Theoretical Investigation on The Kinetics of Free Radical Reactions of Styrene Emulsion Polymerization

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Abstract:

Tables are presented for the calculations of the basic parameters and values, a survey concerning the theoretical equations used for styrene/NaLS/$K_2S_2O_8$ reaction mixture parameters are presented from which the absolute values of the following quantities can be conveniently calculated for any temperature: soap and initiators concentration, particles number according to particle radius containing radicals, rate constants of initiation, propagation and termination and the corresponding energy difference of propagation and termination. The theoretical results are discussed according to the models of Smith theory and Hamielec, is that in emulsion polymerization, Loci (minute particle) of chain propagation, where the monomer concentration is perturbed by conversion to polymer are immediately swamped by un reacted monomer. Numerous data from literature are in good quantitative or qualitative agreement with theories proposed in different research's in field of study.

Introduction:

In emulsion polymerization the system always contains at least four components: water insoluble monomer, water, emulsifier and initiator. The first recipe was discovered purely empirically when attempts were being made to produce latex of natural rubber. This work showed that water soluble initiator (e.g. $K_2S_2O_8$) where more effective than those that where only monomer soluble (e.g. dipenzoyal peroxide). Monomers suitable for emulsion polymerization must be insoluble in water. The effectiveness of water soluble initiators at once suggest that the polymerization, unlike that which occurs in suspension[1], does not take place in the monomer droplets but in "emulsion". This supposition is confirmed by attempts in which a layer monomer is placed over the emulsion phase only being possible via the gas phase. Most monomers are barely soluble for emulsion in pure water. Styrene dissolves to 0.038% in water at 50°c, but to 1.45% in 0.093M aqueous potassium persulfate ($K_2S_2O_8$) solution. This monomer solubilize of by the emulsifier[2] since the monomer in filtrates into micelles formed by the emulsifier sodium lauryl sulphate (NaLS)[3]. What-ever the locus of particle nucleation, the decomposition of persulfate is considered to produce sulfate ion-radicals in the aqueous phase. These ion-radicals are repelled by the negatively charged surface of the monomer swollen emulsifier micelles, polymer particles or monomer droplets and therefore remain in the aqueous phase and add hydrophobic monomer units to form any oligomeric radicals. When this oligomeric radical attains a critical chain length, it

becomes surface-active and adsorbs on the surface of a micelle, polymer particle, or monomer droplet. If it cannot adsorb on a suitable surface, it continuous to grow until it exceed its solubility in water and therefore precipitate to nucleate a latex particles. Initiation in micelles is significant only in the beginning of the polymerization and the monomer droplets usually are not a significant locus of the particle nucleation. Therefore, once the particle nucleation stage is completed the monomer swollen polymer particles are the principal locus of the polymerization[4].

The adsorption of an oligomeric sulfate radical to initiate a polymeric radical and the termination of this polymeric radical should give two surface sulfate groups for each polymer molecule formed assuming that no transfer reactions occur to introduce a different end group, that the termination inside the particle occurs by combination rather than disproportionate and that none of the sulfate end groups become buried inside the particle[5]. Carncio and Williams recently proposed that in styrene emulsion polymerization the latex particles are not uniformly swollen by monomers; rather than the monomer concentration is relatively high at the particle surface and relatively low at the center of the particles. Criticizing this concept Napper favored a reverse picture involving a monomer- poor skin and a monomer rich core, William supplied further details relevant to this controversy in a rebuttal to Napper. Since the postulated existence of monomer concentration gradients within latex particles during polymerization is in consistent with the theory of Smith-Ewart and others[6]. Polystyrene latex have been prepared using persulfate initiator forming sears, but only have method been developed to determine the number and loci of sulfate surface group[7] .

