THE EFFECT OF SOLVENTS ON THE EMULSION POLYMERIZATION

OF VINYL MONOMERS

A Thesis

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Presented to

the Faculty of the Department of Chemistry

College of Arts and Sciences

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Climaco J. Losada

December, 1973

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ABSTRACT

The rate of emulsion polymerization of vinyl compounds such as styrene, methyl methacrylate, acrylonitrile and vinyl acetate may be modified by the use of solvents.

The presence of small concentrations of solvents causes an acceleration of the rate of emulsion polymerization. Increasing the concentration of the good solvent for the polymer results in a gradual decrease in the polymerization rates, but poor solvents accelerate the rate of polymerization, even in relatively large concentrations. High-viscosity-poor solvents also produce an increase in the rate due to an inductive Trommsdorff effect.

Very large concentrations of either good or poor solvents decrease the polymerization rate due to a dilution effect.

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PROBLEM 1

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VINYL-MONOMER-EMULSION-POLYMERIZATION-RATE

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INVESTIGATION IN PRESENCE OF SOLVENTS

SECTION A

INVESTIGATION OF EMULSION POLYMERIZATION RATES OF VINYL MONOMERS IN PRESENCE OF A LARGE CONCENTRATION OF SOLVENT

CHAPTER I

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A - HETEROGENEOUS

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Heterogeneous polymerization may be divided into two different classes. The first type is formed by reactions which are initially homogeneous but in which the polymer forms a second phase as the reaction proceeds. This is the reaction observed in the bulk polymerization of vinylidene chloride¹ and acrylonitrile,² in "gas-phase" polymerization,^{3,4,5,6,7} in certain butadiene polymerizations, and in some high pressure ethylene polymerizations.⁸ A convenient generic name for such reactions is "precipitation polymerization".^{9,10}

The second class of heterogeneous polymerizations involves an initial two phase system, usually with monomer present as a dispersed phase. The well-known and technically important emulsion and suspension polymerizations come into this class.

a) Suspension Polymerization

In suspension polymerization, monomer which is dispersed in the form of small globules or droplets in a non-solvent (usually water) can be polymerized by either oil or water-soluble initiator. The reaction is usually carried out in the presence of a suspension stabilizer whose function is to ensure that the droplets remain dispersed through the reaction. Each monomer droplet functions as an individual reaction vessel.

The general characteristics of these polymerizations are essentially those of a bulk reaction. An insight into the mechanism may be derived from an investigation of the order of reaction and rate constant.

b) Emulsion Polymerization

Emulsion polymerization is a technique of polymerization in which a relatively water-insoluble monomer is emulsified in the water with the aid of a surfactant, adequate agitation and in the presence of an initiator soluble only (or principally) in the dispersing medium.

The Smith-Ewart theory¹¹ based on the emulsion polymerization mechanism put forth by Harkins^{12,13,14} has been well verified experimentally by a number of investigations^{15,16} into the emulsion polymerization of vinyl monomers.

When a relatively water-insoluble vinyl monomer, such as styrene (solubility in water = 0.04%) is emulsified in water using a surfactant such as sodium lauryl sulfate and in the presence of an initiator system such as potassium persulfate/sodium sulfite, the basic mechanism of the polymerization may be described by the following sequence of events: 1 Period: a) Dissolution of a small amount of monomer and surfactant

within the aqueous phase.

- b) Dispersion of the monomer droplets with diameter about 1000 Å.
- c) Formation of oriented cluster of molecules of surfactant called micelles with a diameter about 50 Å.
- d) Diffusion of monomer into the micelles and swelling of the micelles.
- 2 Period: a) Decomposition of the initiator and formation of the radical in aqueous phase.
 - b) Migration of the radical into the micelles.
 - c) Formation of the "activated" micelles.
 - d) Formation of a stationary number of particles.

e) Supply of monomer from the droplets to the particles by diffusion.

3 Period: a) Termination of the polymeric radical by entry of single radicals.

In the first period it is essential that the solubility of the monomer in the aqueous phase be lower than about 0.004 mole/liter. This relative insolubility ensures the fact that the aqueous phase is not a major locus of polymerization.

The surfactant molecules in the aqueous phase have a long, oilsoluble portion attached at one end, whereas there is a water-soluble group at the other end.

A small number of surfactant molecules (about 50-100 molecules) form an oriented cluster, a unit called micelle in which the hydrophilic groups face the aqueous phase whereas the hydrophobic ends face themselves. The actual structure of the micelle still remains a controversial matter but its size is limited by an equilibrium balance of thermodynamic forces. The coalescing factors namely the attractive van der Waals forces of the hydrocarbon chains are just balanced by the repulsive ionic forces of the charged hydrophilic ends of the surfactant molecules.

The critical surfactant concentration which must be surpassed to form micelles in sufficient number to be detected by physical or chemical techniques is known as critical micelle concentration (CMC).

Typical values of CMC at 50° C., in pure water have been reported in the literature:²³

TABLE 1: CMC of Some Surfactants

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Surfactant	CMC, moles/1
Potassium caprylate	0.393
Potassium caprate	. 0.105
Potassium lauryl	. 0.026
Potassium myristate	0.0072 (0.0059)
Potassium palmitate	0.003
Potassium stearate	0.0008
Potassium oleate	0.001
Sodium lauryl sulfonate	0.0098
Sodium lauryl sulfate	0.0057

The fact that the monomer and the initiator exist in different phases is all important and consequently the surfactants play a large part in controlling the kinetics of the reaction.

The monomer dispersed in the aqueous phase seeks oleophilic surroundings and penetrates by diffusion the micelle which swells to saturation. The monomer then, is said to be solubilized. The capacity of the surfactant to form micelles and to solubilize monomer is a function of the molecular structure of the surfactant and the other conditions of the surrounding medium. It appears reasonable to assume orientation and polarization of the monomer molecules within the surfactant micelles. This orientation and polarization of the monomer cause changes in the values of the activation of energy and therefore affects the rate of polymerization.

A lowering of the energy of activation of 8000 calories in emulsion polymerization has been observed.¹⁷ Such decrease in the energy of activation will produce a large increase in the rate or reaction if the collision factor remains constant. Waring and others¹⁸ has shown that the collision factors A in the Arrhenius equation is reduced in surfactant-water systems, this means that the termination constant k_t is reduced, thereby allowing the molecular weight of the polymer to increase. The decrease of collision factors is amply compensated by the decrease in the energy of activation.

The presence of monomer within the micelle has been demonstrated by X-rays¹³ and light-scattering measurements that show that micelles increase

in size when monomer is added. This indicates that the "solubilized" monomer occurs in the micelles presumably along the hydrocarbon chain occupying the interior. According to Harkins, the micelles contain sufficient monomer to produce only low molecular weight polymer.

The various effects which the surfactant exert on heterogeneous polymerizations are not yet understood; nevertheless, a proper description of the phenomenon may well be a prerequisite for the detailed.understanding of the mechanism of emulsion polymerization processes.^{20,21,22} It seems that surfactants are able to influence the polymerization rate in at least three different ways:

- 1 by altering the rate of production of free radicals.¹⁹
- 2 through effects on the colloid stability of the polymer particle. 23,24
- 3 by changing the rate of capture of oligomeric free radicals by latex particle.^{25,26}

In principle, at least, three mechanism may be discussed to explain how surfactants can change the rate of radical capture:

- 1 Particles and free radicals are electrostatically charged, then coulombic interactions may hinder or promote entry of the free radical into the particles.
- 2 nonionic surfactants seem to retard entry of free radicals by providing a high microscopic viscosity around the particles.
- 3 Possibility of chain transfer to the surfactant.²⁷

2 Period:

When a free-radical-producing, water-soluble initiator, such as $K_2S_2O_8$, (potassium persulfate), is added to the emulsion system, the

potassium salt decomposes to form water-soluble sulfate radical anions. A promotor such as $Na_2S_2O_3$, sodium thiosulfite may be used to give:

$$s_2 o_3^{-} + s_2 o_8^{-} \xrightarrow{\text{heat}} s o_4^{-} + s_2 o_3^{-} + s o_4^{-}$$

The generation of free radicals from potassium persulfate in aqueous phase occurs at a constant rate and 100% efficiency.^{23,24,31,32} The system potassium persulfate-sodium bisulfite was studied by Tsuda.³⁰ These sulfate-free radicals are presummed to react with monomer. dissolved in the aqueous phase to form anionic-oligomeric-free radicals:

$$S_2 O_3^{-} + SO_4^{-} + (n + 2)M \longrightarrow SO_4 (M)_{\bar{n}} M^{-} + 2 SO_3 (M)_{\bar{n}} M^{-}$$

It is unlikely that the sulfate anion free radicals leave, the high polar aqueous environment per se³² and enter into the less polar polymer particles. The propagation produces amphipatic free radical oligomers which resemble conventional surfactant molecules, ^{33,23} When the sulfate-free radical has added some units of monomer, will begin to show a strong hydrophobic effect and will seek oleophilic surroundings. These oligomeric radicals may penetrate the micelle where the polymer particle will be formed. Micelles capture many of these anionic-oligomeric-free radicals and therefore constitute the main loci of polymerization. It is unlikely that the entire oligomers penetrate into the swollen particle, partly because of the high internal viscosity of the particle. Further, the polar sulfate ions seem likely to remain at the particle-water interface, Thus the propagation will continue from the outside towards the interior of the particle. The number of radicals captured by monomer large droplets may be neglected for two reasons:

- a) There are more micelles per milliliter of aqueous phase than monomer droplets (about 10¹⁸ vs 10¹¹).
- b) The maximum diameter of the micelles is about 100 Å versus 10,000 Å diameter of dispersed monomer droplets, so the surface to volume ratio is higher in the micelles than in the monomer droplets, thus, the micelles are more efficient collectors.

In a typical emulsion system, free radicals are generated in the aqueous phase at a rate of about 10^{13} p/cm³/sec. As there are about 10^{18} micelles per cubic centimeter, essentially all free radicals get into the micelles on the average of about one per micelle every 10 seconds.

