

CHAPTER II

THEORETICAL BACKGROUND

2.1 Suspension Polymerization [4]

The term suspension polymerization describes a process in which monomer(s), relatively insoluble in water, is dispersed as liquid droplets with steric stabilizer and vigorous stirring (which is maintained during polymerization) to produce polymer particles as a dispersed solid phase. Initiators soluble in the liquid monomer phase are employed in this process. The terms pearl and bead polymerization are also used for the suspension polymerization process. The major aim in suspension polymerization is the formation of an as uniform as possible dispersion of monomer droplets in the aqueous phase with controlled coalescence of these droplets during the polymerization process. The interfacial tension, the degree of agitation, and the design of the stirrer/reactor system govern the dispersion of monomer droplets. The presence of suspending agents (e.g., stabilizers) hinder the coalescence of monomer droplets and the adhesion of partially polymerized particles during the course of polymerization, so that the solid beads may be produced in the same spherical form in which the monomer was dispersed in the aqueous phase. A survey of the materials used as suspending agents is given in Table 2.1 [5].

Suspension polymerization has the following advantages compared with the other polymerization process (bulk, solution, and emulsion): easy heat removal and temperature control; low dispersion viscosity; low levels of impurities in the polymer product (compared with emulsion); low separation costs (compared with emulsion); and final product in particle form. On the other hand, among the disadvantages of suspension polymerization one may refer to lower productivity for the same reactor capacity (compared to bulk); wastewater problems; polymer buildup on the reactor wall, baffles, agitators, and other surfaces; no commercial continuous process operability yet; and difficulty in producing homogeneous copolymer composition during batch suspension polymerization.

Table 2.1 Materials Used in Suspension Polymerization [5]

Suspending agent	Monomer suggested
<p>1. Natural polymeric agents</p> <ul style="list-style-type: none"> - Carbohydrates: starch, agar, tragacanth, pectin, plant gums such as acacia, sodium alginate - Proteinaceous materials: glue, gelatin, isinglass - Alginic acid and salts - Starch with buffer 	<p>Unsaturated esters of organic acids, such as acrylate esters and vinyl esters</p> <p>Vinyl esters, vinyl chloride, etc</p> <p>Methyl methacrylate Vinyl acetate</p>
<p>2. Modified natural polymeric agents</p> <ul style="list-style-type: none"> - Methyl cellulose - Methyl hydroxypropyl cellulose with 0.05-0.2 hydroxypropyl group per C6 unit - Carboxymethyl cellulose sodium salt - Hydroxyethyl cellulose 	<p>Acrylic and vinyl esters Vinyl compound: vinylidene chloride, vinyl chloride, acrylonitrile, etc</p> <p>Vinyl compounds</p> <p>Vinyl chloride</p>
<p>3. Synthetic polymeric agents</p> <p>(a) Containing carboxyl groups:</p> <ul style="list-style-type: none"> - Salts of polyacrylic acid and of poly(methacrylic acid) - Above at pH 5.5-8 with buffers - Na salts of copolymers of methacrylate acid with dichlorostyrene - Salts of copolymers of maleic acid, crotonic acid, with styrene, vinyl ethers, vinyl acetate, etc - Salts of acrylic acid copolymers with acrylic esters or vinyl esters - Copolymers of maleic acid, maleic anhydride with vinyl acetate - Copolymers of vinyl methyl ether and maleic anhydride - Polymers of itaconic, fumaric, maleic, citraconic, aconitic acids also partial esters or their salt 	<p>Acrylic and vinyl esters and homogos</p> <p>Acrylic compounds Dichlorostyrene, acrylonitrile, methyl methacrylate</p> <p>Unsaturated, polymerizable organic compounds generally</p> <p>Vinyl chloride, etc</p> <p>Vinyl halides and comonomers</p> <p>Vinyl halides and comonomers</p> <p>Vinyl compounds including acrylic compounds</p>

Table 2.1 Materials Used in Suspension Polymerization (continued)