The term "compartmentalize free radical polymerization reaction" mean a free radical polymerization which take place within a long number of separate reaction loci are dispersed in a contiguous external phase. The polymerization maybe generated either within the external phase or within the reaction loci, in all cases, the new radicals are assumed to be generated exclusively with the external phase. The theory of compartmentalized free-radical polymerization reaction of the type considered, is of interest primarily because it is believed that the most polymer which is formed in the course of emulsion polymerization reaction is formed by the way of reaction of this type. The objective of the theory is to calculate the relative proportion of reaction loci which may at any instant contain 0,1,2,….,r,…. Propagation radicals and also such properties of the locus population distribution as the average number of propagation radicals per reaction locus and the variance of the distribution of locus population[8].

Method:

Many techniques have been used for the latex preparation as the model were prepared by a semi-path techniques in which a monomer mix was continuously fed into stirred reactor at $80^0C^{[A]}$. The experimental evaluation was done using monodisperse latex particles in the size range 400-1650 A° with a measure of instantaneous rates using an adiabatic calorimeter as reactor. A knowledge of instantaneous rates permits one to determine the variation of K_t and K_p with conversion. In particular for the 400 A° latex particles, one can set the average number of radicals per particles (ň) equal to 0.5 and this permits a direct measure of the decrease of the propagation constant with conversion[B]. Different methods have been used in this research depend on calculating the values of parameters and constants of propagation, termination and rates of initiation, propagation and kinetics of free radical of polymerization of the reactions by using

different equations expressing them. A sets of tables , have been postulated from which graphs were plotted for finding the activation energy and difference between the activation energy of propagation and termination applying equation of Arrhenius form and other parameters. Other graphs for explaining latex preparation model and how the conversion were occurred. The models expressing these parameters, constants, kinetics and the rate of polymerization and calculating their value as follows:

1-The Initiator Parameters:

In order to define the kinetics of free radical polymerization on must consider at least three consecutive reactions, initiation, propagation and termination, plus chain transfer is possible, several compelling reactions unless some mathematical simplification can be made. The kinetics equation which are used describe addition polymerization will be overly complex[C]. And the homolysis of the initiator is the rate determining step in the initiation sequence, the rate of initiation is given by:

$$R_{i=} 2f^*K_d^*[I] \quad \text{---------- (1)}$$

Where f is the efficiency of initiation to cause polymerization which is defined as fraction on radicals produced in homolysis reaction that initiate polymer chain, value of f is less than unity(0.3-0.8) due to the wastage reaction[op.cit.[7]]. The factor(2) takes into account that two radicals are formed from a single initiator molecule. For the commonly used persulfate, K_d was determined by Kolthof and miller, they found it to increase with soap concentration and with decreasing pH. As will be shown , satisfactory agreement between theory and experiment is obtained without taking into account the effect of soap upon initiator decomposition[D]. [I] is the initiator concentration.

2-Kinetics Evidence:

The rate of bimolecular propagation for the same reaction assuming that $M^{.}+M$ reaction proceed at the same rate independently of chain length is determined by ;

$$R_{p=} K_p * [M^{.}] * [M] \text{---------- (2)}$$

Where $[M^{.}]$ is the growing end termination by coupling or by disproportionate in free-radical polymerization is by bimolecular reaction depending only upon$[M^{.}]$, therefore both methods of termination can be expressed by the same relationship.K_p: propagation constant, [M] denotes monomer concentration[op.cit[6]].

$$R_i = 2K_t * [M^{.}] \wedge 2 \quad \text{------------ (3)}$$

At steady-state $R_i = R_t$, The use of factor 2 enters as a result of the disappearance of two radicals at each incidence of termination reaction. Under all ordinary conditions the concentration of chain radicals will assume a value such that the rate of their disappearance through termination will equal their rate of creation in this steady state: Combining (1) and (3) gives:

$$[M^{.}] = (\frac{f*K_d*[I]\wedge\frac{1}{2}}{K_t}) \text{--------------- (4)}$$

$$R_p = K_p * (\frac{f*K_d*[I]}{K_t}) \wedge \tfrac{1}{2} * [M] \ \text{------(5)}$$

$$\frac{f^*K_d*K_p\Lambda2}{K_t} = \frac{R_p\Lambda2}{[I]^*M]\Lambda2} \text{--------(7)}$$

$$\frac{K_p\Lambda2}{K_t} = \frac{2*R_p\Lambda2}{R_i*[M]\Lambda2} \text{------------(8)}$$

