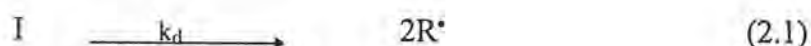


CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Radical Chain Polymerization

Radical chain polymerization has been well known that it consists of three steps: initiation, propagation and termination. The initiation step composes of two reactions including (a) the production of primary radicals (Eq. (2.1)) and (b) the addition of primary radicals produced to the first monomer molecule to obtain the chain initiating species M_1^* [1]. The initiator I is usually homolytically dissociated to yield a pair of radicals R^*



where k_d is the rate constant for the initiator dissociation.

The second reaction of the initiation can be shown as follows



where M is a monomer molecule and k_i is the rate constant for the initiation step.

The propagation step consists of the growth of M_1^* by the addition of large numbers of monomer molecule. Each addition creates a new radical which has the same identity as the one previously, except that it is large by one monomer unit. This step can be presented in general terms as



where k_p represents the propagation rate constant.

The growth of chain take place very rapidly, the average lifetime of the growing chain is short, for instance, a chain of over 1000 units can be produced within 10^{-2} to 10^{-3} s. In theory it could continuously propagate until all the monomers in the system had been consumed. If the radical concentration is high, the short chains are generally produced due to a high probability of radical interactions. The long chains polymer could be produced in the system having low radical concentration [3].

Termination of the growing chains may take place by the reaction of the radical center with initiator radicals; transfer of the radical center to another molecule (such as solvent, initiator or monomer) and interaction with impurities (such as oxygen) or inhibitors. The bimolecular reaction between two radical centers is the most important termination reaction. There are the combination which occurs by the coupling of two radicals center to form one long chain and the disproportionation which a hydrogen atom in the beta position of one radical center is abstracted by another radical center to give a saturated and an unsaturated polymer chains. One or both reactions may be active in any system depending on the monomer and polymerizing condition. The general term expresses the termination step is



where k_t is the combination of the rate constant for the termination step.

2.2 Kinetics of Free Radical Polymerization

The kinetic expression for the overall rate of polymerization is obtained based upon the assumption that k_p and k_t are independent on the radical sizes. The experimental evidence indicates that the effect of size vanishes after the formation of dimer or trimer [1].

The rate of polymerization, which is synonymous with the rate of monomer disappearance, is given by

$$R_i + R_p = -\frac{d[M]}{dt} \quad (2.5)$$

where R_i and R_p are the rates of initiation and propagation, respectively.

In most polymerizations, the addition of primary radical to monomer is much faster than the thermal homolysis of the initiator. Thus, the rate of producing primary radicals is the rate determining step given by

$$R_i = R_d = 2fk_d[I] \quad (2.6)$$

where R_d is the rate of producing primary radicals by thermal homolysis of an initiator.

The factor 2 is due to the production of two radicals in the decomposition reactions. f is the initiator efficiency which is defined as the fraction of the radicals produced in the homolysis reaction that initiate polymer chains. The value of f is usually less than unity.

$[I]$ is initiator concentration which is related to time as Eq.(2.7).

$$[I] = [I]_0 \exp(-k_d t) \quad (2.7)$$

The rate of initiation can be negligible because the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step. Thus, the polymerization rate is expressed by the rate of propagation which is the sum of many individual propagation steps. Since the rate constants for all the propagation steps are the same, one can express the polymerization rate as

$$R_p = k_p[M][M^*] \quad (2.8)$$

where $[M]$ is the monomer concentration and $[M^*]$ is the total concentration of all chain radicals or all radicals of size M_i .

The rate of polymerization R_p expressed in Eq. (2.8) is not directly obtained because $[M^*]$ are difficult to measure quantitatively. The steady state assumption is that the concentration of radicals increases initially, but almost instantaneously reaches a constant. The rate of change of the concentration of radicals quickly becomes and remains zero during the course of the polymerization. Therefore, it is

noted that the steady state assumption is not widely applied in all polymerization kinetics, it is often used for developing the kinetics of many small molecules reaction involving highly active intermediates present at very low concentrations conditions.