Suspending agent	Monomer suggested
- Na salts of copolymers of 1-alkoxybutadiene and maleic acid	Polymerizable vinyl compounds
(b) Containing nitrogen:	
- Poly(vinyl pyrrolidone)	All polymerizable organic compounds
- Polymeric reaction products of methyl methacrylate with ammonia	Acrylic, vinyl esters and mixtures
- Above at pH 5.5-8 with buffers	Acrylic compounds, homologs
- Polymethacrylamide with NaH_2PO_4 and Na_2HPO_4 as buffers	Monomers in general
(c) Containing alcoholic OH groups:	
- Poly(vinyl alcohol)	Acrylic and vinyl esters
- Poly(vinyl acetate) partially saponified, mixtures of different mol. wt. and degrees of saponification	Vinyl acetate
(d) Containing sulfonic acid groups:	
- Sulfonated polystyrene with 0.15-0.5 SO_3H group per ring	Vinyl chloride with less vinylidene chloride
- Reaction products of Poly(vinyl alcohol) with aldehyde sulfonic acids	Polymerizable vinyl compounds
4. Low molecular compounds	
- Ester of organic hydroxyacids, e.g., octyl lactate	Polymerizable vinyl compounds generally
- Aliphatic acid esters of poly(ethylene glycol)	Vinyl chloride
- Partial esters of polyalcohol with fatty acids, e.g., pentaerythryl laurate	Vinyl chloride, vinylidene chloride and other vinyl compounds
- Phthalate esters	Vinyl chloride
5. Condensation polymers	
- Urea-formaldehyde	Vinyl chloride, vinylidene chloride, acrylonitrile
- Water-soluble phenol-formaldehyde	Vinyl chloride polymers

Table 2.1 Materials Used in Suspension Polymerization (continued)

Suspending agent	Monomer suggested
6. Inorganic agents	
- Powder such as kaolin, barium sulfate, talcum, aluminum hydroxide	Polymerizable vinyl and vinylidene compounds
- Addition of powders produced by precipitation together with monomers	Polymerizable vinyl and vinylidene compounds
- Tricalcium phosphate	Polymerizable vinyl and vinylidene compounds
- Difficultly soluble neutral phosphates of 0.2-0.005 μm	Polymerizable vinyl and vinylidene compounds
- Hydrated complex magnesium silicates	Polymerizable vinyl and vinylidene compounds
- Bentonite (colloidal clay)	Polymerizable vinyl and vinylidene compounds

The reactor vessel is usually a stirred tank. The monomer phases subjected to either turbulent pressure fluctuations or viscous shear forces, which break it into small droplets that assume a spherical shape under the influence of interfacial tension. These droplets undergo constant collisions (collision rate $\geq 1 \text{ s}^{-1}$), with some of the collisions resulting in coalescence. Eventually, a dynamic equilibrium is established, leading to a stationary mean particle size.

The most important issue in the practical operation of suspension polymerization is the control of the final particle size distribution. The size of the particles will depend on the monomer type, the viscosity change of the dispersed phase with time, the type and concentration of stabilizer, and the agitation conditions in the reactor. The locus of polymerization is the monomer/polymer beads. Due to the large size of the beads (0.1-1.0 mm), such systems are suspensions rather than emulsions or stable dispersions. The particles must be kept suspended by agitation throughout the course of the polymerization.

2.2 Free-radical Polymerization [6]

All free-radical polymerizations have at least three basic reaction types occurring simultaneously during polymerization. These include: initiation reactions which continuously generate radicals during the polymerization, propagation reactions which are responsible for the growth of polymer chains by monomer addition to a radical center and bimolecular termination reactions between two radical centers which give a net consumption of radicals. Free-radical may be generated by the chemical decomposition of azo and peroxide compounds, thermally and by γ -radiation. The initiation step composes of two reactions including (a) the production of primary radicals (Eq. (2.1)) and (b) the addition of primary radicals produced to the first monomer molecule to obtain the chain initiating species M_1^\bullet . The initiator (I) is usually homolytically dissociated to yield a pair of radicals R:



where k_d is the rate constant for the initiator dissociation.

The second reaction of the initiation can be shown as follows



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

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



where k_p represents the propagation rate constant.

The growth of chain takes place very rapidly, the average lifetime of the growing chain is short, for instance, a chain of over 1,000 units can be produced within 10^{-2} to 10^{-3} s. In theory it could continuously propagate until all the monomers in the system had been consumed. If the radical concentration is high, the short chains are generally produced due to a high probability of radical interactions. The long chains polymer could be produced in the system having low radical concentration.