From which R_i can be evaluated. The theoretical calculations of equations (8) gives the value of R_i is equal to 2.373×10^{-2}. The quantity $\frac{f^*K_d*p\Lambda2}{K_t}$ may be calculated from equation(7). M will be calculated later in section 4.

3- Rate constant in free radical polymerization:

The rate constant of propagation K_p and termination K_t can be existed according to the equations, in which the average life time of growing polystyrene radicals in photosensitized polymerization of liquid monomer have been determined and by determining the rate of initiation, which give a strong evidence that the termination occurs mostly by coupling of radicals[E]. The propagation rate constant is found to be:

$$K_p = 2.17 \times 10^7 e^{\frac{-7760}{KT}} \text{------- (9)}$$

and the termination rate constant:

$$2K_t = 0.59 \times 10^9 e^{\frac{-2370}{RT}} \text{--------(10)}$$

The propagation rate constant is in fair with literature values but the termination rate constant is 20 fold that reported by Bamford and Dewer[F].

Table-1. Shows the calculation of K_p, K_t and the ratio $\frac{K_p}{K_t\Lambda\frac{1}{2}}$. A graph of $\frac{\log K_p}{K_t\Lambda\frac{1}{2}}$ against $\frac{1}{T}$ is plot as in fig.1. To obtain $E_p - E_{t/2}$, the difference between activation energy of propagation and termination, the ratio of frequency factors of propagation and termination $\frac{A_p}{A_t\Lambda\frac{1}{2}}$. By applying the equation[G]:

$$\frac{K_p}{K_t\Lambda\frac{1}{2}} = \left(\frac{A_p}{A_t\Lambda\frac{1}{2}}\right) * e^{-(E_p-E_{t/2})/RT} \text{-- (11)}$$

4- Rate of polymerization:

The classical equation of the rate of emulsion polymerization is given by the equation:

$$Rate = K_p * [M]^*N\tilde{n} \text{----------------(12)}$$

Where K_p is the propagation constant, [M] denotes the monomer concentration at the locus of polymerization in latex particles, N is the particle number and ñ is the number of radical per

particles[H]. According to Smith-Ewart theory ñ=1/2 case II and 0.02 or less case I. The bulk and solution polymerization kinetics depend upon the monomer and radical concentration[I]. It is convenient to replace the molar concentration and radical concentration [M] and [R] with the number of monomer molecules and radicals, m and ñ. In the equations below, K_p is the propagation constant, r is the radius and N_A is the Avogadro number[op.cit[6]].

$$[M] = {3m}/{4\pi r^{3*} N_A} \text{------------(13)}$$

$$[R] = {3m}/{4\pi r^{3*} N_A} \text{--------------(14)}$$

Substituting (13) and (14) into (12):

$$\frac{dm}{dt} = {3K_p * m\tilde{n}}/{4\pi r^{3*} N_A} = \frac{\Delta m}{\Delta t} \text{---- (15)}$$

From (12) m can be calculated which near unity (1.0037-1.010). Table (2) shows the value of N from equation (12), the average value of [M] and [R] from (13),(14) respectively, ñ is equal to $2^{[J]}$ are 3.97×10^{-6} and 7.942×10^{-6} respectively and again the value 0f [R] is twice of that of [M] . And Δt can be calculated from:

$$\Delta t = {4\pi N_A * r^{3*} \gamma}/{3K_p * \tilde{n}} \text{------------ (16)}$$

In which ($\gamma = 10^{-3}-10^{-2}$). Δt = 6.617 sec.