The rates of initiation R_i (Eq. (2.6)) and termination R_t of radicals (Eq. (2.9)) are equal to one another to yield Eq. (2.10).

$$R_t = 2k_t[M^*]^2 \quad (2.9)$$

$$R_p = k_p[M](fk_d[I]/k_t)^{1/2} \quad (2.10)$$

The dependence of polymerization rate on the square root of the initiator concentration has been abundantly confirmed for many different monomer-initiator combinations over wide ranges of monomer and initiator concentrations. However, the deviations from this behaviour are found under certain conditions. R_p may be observed proportional to $[I]$ to the power of less than one-half at very high initiator concentration. This effect may be due to a decrease in f with increasing initiator concentration. Alternatively, the termination mode may change from the normal bimolecular termination between propagating radicals to primary termination which occurs by the combination of the propagating and primary radicals. The primary termination can be possibly occurred in the case of too high concentration of primary radicals produced and/or in the presence of too low monomer concentration. The polymerization rate with the primary termination is given by

$$R_p = \frac{k_p k_i [M]^2}{k_{tp}} \quad (2.11)$$

The polymerization rate expressed in Eq.(2.11) is independent on $[I]$ but dependent on the $[M]^2$.

Primary termination and the accompanying change in the order of dependence of R_p on $[I]$ may also be found in Tromsdorff polymerization region. In this region, if the propagating radicals do not under termination or under certain conditions of chain transfer or inhibition, the order dependence of R_p on $[I]$ will be greater than one-half.

The dependence of the polymerization rate on the first-order of monomer concentration is indeed found to be the general behaviour of many polymerizations. However, there are many of them shown the order dependence of R_p on $[M]$ greater than unity. This may be caused by the dependence of initiation rate on the monomer concentration. Since Eq.(2.7) is derived by assuming R_i being independent of $[M]$, the initiator efficiency f may vary directly with the monomer concentration as

$$f = f[M] \quad (2.12)$$

thus, the dependence of R_i and R_p on $[M]$ is the first-order and 3/2 order, respectively. This behaviour is also observed if the second step of initiation reaction becomes the rate-determining step. It occurs when k_d is higher than k_i or when $[M]$ is low. This effect is also frequently encountered in polymerizations initiated photolytically or by ionizing radiation and in some redox-initiated polymerizations.

Other exceptions to the first-order dependence of the polymerization rate on the monomer concentration occur when termination is not by bimolecular reaction of propagating radicals. Second-order dependence of R_p on $[M]$ occurs for the primary termination.

2.3 Autoacceleration [1]

Normally a reaction rate falls with time since the monomer and initiator concentrations decrease with time. However, it is observed in many polymerizations that the reaction rate increases with conversion. A typical example is shown in Figure 2.1 for the polymerization of methyl methacrylate in benzene solution. The curve for bulk polymerization of methyl methacrylate shows a dramatic autoacceleration in the polymerization rate, which is referred to as the gel effect. Tromsdorff effect or Norrish-Smith effect are also used to name such the gel effect in recognition of the early workers in the field.

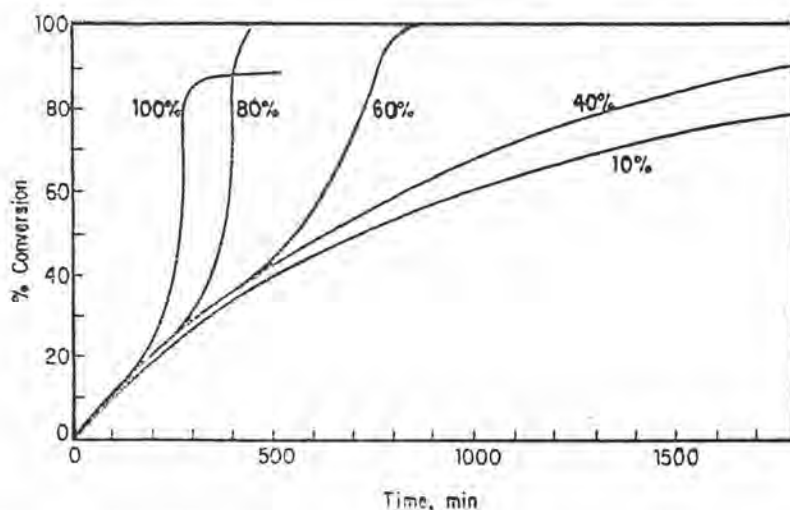


Figure 2.1 Autoacceleration in the benzoyl peroxide initiated polymerization of methyl methacrylate in benzene at 50°C. The different plots represent various concentrations of monomer in solvent [1].

2.3.1 Diffusion-controlled termination

This behaviour is well understood when the termination step is considered to be a diffusion-controlled reaction which proceeds by the three-step processes.