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



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

2.3 Kinetics of Free-radical Polymerization [6]

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

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

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

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

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

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

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

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

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

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

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

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

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

The rate of polymerization R_p expressed in Eq.(2.8) is not directly obtained because $[M\cdot]$ are difficult to measure quantitatively. The steady state assumption is that the concentration of radicals increases initially, but almost instantaneously reaches a constant. The rate of change of the concentration of radicals quickly becomes and remains zero during the course of the polymerization. Therefore, it is noted that the steady state assumption is not widely applied in all polymerization kinetics, it is often used for developing the kinetics of many small molecule reactions involving highly active intermediates present at very low concentration conditions.

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

$$R_i = 2k_t[M\cdot]^2 \quad (2.9)$$

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

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

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

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

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

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

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

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

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

2.4 Study of Polymer Formation Reactions [7]

In reactions for the formation of polymers, volatile substances are generally used as starting materials, and in some reactions (for instance, polycondensation) volatile products are released. As a rule, the presence of a polymer in the reaction mixture does not hinder the use of gas chromatography (GC). GC methods can be used directly for determining the reaction kinetics from the changes in the concentrations of the monomers consumed or the products formed. In connection with the application of GC methods for studying the kinetics of the reactions of formation or transformation of macromolecules in relation to the type of reaction, it was found expedient to consider the application of GC to the study of polymerization (copolymerization) and polycondensation reactions and some chemical transformations of macromolecules.

Experimental methods are usually based on the determination of the time dependence of the polymer concentration in the reaction medium. The kinetic parameters of a reaction can be determined by measuring the decrease in the concentration of the monomer as it is consumed in the polymerization reaction. In order to determine the monomer concentration in the reaction medium, it is useful to apply GC method.

The reaction is usually carried out in a small thermostated reactor in a protective atmosphere of an inert gas, the pressure of which is slightly higher or lower than atmospheric. Samples are collected periodically from the reactor by means of a syringe with a long needle, which is introduced into the reactor through a cap made of self-sealing rubber similar to that used in the sample introduction system of a gas chromatograph. The collected sample is quickly transferred to a test-tube with a reagent that immediately terminates the polymerization reaction. The liquid sample collected from the reactor, together with the polymerization inhibitor introduced into it, is analyzed by GC on standard equipment. In order to separate the non-volatile polymer from the volatile components of the reaction mixture, a special cartridge (a shot column) with an inert packing is introduced between the column and the sample introduction system, or a special sample introduction system is filled with an inert,

friable material (for instance, a support). The non-volatile polymer accumulates on the inert packing, which is replaced periodically.

The degree of conversion in the polymerization reaction is determined by calculating the change in the concentration of the volatile reaction components from the chromatograms of the reaction mixture. There are basically two reasons why composition measurement is needed in polymerization systems [8]:

1. To ensure that proper combination of ingredients is available in the reaction mass at the beginning of or in the course of the polymerization.
2. To determine the extent of reaction (or monomer conversion) which has taken place in the reacting mass in real time to facilitate reaction control.

The use of GC has certain advantages. In Table 2.2 GC is compared with dilatometry, which is evidently the most widely used method for determining the kinetic parameters of polymerization reactions.

The only advantage of dilatometry compared with chromatography is, with concentrated solutions its application in simple cases enables one to determine the degree of conversion of the monomer with greater accuracy, especially at low degrees of conversion. As regards the other characteristics compared in Table 2.2, however, it is preferable to use GC. The field of application of GC is wider; it can be used for determining the kinetic parameters in highly dilute solutions. In studying polymerization kinetics over a wide temperature range, as well as in investigating changes of other parameters (solvent, catalyst, etc.), dilatometry is more laborious than GC because a change in polymerization conditions may lead to a change in the type of polymer obtained (atactic, syndiotactic, etc.), each type having a different density, and also to a change in the rate of side reactions, the products of which may differ in density from that of the initial monomer. Therefore, in experimental investigations of this nature, changes in the polymerization conditions usually necessitate the time-consuming re-calibration of the dilatometer.

From a comparison of the dilatometric and GC methods of the studying polymerization kinetics, one can conclude that GC is the preferred method in most instances. In fact, GC is being used more and more often in investigations of the kinetics and mechanisms of polymerization reactions.