γ a small fraction of all monomers present in a single latex particle is calculable with aid of the diffusion coefficient D by eq. of The diffusive mean free path $X^{/}$:

$X^{/} = 2Dt_\gamma \Lambda^{\frac{1}{2}}$, t is plausible that there will be no core-skin separation if X is equal to or large than the particle radius r, while very small perturbation in monomer concentration induced by polymer formation ($\gamma <<1$). For $D=10 \wedge -12$ cm $\wedge 2.\sec \wedge -1$, $r=5 \times 10 \wedge -6$cm, $X^{/}/r \geq 1$ and $\gamma = 1o^{-2}$. For $D=10^{-9}cm^2.sec^{-1}$, $r=10^{-6}$cm, $X^{/}/r=1$ and $\gamma = 10^{-3}$

The rate of propagation R_p can be calculated by applying the equation:

$$R_p = -\frac{dM}{dt} = {K_p * \tilde{n}M}/{(V^* N_A)} \text{---------(17), in the particles}$$

Where M is the monomer concentration in the particles (gmole.liter^{-1}), K_p the propagation rate constant (liter.gmole^{-1}.sec^{-1}), V the volume of the particle in (liters) and N_A is the Avogadro number. As shown in table-3. It is convenient to remove the monomer concentration from the right hand side of the expression to write the relationship in terms of fractional conversion:

$$\frac{d\ln(1-x)\wedge-1}{dt} = {K_p * \tilde{n}}/{(V^* N_A)} \text{-----------(18)}$$

Table-3- shows the calculated values of $d \ln(1-x)^{-1}$. And a graph of $\ln(1-x)^{-1}$ against time as shown in fig.(2). Where x is the fractional conversion[K].

The overall rate of polymerization [op.cit.[3]]:

$$-\frac{dM}{dt} = R_i + R_p \text{---------------------(19)}$$

$$-\frac{dM}{dt} = 2^*K_t * [M^\cdot]\Lambda 2$$

$$-\frac{dM}{dt} = (2^*K_t * f^*K_d[I])\Lambda\tfrac{1}{2} * [+K_p[M]]^* (\frac{f^*K_d*I}{K_t}) \text{ ---(20)}$$

5- Kinetic chain length and degree of polymerization:

$$Y = (K_p/2^*K_t) [M]/[M^\cdot] \text{ ---------(21)}$$

Eliminating the radical concentration using equation (2):

$$Y = (\frac{K_p\Lambda 2}{2^*K_t}) * [M] \wedge 2/R_p \text{-----------(22)}$$

$$X_n = 2^*Y \text{-----------------------------(23)}$$

Approximately calculated according to equation (22), X_n is the rate of polymerization of undiluted styrene, number average of degree of polymerization, which is directly proportional to the kinetic chain length, Y it should increase with $[M]\Lambda 2$ and decrease inversely with R_p.

Results and Discussion:

The paper has presented a comprehensive set of data for the emulsion polymerization of styrene. Analysis of these data has led to understand the fundamental mechanism of styrene emulsion polymerization, the evidence of substantial of bimolecular propagation for the same reaction as interpreted in equation(2). The rate of initiation R_i as calculated at the steady state condition $R_i = R_t$ has an important effect on the mechanism of chain termination, its average value calculated in temperature range 25-70°C, the chain termination is an instantaneous reaction between two radicals within one particle and the particles are nucleated by radicals absorbed into monomer-swollen soap micelles. The rate constants of propagation K_p and termination K_t, which is also substantial evidence that the termination occurs mostly by coupling of radicals. Applying eq.(11):
$\frac{K_p}{K_t\Lambda\frac{1}{2}} = (\frac{A_p}{A_t\Lambda\frac{1}{2}}) * e^{-(E_p-E_{t/2})/R^*T}$ and from table-1- the graph in fig.-1- the calculated value of $E_p-E_{t/2}$= 7.146 cal.gmole^{-1}.k^{-1}, from the slope and the value of $(\frac{A_p}{A_t\Lambda\frac{1}{2}})$= 1.284 (sec.mole.liter^{-1})$^{-1/2}$, from the intercept. In which E_p and E_t are the activation energy of propagation and termination respectively, A_p and A_t are frequency factors of propagation and termination respectively. The calculated value of molar concentration of monomer [M] and radical concentration in particle [R]

