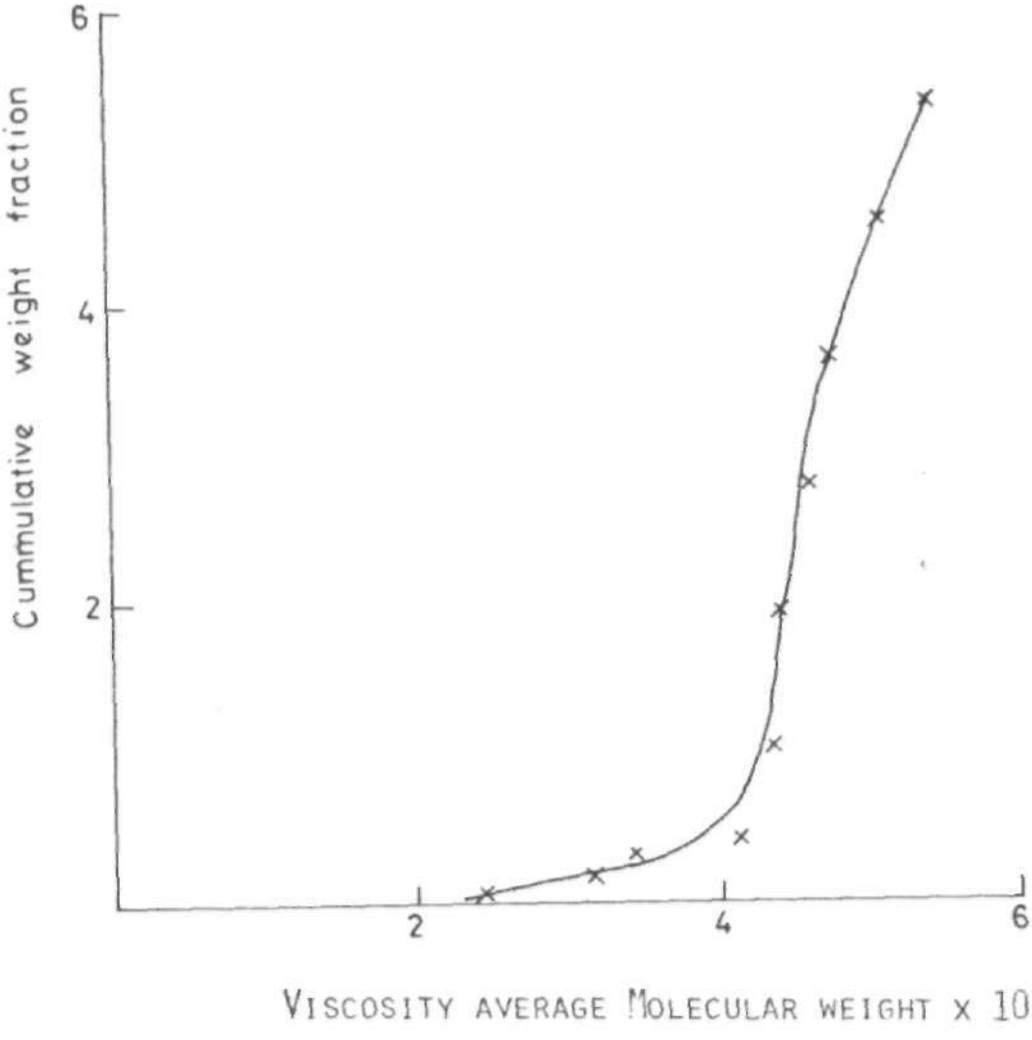


Fig 3.14: Molecular weight distribution of (PMMA) Samples (C_6), Produced under 1.13M/L (MMA) 46.67M/L (H_2O) 3.70×10^{-3} ($K_2S_2O_8$) 6.49×10^{-3}M/L, (SLS) to 94.75% Conversion at 50°C.

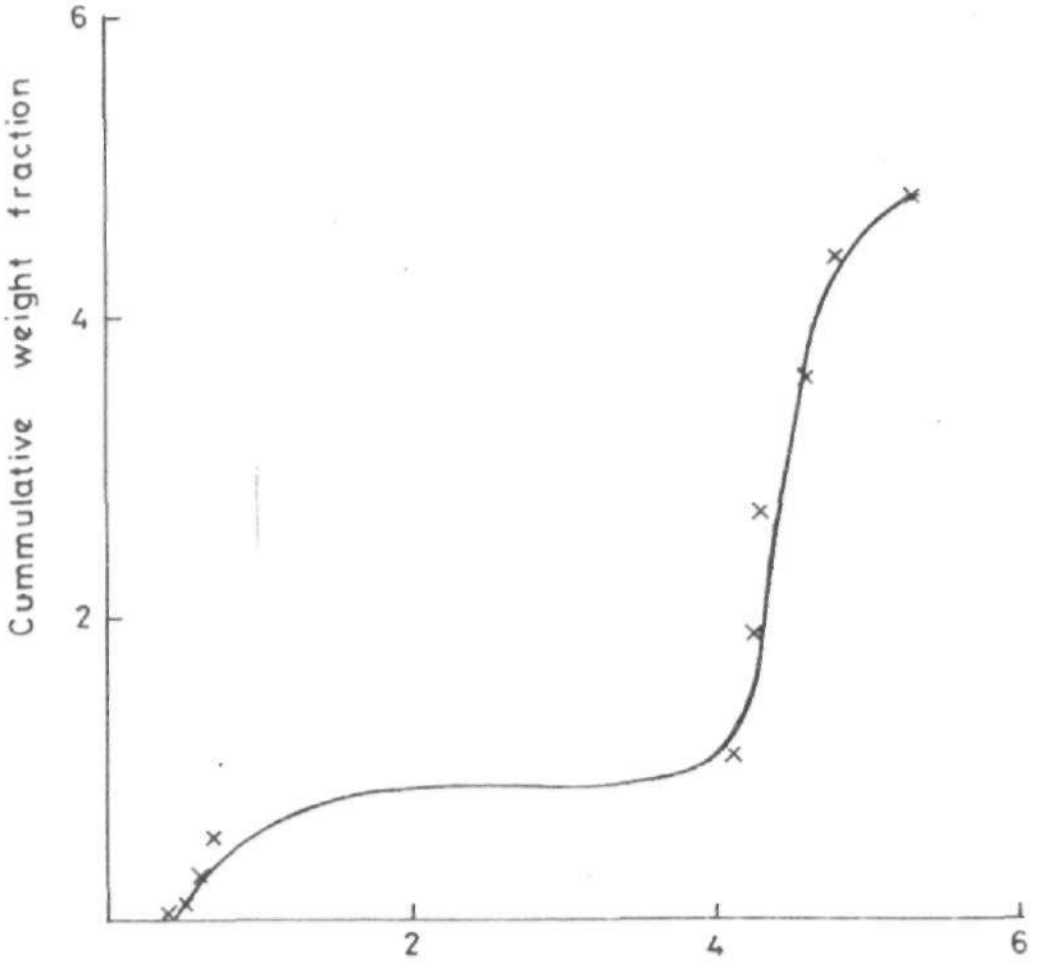


Fig 3.15: Molecular weight distribution of (PMMA) Samples (C_7) Produced under 1.13m/L (MMA), 44.44m/L (H_2O) 3.70×10^{-3}m/L ($K_2S_2O_8$), 12.97×10^{-3}m/L (SLS) to 44.93% conversion at 50°C .