The "activated" micelles consume the solubilized monomer. As the "activated" micelles grow in size, they contain polymer as well as monomer, and absorb more and more surfactant molecules from those that are in the solution. A point is quickly reached at which the surfactant concentration in solution falls below its CMC. This is the concentration of surfactant in solution which must be maintained to form micelles and keep their number constant. When the concentration of surfactant falls below this value, the inactive micelles become unstable and micellar surfactants dissolve. The monomer within the micelles is soon used up and the micelles must be replenished from the aqueous phase. The drops, then, act as reservoirs of monomer which is fed to the growing polymer chain by diffusion through the aqueous phase.

At 2-15% conversion, depending on the particular polymerization system, the "activated" micelles have grown much larger than the original micelles. They are no longer considered as micelles but as polymer particles or, more precisely, as monomer-swollen polymer particles.

The high activity of the propagating chain radicals have very short lifetimes, several seconds at best. This results in a very low stationary concentration of propagating chain radicals. (about 10⁻⁸M in a homogeneous medium). However, during this short lifetime, each growing radical may still have the opportunity of adding thousands of monomer units.

The morphology of the micelle in the growth of polystyrene chains has been studied by Keusch.³⁵ In the compatible monomer-polymer system, the monomer and the polymer are not uniformly distributed through the micelle. The micelle shows a distributed structure in which a monomerrich shell encapsulates a polymer-rich core, 36, 37, 38, 39 This core-shell model implies a two-phase behavior, firstly, one phase where the polymer segment density is higher in the central part of the micelle and secondly, another phase of low density in the peripheral region, Polymerization proceeds homogeneously in the polymer particles as the monomer concentration in the particles is maintained at a constant concentration by diffusion of monomer from the droplets. The number of polymer particles remain then constant throughout the polymerization, During this period the rate of polymerization is constant, The monomer droplets decrease in size as the size of the polymer particles increases, Finally at 50-80% conversion, the monomer droplets completely disappear and the polymer particles contain all the unreacted monomer, Polymerization continues at a steadily decreasing rate as the monomer concentration in the polymer particles decreases,

Final conversions of essentially 100 percent (are usually achieved. The final polymer particles have diameters of the order of 500 to 2000 Å.

B - KINETICS OF FREE-RADICAL POLYMERIZATION,

A mathematical interpretation of emulsion polymerization kinetics according to qualitative and quantitative bases developed by Howard⁴⁰ and Smith^{41,42,43} has been studied by Van der Hoff,⁴⁴ Nomura-Nagata⁴⁵ has presented the kinetics of continuous flow in emulsion polymerization. Gordon^{46,47,48,49,50} has developed a complete mathematical approach for emulsion polymerization kinetics.

Emulsion polymerization follows the same kinetics laws established for homogeneous polymerization in bulk and solution. However in the mechanism, the loci of polymerization are isolated from one another so that in each swollen micelle a homogeneous polymerization takes place independently of the other micelles in the system. 52,53

The mechanism for emulsion polymerization 54,55 may be symbolized by the following equations:

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I - Initiation;

$$I \xrightarrow{K_{d}} 2I'$$

$$R_{d} = -\frac{d[I]}{dt} = 2fK_{d}[I] \qquad (1)$$

$$I' + M \xrightarrow{K_{1}} M'$$

$$R_{1} = -\frac{d[M]}{K_{1}} = K_{1}[I'][M] \qquad (2)$$

Where;	ľ	Ħ	initiator molecule,
	I,	=	initiator radical,
	М	Ħ	monomer,
	M،	=	radical monomer,
	к _d	Ħ	decomposition constant.
	ĸ	H	initiation constant,
	^R d	8	decomposition rate,
	R _i	Ħ	initiation rate.
	f	=	fraction of effective radicals

The factor 2 arises because each initiator molecule forms two radical, 56,57,58 When the initiator is 100% efficient in starting polymer chains, then K_i equals fK_d and is equal to K_d being (f = 1) so:

$$R_{i} = 2fK_{d}[I] = 2K_{i}[I]$$
(3)

II - Propagation:

The simplifying assumption that the rate constant for any reaction is independent of the chain length of the polymeric radical taking part in the reaction is necessary in order to derive the addition polymerization rate.⁵⁹ In homogeneous systems at relatively low conversion there are no complications introduced by increases in viscosity with conversion of polymer separation. It follows, then, that the disappearance of monomer may be represented as

$$\pi \frac{d[M]}{dt} = K_{i}[I'][M] + K_{p}[M'][M]$$
(4)

where K_p is the propagation constant and [M·] the concentration of polymeric radical of any length. Since the polymer approaches high molecular weight in 1 to 10 sec., and the remaining species are almost entirely monomer, it is clear that the disappearance of monomer is not essentially influenced by the initiating rate $K_i[I\cdot][M]$, so:

$$R_{p} = -\frac{d M}{dt} = K_{p}[M^{\prime}][M]$$
 (5)

III - Termination;

Chain termination can occur either by coupling or by disproportionation. Termination is a bimolecular reaction depending on M'; therefore both methods of termination can be expressed by:

a) By coupling (combination of radicals):

$$2M' \xrightarrow{K_{tc}} M_{tc}M$$

$$R_{tc} = -\frac{d[M']}{dt} = 2K_{tc}[M']^2 \qquad (6)$$

b) By disproportionation:

$$M_{n}^{\prime} + M_{n}^{\prime} \xrightarrow{K_{td}} M_{n} + M_{m}^{\prime}$$

$$R_{td} = -\frac{d M^{\prime}}{dt} = 2K_{td}[M^{\prime}]^{2} \qquad (7)$$

Where; K_{tc} = Termination constant by coupling, K_{td} = Termination constant by disproportionation. R_{tc} = Termination rate by coupling, R_{td} = Termination rate by disproportionation,

Although the two termination reactions are quite different and can substantially influence molecular weight (particularly when both processes occur in varying degrees), both processes lead to radical destruction and the same kinetic effect, Accordingly:

$$k_{t} = k_{tc} + k_{tp}$$
(8)

So the rate of termination is given by:

$$R_{t} = -\frac{d[M']}{dt} = 2k_{t}[M']^{2}$$

where the factor 2 accounts for the destruction of two radicals in each reaction. Termination by coupling and termination by disproportionation follow the same kinetic law.

The Bodenstein stationary state approximation⁵⁹ is a reasonable assumption by which a steady state (stationary concentration) in radical concentration will be rapidly reached, at which the rates of formation and termination of radicals are equal, because the rate of change of radical M' is a function of the difference between their rates of formation and termination:⁶⁰

$$\frac{d M'}{dt} = k_{i}[I'][M] - 2k_{t}[M']^{2}$$
(10)

Radicals by virtue of their great reactivity simply do not last long compared with the over-all process of converting monomer to polymer. Therefore, the rate of change of radical concentration, d M'/dt relative to the rates of formation and termination is very small. Hence, at the steady state:

$$k_{i}[I'][M] = 2k_{t}[M']^{2}$$
(11)

Furthermore, the rate of change of initiating radical concentration is a function of its appearance minus its rate of disappearance,

 $\frac{d[I^{*}]}{dt} = 2fk_{d}[I] - k_{i}[I^{*}][M]$ (12)

- In the steady-state assumption when d[[']/dt is extremely small, then

 $2fk_{d}[I] = k_{i}[I'][M]$ (13)

Equating eq. (11) and (13);

$$2fk_{d}[I] = 2k_{t}[M']^{2}$$
(14)
[M'] = $\frac{fk_{d}[I]^{\frac{1}{2}}}{kt}$ (15)

Combination of (15) and (5);

$$R_{p} = k_{p} \left[\frac{fk_{d} [I]}{k_{t}} \right]^{\frac{1}{2}} [M]$$
 (16)

By combining eq. (16) and (3):

$$R_{p} = k_{p} \left[\frac{k_{1}[I]}{k_{t}} \right]^{\frac{1}{2}} [M]$$
 (17)

The over-all rate constant is, then, given by

$$k_{o} = k_{p} (k_{i}/k_{t})^{k_{2}}$$

It k_t decreases and k_p and k_i remain the same, then k_o will be larger. The reaction of radicals with each other (or termination) is a diffusion-controlled reaction, therefore inversely proportional to the viscosity of the medium. So an increase in the viscosity by any means should produce an increase in k_o . If the termination is diffusion-controlled an increase in the molecular weight would be expected. If the molecular weight does not increase, an effect of the viscosity on the activation energy should be postulated. Equations (16) and (17) illustrate the dependency of the over-all rate of polymerization on the initiator and monomer concentration. The half-power dependency of the rate on the initiator concentration appears to be a universal feature of the free radical mechanism and has been used as a diagnostic test for the presence of this mechanism.

The quantity $fk_d k_p^2/k_t$ may be calculated in eq. (16) from the rate of polymerization and the concentrations of monomer and initiator. The ratio k_p^2/k_t may then be evaluated if the rate constant k_d for the decomposition of the initiator and its efficiency has been determined.

Combination of eq. (1) and (16) gives the evaluation of the ratio k_p^2/k_t :

$$\frac{k_{\rm p}^2}{k_{\rm t}} = \frac{2R_{\rm p}^2}{R_{\rm d}[M]^2}$$
(18)

The kinetic chain length that represents the number of monomer molecules consumed by each primary radical is given by:

$$v = \frac{\text{Rate of propagation}}{\text{Rate of formation}} = \frac{R_p}{R_i}$$
 (19)

$$v = \frac{k_p [M^*] [M]}{2fk_d [I]}$$
(20)

By using eq. (14):

$$v = \frac{R_{p}}{R_{t}} - \frac{k_{p}[M^{*}][M]}{2k_{t}[M^{*}]^{2}} = \frac{k_{p}[M]}{2k_{t}[M^{*}]}$$
(21)

In eq. (20 the chain length is inversely proportional to the rate of initiation, consequently faster rates of initiation lead to lower-molecularweight polymers.

The combination of eq. (5) and (21) gives:

$$\gamma = \frac{k_p^2 [M]^2}{2k_t R_p} = \frac{k_p}{2K_t^{\frac{1}{2}} K_d^{\frac{1}{2}} [I]^{\frac{1}{2}}} [M]$$
(22)

this means the chain length is a function of the concentration of monomer.