Table 2.2 Comparison of GC and Dilatometric methods for determining the kinetic parameters of polymerization reactions [7]

Characteristic	Dilatometric method	GC method
Principle	Determination of decrease in volume of reaction mixture as a result of formation of a polymer characterized by higher density than that of initial monomer.	GC determination of monomer concentration in samples periodically collected from reactor.
Accuracy	Degree of conversion with concentrated solutions can usually be determined to within 0.1%.	Degree of conversion can be determined to within 0.5-5% (relative).
Field of application	Study of polymerization reactions using pure monomers and concentrated solutions; sensitivity of the method reduces with decreasing monomer concentration in reaction mixture.	Study of polymerization reactions in concentrated and highly dilute solutions (up to 0.001-0.0001% initial concentrations of monomers in reaction medium).
Volume of reaction mixture	Sensitivity of method increases with amount (volume) of reacting monomer in reaction mixture; necessary monomer volume is 10-50 ml.	Minimal amount (volume) of monomer necessary for one experiment is small, and when using dilute solutions is 0.01-0.005 g.
Equipment and experimental procedure	Equipment is simple but non-standard; method is rather time consuming as any change in polymerization.	Analytical equipment (chromatograph) is complex, but standard. Calibration of chromatograph is independent of polymerization conditions.

2.5 Polymer Solubility [9]

2.5.1 General Rules for Polymer Solubility

Some general qualitative observations on the dissolution of polymers:

1. Like dissolves like; that is, polar solvents will tend to dissolve polar polymers and nonpolar solvents will tend to dissolve nonpolar polymers. Chemical similarity of polymer and solvent is a fair indication of solubility; for example, polystyrene, in toluene, $\phi\text{-CH}_3$

2. In a given solvent at a particular temperature, the solubility of a polymer will decrease with increasing molecular weight.

3. a. Crosslinking eliminates solubility.

b. Crystallinity, in general, acts like crosslinking, but it is possible in some cases to find solvents strong enough to overcome the crystalline bonding forces and dissolve the polymer. Heating the polymer toward its crystalline melting point allows its solubility in appropriate solvents.

4. The rate of polymer solubility decreases with increasing molecular weight. For reasonably high molecular weight polymers, it can be orders of magnitude slower than that for nonpolymeric solutes.

It is important to note here that items 1, 2, and 3 are equilibrium phenomena and are therefore describable thermodynamically, while item 4 is a rate phenomenon and is governed by the rates of diffusion of polymer and solvent.

2.5.2 The Thermodynamic Basis of Polymer Solubility

Consider the process of mixing pure polymer and pure solvent (state 1) at constant pressure and temperature to form a solution (state 2) by the sign of the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \quad (2.13)$$

where ΔG = the change in Gibbs free energy

T = the absolute temperature

ΔH = the change in enthalpy

ΔS = the change in entropy

Only if ΔG is negative will the solution process be thermodynamically feasible. The absolute temperature must be positive, and the change in entropy for a solution process is generally positive, because in a solution, the molecules are in a more random state in the solid. The positive product is preceded by a negative sign. Thus, the third $(-T\Delta S)$ term in Eq. 2.13 favors solubility. The change in enthalpy may be either positive or negative. A positive ΔH means the solvent and polymer "prefer their own company," that is, the pure materials are in a lower energy state, while a negative ΔH indicates that the solution is the lower energy state. If the latter obtains, solution is assured. Negative ΔH 's usually arise where specific interactions such as hydrogen bonds are formed between the solvent and polymer molecules. But, if ΔH is positive, then $\Delta H < T\Delta S$ if the polymer is to be soluble.

2.5.3 The Solubility Parameter

The formation of regular solutions (those in which solute and solvent do not form specific interactions), the change in internal energy per unit volume of solution is given by

$$\Delta H \approx \Delta E = \phi_1\phi_2(\delta_1 - \delta_2)^2 \quad [=] \text{ cal/cm}^3 \cdot \text{soln} \quad (2.14)$$

where ΔE = the change in internal energy per unit volume of solution

ϕ_i = volume fractions

δ_i = solubility parameters

The subscripts 1 and 2 usually refer to solvent and solute (polymer), respectively. The solubility parameter is defined as follows:

$$\delta = (CED)^{1/2} = (\Delta E_v / v)^{1/2} \quad (2.15)$$

where CED = cohesive energy density, a measure of the strength of the intermolecular forces holding the molecules together in the liquid state

ΔE_v = molar change in internal energy on vaporization

v = molar volume of liquid

Traditionally, solubility parameters have been given in $(\text{cal}/\text{cm}^3)^{1/2} =$ hildebrands, but they are now more commonly listed in $(\text{MPa})^{1/2}$ (1 hildebrands = $0.4889 (\text{MPa})^{1/2}$).