as indicated from equation (13) and (14) in the range of temperature 25-70°C, this is as discussed above the reaction is between two radicals within one particle. The calculated number of particles and the fact n is in the range 0.02 or less[op.cit[I]]. as shown in table-2- is decrease at the beginning of the reaction, then has increased specially at time interval 27.66x10^3 sec. and there is a sudden decrease in time interval at temperatures 40°and 80°C. When the conversion has proceed far enough , the monomer droplets disappear and the reaction mixture becomes a two phase system of monomer-swollen latex particles and aqueous phase in time intervals. Fig-2- the number of particle with time, the conversion show an oscillation with time intervals. Having once entered a locus, suppose that a free radical continues to cause polymerization until its activity is destroyed or transferred out of the locus and the interfacial area through which the transfer take place and again the equation of steady state $R_i = R_t$[L] applicable and the event in which two free radicals are disappeared at each incident for each event of termination. Table-3- indicate the fractional conversion with time interval and there is increase in fractional conversion specially at 80°C in which the time interval is 0.032x10^3 sec was chosen from column (3) of life time. The curve in figure(3) give an evidence to case that the conversion is occur in a harmonic oscillations, which give rise to particles to nucleate. Table-4- indicate the rate of propagation at the operated reaction 40-80°C. Fig.(4) show the inverse dependant of R_p on temperature, the graph is a straight line and using equation of Arrhenius type:

$$R_p = \text{constant} \exp^{(- E/R^*T)} ,$$ from

which E =8.816 cal.gmole^{-1}. And the constant = 6.66 sec^{-1}. As calculated from the intercept of the graph.

According to equation (20) the overall rate of propagation as calculated at 60°C, which is equal to 1.196x10^{-4}sec^{-1}. In which the decomposition rate constant[op.cit[J]]. K_d = 1.5x10^{-6}sec^{-1}. From the information, the concentration of monomer in loci and the number of loci (polymer particles) produced in emulsion polymerization of styrene, needed for calculating the kinetic chain length, applying equation (22) is equal to 5.37x10^{-2}sec^{-1}.The value of the number average degree of polymerization of styrene according to equation (23) is equal to 10.614x10^{-2}sec^{-1}. A retard or inhibition in reaction mechanism depend on whether the free radicals were chosen to be a flow reactivity for other-wise it may be initiate chains as well as termination.

Emulsion polymerization is a type of radical polymerization that usually start with an emulsion incorporating water and surfactant. The most common type of emulsion polymerization is an oil in water emulsion in which droplets of monomer of (the oil) are emulsified (with surfactant) in continuous phase of water. The emulsion polymerization is an isomer that arise from historical misconception. Rather than occurring in emulsion droplets polymerization takes place in the latex particles that forms a spontaneously in the first few minutes of the process. These latex particles are typically 100 nm. In size and comprise many individual polymer chains. The particles are stopped from coagulation with each other because each particles surrounding by surfactant (soap) the change of the surfactant repels other particles electrostatically. When water soluble polymers, such as polyvinyl alcohol or hydroxyethyl cellulose are used as stabilizers instead of soap, the repulsion between particles arises because forming a hairy layer around the particles that repels other particles, because pushing particles together would involve compressed these chains. Emulsion polymerization is used to manufacture several commercially important polymers. Many of these polymers are used as a solid materials and must be isolated from aqueous dispersion after polymerization . in other cases the dispersion itself is the end product. A dispersion resulting from emulsion polymerization is often called latex (refer to a dispersion from a liquid to water)[(M)]. Free

radical polymerization, in which propagating species is a long chain free radical, usually initiated by the attack of free radicals derived by thermal or photo-chemical decomposition of unstable materials called initiators. Polymerization process by the chain reaction addition of monomer molecules to the free radical ends of growing chain molecules. Finally two propagating species (growing free radicals) combine or disproportionate to terminate chain growth and form one or more polymer molecules[N].