The degree of polymerization, \overline{DP} , is the number of monomer units in the average polymer molecule. If termination occurs by disproportionation the degree of polymerization equals to the kinetic chain length,

If termination is by combination, the \overline{DP} is equal to twice the kinetic chain length:

$$\overline{\rm DP} = 2\nu \tag{24}$$

In cases where the termination mechanism takes place by both combination and disproportionation of growing chains the average \overline{DP} has an intermediate value between one or two kinetic chain lengths. If, y, represents the fraction of the termination by combination, then:

$$y = \frac{k_{tc}}{k_t} = \frac{k_{tc}}{k_{tc} + k_{td}}$$
(25)

A general expression relating the average \overline{DP} to the kinetic chain length can be represented by:

$$\overline{DP}_n = \frac{2v}{2 - y}$$
(26)

Hence by substituting eq. (17) in (21) and the results into eq. (26) and then obtaining reciprocals:

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$$\frac{1}{DP_n} = \frac{(2-y)k_1^{\frac{1}{2}}k_t^{\frac{1}{2}}[I]^{\frac{1}{2}}}{k_p[M]}$$
(27)

Thus a plot of the reciprocal average degree of polymerization $1/\overline{P}_n$ vs the square root of the initiator concentration [I] gives a straight line whose slope is $(2 - y)k_i^{\frac{1}{2}} (k_t^{\frac{1}{2}}/k_p)/[M]$. From the value of the slope it is possible to calculate y.

C - QUANTITATIVE THEORY OF EMULSION POLYMERIZATION SYSTEM.

The kinetics of emulsion polymerization do not obey the relationships discussed above. There are slight, modifications because the locus of polymerization -the micelles and the monomer-polymer particles- is subdivided into many small, discrete volumes.

The deviations observed during emulsion polymerization must be studied independently. The first of these deviations is the very fast rate of polymerization giving a high-molecular-weight polymer. The second deviation is the fact that in many systems after 20-30% conversion, the addition of a large quantity of initiator does not affect the rate of polymerization. The first deviation has been explained as due to an abnormally low termination rate in the highly viscous monomer-polymer particles. The second deviation has been discussed by Smith and Ewart^{41,42,43},

The Smith-Ewart-theory-calculation base is that no new micelles can be formed after a certain time, because the total surface area of the particles in the system increases, and then the surfactant concentration in the aqueous phase is reduced to below the CMC for the surfactant.⁶⁰

The rate of generation of free radicals in the aqueous phase is ρ and the rate of entry of the radical into the micelles is ρ '. If there are N isolated reaction nuclei per millimeter of the external phase, each having a volume, ν , and an interfacial area a, the rate of entry will be:

$$dn/dt = \rho'/N$$
[1]

When a radical has penetrated a particle it will continue to grow until its reactivity is destroyed by its interaction with another radical or by its physical removal from the site. The rate of physical transference will be:

$$dn/dt = -k_a(n/v)$$
 [2]

where k_0 is the rate constant for this process and n/v is the concentration of radicals in the particle. If the termination of radicals takes place only by recombination, the rate of termination in a single particle will be given by:

$$dn/dt = -2k_{+}[n(n-1)/v]$$
 [3]

where k_t is the termination constant. The factor 2 arises from the fact that two radicals are destroyed in each termination event; (n - 1)/v is the concentration of radicals with which any one free radical in the particle can react, since it cannot react with itself. At the steady state, the rate of entry of radicals into the particles is equal to the rate at which radicals are lost to the particles by transfer out of them or by termination within them. At any instant, of all the N particles, there will be a certain number having no radicals in them, N_0 , a certain number having one radical, N_1 , a certain number having two radicals, N_2 , or in general, N_n particles having n radicals each.

By each entry of a radical, an N_{n-1} particle becomes an N_n , then:

$$N_{n-1}(d/N) = N_n(o'/N)$$
 [4]

By each transfer of a radical out of a particle, an N_{n+1} particle becomes an N_n particle:

$$N_{n+1}k_{o}a\left[\frac{(n+1)}{v}\right] = N_{n}k_{o}a\left(\frac{n}{v}\right)$$
[5]

By each termination within a particle an N_{n+2} particle becomes an N_n particle:

$$N_{n+2}k_{t}\left[\frac{(n+2)(n+1)}{v}\right] = N_{n}k_{t}\left[\frac{n(n-1)}{v}\right]$$
[6]

At the steady state, the number of particles with N_n radicals in them will be constant, and the rate at which N_n particles are formed from N_{n-1} , N_{n+1} , and N_{n+2} particles will be equal to the rate at which they are lost. This is expressed by the formula:

$$N_{n-1}(\rho'/N) + N_{n+1}K_{0}a\left[\frac{(n+1)}{V}\right] + N_{n+2}k_{t}\left[\frac{(n+2)(n+1)}{V}\right] = N_{n}(\rho'/N) + N_{n}k_{0}a\left(\frac{n}{V}\right) + N_{n}k_{t}\left[\frac{n(n-1)}{V}\right]$$
[7]

Because the general solution of this problem is not easy, Smith-Ewart proposed three limiting cases:

CASE I: Number of free radicals per particle is small compared with the unity.

If the probability of physical transference of the radical out of the particles is sufficiently great, the number of particles containing radicals will be very small, i.e. the condition is that $\rho'/N \ll k_0(a/v)$. Under these conditions it is necessary to consider only the relationship expressed in eqs. 4 and 5. That is in the steady-state conditions only the conversion of N₁ to N₀ particles and vice versa need be considered:

$$N_{o}(\rho'/N) = N_{1}k_{o}a/v$$

but $N_0 \simeq N$, so that

$$\rho' = N_1 k_0 \alpha / v$$
 [8]

and

$$N_1 \simeq \rho' v / k_0 a \simeq R^{\bullet}$$
 [9]

because of the limiting conditions of the total number of radicals, R, must be equal to N_1 and the rate of the reaction will be:

$$- d[M]/dt = k_{p}[M][R^{*}]$$

$$= k_{p}[M]N_{1}$$

$$= k_{p}[M][p'v/k_{0}a]$$

$$= k_{p}[M]V_{p}C_{p}$$
[10]

where V_p is the actual volume of the polymer particles in 1 ml of the water phase, and C_p is the average concentration of the radicals in the particles.

Here the rate of reaction is independent of the number of particles and depends only on the total volume of the particles and the concentration of the radicals. If the final termination takes place in the water phase:

$$dn/dt = -2k_t C_w^2 = -\rho$$
 [11]

where C_w is the concentration of the radicals in the water phase. From eq. 11 then:

$$C_{W} = \frac{\rho^{\frac{1}{2}}}{(2k_{+})^{\frac{1}{2}}}$$
[12]

Since the exchange of radicals between the water and the oil phases is rapid, a partition constant, α , defined by the ratio:

 $C_p/C_w = \alpha$

 $C_p = \alpha C_w$

or

then

$$C_{p} = \alpha p^{\frac{1}{2}} / (2k_{t})^{\frac{1}{2}}$$
 [13]

and the rate of polymerization will be:

$$- d[M]/dt = k_p [M] V_p C_p$$
$$= k_p M V_p \alpha \rho_{\bullet}^{\frac{1}{2}} / (2k_t)^{\frac{1}{2}}$$
[14]

The average lifetime, $\boldsymbol{\tau}_p,$ of a growing radical will be given:

$$\tau_{\mathbf{p}} = \frac{[\mathbf{R}^{\bullet}]}{\rho} = \frac{V_{\mathbf{p}}C_{\mathbf{p}}}{2k_{\mathbf{t}}C_{\mathbf{w}}} = \frac{V_{\mathbf{p}}\alpha}{(2k_{\mathbf{t}}\rho)^{3}}, \quad [15]$$

Ű
If the final termination takes place within the particles it can be assumed that this occurs whenever two radicals coexist in the same particle, then:

$$dn/dt = -2(\rho'/N)N_1 = -2(\rho'^2/N)(v/k_0a)$$

and

$$\tau_{\rm p} = N/2\rho' = (V_{\rm p}/2k_{\rm o}a)^{\frac{1}{2}}$$
 [16]

Under these circumstances the rate of reaction is

$$- d[M]/dt = k_p[M] [V_p/2k_0a]^{\frac{1}{2}}$$
 [17]

CASE II: The number of radicals per particle is 0.5.

In this case the rate of transfer of radicals out of the polymer particles is negligible or zero compared with their rate of entrance, and the termination of an existing radical in a particle takes place very rapidly on the entrance of another radical, compared to the interval between the entrance of one radical and the next. These are the actual circumstances during most emulsion polymerizations. Under these conditions the Smith-Ewart theory has found that, when the number of particles is fairly large, the number of radicals is approximately one-half the number of particles, or, at any instant, one-half of the particles contain a radical, while the remainder contain none. The existence of a radical in a particle and the termination of this radical are both dependent upon the same event, i.e. the entrance of another radical. It therefore follows that, in a large number of particles in a polymerizing system, the probabilities of any given particle having and not having a radical are equal, and so on the average one-half of them must contain a radical. The mathematical formulation of this condition is that:

$$k_{o}a/v <<\rho'/N < k_{t/v}$$
 [18]

So the eq. 7 becomes:

$$N_{n-1}(\rho'/N) + N_{n+2}k_{t}(n+2)(n+1)/\gamma = N_{p}\left[(\rho'/N) + k_{t}n(n-1)/\gamma\right]$$
[19]

This can be rewritten:

$$N_{n-1} + N_{n+2}^{\beta(n+2)(n+1)} = N_n \left[1 + \beta_n(n-1) \right]$$
 [20].