For a process that occurs at constant volume and constant pressure, the changes in internal energy and enthalpy are equal. Since the change in volume on solution is usually quite small, this is a good approximation for the dissolution of polymers under most conditions, so Eq. 2.13 provides a means of estimating enthalpies of solution if the solubility parameters of the polymer and solvent are known.

Note that regardless of the magnitudes of δ_1 and δ_2 (they must be positive), the predicted ΔH is always positive, because Eq. 2.13 applies only in the absence of the specific interactions that lead to negative ΔH 's. Inspection of Eq. 2.13 also reveals that ΔH is minimized, and the tendency toward solubility is therefore maximized by matching the solubility parameters as closely as possible. As a very rough rule-of-thumb,

$$|\delta_1 - \delta_2| < 1 (\text{cal}/\text{cm}^3)^{1/2} \text{ for solubility} \quad (2.16)$$

Measuring the solubility parameter of a low molecular weight solvent is no problem. Polymers, on the other hand, degrade long before reaching their vaporization temperatures, making it impossible to evaluate ΔE_v directly. Fortunately, there is a way around this impasse. The greatest tendency of a polymer to dissolve occurs when its solubility parameter matches that of the solvent. If the polymer is crosslinked lightly, it cannot dissolve, but only swell. The maximum swelling will be observed when the polymer and solvent solubility parameters are matched. So polymer solubility parameters are determined by soaking lightly crosslinked samples in a series of solvents of known solubility parameters. The value of the solvent at which maximum swelling is observed is taken as the solubility parameter of the polymer (Figure 2.1).

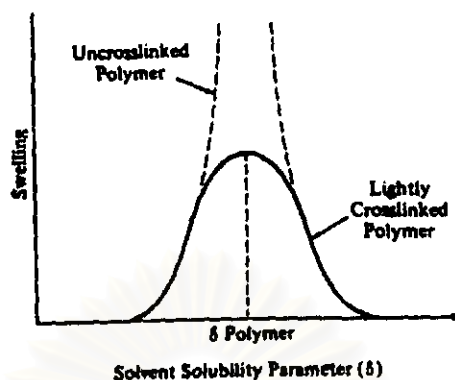


Figure 2.1 Determination of polymer solubility parameter by swelling lightly crosslinked samples in a series of solvents. [9]

Table 2.3 Classification of the solvating power of the diluents according to their solubility parameters [10]

Diluent	$ \delta_1 - \delta_2 $ (MPa) ^{1/2}	Prevision
EtAc	0.2	Good Solvents $ \delta_1 - \delta_2 < 1.0$
Tol	0.4	
DIBP	0.4	
Deacl	0.6	
BuAc	1.2	Intermediary Solvents $1.0 < \delta_1 - \delta_2 < 3.0$
MIBK	1.4	
DEP	1.8	
i-AmA	1.9	
DOP	2.4	
i-AmAc	2.6	
ACP	3.1	Poor Solvents $ \delta_1 - \delta_2 > 3.0$
Hep	3.5	
BA	6.1	

2.5.4 Hansen's Three-Dimensional Solubility Parameter

According to Hansen, the total change in internal energy on vaporization, ΔE_v , may be considered the sum of three individual contributions: one due to hydrogen bonds ΔE_h , another due to permanent dipole interactions ΔE_p , and a third from dispersion (van der Waals or London) forces ΔE_d :

$$\Delta E_v = \Delta E_d + \Delta E_p + \Delta E_h \quad (2.17)$$

Dividing by the molar volume v gives

$$\frac{\Delta E_v}{v} = \frac{\Delta E_d}{v} + \frac{\Delta E_p}{v} + \frac{\Delta E_h}{v} \quad (2.18)$$

or
$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.19)$$

where
$$\delta_j = (\Delta E_j/v)^{1/2} \quad j = d, p, h$$

Thus, the solubility parameter δ may be thought of as vector in a three-dimensional d, p, h space. Equation 2.19 gives the magnitude of the vector in terms of its components. A solvent, therefore, with given values of δ_{p1} , δ_{d1} , and δ_{h1} is represented as a point in space, with δ being the vector from the origin to this point.