- (1) Translational diffusion where two propagating radicals move to proximity close to each other.
- (2) Segmental diffusion occurs by the movement of segments of a polymer chain relative to other segments in order to rearrange the radical ends of each chain to sufficiently close for chemical reaction.
- (3) Chemical reaction of two radical ends.

Recently, it has found that the segmental and translational diffusion are expected to be affected differently with conversion. In the case of increasing conversion, the polymer concentration is also increased which causes the polymerization medium becomes a poorer solvent. Then the size of the propagating radicals in solution are randomly coiled up and become smaller. Such the condition,

there is an effective higher concentration gradient across the coil. The segmental diffusion of the radical end out of the coil to encounter another radical increases. Simultaneously, the translational diffusion decreased. At sufficiently high polymer concentrations, the polymer radicals become more crowded and entangled with each other. This leads to a faster decrease in translational diffusion relative to the decrease with increasing viscosity.

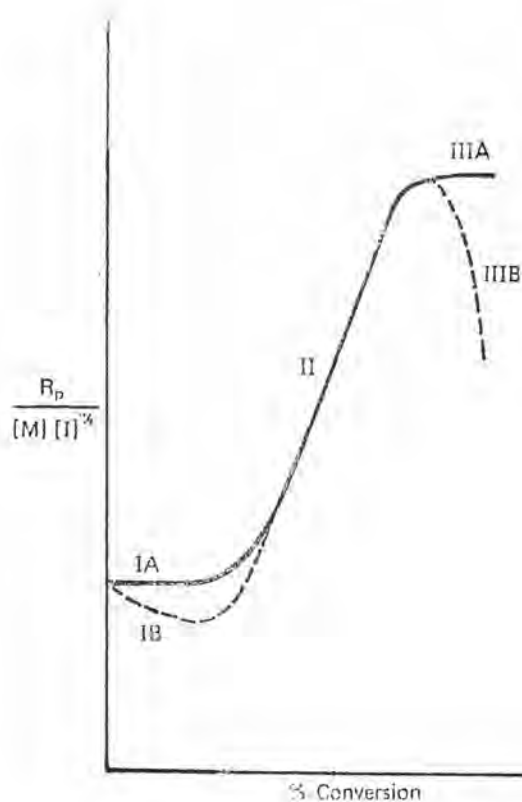


Figure 2.2 Effect of conversion on polymerization rate [1].

The value of $R_p/[M][I]^{1/2}$ is used instead of percent conversion takes into account the concentration changes in monomer and initiator with time (see Figure 2.2). There are three distinct stages that can be distinguished in some polymerizations. Stage IA generally observed for many monomers where the segmental diffusion is apparently counterbalanced by the decreasing of translational diffusion, i.e., k_t remains constant. In contrast to Stage IB, the initial increase in segmental diffusion is greater than the decrease in translational diffusion, k_t increases

and the polymerizations rate decreases. Stage II corresponds to the gel effect. In this stage the translational diffusion decreases faster than the increase in segmental diffusion, and rapid autoacceleration occurs. As the polymerization proceeds, the viscosity of system increase with subsequent chain entanglement and termination becomes much slower. The propagation is also slightly affected. Since the termination involves the reaction of two large propagating radicals, while the propagation involves the reaction of one large propagating radical and the small monomer molecule. Accordingly, the high viscous medium affects the termination reaction much more than the other. The second consequence of this effect is an increase in the molecular weight with conversion. At higher conversion, both k_p and k_t are lower, but k_t is much more lower than k_p . This leads to the increase in the radical lifetime with increasing conversion. At very high conversion, k_p becomes sufficiently affected. The value of $R_p/[M][I]^{1/2}$ begins to level off or decrease corresponds to stage IIIA and IIIB, respectively. But the behaviour of stage IIIB is much more common than stage IIIA and sometimes refers to as the glass or vitrification effect.

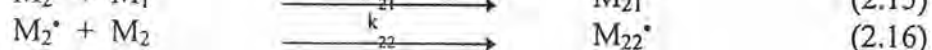
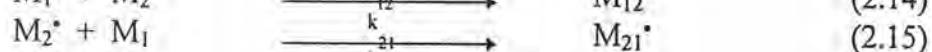
Recently, it has been reported that the variations in the initiator efficiency f affected the rate and degree of polymerization. Because the calculation of k_p and k_t were assumed that f was independent of conversion. But the recent work has indicated that f varied with conversion, i.e., it decreased with conversion in an approximately linear manner. A much steeper drop in f with conversion was found thereafter the high conversion of Stage IIIB were reached. The behaviour observed in Stage IIIB was a consequence of decreases in both k_p and f , not just only the decrease in k_p .