Conclusion:

The analysis of the sulfate end-groups of the oligomers produced in the styrene system was carried out to understand the mechanism the initiation, transfer and termination[O].

1-In the initiation step the decomposition of persulfate is considered to produce ion-radicals, which repelled by the negatively surface because of the anions of the emulsifier sodium lauryl sulfate (NaLS). The development of the kinetic of free radical polymerization of styrene, the principal locus of polymerization is in the polymer-monomer particles, as pointed in table (1) the value of (r) A°[op.cit[B]] refer to extremely minute polymer particle are initiated in and grow in this monomer layer[p]. These polymer particles carry soap with them, at a yield as many as 10^{20} particles, such particles, the rate of production of them provides a locus for the monomer present and as the conversion proceed the monomer-polymer particles rapidly larger as the concentration of soap increase many more polymer particles are formed as it reach its maximum value, the yield also increased.

2- The investigation introduced two types of loci;

A- in which minute particles are initiated; B- The locus in which most of the polymer formed.

A-1- Early in the reaction nearly all of the polymer particles nuclei are formed in monomer solubilized in the core of oil in the soap micelles. The polymer molecules thus formed grow from the soap micelles into the aqueous phase, the soap of the micelles become adsorbed soap. This locus ceases to be active with growing yield. A-2- The locus for initiation; the aqueous phase, the relative importance of which rises with decrease in the initial amount of soap, this hold up to some extent with increasing soap concentration and yield above which all the monomer is dissolved in the polymer, except a very slight amount of monomer dissolved in the water. B- Locus in which nearly all of the molecules polymer, formed the polymer particles themselves. These take up monomer molecules from the aqueous phase and the polymer-monomer particles then formed undergo polymerization while simultaneously the particles take up more monomer[Q].

3- In free kinetics of free radical chain polymerization, the rate of polymerization is directly proportional to the kinetic chain length, and inversely decreases with rate of propagation, $X_n \sim 1 / R_p$. and Y should increase with concentration, between R_i and R_t are longitudinal for high degree of polymerization.[op.cit[K]].

4-Emulsion polymerization is used to manufacture several commercially important polymers. Many of these polymers are used as solid materials and must be isolated from the aqueous dispersion after polymerization. In other cases the dispersion itself is the end product. A dispersion resulting from emulsion polymerization is often called a latex (especially if derived from a

synthetic rubber) or an emulsion (even though "emulsion" refers to a dispersion of an immiscible liquid in water)[R].

5-There is no single branch of science and technology or industry that is not affected by nanotechnology. The development and innovation in the next 10 years or so would even be showing stronger influence of nanotechnology on most material we are surrounded. To date it has accommodated the multiplication of applications, in industrial manufacturing (more importantly in polymer modification and synthesis), computer/electronic chips, medical diagnosis, health care, finishing formulations, energy, automation biotechnology, packaging, space, aircraft, protection and security[S].

Table-1-The values of rate constant of propagation and termination K_P, K_t at different temperatures

t°C	1000/Tk^{-1}	K_p l.mole^{-1}.sec^{-1}	k_tl.mole^{-1}.sec^{-1}x10^{-7}	2.302logk_p/$k_t^{1/2}$ (l.mole^{-1}.sec^{-1})$^{-1/2}$
25	3.335	44	2.365	-2.043
30.5	3.294	55	2.527	-1.936
40	3.194	82.72	2.866	-1.812
50	3.095	121.73	3.225	-1.664
60	3.003	175.02	3.6	-1.532

70	2.915	246.37	7.999	-1.409
80	2.835	340.157	8.827	-1.441
90	2.754	461.36	9.699	-1.329