A polymer is also characterized by δ_{p2} , δ_{d2} , and δ_{h2} . Furthermore, it has been found on a purely empirical basis that if δ_d is plotted on a scale twice the size as that used for δ_p and δ_h , then all solvents that dissolve that polymer fall within a sphere of radius R surrounding the point (δ_{p2} , δ_{d2} , and δ_{h2}).

The three-dimensional equivalent of Eq. 2.16 is obtained by calculating the magnitude of the vector from the center of the polymer sphere (δ_{p2} , δ_{d2} , and δ_{h2}) to the point representing the solvent (δ_{p1} , δ_{d1} , and δ_{h1}). If this is less than R , the polymer is deemed soluble:

$$[(\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 + 4(\delta_{d1} - \delta_{d2})^2]^{1/2} < R \quad \text{for solubility} \quad (2.20)$$

(The factor of 4 arises from the empirical need to double the δ_d scale to achieve a spherical solubility region).

Table 2.4. Hildebrand solubility parameters, coordinates of three-dimensional solubility parameters δ_t (δ_p , δ_d , and δ_h) [10]

Diluent	δ (MPa) ^{1/2}	δ_t (MPa) ^{1/2}		
		δ_d	δ_p	δ_h
Acetophenone (ACP)	21.7	19.6	8.6	3.7
Benzyl alcohol (BA)	24.7	18.4	6.3	13.7
Butyl acetate (BuAc)	17.4	15.8	3.7	6.3
Decaline (Dec)	18.0	18.4	0.0	0.0
Diethyl phthalate (DEP)	20.5	17.6	9.6	4.5
Diisobutyl phthalate (DIBP)	19.0	17.8	8.6	4.1
Dioctyl phthalate (DOP)	16.2	16.6	7.0	3.1
Ethyl acetate (EtAc)	18.6	15.8	5.3	7.2
Heptane (Hep)	15.1	15.3	0.0	0.0
Isoamyl acetate (I-AmAc)	16.0	15.3	3.1	7.0
Isoamyl alcohol (I-AmA)	20.5	16.0	4.5	13.9
Methyl-isobutyl ketone (MIBK)	17.2	15.3	6.1	4.1
Toluene (Tol)	18.2	18.0	1.4	2.0

2.5.5 The Flory-Huggins Theory

Theoretical treatment of polymer solutions was initiated independently and essentially simultaneously by Flory and Huggins in 1942. By statistically evaluating the number of arrangements possible on the lattice, Flory and Huggins obtained an expression for the (extensive) configurational entropy changes (that due to geometry alone), ΔS^* , in forming a solution from n_1 moles of solvent and n_2 moles of solute:

$$\Delta S^* = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (2.21)$$

where the ϕ 's are volume fractions,

$$\phi_1 = \frac{x_1 n_1}{x_1 n_1 + x_2 n_2} \quad (2.22a)$$

$$\phi_2 = \frac{x_2 n_2}{x_1 n_1 + x_2 n_2} \quad (2.22b)$$

and the x 's are the number of segments in the species. For the usual monomeric solvent, $x_1 = 1$. For a polydisperse polymeric solute, strictly speaking, a term must be included in Eq. 2.21. For each individual species in the distribution, but x_2 is usually taken as \bar{x}_n , the number-average degree of polymerization, with little error.

Table 2.5 Classification of the solvating power of the diluents according to diluent-polymer distances (R) in a three-dimensional δ_p , δ_d , and δ_h space [10]

Diluent	R (MPa) ^{1/2}	Prevision
ACP	3.5	Good Solvents $R < 10.0$
DIBP	7.5	
Tol	8.3	
DEP	8.3	
Dec.	9.3	
DOP	9.5	
BA	11.1	Intermediary $10.0 < R < 12.7$
EtAc	11.4	
BuAc	11.4	
MIBK	12.0	
i-AmAc	12.4	
Hep	14.0	Poor Solvents $R > 12.7$
i-AmA	14.4	

2.5.6 Properties of Diluent Solutions

For typical polymer-solvent systems this usually works out to a few percent polymer.

In a “good” solvent (one whose solubility parameter closely matches that of the polymer), the secondary forces between polymer segments and solvent molecules are strong, and the polymer molecules will assume a spread out conformation in solution. In a “poor” solvent, the attractive forces between the segments of the polymer chain will be greater than those between the chain segments and the solvent; in other words, the chain segments “prefer their own company,” and the chain will ball up tightly (Figure 2.2).