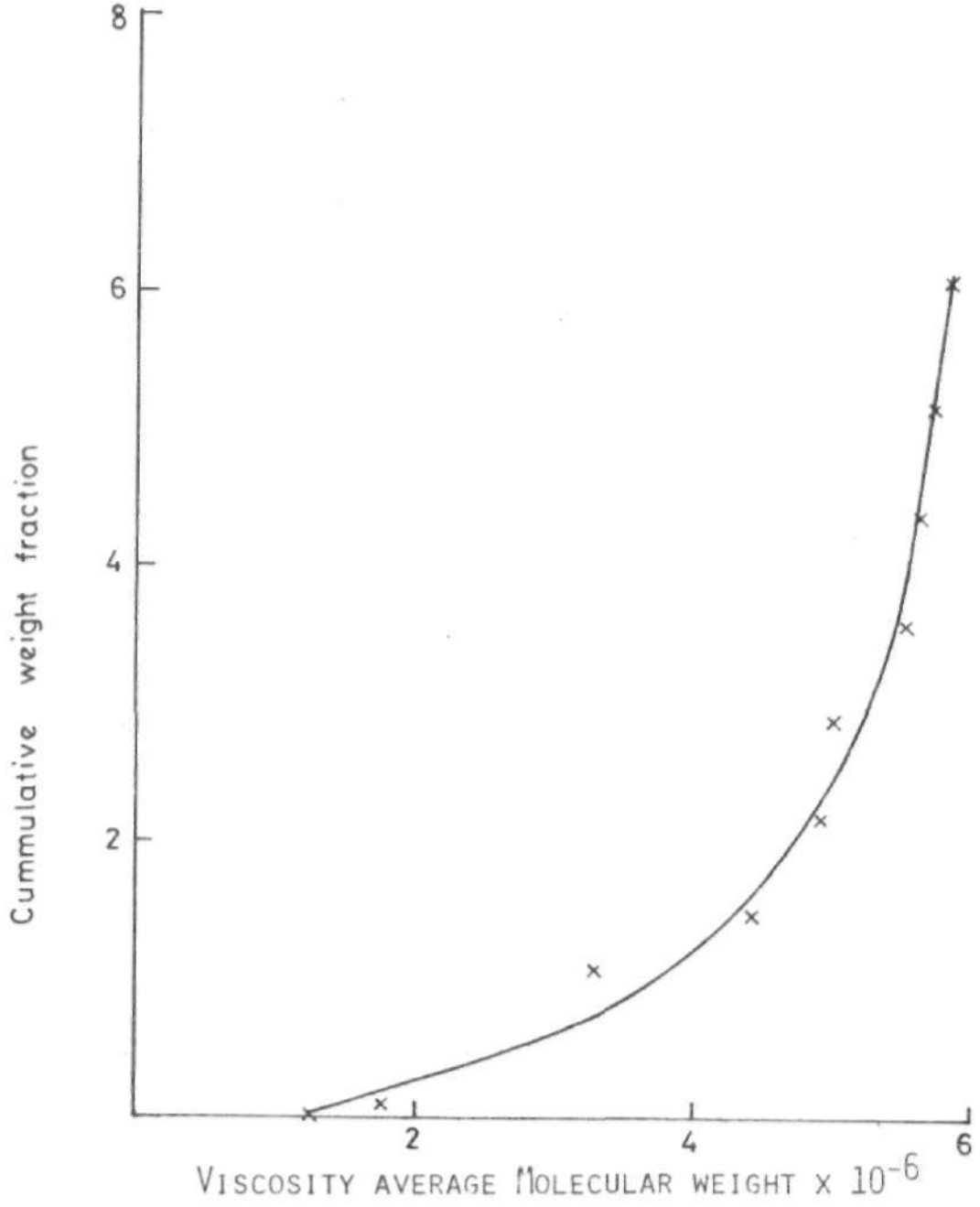


Fig. 3.16: Molecular weight distribution of PMMA Samples (C_8) produced under 1.13 m/l (MMA), 44.44 m/l (H_2O), 3.70 x 10^{-3} m/l ($K_2S_2O_8$), 12.97 x 10^{-3} m/l (SLS), to 9 0.25% conversion at 50°C.

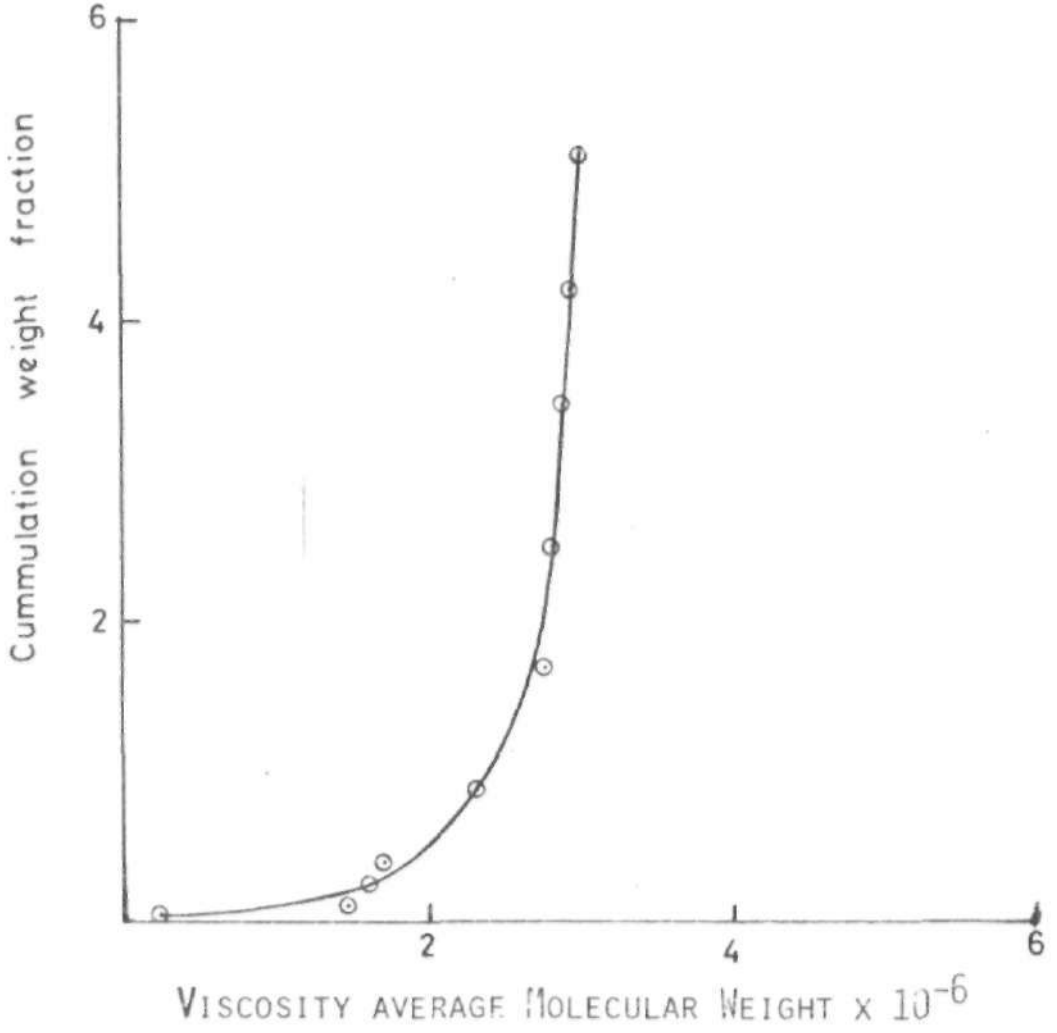


Fig. 3.17: Molecular Weight distribution of PMMA Samples (C_9). Produced under 1.13M/L (MMA) 48.33M/L (H_2O) 4.44×10^{-3}M/L ($K_2S_2O_8$), 1.63×10^{-3}M/L (SLS), to 25.59% conversion at 50°C.