Table-2- The number of particles at time interval

t°C	r A$^{°*}$	N(particles) x10^{-20}	t secx10^{-3}
25	565	1.324	5.168
30.5	790	0.482	11.302
40	430	3	0.441
50	580	1.224	20
60	338	6.183	27.66
70	482	2.132	57.31
80	332	6.071	0.135
90	420	3.223	20.5

* Gardon$^{(D)}$

Table-3- The values of $d \ln(1-x)^{-1}$ and time

t°C	$d \ln(1-x)^{-1}$x10^4	t secx10^{-3} life time
25	8.1	1.234
30.5	3.704	2.699
40	34.547	0.289
50	20.717	0.482
60	150.484	0.0644
70	146.114	0.1369
80	202.448	0.0323
90	308.661	0.0483

Table-4- rate of propagation

t°C	1000/T k^{-1}	R$_p$ x10^8 sec^{-1}.	2.302 log R$_p$
40	3.194	1.722	-7.763
50	3.095	0.421	-8.375
60	3	15.44	-6.811
70	2.915	2.581	-7.587
80	2.832	33.41	-6.467
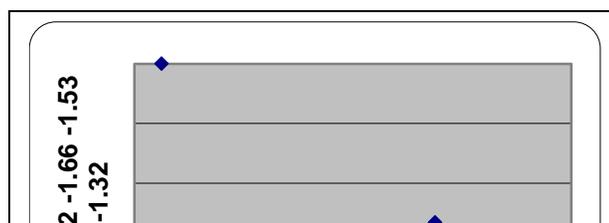
$\text{Lo g } K_p/K_t$

$1000/\text{T K}^{-1}$
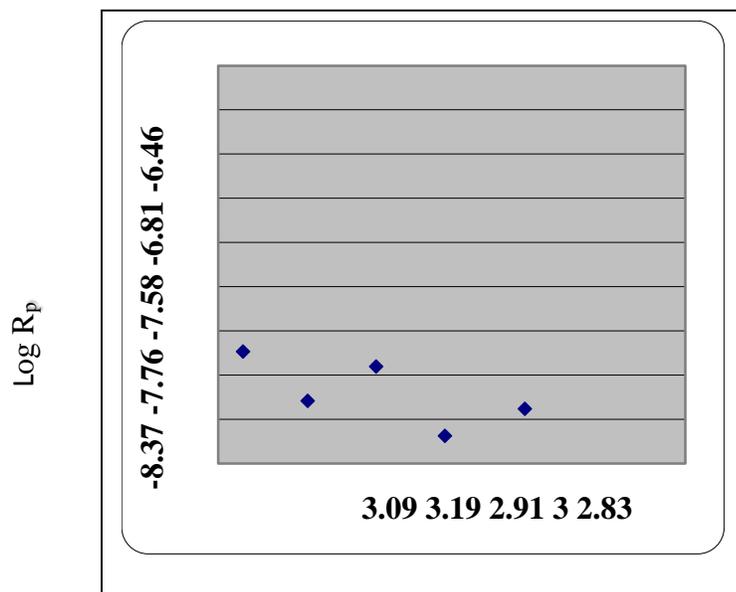
Fig.-1-Arrhenius plot for calculation E_p-$E_{t/2}$.