2.4 Copolymerization

2.4.1 Copolymerization equation [1,3]

The composition of the copolymer can be predicted based on a kinetic model which assumed the chemical reactivity of the propagating chains (which may be free radical, carbocation, or carbanion) in a copolymerization depend only on the identity of the monomer unit at the growing end and independent on the penultimate unit. It is further assumed that the monomer consumed in reactions other than propagation is negligible so that only copolymer molecules of high molar mass are formed. This is referred to as the terminal or first-order Markov model of copolymerization.

Consideration of the copolymerization of two monomers M_1 and M_2 . Two types of the propagating species $\sim M_1^*$ and $\sim M_2^*$. Based on the above assumption, four irreversible propagation reactions take place



where k_{11} and k_{22} are respectively the rate constant for the homopropagation or self-propagation, which is the addition reaction of M_1 or M_2 to $\sim M_1^*$ or $\sim M_2^*$, k_{12} and k_{21} are the rate constant for addition of the different monomers to the propagating chain end, which is usually referred to as cross-propagation or crossover reaction.

The rates of disappearance of two monomers, which are synonymous with their rates of entry into the copolymer, are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \quad (2.17)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \quad (2.18)$$

The steady state assumption is applied in that the rates of generation and of disappearance of the radicals are practically equal.

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \quad (2.19)$$

Divide Eq.(2.17) by Eq.(2.18), later substitute Eq.(2.19); and finally rearrange minorly, the copolymerization equation below (Eq.(2.20)) is obtained.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] (r_1[M_1] + [M_2])}{[M_2] ([M_1] + r_2[M_2])} \quad (2.20)$$

where r_1 and r_2 are monomer reactivity ratios defined as the ratio of the rate constant for a reactive propagating species adding its own type of monomer to the rate constant for its addition of the other monomer, i.e.,

$$r_1 = \frac{k_{11}}{k_{12}} \quad (2.21)$$

and

$$r_2 = \frac{k_{22}}{k_{21}} \quad (2.22)$$

The tendency of two monomer to copolymerize is noted by r values between zero and unity.

The term $d[M_1]/d[M_2]$ in Eq. (2.20) is the molar ratio of the two monomer units in the copolymer which is related to the concentration of the monomers in the feed.

The compositions of the monomer feed and of the polymer formed may be expressed as mole fractions instead of the mole ratios. Let's F_1 and F_2 represent the fraction of monomer M_1 and M_2 in the increment of copolymer formed at a given stage in the polymerization, i.e.,

$$F_1 = \frac{d[M_1]}{d([M_1]+[M_2])} = 1-F_2 \quad (2.23)$$

Let's f_1 and f_2 represent the mole fraction of unreacted monomer M_1 and M_2 in the feed, then

$$f_1 = \frac{[M_1]}{([M_1]+[M_2])} = 1-f_2 \quad (2.24)$$

The other form of copolymer composition equation which is often more convenient than Eq. (2.20) is

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (2.25)$$

The copolymerization equation is equally applicable to radical, cationic and anionic chain copolymerizations, although the value of r_1 and r_2 for any particular comonomer pair can be drastically different depending on the mode of initiation. This was confirmed by the following reactivity ratios of styrene (M_1) and methyl methacrylate (M_2), r_1 and r_2 are 0.52 and 0.46 in radical copolymerization, 10 and 0.1 in cationic polymerization and 0.1 and 6 in anionic copolymerization. The ionic copolymerization are predictably much more selective than radical copolymerization, but the former limited its practical use. Since only a small number of monomers underwent ionic copolymerization, the ranges of copolymer products obtained was therefore limited. In contrast, almost all of monomers can undergo the radical copolymerization, therefore a wide range of products can be synthesized.

For any specific type of initiation the monomer reactivity ratios and therefore the copolymer composition equation are independent of many reaction parameters such as the termination and initiation rate constants, the presence or absence of inhibitors or chain transfer agents, the initiation system used to produce the free radical in radical polymerization and the degree of polymerization. This generalization is only limited in the case that the copolymer being a high polymer.