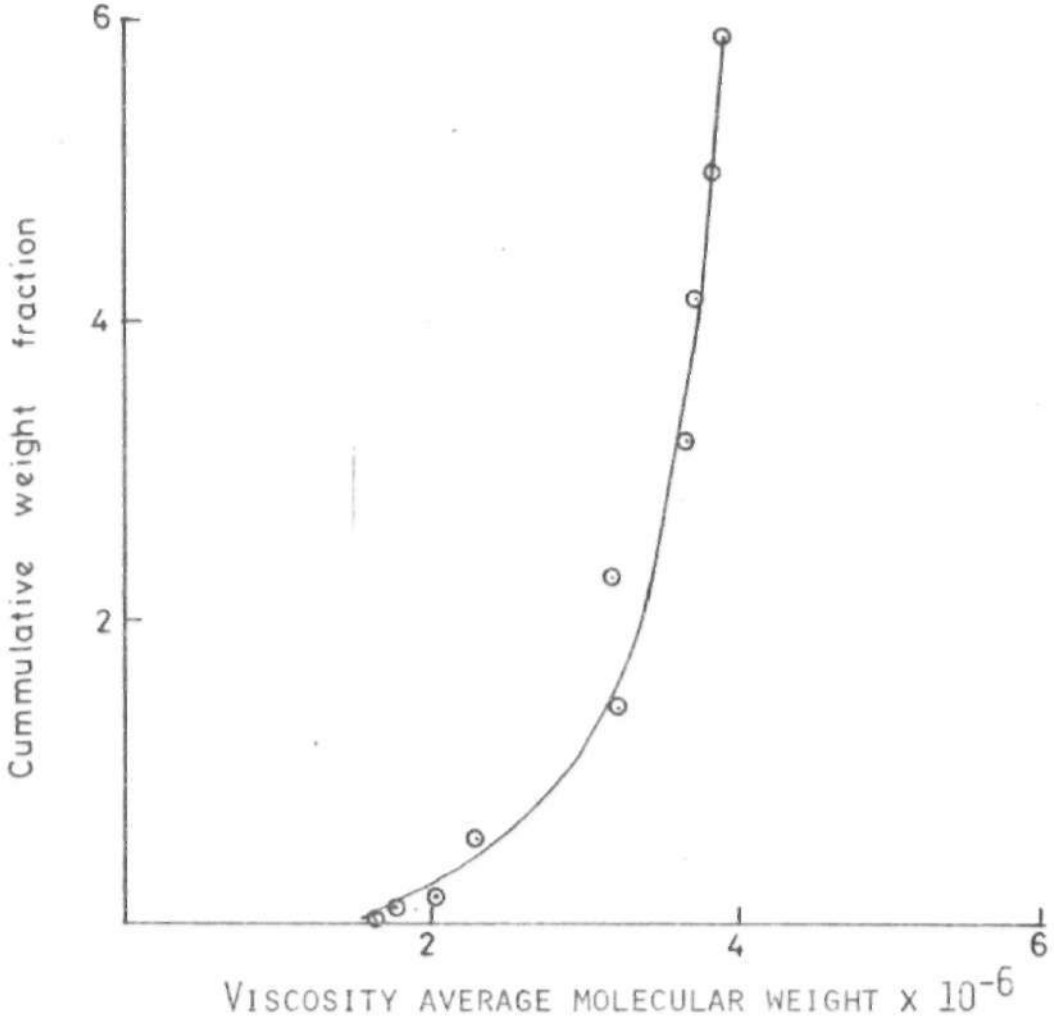


FIG 3.18: MOLECULAR WEIGHT DISTRIBUTION OF PMMA SAMPLE (C_{10}). PRODUCED UNDER 1.13M/L (MMA), 48.44M/L (H_2O), 4.44×10^{-3} ($K_2S_2O_8$) 1.63×10^{-3}M/L (SLS) TO 66.92% CONVERSION AT 50°C.

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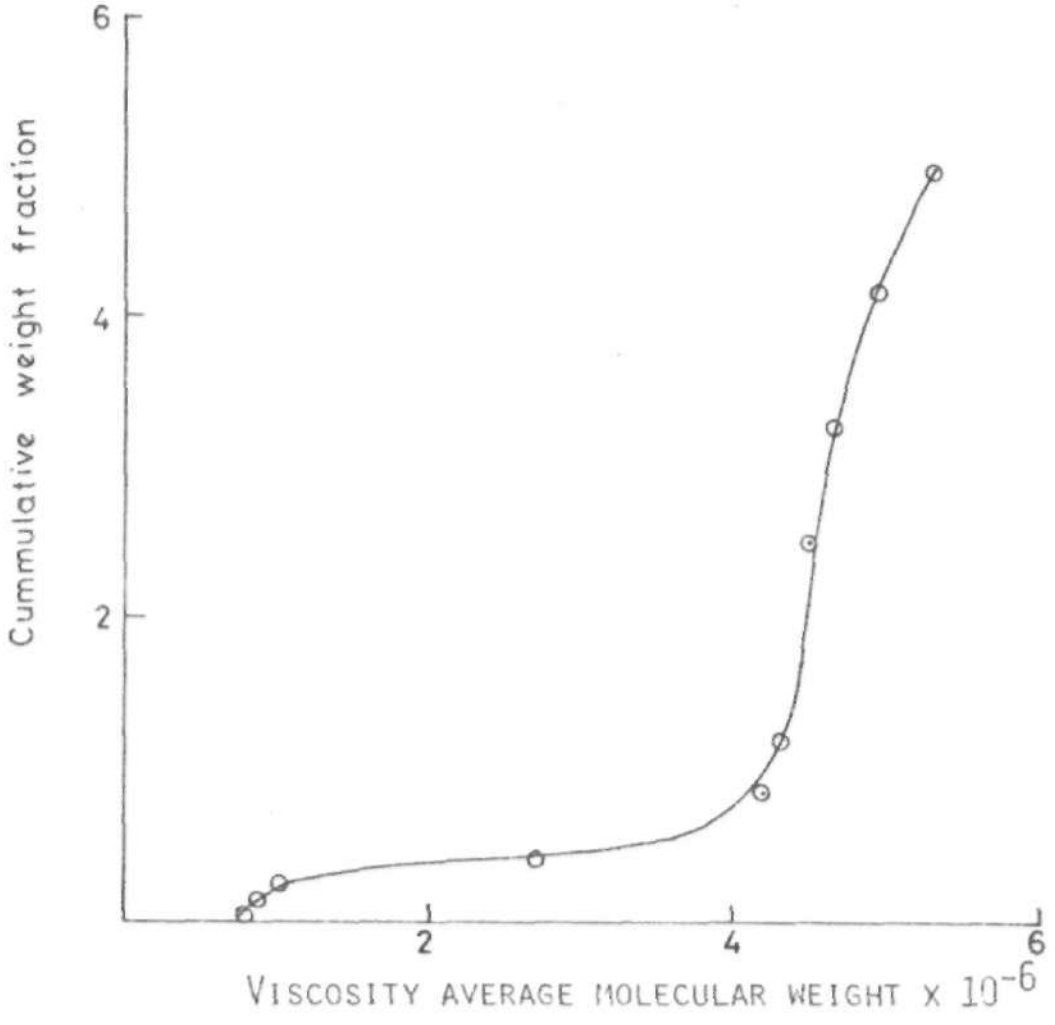


FIG. 3.19: MOLECULAR WEIGHT DISTRIBUTION OF PMMA SAMPLES (C_{11}). PRODUCED UNDER 1.13 M/L (MMA), 47.78M/L (H_2O), 4.44×10^{-3} ($K_2S_2O_8$) 3.25×10^{-3}M/L (SLS) TO 57.25% CONVERSION AT 50°C.