$N \times 10^{-20}$

7
6 3.26
5 2.13
4 6.13
3 1.22
2 0.48
1 1.32
0
6 3

0   20   40   60   80

0.13 0.44 5.16 11.3 20 27.66 57.31 20.5
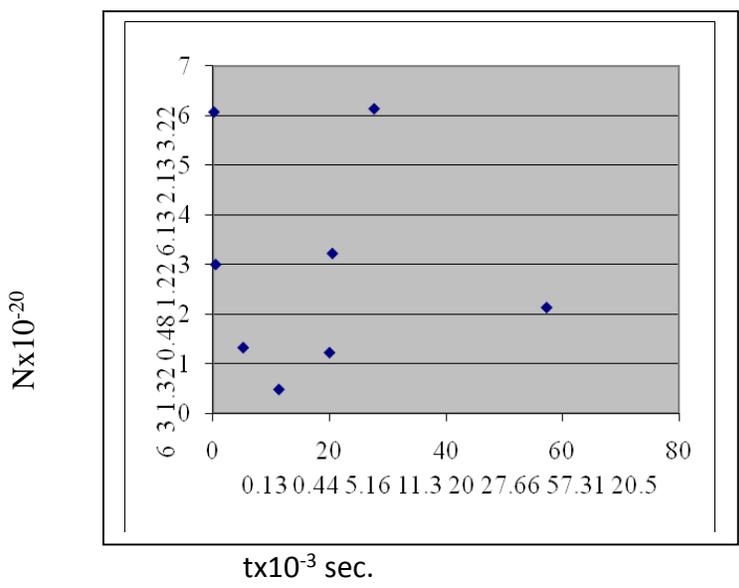
$t \times 10^{-3}$ sec.

Fig-2- The nucleation of the number of particles

$Ln(1-x)^{-1} \times 10^4$

202.4
146.1
150.4
20.7
34.5
3.7
8.1
308.6

1.23 2.69 0.28 0.48 0.06 0.13 0.03 0.04
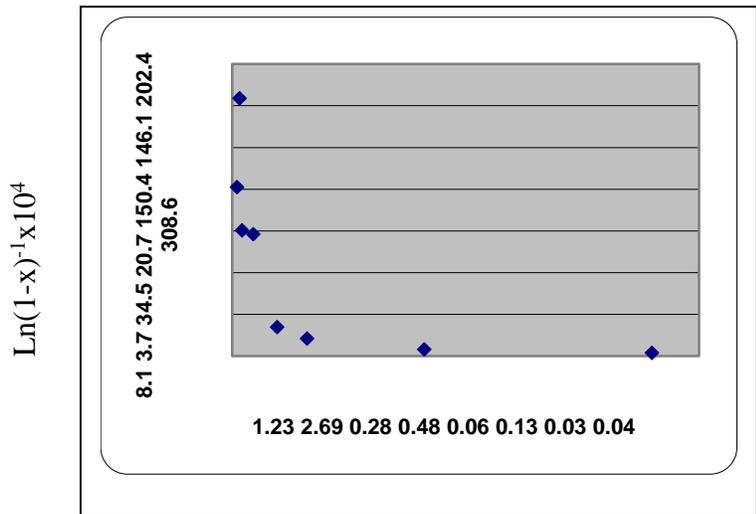
$tx10^{-3}$sec.

Fig.-3- The fractional conversion of styrene

$1000/T \; K^{\circ} - 1$

Fig.-4- Arrhenius plot of $1/T$ with $\log R_p$

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تحقيق نظري على ديناميكية تنشيط تفاعلات الجذور الحرة للستايرين البلمرة

بالاستحلاب

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الخلاصة :-

جداول من الحسابات النظرية التي تظهر قيم المعاملات الأساسية التي تهتم بالمعادلات النظرية المستخدمة بالنسبة إلى تفاعلات معاملات مزيج SO_4 $styrene/Nals/k_2$ والتي تبدأ من الحسابات الملائمة للقيم المطلقة

لتركيز كميات الصابون (Soap) والبادئات وعدد الجسيمات نسبة إلى قطر الجسيم الذي يحتوي على جذور, معدل الثوابت للابتداء, الانتشار والانتهاء واختلاف الطاقة للانتشار والانتهاء على التعاقب لأي درجة حرارة. هن النتائج النظرية نوقشت نسبة إلى النموذج النظري لـ(Smith) و(Hamielec) الذي ينص إن البلمرة بالاستحلاب تتم عندما يغمر جسيم صغير(Loci) مباشرة بواسطة مونيمر غير متفاعل في مكان تواجده الذي بدوره يتعرض تركيز المونيمر إلى اضطراب نتيجة التحول إلى بوليمر