2.4.2 Kinetics of copolymerization [1,3,6]

The kinetic of copolymerization is similar to that of homopolymerization. The rate of copolymerization in a binary system depends not only on the rates of the four propagation steps as mentioned above but also on the rates of initiation and termination. The rate of initiation is simplified due to its independence of the monomer composition. the rate of initiation, R_i , of M_1^* and M_2^* can be written as

$$R_i = 2fk_d[I] \quad (2.26)$$

The overall rate of propagation R_p is (see Eq. (2.13) - (2.16))

$$R_p = -\frac{d[M_1] + d[M_2]}{dt} \quad (2.27)$$

$$= k_{11}[M_1^*][M_1] + k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] + k_{21}[M_2^*][M_1] \quad (2.28)$$

Two different types of termination are taken into account including the chemical-controlled and diffusion-controlled terminations.

(1) Chemical-controlled determination

This type of termination involve three reactions, i.e.,



Eq. (2.29) and (2.30) correspond to termination between radicals having similar terminal structure (the like radicals) and Eq. (2.31) represents the cross termination between unlike radicals.

Two steady state assumptions are used to eliminate the radical concentration. First, each type of radical is assumed to be equal

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \quad (2.32)$$

The second assumption applied to the total radical concentration requires that the combined rate of termination will be equal to the combined rate of initiation.

$$R_i = 2k_{11}[M_1]^2 + 2k_{12}[M_1][M_2] + 2k_{22}[M_2]^2 \quad (2.33)$$

Thus the rate of copolymerization obtains as

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2) R_i^{1/2}}{(r_1^2 \delta_1^2 [M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2] + r_2^2 \delta_2^2 [M_2]^2)^{1/2}} \quad (2.34)$$

$$\text{where } \delta_1 = (2k_{t11}/k_{11}^2)^{1/2} \quad (2.35)$$

$$\delta_2 = (2k_{t22}/k_{22}^2)^{1/2} \quad (2.36)$$

$$\phi = k_{t12}/2(k_{t11}k_{t22})^{1/2} \quad (2.37)$$

δ represents the reciprocals of the familiar $k_p/(2k_t)^{1/2}$ ratios for the homopolymerizations of the individual monomers. The ϕ term represents the ratio of half the cross-termination rate constant to the geometric mean of the rate constants for self-termination of like radicals. The factor of 2 is present in the denominator of Eq. (2.37) since the cross-termination is statistically favored over termination by the like radicals with a factor of 2. $\phi < 1$ represents the cross-termination is not favored, while $\phi > 1$ means that cross-termination is favored. The tendency toward cross-termination parallels the tendency toward cross-propagation in that the increases as $r_1 r_2$ approaches zero. This has led to the conclusion that polar effect is responsible for the tendency toward the cross-termination. The reaction between radicals of dissimilar polarity is enhanced because of stabilization of the transition state for termination by electron-transfer which the effect is analogous to those used to describe enhanced chain transfer and alternation.

(2) Diffusion-controlled termination

It is well established that termination in radical polymerization is generally diffusion-controlled. The value ϕ cannot be interpreted primarily in terms of the chemical effect of the radical chain ends. The ϕ value different from unity should be interpreted in terms of the changes that occur in the translational and segmental diffusion of the chains according to their composition. The termination reactions involve in this termination are



where k_{t12} is a function of the copolymer composition. It is expected to be a function of the termination rate constants for the corresponding two homopolymerizations. In the ideal situation this dependence might be

$$k_{t12} = F_1 k_{t11} + F_2 k_{t22} \quad (2.39)$$

where k_{t12} is the average of k_{t11} and k_{t22} each weighed on the basis of the mole fraction of monomer in the copolymer composition.

The rate of copolymerization can be expressed as

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2) R_i^{1/2}}{k_{t12}^{1/2} \{(r_1[M_1]/k_{11}) + (r_2[M_2]/k_{22})\}} \quad (2.40)$$

and the propagation rate constant (k_p) can be written as

$$k_p = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{(r_1 f_1/k_{11}) + (r_2 f_2/k_{22})} \quad (2.41)$$

2.4.3 Methods for determination of monomer reactivity ratios

The copolymerization data obtained from several experimental methods are further employed to calculate the monomer reactivity ratios using the following methods.

(1) Curve-fitting method (Lewis-Mayo equation)

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])} \quad (2.42)$$

where $[M_1]$ and $[M_2]$ are the initial concentrations of monomers M_1 and M_2 , respectively.