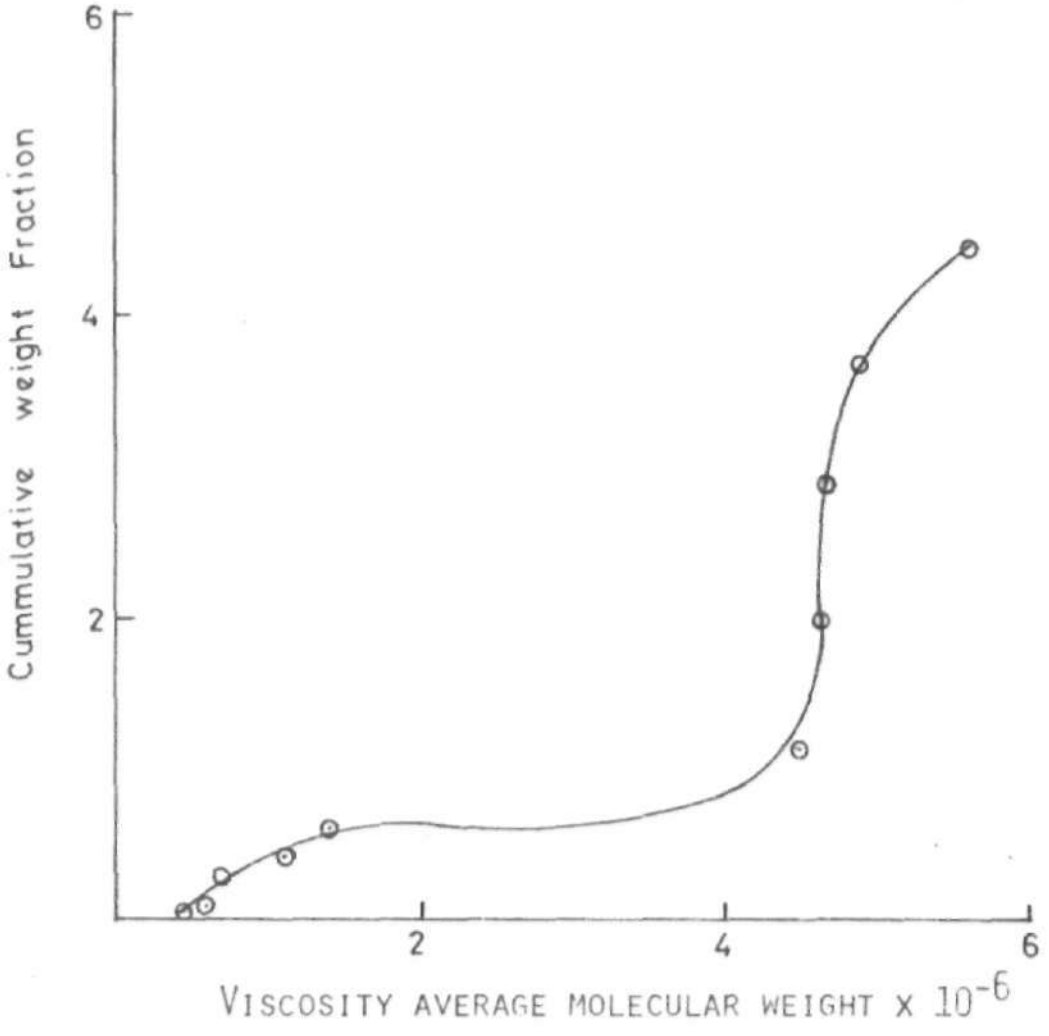


Fig 3.20: Molecular weight distribution of PMMA Samples (C_{12}), Produced under 1.13M/L (MMA) 47.78M/L (H_2O), 4.44×10^{-3}M/L ($K_2S_2O_8$), 3.25×10^{-3} (SLS) to 90.18% Conversion at 50°C.

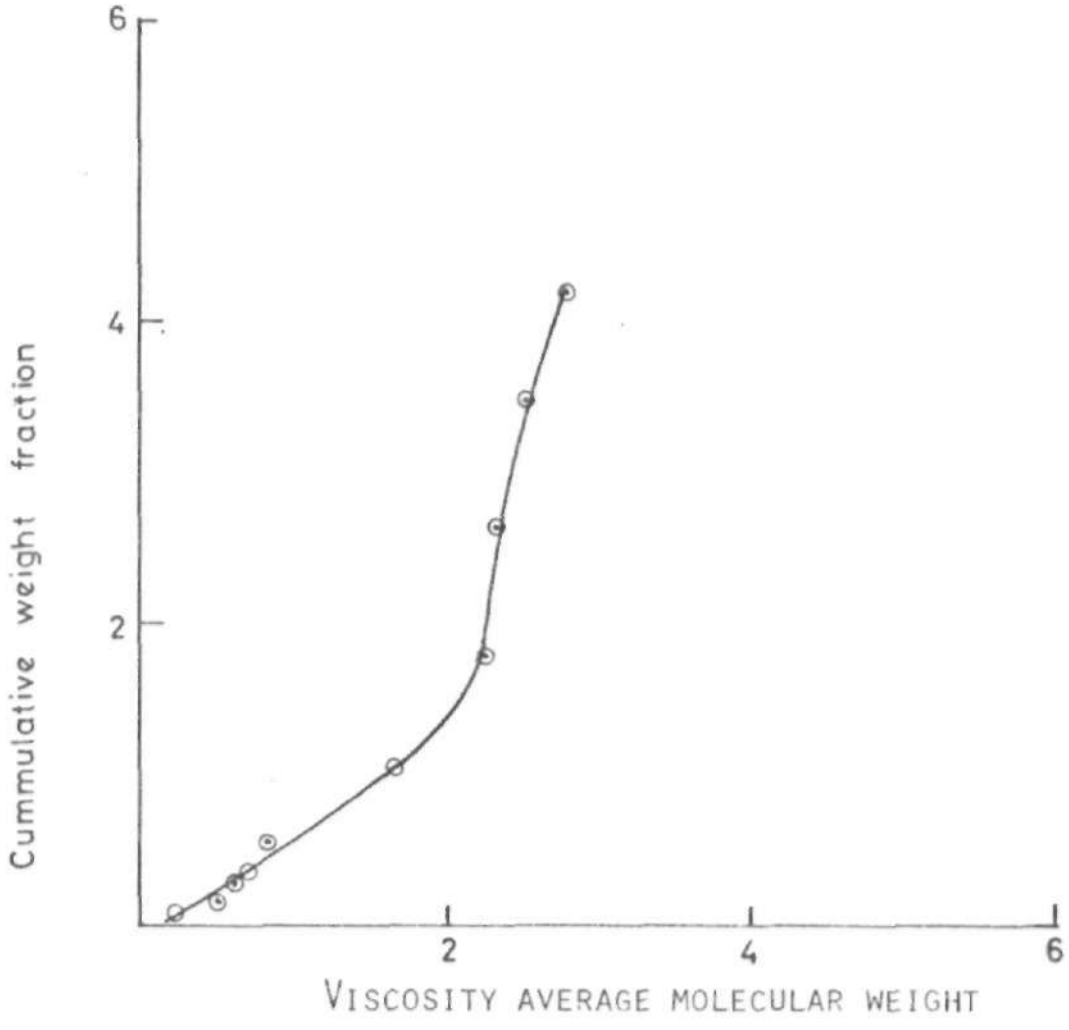


FIG. 3.21: MOLECULAR WEIGHT DISTRIBUTION OF PMMA SAMPLE (C_{13}). PRODUCED UNDER 1.13M/L (MMA), 46.67M/L (H_2O) 4.44×10^{-3} ($K_2S_2O_8$), 6.49×10^{-3} (SLS) TO 36.10% CONVERSION AT 50°C.