Defining $\beta = k_t N/v \rho^* > 1$, la solution of the eq. 20 is

$$N_{n-1}/N_n = 1 + \beta n(n-1)$$
 [21]

From eq. 20, if

$$n = 0$$
 $N_2 = N_0/2\beta$ [22]

$$n = 1$$
 $N_1 = N_0 + 6N_3\beta$ [23]

From eq. 21:

$$N_3 = \frac{N_2}{1+6\beta} = \frac{N_0/2\beta}{1+6\beta} = \frac{N_0}{2\beta(1+6\beta)}$$
 [24]

And therefore: N_1 from eq. 20:

$$N_1 = N_0 (4 + 6\beta) / (1 + 6\beta), \text{ etc.}$$
 [25]

to any desired degree of approximation. The total number of free radicals present is given by:

$$n_t = 1N_1 + 2N_2 + 3N_3 + \dots + N_n$$
 [26]

while the total number of particles is:

$$N = N_0 + N_1 + N_3 + \dots + N_n$$
 [27]

From these relationships and those above it is found that:

$$n_{t} = (N/2)(1 + 1/\beta - 1/3\beta^{2} + ...)$$
 [28]

or if β is large:

$$n_{+} \simeq N/2 \simeq R^{*}$$
 [29]

and the rate of polymerization is:

$$- d[M]/dt = k_{\rm p} M(N/2)$$
 [30]

The mean lifetime $\tau_{\rm p}$ of the growing radical will be:

$$\tau_{\rm p} = N/2\rho \, (31)$$

If it can be assumed that $\rho' = \rho$ (this probably nearly the case), then:

$$\tau_{\rm p} = N/2\rho \qquad [32]$$

The concentration of free radicals during bulk or solution polymerization is very small, usually of the order of 10^{12} radicals per milliliter. In 1 ml of polystyrene particles of 1000 A. diameter there will be about 10^{14} radicals. This rough comparison indicates that emulsion polymerization can be expected to be 100 times faster than solution polymerization at comparable concentration. The more rapid rate of polymerization in emulsion systems is thus due to the higher concentration of radicals. The radical lifetimes are relatively long, moreover increase with the number of particles present. Thus, as distinct from the first case, the rate of the reaction is proportional to the number of particles present only and is independent of all other variables except the temperature.

CASE III: Number of free radicals per polymer particle large compared with unity.

This case is essentially an oil-phase polymerization carried out in a large number of discrete loci, with the difference that the radicals originate in the exterior, aqueous phase. These loci will, in general be much larger than the typical polymer particles formed in true emulsion polymerizations. The steady-state condition can be written down by assuming that the loci are uniform in size and so large that all contain about the same number of radicals. From eq. [1] and [3], the steady-state condition can be written as:

$$\rho^{\prime}/N = 2k_{+}(n^{2}/v)$$

from which

$$\mathbf{n} = (\mathbf{v} \mathbf{p}'/2\mathbf{k}_{+} \mathbf{N})^{\frac{1}{2}}$$

and

$$[M]/dt = k_p [M] (V_p '/2k_t)^{\frac{1}{2}}$$

and the mean lifetime of radical will be:

$$\tau_{\rm p} = (V_{\rm p}/2k_{\rm t}\rho')^{\frac{1}{2}}$$

The rates, thus, of polymerization and lifetime of the radicals depend only on the total volume of the polymer particles, and not on their number.

D - SOLUBILITY PARAMETERS.

The criteria⁶¹ which determine whether or not a given polymer is soluble in a given solvent are best discussed in thermodynamic terms.

Every chemico-physical system at equilibrium has a definite value of an energy parameter G, the Gibbs Free Energy. The actual value taken by G depends on the temperature and pressure of the system as well as on the number of moles present. If two systems with G values G_1 and G_2 are mixed at constant temperature and pressure, then only those changes occur which result in the value of G for the mixture being less than $G_1 + G_2$. If a change does occur, the new equilibrium position corresponds to the lowest value of G. The change in G is given by ΔG :

 $\Delta G' = G_{final} - G_{initial}$

 ΔG is always negative for a spontaneous change.

For polymer in solution, the changes in G which result on mixing solvent and polymer is by definition:

$$\Delta G_{mix} = G_{solution} - (G_{polymer} + G_{solvent})$$

The values of ΔG_{mix} depends on three factors:

1 - The heat release on mixing polymer and solvent, ΔH_{mix} ,

2 - The temperature, T.

3 - A parameter measuring the increase in disorder resulting from mixing polymer and solvent, ΔS_{mix} .

At constant temperature and pressure:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Any process in solution is accompanied by an increase in disorder so that ΔS_{mix} is positive.

For a solution to take place at a given temperature, ΔG_{mix} will be negative, if:

- ΔH is negative, i.e. heat is given up on polymer dissolving in the solvent.
- b) ΔH_{mix} is zero, i.e. heat is neither required for nor obtained from the disolution of polymer in the solvent.
- c) ΔH_{mix} is positive but small, i.e. some heat is absorbed from the system but insufficient to offset the product $T\Delta S_{mix}$.

The polymer will not dissolve to any appreciable extent if a large amount of heat has to be supplied, for then ΔH_{mix} is sufficiently positive to exceed TAS_{mix}. In polymer-solvent systems in which ΔH_{mix} is negative or zero complete miscibility is observed.

The behavior of each system is determined essentially by two fundamentally different factors, namely, by the decrease in free energy and by the increase in entropy. The former demonstrates that the forces acting in the system try to effect a minimum of potential energy by displacing the polymer chains until further deformations are no longer compatible with the geometrical possibilities of movement; the latter signifies, however, that there is a constant striving towards the most probable state of distribution, as a result of the irregular motions to which the individual particles are subjected. This position ' may also be, expressed as follows: in any isolated system, the total energy is composed of a potential and a kinetic component. Attractive forces between the particles are connected with the decrease of the potential energy while the kinetic energy -in so far as it is present as random molecular motion- results in the increase in entropy and opposes the collective influence of the forces.

Mixing is influenced by forces which the individual particles exert upon one another and by the possibilities of geometrical packing and arrangement of molecules endowed with different forms and sizes.

Particularly strong forces of attraction between components A and B and unusually favorable packing conditions between the two kinds of molecules will promote the occurrence of mixing beyond the ideal entropy effect. If, however, the forces between A and A and B and B are greater than the interaction between A and B, the result is that the free energy of the mixture can be greater than that of the components; the mixed liquids would then automatically separate. The influence of the forces effecting separation would then exceed that of the entropy increase which favors mixing.

Polymer-solvent interactions greatly affect the average shapes and extensions of polymer chains in solution, if solvent molecules are strongly attracted by atoms or groups in the polymer molecules, they may restrict the orientations of the segments in much the same way as do the attractions and repulsions of the second-nearest neighbor segments. Probably more important is the dependence of the energy of the solution on the degree of extension. Extending the molecule increases the number of segment-solvent

contacts and decreases the numbers of segment-segment and solvent-solvent contacts. If this results in a net decrease in energy (increase in stability), the average polymer molecule dimensions will be greater than they would be in the absence of solvent.

The requirement that different portions of a polymer chain cannot occupy the same space, tends to favor the more open chain configurations, with larger end-to-end dimensions. If this expansion tendency is just balanced by a contraction tendency, resulting from a net excess of polymerpolymer and solvent-solvent attraction over the polymer-solvent attraction in the average chain dimensions should be those given for the freely jointed chain model, modified by constant-bond-angle and second-preceding-segment limitations. Otherwise expressed, the "unperturbed" average molecular dimensions should exist, if the average change in free energy on expansion of the polymer molecules is zero.

Cases in which ΔH_{mix} is positive lead to incomplete miscibility below a certain temperature. This temperature is the critical solution temperature or theta temperature.⁶² The greater the value of ΔH_{mix} the higher will be the value of the critical solution temperature.

Since the dissolution of a polymer always is connected with a large increase in entropy, the magnitude of the heat term H_{mix} is a deciding factor in determining the sign of the free energy change.⁶³

Hildebrand states that:

$$\Delta H_{\text{mix}} = V_{\text{mix}} \left[(\Delta E_1 / V_1)^{\frac{1}{2}} - (\Delta E_2 / V_2)^{\frac{1}{2}} \right]^2 \phi_1 \phi_2$$

where:

The expression ($\Delta E/V$) is the energy of vaporization per cubic centimeter, This has been described as the "internal pressure" or the "cohesive energy density". The equation may be rearranged:

$$\frac{\Delta H_{\min}}{V_{\min x \phi_1 \phi_2}} = \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2$$

This means that the heat of mixing per cubic centimeter at a given concentration is equal to the square of the difference between the square roots of the cohesive energy densities of the components.

If the symbol \S is equal to $(E/V)^{\frac{1}{2}}$

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}$$

where ΔE is the energy of vaporization, then

$$\Delta H_{\text{mix}} = (\delta_1 - \delta_2)^2 V_{\text{mix}} \phi_1 \phi_2$$

The term $(\delta_1 - \delta_2)^2$ has to be small for two substances to be miscible. It is the Hildebrand solubility parameter.

Solubility parameters for volatile substances have been estimated from the latent heat of vaporization (AH), but this technique is not applicable to resinous products, The Hildebrand parameter of a volatile liquid may be calculated from:

$$\delta = \left(\frac{\Delta H_{V} - RT}{M/D}\right)^{\frac{1}{2}}$$

where:

R = gas constant (1.986).
T = Absolute temperature,
V = Molar volume = M/D,

The solubility parameter of any substance may also be estimated from Small's molar attraction constants, G:

$$\delta = \rho \frac{\Sigma_{G}}{M/D}$$

A graphic technique has been provided for estimating these parameters for compounds in homologous series.⁶⁴ Another method in solvent selection has been suggested via miscibility number.⁶⁵

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SOLUBILITY PARAMETERS OF SOLVENTS

$\delta(ca1/cc)^{\frac{1}{2}}$	Name	H-bonding group
4.9-5.9	dimethyl siloxanes	p
5.4	methane	þ
6.0	ethane	р
6.3	neopentane	p ·
6.4	propane	р
6.6	n-decane	p
6.9	Mineral Spirits	. p
7.0	pentane	р
7.2	diisodecyl phthalate	m
7.3	n-hexane	p
7.4	n-heptane	р
7.6	n-octane	ŗ b
7.8	vinyl chloride	m
8.8	methyl methacrylate	m
9.2	benzene	р
9.3	styrene	р
10.5	acrylonitrile	р

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E - VISCOSITY.

The viscosimetric method introduced by Staudinger for determining molecular weights is based on the phenomenon that threadlike molecules cause a marked increase in the viscosity of the solvent in which they are dissolved, with increase being proportional to the molecular weight of the polymer. This method is valid only for linear or slightly branched molecules.