This method is the graphical comparison of the experimental monomer-copolymer composition curves with that calculated for the selected r_1 and r_2 values by trial and error. The plots of monomer-copolymer composition were based on the copolymer composition equation.

An advantage obtained from this method is that the monomer reactivity ratios are weighed from the experimental points. However, at least two disadvantages are observed. Firstly the initial composition of monomer feed is used instead of the instantaneous composition. An error may be due to the difference of reactivity of two monomers. Since the more reactive monomer can easily add to the copolymer chain than the less reactive one, so that the monomer feed compositions are progressively changed or the concentration of the more reactive monomer is relatively decreased. The initial composition of the feed monomers can be approximately used if the copolymer formed was isolated at a conversion as low as possible due to the changes of copolymer compositions with conversion. Such a limiting conversion is dependent upon composition and the reactivities of monomers feed. The error caused by this factor seems to be expected to increase with increase of the difference between the reactivities of two monomers. The other disadvantage may come from the arbitrariness contained in the visual best fit; however, it has been already solved using a graphical least-squares procedure.

(2) Fineman-Ross method

$$F(f-1)/f = (r_1F^2/f) - r_2 \quad (2.43)$$

where $F = [M_1]/[M_2]$ and $f = d[M_1]/d[M_2]$.

The equation used for this method is one of the linearized forms of Lewis-Mayo equation. The plot of $(F/f)(f-1)$ against F^2/f gives the slope and the intercept on abscissa of the curve equal to r_1 and r_2 , respectively. The method has been widely used; however, some disadvantages have been pointed out. The slope of the plot is normally determined by the furthest point from the abscissa, which has the largest value of F^2/f . However, in the original equation, the experimental point of extremely large F or f is insensitive to the values of r_1 and r_2 . Moreover, this plot may give a negative r_1 value which has no meaning. Although calculation by an electronic computer and modification of this method can solve partly the problems mentioned above.

(3) Intersection method

$$r_2 = \frac{[M_1]}{[M_2]} \left\{ \left(\frac{d[M_2]}{d[M_1]} \right) (1 + r_1 \frac{[M_1]}{[M_2]}) - 1 \right\} \quad (2.44)$$

For this method, the monomer feed and copolymer compositions for each copolymerization are substituted into Eq.(2.44), and r_2 is plotted as a function of various assumed values of r_1 . $(\frac{[M_2]^2}{[M_1]^2} \frac{d[M_1]}{d[M_2]})$ and $(\frac{[M_2]}{[M_1]} (\frac{d[M_1]}{d[M_2]} - 1))$ are obtained as the slope and the intercept, respectively. The intersection of the straight lines determines r_1 and r_2 . The points of intersection of various lines may have variation and these are the indication of the experimental errors in the composition data and the limitation of the mathematical treatment. The composition data can also be treated by linear least-square regression analysis instead of the graphical analysis. However, this method has at least three disadvantages. Two of these are the same as those mentioned earlier in the Fineman-Ross method, and the other is that the value of r_1 and r_2 are hardly to determine since the n of straight lines usually give $n(n-1)/2$ intersection.

(4) Integration method

$$r_2 = \frac{\log([M_2]_0/[M_2]) - 1/p \log((1-p[M_1]/[M_2])/(1-p[M_1]_0/[M_2]_0))}{\log([M_1]_0/[M_1]) + \log((1-p[M_1]/[M_2])/(1-p[M_1]_0/[M_2]_0))} \quad (2.45)$$

where $p = (1-r_1)/(1-r_2)$

$[M_1]_0$ and $[M_2]_0$ are the initial concentrations of the respective monomers.

$[M_1]$ and $[M_2]$ are their concentrations at the time which copolymerization was stopped.

The integrated form can solve the disadvantages inherent in the use of the initial composition of the feed. However, since the calculation of this method seems to be more complicated than the others and the larger arbitrariness in the r_1 and r_2 determination, it has been employed not so often.