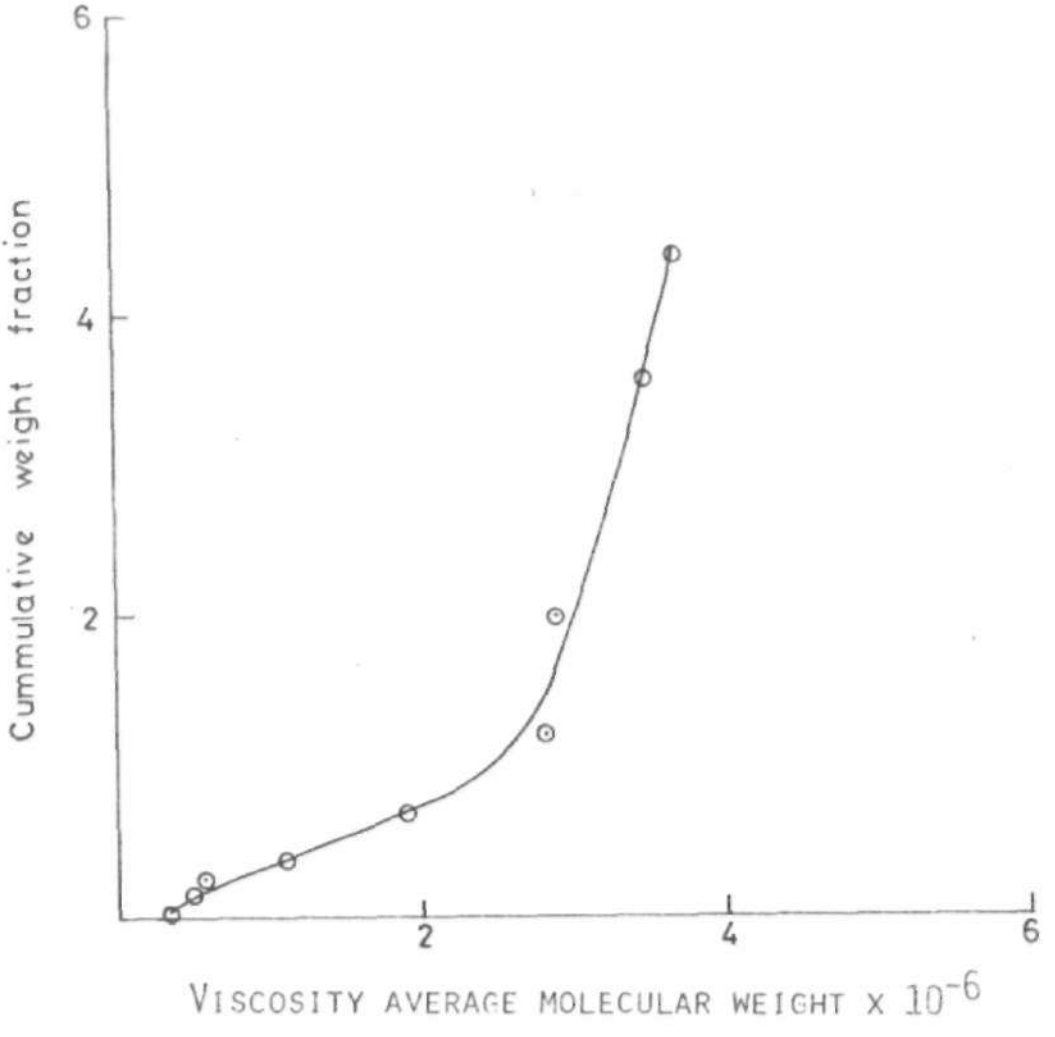


FIG. 3.22: MOLECULAR WEIGHT DISTRIBUTION OF PMMA SAMPLES (C_{14}). PRODUCED UNDER 1.13M/L (MMA), 46.67M/L (H_2O), 4.44 x 10^{-3}M/L $K_2S_2O_8$, 6.49 x 10^{-3}M/L (SLS), TO 36.10% CONVERSION AT 50°C.

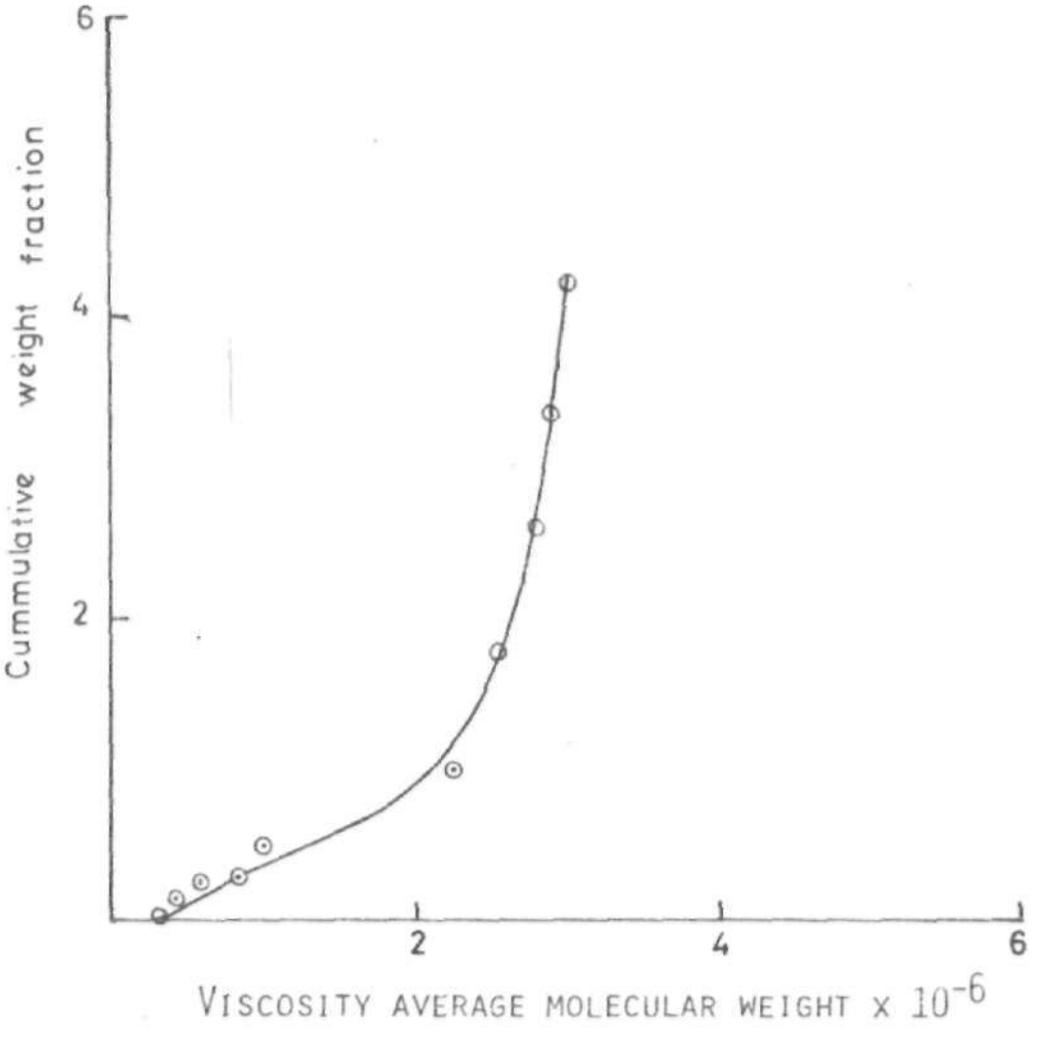


Fig. 3.23: Molecular weight distribution of PMMA Samples (C_{15}). Produced under 1.13M/L MMA, 44.44M/L H_2O, 4.44 x 10^{-3}M/L $K_2S_2O_8$ 12.97 x 10^{-3}M/L (SLS), to 28.25% at 50°C.