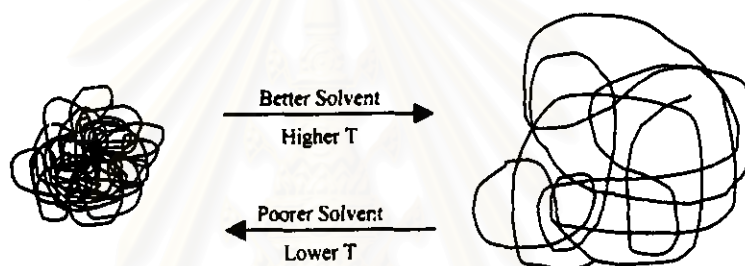


Figure 2.2 The effects of solvent power and temperature on a polymer molecule in solution [9].

2.6 Absorption-Desorption Kinetics

2.6.1 Absorption Kinetics

When a piece of polymer is added to a solvent, the polymer chains interact with the molecules of the solvent, which is absorbed by the polymer. As the contact with the solvent continues, these chains gradually extend and relax. They may then disentangle, diffuse into the bulk of the solvent, and become dissolved [11]. If the polymer is crosslinked the chains remain linked to each other through chemical bonds. The polymer will swell but not dissolve in the solvent. The swelling of these materials is determined by the solvent properties of the liquid for the polymer and the degree of crosslinking. The positive entropy of mixing of the polymer and the solvent enhances swelling. The heat of mixing may enhance (if negative) or retard (if positive) swelling. The tension set up in the polymer subchains resists swelling. A

"good" solvent will give a high degree of swelling. A lightly crosslinked polymer will give a high degree of swelling, a heavily crosslinked a smaller degree of swelling.

Tanaka and Fillmore [12] characterized the swelling of spherical gels in liquids as a relaxation process. They defined the diffusion coefficient of the gel in the liquid by:

$$D = [(4u/3) + K] / f \quad (2.23)$$

where u is the shear of polymer network alone

K is the bulk modulus of polymer network alone

f is frictional coefficient between the network and the fluid medium

A characteristic swelling time τ was defined by:

$$\tau = a^2 / D \quad (2.24)$$

where a is the final radius of the fully swollen gel. For $t/\tau > 0.25$, the following equation was obtained:

$$\ln(\Delta a_t / \Delta a_0) = \text{const.} - t / \tau \quad (2.25)$$

where Δa_t is the difference between the size at time t and that at a saturation swelling

Δa_0 is the total change in radius throughout the entire swelling process

The characteristic swelling time τ can be obtained from the slope of the $\ln(\Delta a_t / \Delta a_0)$ - time plot.

2.6.2 Desorption Kinetics

By bringing the swollen gel into contact with a substrate and separated from the bulk of the swelling liquid, the imbibed solvent may be released. If the substrate competes favorably for the solvent the desorption will be effective, if the substrate competes poorly

the desorption will be incomplete. A rapid sorption by the substrate makes the desorption from the bead rapid. A slow sorption by the substrate makes the desorption slow. The diffusion of solvent into substrate has been shown to follow the Rideal-Washburn equation, which describes the penetration of a liquid into capillary pores:

$$I^2 = rt \gamma \cos\theta / 2\eta = Kt \gamma \cos\theta / 2 \quad (2.26)$$

where I is the depth of penetration

r is the radius of the cylindrical capillaries

t is the time of penetration

η is the viscosity of the liquid

γ is the surface tension of the liquid

θ is the contact angle of the liquid on the capillary walls

K is the effective radius of non- cylindrical capillary pores including a tortuously factor

2.7 Literature Review

So far the synthesis of the porous polystyrene crosslinked with divinylbenzene for the use as raw materials for polymeric supports in chromatography, ion exchange and absorbents in medical, chemical and agricultural applications. Recent works on the study of synthesis of styrenic imbibed beads by suspension polymerization are listed below.

Asaworarith [13] synthesized polystyrene crosslinked with divinylbenzene by suspension and seed suspension polymerization using the mixture HPMC and HEC as suspending agents and BPO as an initiator. The properties of copolymer beads are: specific area of 0.1-0.8 m²/g, density of 1.05 g/cm³, maximum absorption at 13.2 times its own dimension and complete desorption time of absorbed toluene at 23 hr.