2.5 Studies on the Kinetics of Polymerization using DSC technique [7,8]

Differential scanning calorimetry (DSC) is a thermal analysis technique measured the heat flow into or out of a sample as it is exposed to a controlled thermal profile. It has been widely used to study not only the kinetics of chemical reaction but also that of the polymerization. Generally, the experimental methods used for kinetics investigation are operated under the isothermal and the dynamic modes. In dynamic mode, the kinetic parameters are evaluated from the DSC thermogram which may be obtained from three different conditions [8] including (a) obtain at a constant heating rate, (b) obtain at variation of heating rate effect on the peak exotherm, and (c) obtain at variation of heating rate effect on temperature at a constant conversion. In the isothermal condition, the DSC thermogram obtained are the record of the electrical signal which is proportional to the reaction heat produced versus time. This data can be used to evaluate the kinetic parameters of the free radical polymerization by assuming that the total peak area located between the exothermic curve and the baseline of DSC thermogram corresponds to the heat evolved during the polymerization. In order to evaluate properly the initial rate, generally it is necessary

to follow the polymerization until no heat evolution can be detected and subsequently to run the reaction to 100% conversion by a dynamic scan up to higher temperature [9,10,11]. The monomer conversion up to time t can be expressed as

$$x = \frac{[M]_0 - [M]}{[M]_0} = \frac{a_t}{A_T} = \frac{a_t}{\Delta H_I + \Delta H_R} \quad (2.46)$$

where x is the monomer conversion at time t ,

a_t is the accumulated area under the isothermal DSC curve from the initial time to time t ,

A_T is the total peak area for the monomer conversion up to 100%,

ΔH_I is the total heat of isothermal polymerization or the total peak area under the isothermal DSC curve, and

ΔH_R is the total heat of polymerization of the residual monomer or the total peak area under the dynamic DSC curve.

The value of a_t are manually or automatically determined by dividing the total peak area into a number of partial area. This procedure was performed by drawing a horizontal baseline located between the two “no reaction” point on curve and a vertical line between the horizontal baseline and the exotherm curve. The accumulate of the partial peak area from the initial time to time t is the value of a_t . The total peak area obtains from the isothermal mode represented the heat of polymerization at the isothermal condition (ΔH_I). However, the value of A_T assumed to correspond to the total heat of polymerization is evaluated from the addition of total peak area of the exotherm curve obtained from the isothermal mode and that obtained from the dynamic mode [9,10]. In order to proceed the polymerization up to 100% conversion, the residual monomer was then totally polymerized at the higher temperature and evaluated from the heat evolved at this stage represent the heat of polymerization of the residual monomer (ΔH_R) which can be expressed as

$$R = \frac{\Delta H_R}{\Delta H_I + \Delta H_R} \quad (2.47)$$

where R is the residual monomer content.

Besides the above parameters, the other parameters such as the rate of polymerization (R_p), the overall rate constant (k_{ov}), etc. can be calculated from the relation of conversion-time. The rate of polymerization is given by

$$R_p = \frac{-d[M]}{dt} = [M]_0 \frac{dx}{dt} \quad (2.48)$$

where dx/dt is the rate of monomer conversion obtained from the slope of the plot of monomer conversion against time.

2.6 Relevant Literature Review

Malavasic, T.; Vizovisek, I.; Laponje, S. and Moze, A. [9] studied the isothermal bulk polymerization of methyl methacrylate by differential scanning calorimetry. The polymerizations were carried out under the isothermal condition at 70-90°C using 0.05 mol/L AIBN initiator. The heat of polymerization was evaluated by the addition of the total heat of isothermal and dynamic conditions. The value observed at 70°C is 52.3 kJ/mol and becomes more increasing with increase of temperature. The overall activation energy was determined to be 77 kJ/mol. Another series of polymerization experiments were performed at 80°C with various amount of initiator. The heat of polymerization detected is 52.8 kJ/mol and seems to increase slightly with the increasing initiator concentration. The overall rate of polymerization at low degree of conversion depends on $[I]^{1/2}$.

Armitage, P.D.; Hill, S., Johnson, F., Mykytiuk, J. and Turner, J.M.C. [10] investigated the kinetics of bulk polymerization of methyl methacrylate. Two different methods used to follow the polymerization course included differential scanning calorimetry and gel permeation chromatography. The former was carried out

by allowing the polymerization to occur in small aluminium pans in the DSC furnace. The initiator used was AIBN and the polymerization temperatures were at 65-95°C. The monomer conversions, the heat of polymerization and some kinetic parameters are calculated from the data given. The other method was used to follow the polymerization that occurred in the glass ampoules. The residual monomer content and the molecular weight of polymer produced were measured. The kinetic parameters obtained from both methods were different which could be resolved by consideration of the measured temperature rise during of the polymerization carried out in the ampoule.