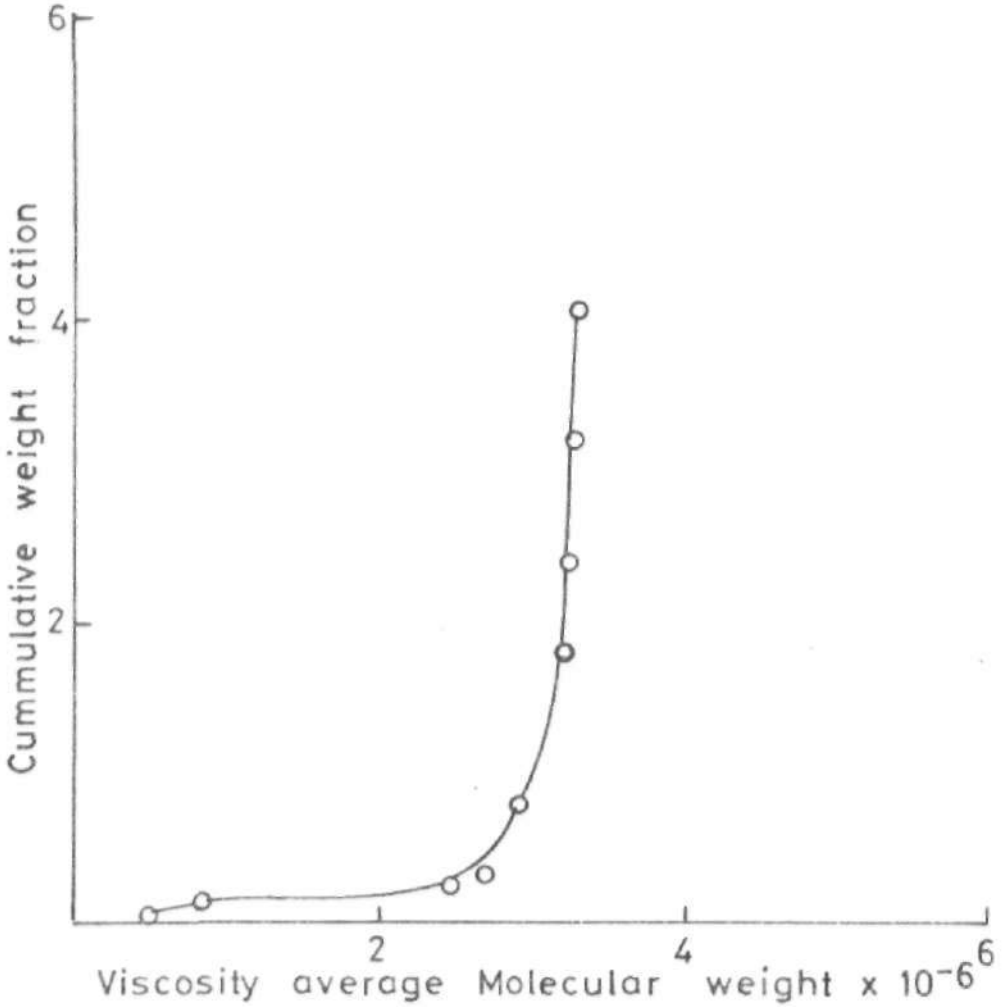


FIG. 3·24: MOLECULAR WEIGHT DISTRIBUTION OF PMMA SAMPLES (C_{16}). Produced under 1·13M/L(MMA), 44·44 M/L (H_2O), $4·44 \times 10^{-3}$ M/L ($K_2S_2O_8$), $12·97 \times 10^{-3}$ M/L (S L S), to 85·56% Conversion at 50°C.

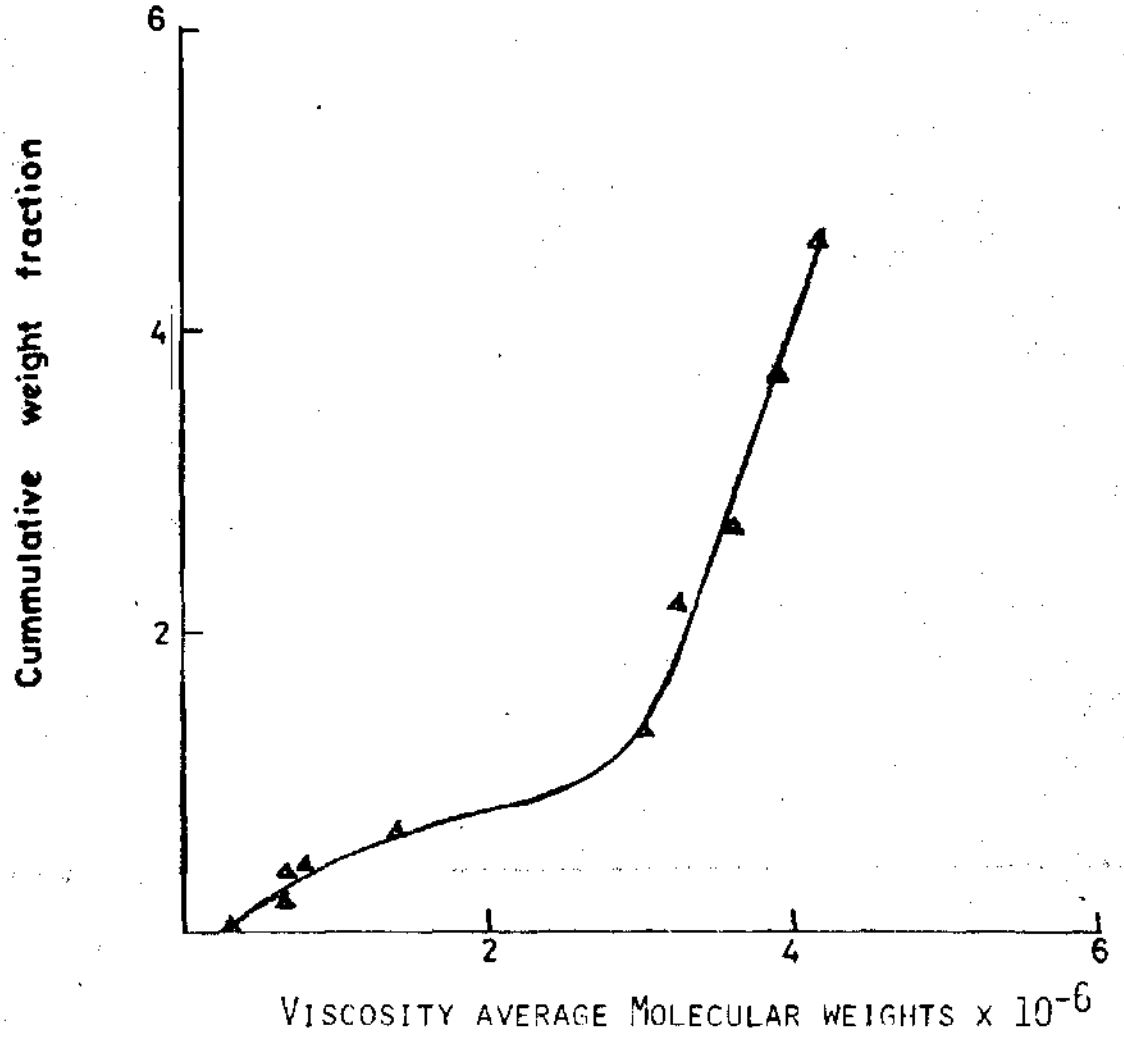


Fig. 3.25: Molecular weight distribution of (PMMA) Samples (D_1) produced under 1.13M/L (MMA) 46.67M/L (H_2O) 4.44 x 10^{-3}M/L ($K_2S_2O_8$), 6.49 x 10^{-3}M/L (SLS), to 40.85% conversion, at 50°C.