In molecular weight determinations, the increase in the relative viscosity is important while knowledge of the absolute viscosity is not necessary. Hence, the viscosity of the solution of the polymer (n) and that of the solvent (n_0) is measured and the specific viscosity (n_{sp}) is determined from that:

$$n_{\rm sp} = \frac{n - n_0}{n_0} \tag{1}$$

If the measurements are made in capillary viscometers and at low concentrations (so that the density of solution is nearly equal to that of the solvent), then the flow time t (solution) and t_0 (solvent) may be used in good approximation. Eq. (1) then becomes:

$$\eta_{\rm sp} = \frac{t - t_0}{t_0}$$

If the relation is divided by the concentration of the polymer in the solution, the reduced specific viscosity n_{sp}^{\prime}/c is obtained. Since this quantity is, however, dependent upon the concentration, the limiting viscosity number [n] is used to evaluate the viscosimetric behavior of threadlike molecules:

$$[n] = \lim_{c \to 0} \frac{n_{sp}}{c}$$

This quantity was formerly termed the intrinsic viscosity, but in accordance with the recommendations of the Commission on Macromolecules of the I International Union of Pure and Applied Chemistry, the above nomenclature will be adopted here.

Frequently, the relative viscosity:

$$\eta_{rel} = \frac{t}{t_0}$$

and the inherent viscosity:

$$n_{inh} = \left(\frac{\ln n_{rel}}{c}\right)$$

are used. Because the relative viscosity $n_r = \frac{n}{n_0} = \frac{t}{t_0}$ approaches 1 and not zero as the solution becomes more dilute, n_r does not denote the polymer's ability to increase the viscosity of the dispersion mediu. To compensate this, n_r is diminished by 1 to give the specific viscosity:

$$n_{sp} = \frac{n}{n_0} - 1 = \frac{t}{t_0} - 1 = \frac{n - n_0}{n_0}$$

The original law, due to Staudinger stated that the specific viscosity was directly proportional to the molecular weight of the solution and its concentration:

$$n_{sp} = \frac{(n - n_0)}{n_0} = KMc$$

the constant, K, was assumed to be typical of a given homologous series and M and c were the molecular weight and concentration respectively. Experimental and theoretical investigations have made it clear that the effects of mechanical and structural interference are to be separated from the effects due to the molecular size of the solute, and so the experimental data must be extrapolated to infinite dilution, giving

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c} \right) = KM$$

Huggins obtained a direct proportionality between the specific viscosityconcentration ratio and the molecular weight. This work may be summarized by the statement that, if the conditions of flow are such that Brownian movement is sufficient to counteract orientation effects, the presence of a suspension of large molecules causes an extra dissipation of energy to maintain the flow. This is reflected in the expression:

$$\frac{n_{sp}}{c} = KM^{\alpha}$$

where K is a constant whose value is independent of molecular weight, but depends on the polymer, solvent and temperature. The second constant, α , is dependent on the shape of the solute molecule and ranges in value from zero for perfect spheres to 2 for rigid rods.

The final form of the limiting visconsity number becomes:

$$[n] = \lim_{c \to o} \left(\frac{n_{sp}}{c} \right) = \lim_{c \to o} \left(\frac{\ell n_r}{c} \right) = KM^{\alpha}$$

Schulz has proposed a formula which, in effect, allowed the limiting viscosity number to be computed from measurements of the specific viscosity and the concentration:

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$$\lim_{c \to 0} \frac{\left(\eta_{sp} \right)}{c} = \left(\frac{\eta_{sp}}{c} \right) / (1 + K \eta_{sp})$$

The empirical formula:

$$[n] = \frac{n_{sp}}{4c} + \frac{3ln n_{rel}}{4c}$$

is used with good agreement with the reported results.

CHAPTER II

EXPERIMENTAL

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FIGURE 1: Emulsion Polymerization Apparatus.

- A 500 ml reaction flask
- B Constant temperature bath
- C Condenser
- D Sampling tube
- E Thermometer
- F Stirring motor
- G Control valve
- $H N_2$ purge line
- I Sampling syringe
- J Magnetic stirring bar



Experimental

1 - Purpose of the experiments:

To determine the rate of polymerization of styrene, methyl methacrylate and vinyl acetate in the presence of different concentrations of solvents and non solvents.

2 - General Technique

a) Apparatus:

A 500 ml four necked reaction flask (K-606220 Kontes General Catalog TG-40). One side neck is a 10/30 outer neck for a thermometer (k-871000 immersion length 75 mm.). The other side necks (24/40) are at an angle. The central neck is fitted with an adapter to a Teflon-blade glass-stirrer shaft (K-782030) and an electrical stirring motor made by Matheson Scientific (60002-10 with support arm, T-Line No. 105) and controlled by an electrical Synchro-Tork Stirrer made by Inframo, Wayne, N.J. One side neck is fitted with a condenser (K-4470000) and an adapter at the top (K-199000) through which zero grade-nitrogen inlet and simultaneously bleeding tube reaches the bottom of the liquid. The water-inlet of the condenser is sealed; the water-outlet is fitted with a rubber tubing whose end is submerged in a water trap to monitor the bubbling nitrogen gas.

The bleeding tube is connected with a three-way adapter to a 10 cc syringe to take samples. The three-way adapter stops the nitrogen stream to take the sample, followed by an immediate flushing of the bleeding tube with nitrogen forcing the solution back into the flask.

The second side neck is fitted with a stopper 24/40 (K-851000) or alternately with a separatory funnel 24/40 (K-636280) for copolymer preparation.

The complete set-up was located in a constant temperature bath $(50^{\circ}C \pm 1)$ controlled with a Thermis-temp Temperature Controller, Model 71, made by W. H. Curtin Co.

b) Chemicals

Monomers:

Monomers were distilled under reduced pressure and stored in amber glass bottles at 4°C and checked periodically for contaminations with oligomers by shaking aliquots with methanol.

Surfactants:

Triton X-405, $(C_8H_{15}C_6H_4-0-(CH_2-CH_2)_n-0H$, octylphenoxypolyethoxyethanol) technical grade, a nonionic surfactant,¹ was supplied by Rohm and Haas, Philadelphia, PA. Sodium lauryl sulfate USP $(CH_3(CH_2)_{10}CH_2OSO_3Na)$ an anionic surfactant was supplied by Fisher Scientific Co, Fairlawn, N.J. Initiators:

Potassium peroxidisulfate, $K_2S_2O_8$ and Sodium thiosulfate, $Na_2S_2O_3$ as promotor, both reagent grade, were prepared by Matheson and Coleman, Norwood, Ohio. 2,2'-Azobisisobutyronitrile (AIBN) supplied by E.I. Du Pont de Nemours and Co., was recrystallized from chilled ethanol by the addition of distilled water, dried in the vacuum and stored in amber glass bottles. Protective Atmospheric Medium:

Zero grade nitrogen was used as supplied by the Union Carbide Corp., Linde Div.

¹With 40 avg. EO units and 2066 avg. MW.

Flocculants:

1-N. sulfuric acid solution, and sodium chloride (saturated solution) was ordinarily used.

Solvents:

Silicone oil, benzene, hexane, heptane, octane; all were reagent grade and Nujol (mineral oil) and kerosene in technical grade were used. 3 - General Procedure:

Surfactants were dissolved in boiled-distilled water. Freshly distilled monomers were deoxygenated by bubbling zero-grade nitrogen through them for 30 minutes. The reaction flask was charged with the surfactant solution and deoxygenated with a nitrogen stream. The monomer, or the mixture solvent-monomer was added and enough time was allowed for the system to reach the equilibrium temperature. The initiator solution $(K_2S_2O_8/Na_2S_2O_3)$ was added to the flask after its contents had reached 50° C. while nitrogen was passed through the system. The stirring motor was set at 680 rpm.

4 - Recipe:

The general recipe used in the experiments was of the type called high-concentration-surfactant recipe due to the formation of mixed micelles.

Monomer	40.0 gr
Solvent	(different in %)
Water	320.0 cc
Triton X-405	2.0 gr.
Potassium Peroxidisulfate	0.1 gr

Ingredient

Ingredient (continued)

Sodium	thiosul	lfate	0.03	gr
Sodium	Lauryl	Sulfate	0.6	gr

5 - Collection of Samples:

Periodically, samples were taken from the reaction flask through the syringe and the volume and time of collection were recorded. The sample was added to 5 cc of 2% hydroquinone solution. The emulsion was acidified with 5-10 cc sulfuric acid and broken with 10-15 cc saturated sodium chloride solution. The precipitated polymer was filtered on preweighed quantitative filter paper, washed at least three times with both methanol and distilled water, and finally dried in vacuum until no change in weight was observed.

6 - Method of Obtaining Yield Data:

a) Gravimetric procedure:

The %-yield was obtained for every sample by the formula:

Weight of the sample Total monomer weight Total volume (Monomer + Water) x Sample Volume

b) Viscosities:

The viscosity of every sample was determined by dissolving the polymeric sample in benzene (spectrograde, J. T. Baker). The polymer was precipitated from solution by addition of an excess of methanol. After drying, each sample was redissolved in spectrograde benzene at concentrations about 0.5%. An Ubbelohde viscometer no. 2031 was used. The viscometer and the solution were allowed to reach thermal equilibrium in a 25°C constant temperature bath. Each sample was run at least three times and the reduced viscosity was calculated.

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F - EXPERIMENTS.

The experiments were conducted as follows: Exp. No. 1 - Comparison between emulsion and suspension polymerization. Exp. No. 2 - Contrast of a good solvent present in emulsion polymeriza-

tion and a standard emulsion polymerization. Exp. No. 3 - Solvents with different $\Delta \delta_{p-s}$ at the same concentration. Exp. No. 4 - Solvents with the same $\Delta \delta_{p-s}$ at different concentration

The solvent (good and/or poor solvent) was selected as nonreactive solvent with the monomer, and was expected then to be emulsified with the monomer, thus it would be present with the reactive species and later with the monomer-polymer particle.

Criteria to determine whether a polymer is dissolved in a specific solvent or not were estimated by Seymour <u>et al.</u>⁶⁶ A solvent for a specific polymer is considered a good solvent if the difference between solventpolymer hildebrand-solubility-parameters is less than 1.8 hildebrands. For poor solvents, the solvent-polymer-parameter difference must be greater than 1.8. Poor solvents can be viscous or non-viscous.

Experiment No. 1.