Alberda, G.O.R. and Roman, J.S. [11] investigated the use of the calorimetric method to determine the initial rate of the free radical polymerization of methyl methacrylate in dimethylformamide. The polymerizations were performed using 0.015 mol/L AIBN at 40-70°C. The rate of polymerization and rate constants determined using the method so-called $v_{p,max}$ method. The values obtained were closed to those obtained from the conventional technique. The overall activation energy and $\ln A$ calculated from the Arrhenius equation were 76.4 kJ/mol and 19.5, respectively.

Horie, K.; Mita, I. and Kambe, H. [12] used the calorimetric method to follow the bulk copolymerization of diethyl fumarate and styrene initiated by benzoyl peroxide or AIBN. The heat of copolymerization decreased almost linearly with the increase in diethyl fumarate content in copolymer. The rate copolymerization was determined over the whole range of conversion. The monomer reactivity ratios at 100°C were also determined.

Ebdon, J.R. and Hunt, B.J. [13] used the differential scanning calorimetry to follow the course of free radical polymerization of styrene. The reaction order with respect to benzoyl peroxide at 80°C was 0.53 ± 0.06 . The order of reaction with respect to the monomer concentration at 80°C was 1.2 ± 0.3 . The activation energy

for the polymerization is 19 kcal. The values of heat of polymerization are in the ranges of 12 to 14 kcal/mol.

Khan, H.U. and Wadehra, B.M.L. [14] studied the kinetic of free radical bulk copolymerization of styrene and methyl methacrylate (MMA), conducted in sealed glass ampoules at constant temperature using benzoyl peroxide initiator. The comonomer feed compositions were varied from 0.2 to 0.8. The rate of copolymerization was lower than the homopolymerization of styrene or MMA, and it decreased gradually with increasing styrene content in feed. The termination mechanism was controlled by diffusion.

Rim, P.M. and O'Connor, K.M. [15] studied the possibility of using differential scanning calorimetry in the temperature scanning mode to monitor the polymerization course. Three systems were investigated, i.e., homopolymerization of styrene and the copolymerization of maleic anhydride (MAH) with styrene and 1-decene. Polymerizations were initiated with di-tert-butyl peroxide and were performed in carbitol acetate solution. The total heat of polymerization, the overall activation energy and the frequency factor of three systems are evaluated. The kinetics of the decomposition of initiator was also studied and the consumption of initiator has been determined to be important variable influencing polymerization rate constants.

Maffezzoli, A. [16] studied the polymerization kinetics of acrylic bone cement by differential scanning calorimetry. A simple phenomenological model, accounting for the autoacceleration effect, for a diffusion controlled termination mechanism, and for the reaction between inhibitor and initiator was proposed. DSC was used for the determination of the rates of polymerization under isothermal and non-isothermal conditions. The parameters of the proposed phenomenological kinetic model were calculated.

Gorna, K. and Polowinski, S. [17] studied the kinetics of radical bulk polymerization of methyl methacrylate using differential scanning calorimetry technique. The polymerization reactions were carried out under the isothermal (75-90°C) and temperature scanning conditions. At low conversions, the overall rate constant and some thermodynamic parameters such as enthalpy of polymerization, activation energy and entropy were evaluated from the isothermal condition. The value of activation energy and entropy were also determined from the temperature scanning condition. At high conversion, the polymerization course was found to obey the Sawada equation.

The literature values of the monomer reactivity ratio of styrene and MMA are summarized in Table 2.1.

Table 2.1 The monomer reactivity ratio of styrene and MMA obtained from the literature [18].

Monomer reactivity ratio	
Styrene	MMA
0.490	0.418
0.564	0.540
0.440	0.450
0.485	0.409
0.480	0.504
0.371	0.611
0.396	0.220
0.585	0.478
0.420	0.320
0.540	0.420
0.480	0.420
0.500	0.440

Table 2.1 (Continued).

Monomer reactivity ratio	
Styrene	MMA
0.520	0.450
0.470	0.450
0.490	0.460
0.520	0.460
0.450	0.470
0.520	0.470
0.580	0.480
0.380	0.480
0.560	0.490
0.530	0.490
0.540	0.490
0.440	0.500
0.500	0.500
0.620	0.590
0.520	0.600
0.500	0.630
0.550	0.580
0.550	0.640
0.410	0.410
0.472	0.454
0.497	0.464
0.432	0.422
0.275	0.314
0.570	0.410