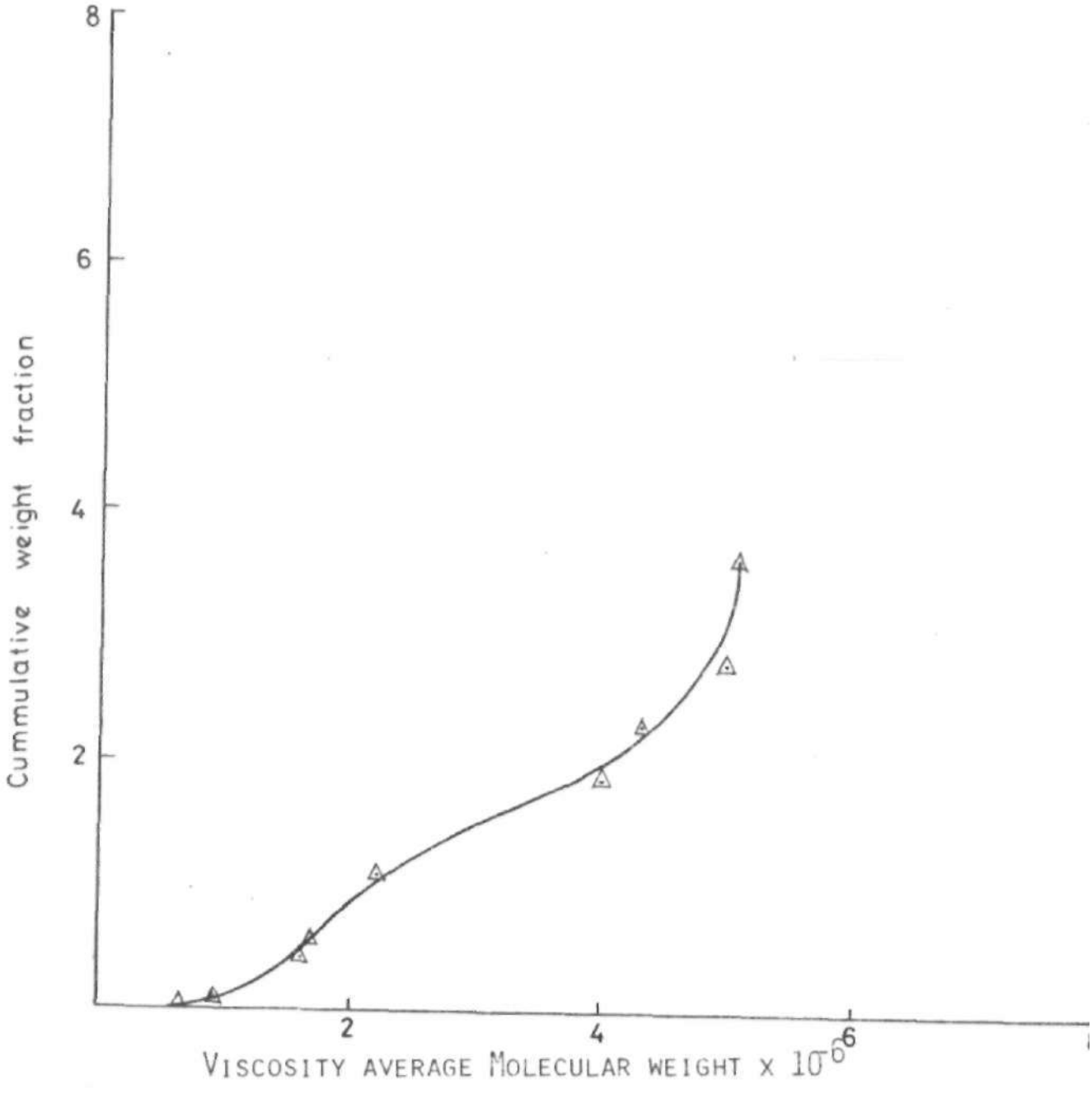


Fig. 3.26: Molecular weight distribution of (PMMA) Sample (D_2). Produced under 1.13M/L (MMA) 47.78M/L (H_2O) 4.44×10^{-3}M/L ($K_2S_2O_8$) 6.49×10^{-3}M/L (SLS) to 83.01% conversion at 55°C.

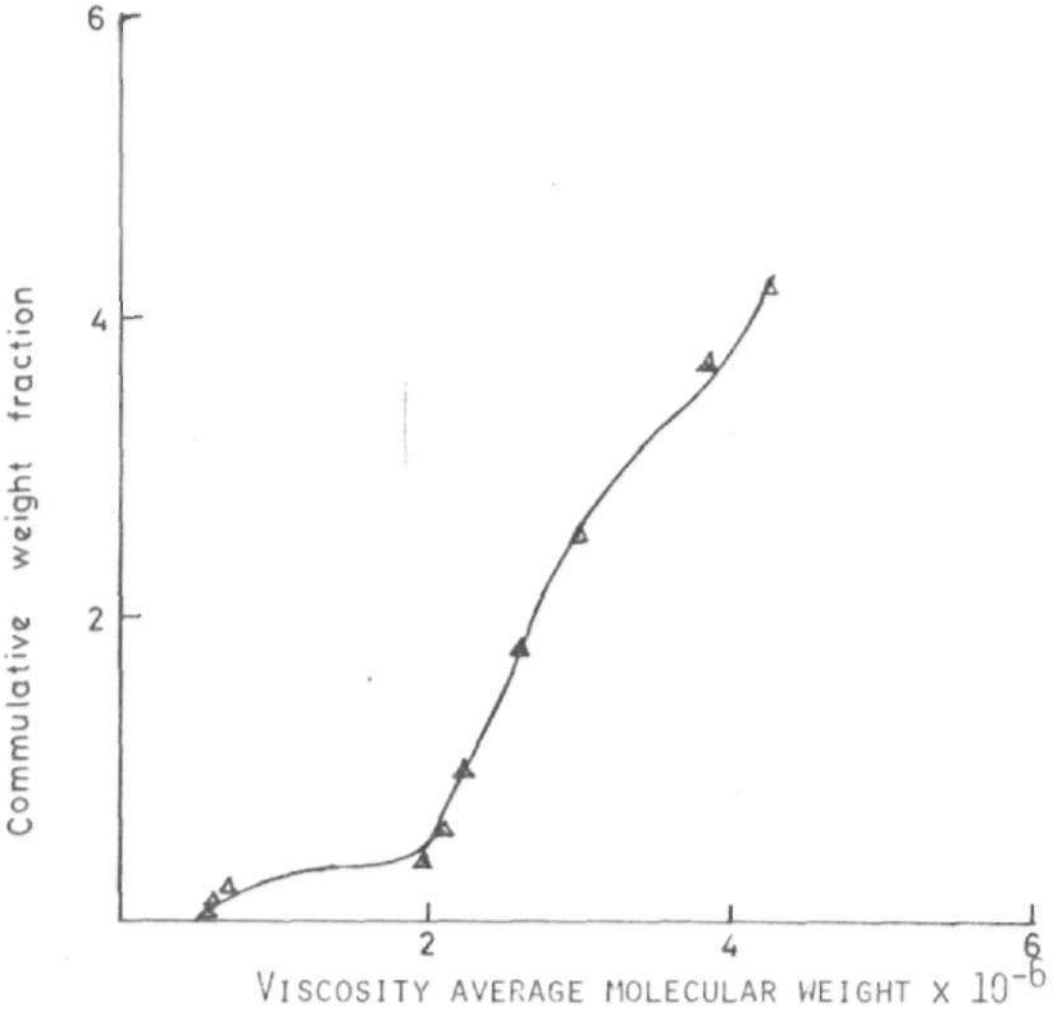


FIG. 3.27: MOLECULAR WEIGHT DISTRIBUTION OF PMMA SAMPLES (D_3). PRODUCED UNDE R 1.13M/L (MMA) 44.44 x 10^{-3}M/L (H_2O), 4.44 x 10^{-3}M/L ($K_2S_2O_8$), 12.97 x 10^{-3}M/L (SLS), TO 21.63% CONVERSION AT 55°C.