Graph 1 shows the differences in rate between the suspension polymerization, Run 1 and the emulsion polymerization of styrene, Run 2. The reduced viscosity for emulsion polymerization of styrene was 8.6 indicating high molecular-weight polymer in contrast with the reduced viscosity of styrene in suspension polymerization, 0.94.

GRAPH 1: Contrast of Rates of Styrene in Emulsion and Syspension Polymerizations.

Emulsion;

Run () 2

Suspension:

Run 🛆 1

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Experiment No. 2.

The effect of the presence of a good solvent in the styrene emulsion polymerization was investigated using Benzene ($\Delta \delta_{p-s} = 0.1$). The benzene was 300% in volume respect to the monomer. The Graph 2 shows a very poor conversion and the polymeric product isolated was low-molecularweight oil.

Several factors may explain this unexpected rate decrease:

- a) Obviously, the exponential dilution factor reduces the polymerization rate.
- b) The benzene can increase the collision propolymeric-chain end and as a result an increase in the termination rate.
- c) Burnett has given an explanation based on some evidences that the growing radical forms a complex with solvent and that it is the unstability and reactivity of this complex which determines the rate decrease.⁶⁹

Experiment 3.

The effect of $\Delta \delta_{p-s}$ on the polymerization rate of styrene with different solvents at concentrations 300% solvent respect to the monomer is presented in graph 3.

The $\Delta\delta$ values for the styrene-solvent system on the graph are:

 $\Delta\delta$ Nujol > 3.8Run 4 $\Delta\delta$ Hexane = 2.0Run 5 $\Delta\delta$ Heptane = 1.9Run 6 $\Delta\delta$ Octane = 1.7Run 7 $\Delta\delta$ Benzene = 0.1Run 3

The Nujol, hexane and heptane, graph 3, are poor solvents for styrene, but not sufficiently poor to bring about complete precipitation of the polystyrene. Under such conditions, the polymer molecules and the particles remain in solution but assume a tightly coiled conformation as opposed to the expanded conformation of polymer molecules in good solvents.

Obviously, a decrease in solubility is accompanied by an increase in the ratio $k_p/k_t^{\frac{1}{2}}$. This increase could be caused by a decrease in k_t , an increase in k_p , or both. In the case in which the poor solvent is somewhat more viscous than pure monomer, it has been demonstrated^{67,68} that for styrene $k_t \alpha 1/n_{mix}$. It seems ^{69,70,71} that the viscosity of the medium is not the only controlling parameter on the termination rate. The conformation of the polymer chain is also an important factor, because when the chain is tightly coiled, due to low macroradical-solvent interaction, termination is hindered. The Graph 3 demonstrates a strong dependence of the styrene polymerization rate upon the effectiveness of the solvent used and hence on the degree of macromolecule coiling.

Octane and benzene on the other hand are good solvents for styrene and thermodynamically exert their influence on the termination through their effect on the solubility of the reaction medium. The termination rate of styrene polymerization is a diffusion-controlled process and the rate coefficient for termination k_t , is inversely proportional to the viscosity of the medium; hence good solvents accelerate termination because they increase the viscosity-dependent segmental rearrangement

which brings the polymer-particle ends into a position where they can react.

Graph 3 shows representative conversion-time curves over the range of polymerization rates encountered for each system.

The initial inductive period was longer for hexane (5-15% conv.) and heptane (5-20% conv.) than for the Nujol. Assuming no retardation in the polymerization, this means that there is a particle formation over a wider conversion range during styrene-heptane polymerization than for styrene-Nujol system.

With each system, the polymerization rate went through the usual zero-order period characteristic of a constant concentration of both chain radicals and monomer into the micelles. When the monomer concentration decreased because the monomer was used up, the conversion-time curve followed a first order period.

As expected, the larger the value $\Delta\delta$ the faster the rate, this means that the smaller the value $\Delta\delta$ the higher, the entropy and the higher the termination rate. Consequently any factor that increases the mobility of monomer-polymer particle increases the termination rate as well.

Experiment No. 4.

This investigation was conducted to determine the effects of change in the rate of polymerization when the concentration of solvent was varied.

The solvent and their concentrations were:

Run	2	S (standard)	
Run	8	S-Nujol	(100% solvent)
Run	9	S-Nujol	(200%)
Run	10	S-Nujol	(300%)

Experi	ment No.	4 (continued)
Run	10	S-Nujol (300%)
Run	11	MMA (standard)
Run	12	MMA-Nujol (100%)
Run	13	MMA-Nujol (200%)
Run	14	MMA-Nujol (300%)
Run	15	S-hexane (100%)
Run	16	S-hexane (200%)
Run	5	S-hexane (300%)
Run	17	S-hexane (400%)
Run	18	MMA-hexane (100%)
Run	19	MMA-hexane (200%)
Run	20	MMA-Hexane (300%)
Run	21	MMA-hexane (400%
Run	22	S-heptane (100%)
Run	23	S-heptane (200%)
Run	6	S-heptane (300%)
Run	24	S-heptane (400%)
Run	25	MMA-heptane (100%)
Run	26	MMA-heptane (200%
Run	27	MMA-heptane (300%)
Run	28	MMA-heptane (400%)
Run	29	S-octane (100%)
Run	30	S-octane (200%)
Run	7	S-octane (300%)
Run	31	S-octane (400%)

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Experiment No. 4 (continued)

Run	32 ·	MMA-octane	(100%)
Run	3 3	MMA-octane	(200%)
Run	34	MMA-octane	(300%)
Run	35	VAC (standa:	rd)
Run	36	VAC-hexane	(100%)
Run	37	VAC-hexane	(200%)

Obviously in graphs 6, 7, 8, 9, 10, 11 and 12 a systematic decrease in the concentration of the solvent produces a gradual decrease in the polymerization rate due to a dilution effect.

The Graph 13 shows the dependence of the % conversion vs. Hildebrand solubility parameters after 150 minutes of polymerization.

The four curves represent four different concentrations of solvent: 100%, 200%, 300%, and 400%.

The styrene polymerization rate obtained in presence of solvents with different solubility parameters has been represented on each curve.

An unusual acceleration in the rate is observed when the difference between styrene-solvent solubility parameter is above 1.8 Hildebrand values. Presumably, this acceleration is due to the coiling of the polymerparticle burying the active end into the chain and causing a net decrease in the termination rate. Obviously, the extent of the coiling is governed by the ratio monomer-solvent. GRAPH 2: Contrast of the Standard Emulsion Polymerization and the Emulsion Polymerization of the Styrene in the Presence of Benzene as a Solvent.

Run O 2 Styrene standard polymerization.
Run A 3 Styrene polymerization in the presence of benzene (300%).



GRAPH 3: Effects on the Polymerization Rate of Styrene with Different Solvents, at the Same Concentration 300% Volume, with Respect to the Monomer.

Run	∇	2	Styrene (standard)
Run	$\overline{\mathbf{\cdot}}$	4	Nujol
Run	$\overline{}$	5	Hexane
Run	\triangle	6	Heptane
Run	\odot	7	Octane
Run	\diamond	3	Benzene



GRAPH 4: Polymerization of Styrene in Different Concentrations of Nujol

Run	\odot	2	Styrene	(standard)
Run	\triangle	8	S-Nujol	(100%)
Run	$\overline{}$	9	S-Nujol	(200%)
Run	∇	4	S-Nujol	(300%)
Run	\Diamond	10	S-Nujol	(400%)


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GRAPH 5: Polymerization of MMA in Different Concentrations of Nujol.

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Run 11 MMA (standard) \odot Run (100%) \triangle 12 MMA-Nujol (200%) Run 13 MMA-Nujol \odot 14 MMA-Nujol (300%) Run



GRAPH 6: Polymerization of Styrene in Different Concentrations of Hexane.

S (standard) Run 2 (\cdot) S-hexane (100%) Run 15 $\left[\cdot \right]$ 16 Run Γ. S-hexane (200%) Run 5 S-hexane (300%) Run 17 S-hexane (400%) $\overline{)}$



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GRAPH 7: Polymerization of MMA in Different Concentrations of Hexane.

Run	\odot	11	MMA (standa	rd)
Run	\triangle	18	MMA-hexane	(100%)
Run	$\overline{\cdot}$	19	MMA-hexane	(200%)
Run ·	\square	20	MMA-hexane	(300%)
Run	∇	21	MMA-hexane	(400%)



GRAPH 8: Polymerization of Styrene in Different Concentrations of Heptane.

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S (standard) Run 2 (\cdot) Run $\overline{\nabla}$ 22 S-heptane (100%) • 23 S-heptane (200%) Run Δ 6 S-heptane (300%) Run Run $\langle \cdot \rangle$ 24 S-heptane (400%)

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GRAPH 9: Polymerization of MMA in Different Concentrations of Heptane.

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MMA (standard) Run 11 \bigcirc A Run 25 MMA-heptane (100%) Run 26 MMA-heptane (200%) \Box 27 MMA-heptane (300%) Run $\langle \cdot \rangle$ Run 28 MMA-heptane (400%) $\nabla 7$

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GRAPH 10: Polymerization of Styrene in Different Concentrations of Octane.

Run 2 S (standard) (\cdot) S-octane (100%) Run 29 \Box 30 \triangle Run S-octane (200%) Run \odot 7 S-octane (300%) Run 57 31 S-octane (400%)



GRAPH 11: Polymerization of MMA in Different Concentrations of Octane.

Run	Ó	11	MMA (standa	rd)
Run	\triangle	32	MMA-octane	(100 [°] %)
Run	$\overline{}$	33	MMA-octane	(200%)
Run	∇	34	MMA-octane	(300%)



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GRAPH 12: Polymerization of Vinyl Acetate (VAC) in the Presence of Hexane.

Run	\odot	35	VAC (standard)	
Run	\triangle	36	VAC-hexane (100%)	
Run	$\left[\cdot \right]$	37	VAC-hexane (200%)	



GRAPH 13: Polymerization of Styrene at 150 Minutes vs. Solubility

Solubility Parameter Solvent 9.3 Styrene 9.2 Benzene \odot ▽
○ Cyclohexane 8.2 n-Octane 7.6 n-Heptane 7.4 n-Hexane 7.3

Parameters of the Solvents.

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TABLE III: VISCOSITIES

System	n_{rel} Relative viscosity t_p/t_s	n _{sp} Specific viscosity t _p /t _s -1	n _{red} Reduced viscosity n _{sp} /C	
Ps/Nujol		- - -		
100%	1,554	0,554	5.54	
200%	3,50	2.50	5,00	
300%	2,70	1,70	3,40	
400%	2.66	1.66	3.32	
Ps/Hex.				
100%	3/58	2,58	5,15	
200%	2,72	1.72	3,50	
300%	2.25	1,25	2.50	
400%	1.58	0.58	1,16	
Ps/Hept.				
100%	3.1	2.1	4,2	
200%	2.0	1.0	2,44	
300%	1.44	0,44	0.89	
Ps/Oct.				
100%	3.93	2,93	5,86	
200%	3,00	2,00	4,09	
300%	2.32	1,32	2,65	

CHAPTER III

RESULTS AND DISCUSSION

TABLE IV: VISCOSITIES

System	ⁿ rel Relative viscosity t/t p s	n _{sp} Specific viscosity t _p /t _s -1	n _{red} Reduced viscosity n _{sp} /C
PMMA/Nujol			,
100%	3.320	2.320	9,28
200%	3.055	2.055	8,22
300%	2.836	1.836	7,344
400%	1.26	0.26	1.04
PMMA/Hex.			
100%	3.315	2.315	9,26
200%	3.027	2.037	8,1
300%	2,945	1.045	7,78
400%	2 .9 04	1.904	7.62
PMMA/Hept.			
100%	8.972	7.972	7,972
200%	7.301	6.301	6.3
300%	5.493	4.993	4.5
400%	3.698	2.698	2,7
PMMA/Oct.		1	
100%	2.931	1,931	7.7

RESULTS AND DISCUSSION

S-Nujol and MMA-Nujol systems.

The marked accelerations observed (Graph 4 and 5) in the polymerization rate may be explained by two factors: a) an increase in the viscosity of the medium due to the Nujol, b) a large difference in $\Delta \delta_{p-s}$ giving as a result an inductive Trommsdorff effect. The accelerative effects observed in these instances of heterogeneous polymerization are similar to the gel effect and are caused by a decrease in k_t relative to k_p .

The conversion at which autoacceleration is observed varies depending on the reaction conditions and the order the procedure was performed. The S-Nujol and MMA-Nujol systems show the $k_p/k_t^{\frac{1}{2}}$ ratio as increasing from the very beginning or after only a few percent conversion, substantiating the conclusion that the termination reaction is a diffusioncontrolled process. This autoacceleration is caused by a decrease in the termination rate constant with increasing conversion. As the polymerization proceeds the viscosity of the system increases and the termination becomes increasingly slower.

The growing polymeric radicals become coiled up since they are essentially insoluble in the Nujol.

Although propagation is also hindered the effect is much smaller since k_p values are smaller than k_t values by a factor of $10^4 - 10^5$. High viscosity affects the former much more than the latter. Therefore, the quantity $k_p/k_t^{l_2}$ increases and the result is an increase in R_p with conversion. A second consequence of this effect is an increase in molecular weight with conversion as required by $v = R_p/R_t$ in eq. 21.

As was noted before, the autoacceleration is an autogeneous increase in the rate of polymerization due to a gradual increase in the medium viscosity as the polymerization progresses.

It seems to be logical to inquire more closely into the behavior of the reactions in solvents which are themselves inherently as viscous as Nujol.

The Nujol-Nujol intermolecular interaction is very strong (about 1000 cps); even more, the Nujol does not permeate the polymer-particle, then, it gives step to a higher shielding effect of the polymer-radical. The dramatic increase in the polymerization rate due to the Nujol presence may be explained as a cummulative effect of : a) the inherent autoacceleration of the MMA in the polymerization, b) the inductive acceleration produced by a initial increase in the medium viscosity, c) the large different in solubility parameters between the Nujol and the polymer.

Since the average size of the particle increases during the reaction, there is, then, a progressive trapping of polymer-radicals, and consequently the termination velocity coefficient progressively falls leading to the observed acceleration. The rate of polymerization is then a function of the degree of occlusion. A moderate degree of occlusion gives rise to an increase in the over-all rate of reaction. An extreme degree of occulsion may cause complete trapping of radicals and k_t may become very small, and even tend to zero. This means that at infinite high viscosity k_t must approach zero, since the polymer-radicals are immobilized.

The inductive Trommsdorff effect seems to be a physical ability of the solvent to encapsule the polymer-chain. Radicals can be so impeded that they remain indefinitely stable inside a protective coating of coiled, coalesced polymer-particles.

S-hexane and MMA-hexane systems.

Hexane is a poor solvent for Ps and PMMA. The hexane-hexane interactions are weak. In small concentrations, hexane does not permeate the polymer-radical, so produces the coiling of the polymeric chain and accelerates the rate. High concentrations of hexane seem to swell the polymer-radical reducing the rate (Graph 6 and 7). The molecular weights are consistent with the changes in the concentration of hexane: the larger the concentration of the solvent the smaller the molecular weight, (Table 3 and 4).

S-heptane and MMA-heptane systems.

Heptane has a $\Delta \delta = 1.9$ respect to the Ps, and a $\Delta \delta = 1.4$ in respect to the PMMA, consequently heptane is a poor solvent for the Ps and a fair solvent for PMMA. Its ability to increase the rate of polymerization of S is observed in Graph 13. Increase in MMA polymerization rate has not been observed.

VAC-Hexane system.

The difference between the kinetics of styrene and vinyl acetate emulsion polymerization seems to be due mainly to the different water solubility of the monomers, but it should be due also to the different reactivities of the styrene and vinyl acetate radicals. From the literature the following solubility data were obtained:

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Monomer		Wt-% water solubility
Styrene	45	3.6×10^{-2}
MMA	45	1,50
VAC	28	2.5
AN	50	8.5

As predicted by the Smith-Ewart theory and reported by Okamura,⁷² the rate of polymerization of styrene is very small below the CMC and increases abruptly above it. This is not so of vinyl acetate, which polymerized with an appreciable rate even without surfactant. In conclusion most of the polymerization of VAC takes place in the water phase. The presence of a solvent in the VAC emulsion polymerization seems to indicate that the PVAC in the water phase is permeated by the solvent giving as a result a increase in the mobility of the chain-radicals and a decrease in the polymerization rate, Graph 12.

SECTION B

INVESTIGATION OF EMULSION POLYMERIZATION RATES OF VINYL MONOMERS IN PRESENCE OF A SMALL CONCENTRATION OF SOLVENT

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CHAPTER I INTRODUCTION

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The effect of small concentrations of some diluents produces an antidiluent effect as was reported by Seymour.⁷³ This antidiluent action has been attributed to an enhancement of the degree of structural ordering. The breaking down of this ordered structure has been observed by infra-red spectrosopy and X-ray diffraction measurements by Lebedev et al.⁷⁴

Measurements⁷⁵ have been made to determine the microviscosity of the interior of the micelles giving larger values than that of bulk viscosities of liquid long-chain hydrocarbons. Recently Dorrance and Hunter⁷⁶ concluded that pyrene solubilized in the long-chain-cationic micelles that the micelles have a solid core at room temperature, but this conclusion has been controverted by Gratzel.⁷⁷

Spin resonance technique have been applied to study the position of solubilizates in the micelle.⁷⁸ The movement of molecules across the water-micelle interface has been investigated by means of the nanosecond laser photolysis technique.⁷⁹

Since the micelles play a central role in polymerization processes, a systematic study of their behavior in microenvironment due to the presence of small concentration of poor and good solvents had been conducted. A kinetic analysis of the conversion-time dependency yields information about the permeability of the micellar shell and the solvent power, as well as the position of the solubilized monomer-polymer in the hydrocarbon interior of the micelle.

CHAPTER II

1

EXPERIMENTAL AND RESULTS

The experiments were conducted as follows: Section A.

Exp. No. 1 - Styrene + viscous-poor solvents. Exp. No. 2 - Styrene + poor solvents. Styrene + mixtures (viscous/poor solvent),' Exp. No. 3 - Styrene + good solvents. Exp. No. 4 - Methyl methacrylate + good solvent. Methyl methacrylate + poor solvent.

Results and discussion of experiments 1, 2, 3 and 4

Section B.

Exp. No. 5 - Vinyl acetate + poor solvent.

Vinyl acetate + good solvent.

Exp. No. 6 - Acrylonitrile + poor solvent.

Acrylonitrile + viscous poor solvent

Results and discussion of experiments 5 and 6.

Section A

Experiment No. 1.

The object of this experiment is to investigate the effect of small concentration of Nujol and Dow 710 Silicone oil on the styrene emulsion polymerization.

The Nujol and the Dow 710 Silicone oil were selected because it was expected to produce two effects:

 a) an induced strong autoacceleration due to their high viscosities (about 1000 cps). b) a strong coiling due to the difference of solubility parameters,

 $\Delta \delta > 3.8.$

The concentration of the solvents were:

Run	38	S-Nujol	(1:0,25)
Run	39	S-Nujol	(1;0.025)
Run	40	S-Nujol	(1:0.0125)
Run	41	S-Silicone	(1:0.025)

Experiment No. 2.

The object of this experiment is to investigate the effect of small concentrations of:

a) a poor solvent,

 b) a viscous + a poor solvent, (50-50), in styrene emulsion polymerization

The concentration of the mixtures was 50% 50 and the runs were as follows:

Run	42	S-Hexane	(1:0,025)
Run	43	S-Hexane	(1:0.0125)
Run	44	S-Nujol/hexane	(1:0.0125)
Run	45	S-Silicone/hexane	(1:0.0025)

Experiment No. 3.

The object of this experiment is to investigate the effects of the presence of good solvent in styrene emulsion polymerization. Benzene was selected as good solvent for Ps. GRAPH 14: Styrene Emulsion Polymerization in the Presence of Small Concentrations of Nujol and Dow 710 Silicone Oil.