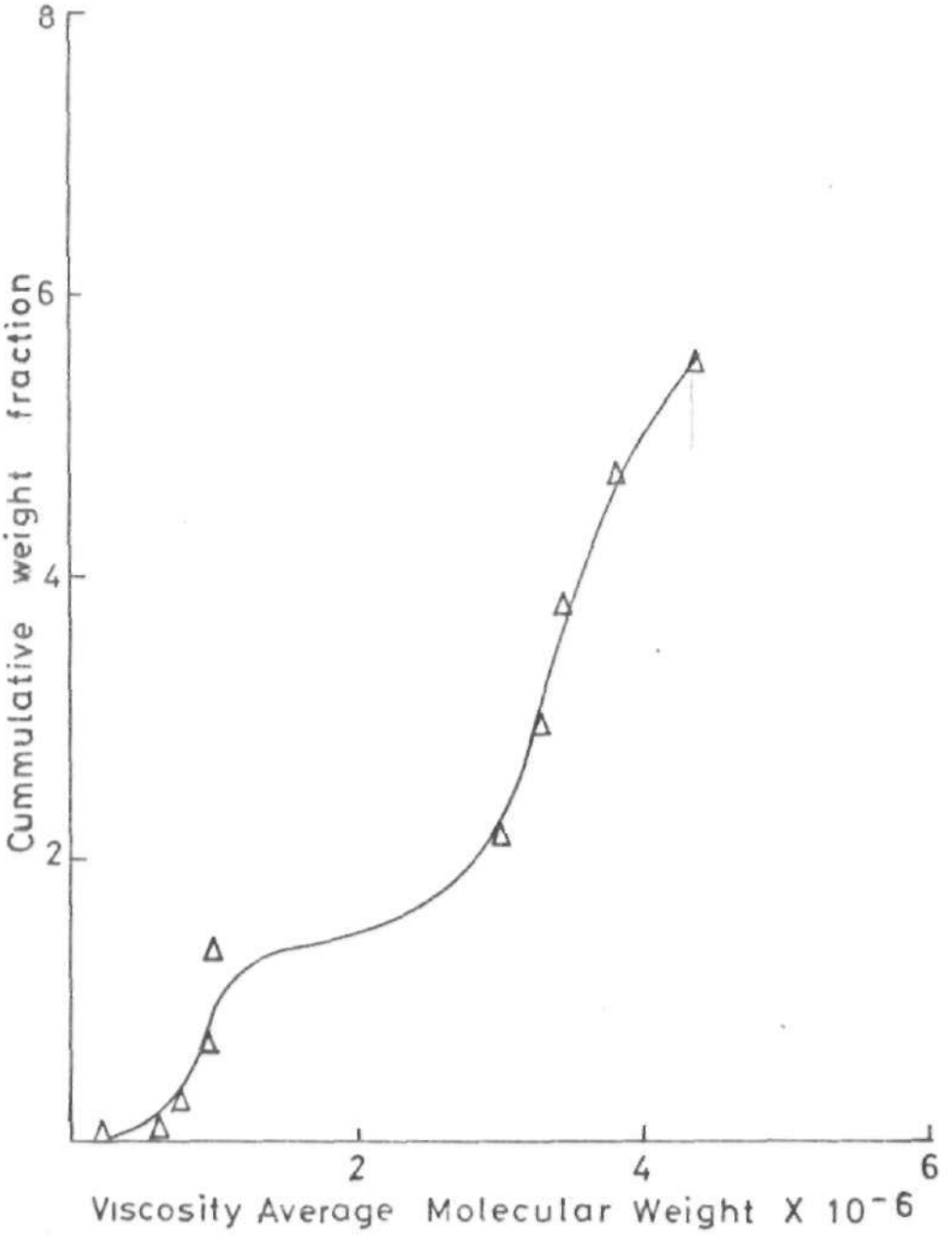


FIG. 3·28: MOLECULAR WEIGHT DISTRIBUTION OF (PMMA) SAMPLES (D_4). Produced under 1·13M/L (MMA), 44·44 M/L (H_2O), 4·44 X 10^{-3} M/L ($K_2S_2O_8$), 12·97X10^{-3} M/L (S L S) to 76·21% Conversion at 55°C.

CHAPTER FOUR

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions.

From the results of the present investigations, a number of conclusions have been drawn about the kinetics of emulsion polymerisation of methylmethacrylate below cmc of (SLS) and the pattern of the molecular weight distribution in the PMMA samples produced.

(i) The results have proved that polymerisation will occur below the cmc of (SLS) tc a significant extent, and rapidly too.

(ii) From the kinetics study of the emulsion polymerisation of (MMA) below the cmc of (SLS), three intervals I, II and III were recognised as in typical emulsion polymerisation of MMA above the cmc of sodium laurylsulphate. Rate of polymerisation (R_p) i.e. of the propagation step is affected by $[E]$, $[I]$ and temperature. Rate was observed to increase with $[E]$, $[I]$ and with temperature. The following relationships have been established

(a) $R_p \alpha [E]^{0.44}$ with 3.70×10^{-3} M/l $[I]$ at 50°C

(b) $R_p \alpha [E]^{0.50}$ with 4.44×10^{-3} M/l $[I]$ at 50°C

(c) $R_p \alpha [E]^{0.60}$ with 4.44×10^{-3} M/l $[I]$ at 55°C.

The exponent of $[E]$ in the relation $R_p \alpha [E]^a$ depends on $[I]$, temperature and the range of $[E]$.

(iii) Polymer samples produced during polymerisation below cmc of (SLS) have high molecular weight values. Molecular weight of the polymer samples depends on [E], [I] and temperature of polymerisation. Molecular weight observed is in the order of a million and increases with increase in [E], decrease in [I] and with increase in temperature.

(iv) The results of the fractionation study show that only two distinct fractions could be obtained with the method employed for the fractionation of the polymer samples obtained while polymerisation of MMA is done below the cmc of (SLS). The number of fractions might possibly increase for samples produced during polymerisation above the cmc of (SLS).

(v) The pattern of molecular weight distribution depends upon [I], [E], percentage conversion and on temperature of polymerisation. Narrow distribution is obtained at low conversion, low [I], low [E] and with low temperature of polymerisation. On the other hand the distribution becomes broader with increase in [I], [E], temperature and (%) conversion.

4.2 Recommendations.

A further research into the emulsion polymerisation of methylmethacrylate in water above the cmc of other emulsifiers and (SLS) will be necessary.

It would also be valuable to conduct further research on the emulsion polymerisation of other water insoluble monomer in water below the cmc of the various emulsifiers in order to be able to explain better the polymerisation of these monomers. The finding would help to explain further the mechanism of the polymerisation reaction.

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