Run	\odot	97	S (standard))
Run	∇	38	S-Nujol	(1:0.25)
Run	\diamond	39	S-Nujol	(1:0.025)
Run		40	S-Nujol	(1:0.0125)
Run	\triangle	41	S-Silicone	(1:0.025)

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System		n _{rel}	n _{sp}	nred
S-Nujol	(1:0.25)	2.109	1.109	4,44
S-Nujol	(1:0.025)	1.808	0.808	9,08
S-Nujol	(1:0.0125)	2.273	1.273	12.73
S-Silicone	(1:0.025)	4.397	3.397	6.79

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GRAPH 15: Styrene Emulsion Polymerization in the Presence of Hexane and Mixtures of Hexane/Nujol and Hexane/Dow 710 Silicone Oil

Run	0	2	S (standard)	
Run	∇	42	S-hexane	(1:0.025)
Run	\odot	43	S-hexane	(1:0.0125)
Run		44	S-Nujol/hexane	(1:0.0125)
Run	Δ	45	S-Silicone/hexane	(1:0,0025)


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System		^(†) rel	n _{sp}	n _{rel}
S-hexane	(1;0,025)	5,575	4,575	9.15
S-hexane	(1;0.0125)	3.260	2.260	4.5
S-Nujol/hex.	(1:0.0125)	1.370	0.370	3.7
S-Silicone/hex.	(1:0.0025)	3,616	2.616	5.23

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TABLE VII

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GRAPH 16: Styrene Emulsion Polymerization in Different Concentrations

of Benzene

S (standard) Run \odot 2 Δ Run 46 S-benzene (1:0.0125) (1:0.0375) ∇ 47 Run S-benzene (1:0.05) Run 48 S-benzene \Box



GRAPH 17: Methyl Methacrylate Emulsion Polymerization in Different Concentrations of Benzene and Diundecyl Phthalate (DUP).

Run	Ō	54	MMA (standard	.)
Run	∇	49	MMA-benzene	(1:0.125)
Run		50	MMA-benzene	(1:0.05)
Run	\diamond	51	MMA-benzene	(1:0.025)
Run	\odot	52	MMA-DUP	(1:0.025)
Run	Δ	53	MMA-DUP	(1:0.0125)



The concentrations were:

Run	46	S-benzene	(1:0.0125)
Run	47	S-benzene	(1:0.0375)
Run	48	S-benzene	(1:0.05)

Experiment No. 4.

The object of this experiment is to investigate the effects of the presence of

a) a good solvent,

b) a viscous-poor solvent, in the MMA emulsion polymerization.

Benzene, a good solvent, and diundecyl phthalate (DUP), a viscouspoor solvent, were selected for methyl methacrylate.

The concentrations of the solvents were:

Run	49	MMA-benzene	(1:0.125)
Run	50	MMA-benzene	(1:0.05)
Run	51	MMA-benzene	(1:0.025)
Run	52	MMA-DUP	(1:0.025)
Run	53	MMA-DUP	(1:0.0125)

Results and discussion of experiments 1, 2 and 3:

The graph 14 shows the progressive acceleration of the rate with an increase in the concentration of Nujol. This suggests an early Trommsdorff effect due to Nujol-protective shell covering the micelle and the polymer-particle.

Mathematical calculations based on Williams data that the polymerparticle has a 1520 Å diameter show that with 40 g of monomer used in the experiments is possible to form 2.4 x 10^{16} particles, supposing they are ideal spheres. If the particle is shielded with a shell 5 Å wide, then 1 cc of Nujol (1 x 10^{24} Å³) may form 2.7 x 10^{16} protective shells.

Runs 38 and 39 show acceleration due to sufficient concentration of Nujol to protect the micelles. In run 40 there is deficiency in the protecting shell and the rate decreases. The study of the viscosities for the Ps-Nujol system shows a progressive decrease in the reduced viscosity when the concentration of Nujol was increased. This means that large concentrations of nonsolvents can swell the polymer particle causing the expansion of the polymeric chain and a fast termination.

The Graph 15 shows the acceleration of the rate in the mixture Ps-Nujol/hexane, where the Nujol is present in enough amount to cover most of the micelles.

Small concentration of Silicone hexane mixture (1:0.0025) does not seem to deviate from the standard rate appreciably,

Ps-Hexane system (1:0.025) presents acceleration of the rate at 50% conversion, this means that the micelle needs a "aging time" for building up a structural solvent layer on the surface of the micelle.⁸⁰ The protecting solvent layer may slow down the entry rate of a quenching radical into the micellar core, giving a sensitive acceleration of the rate.

Ps-hexane system (1:0.0125) presents a initial increase in the rate due to the still small volume of the micelle, but after 50% conversion the rate decreases showing that the hexane increases the termination rate giving more mobility to the chain radicals. On the other hand, as discussed in Section A, large concentrations of hexane reduce the rate as well. This means that the swelling produces an "opening" of the sodium lauryl sulfate micelles facilitating the termination.

The study of the values of the reduced viscosity shows that poor solvents give higher M.W. than solvents predominantly viscous.

The S-benzene and MMA-benzene systems, graph 16 and 17 in experiments 3 and 4, show an acceleration in the rate opposite to the expected progressive deacceleration due to the small difference in the solubility parameter. It seems that the benzene, in small concentrations, is absorbed on the long-hydrocarbon-surfactant chains before permeating the polymerparticle. The values of the reduced viscosity for both systems show a high M.W. with the increase in the rate as was expected.

The increase in the reduced viscosity due to an increase in the concentration of DUP was expected.

The correlation between the rates and the reduced viscosities shows that the higher the rate, the higher the M.W. Although it is known that the greatest percentage of the emulsion polymerization is in water, it seems that the presence of DUP (1:0.025) affects that part of the polymerization made in the micelle because the amount of solvent used is only enough to protect the micelle. Large concentrations of DUP seem to interfere with that part of the polymerization made in water reducing the rate and decreasing the M.W.

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System		ⁿ re1	n _{sp}	ⁿ red
Ps-benzene	(1;0,0125)	2.233	1,233	12.33
Ps-benzene	(1:0.0375)	1.725	0.725	7.25
Ps-benzene	(1:0.05)	1.643	0.643	6.43
-				:
PMMA-benzene	(1;0,125)	2.092	1.092	2.18
PMMA- benzene	(1:0.05)	6.43	5.43	10.8
PMMA-benzene	(1:0.025)	5.73	4.73	9.5
PMMA-DUPh	(1:0.025)	8.86	7.86	15.9
PMMA-DUPh	(1:0.0125)	7,39	6.39	12.8

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SECTION B

Experiment No. 5

The object of this experiment is to investigate the effect of the presence of good and poor solvents in VAC emulsion polymerization.

The concentration of the solvents was:

Run	55	VAC-DUPh	(1:0,25)
Run	56	VAC-DUPh	(1:0.025)
Run	57	VAC-DUPh	(1:0.0125)
Run	58	VAC-Benzene	(1:0,025)

Experiment No. 6

The object of this experiment is to investigate the effect of the presence of good and poor solvents in the AN emulsion polymerization.

The concentration of the solvents was:

Run	60	AN-DMF	(1:0.25)
Run	61	AN-DMF	(1:0.05)
Run	62	AN-DMF	(1:0.025)
Run	63	AN-DMF	(1:0.0125)
Run	64	AN-hexane	(1:0.025)
Run	65	An-hexane	(1:0.0125)

Results and discussion of experiments 5 and 6.

Small concentration of viscous-poor solvents as DUPh accelerate the polymerization rate, of VAC, although the monomer has a high percent solubility in water. This seems to say either that the small concentration of the viscous-poor solvent affects the micelle, surface or that the DUPh helps the polymerization in water by a mechanism not yet understood. GRAPH 18: Vinyl Acetate Emulsion Polymerization in the Presence of Diundecyl Phthalate (DUP) and Benzene.

Run	\odot	59	PVAC (standard)	
Run	Δ	55	PVAC-DUP	(1:0.25)
Run	∇	56	PVAC-DUP	(1:0.025)
Run	$\overline{}$	57	PVAC-DUP	(1:0.0125)
Run	\bigcirc	58	PVAC-benzene	(1:0.025)



, System		ⁿ rel	η sp	nred
PVAC-DUPh	(1;0.25	1.137	0.137	1.37
PVAC-DUPh	(1;0,025)	1,192	0.192	1.92
PVAC-DUPh	(1:0.0125)	1.178	0.178	1.78
PVAC-Bz	(1:0,025)	1.288	0.288	2.9
PVAC-std		1,822	0.822	3.3

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GRAPH 19: Acrylonitrile Emulsion Polymerization in the Presence

of Dimethylformamide and Hexane.

Run	O	66	AN (standar	d)
Run	\square	60	AN-DMF	(1:0.25)
Run	∇	61	AN-DMF	(1:0.05)
Run	\diamond	62	AN-DMF	(1:0.025)
Run	\odot	63	AN-DMF	(1:0.0125)
Run	◬	64	AN-hexane	(1:0.025)
Run		65	AN-hexane	(1:0.0125)

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TABLE X: VISCOSITIES

System			ⁿ rel	n _{sp} .	nred
PAN-DMF		(1;0.25)	1,415	0.415	4.15
PAN-DMF		(1;0,05)	1.550	0.550	5.5
PAN-DMF		(1;0,025)	1.623	0.623	6.23
PAN-DMF	,	(1:0.0125)	1.477	0.477	4.77
PAN-hexane		(1:0.025)	5.9	4.9	9.8
PAN-hexane		(1:0.0125)	5.48	4.48	8.9
PAN-standard			4.79	3.97	7,9

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Although DMF is a good solvent for the PAN, however small concentrations of DMF produce an acceleration in the polymerization rate. The graph shows that concentration of (1:0.0125) produces a decrease in the rate, but an increase in the concentration (:0.025) and (1:0.05) caused an increase in the rate, and as expected in a good solvent further increments in the solvent slow down the rate The viscosities are in accord with the observed rates, The higher the rate the higher the M.W.

CHAPTER III

CONCLUSIONS

Very large concentrations of either good or poor solvents slow down the emulsion polymerization rate due to a dilution effect.

Small concentrations of good solvents cause an enhancement of the degree of structural ordering of the solvent around the micelles. Increasing the ratio solvent/polymer results in a progressive decreasing of the polymerization rate.

Poor solvents accelerates the polymerization rate even in relatively large concentration. Solvents with inherent high viscosity produce an increase in the rate due to an inductive Trommsdorff effect.

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