Karoowanchareern [14] studied effect of such influential parameters as monomer fraction, temperature and time schedule, concentrations of diluent and inhibitor on absorption properties of styrene-divinylbenzene beads. The properties of copolymer beads are pore volume of $0.28 \text{ cm}^3/\text{g}$, specific surface area of $94.4 \text{ m}^2/\text{g}$, density of 0.618 g/cm^3 , and swelling ratio of 17.7 within 20 hr.

Traisaranapong [15] studied the effects of such influential parameters as temperature and time schedule, inhibitor concentration, nitrogen flowrate and diluent concentration, on absorption properties of styrene-divinylbenzene beads. The copolymer beads were prepared by conventional and seed suspension polymerization. The properties of copolymer beads are specific surface area of $139.87 \text{ m}^2/\text{g}$, pore volume of $0.12 \text{ cm}^3/\text{g}$, density of 0.9667 g/cm^3 , swelling ratio of 16.4 within 50 min.

Wiley [16] studied the differences in properties of pure m- and pure p-DVB crosslinked polystyrene and their sulphonated products have been correlated with probable network structural differences. The p-DVB copolymerized more slowly than the meta isomer to give a crosslinked copolymer which swelled less, sulphonated less rapidly, and, when sulphonated, gave an ion exchanger which had lower selectivity. It was concluded, that the para crosslinked network was tighter and less uniform than that of the meta crosslinked network. Kinetics of the polymerization and copolymerization was determined by radiocarbon techniques and computer analysis of high-conversion data. The preparation and sulphonation of the bead copolymers of styrene with the pure meta- and para-DVB was developed in detail and the exchange isotherms of the sulphonated beads were evaluated.

Kwant [17] studied the copolymerization of styrene with small amounts of divinylbenzenes ($\leq 0.04 \text{ wt}\%$) which offered advantages over similar studies made at high DVB concentrations. Experimental data showed that the copolymerization constants for the copolymerization of the first double bonds of m- and p-DVB with styrene were 0.85 and 0.43, respectively. The results reported that at low concentration of DVB the

copolymerization constants were not dependent on the conversion, at least in the low conversion range in which no Trommsdorff effect occurred. In earlier studies performed at higher DVB concentrations, the copolymerization constants changed with conversion. After 50% conversion an autoacceleration effect reduced the selectivity of the growing polystyrene radical.

Hild and Rempp [18] investigated the kinetics of the radical copolymerization which was carried out on several systems of this type: styrene-divinylbenzene, styrene-diisopropenylbenzene, styrene-ethylenedimethacrylate, methylmethacrylate-ethylene dimethacrylate. In some cases, a chain transfer agent was added to the system to delay the occurrence of network formation. From conversion curves of each individual monomer - that were obtained from vapor phase chromatography taken at regular time intervals - the instantaneous composition of the copolymers formed were determined. This was clearly evidenced by recent works carried out on the system styrene-divinylbenzene in which it was shown that, once the gel point was reached, cross-linking went on; more links between individual chains were formed, whereby the crosslink density increased and the average length of the elastically effective network chain decreased.

Chung, et al. [19] prepared macroporous with varying diluent amount of benzyl alcohol. From sample analysis, the copolymerization kinetics concerning both monomer consumption and residual double bond amount were determined. Porous texture and morphology were analyzed by BET, BJH, mercury porosimetry, and scanning electron. Depending on diluent amount, the final product was classified as inside or outside the macroporous domain. Texture evolution was clearly different for the two classes of products, although their chemical evolutions were almost the same. A qualitative discussion of porous texture formation was presented, based on occurrence of three critical events: gelation, phase separation and molecular overlap.

Mikos et al. [20] developed a new kinetic model for free radical monovinyl-divinyl monomer copolymerization/cross-linking reactions. The model included kinetic

information of the initiation, propagation and cross-linking, termination, and chain transfer to monomer steps of the polymerization. The kinetics was described in terms of the concentrations of the monovinyl, divinyl, and pendent vinyl species. The gel point, number-average molecular weight of linear polymer, and average number of cross-links per polymer chain were calculated for both the styrene/p-divinylbenzene and styrene/m-divinylbenzene reaction schemes using the moments of the molecular weight distribution of the cross-linked copolymers.

Okay [21] presented a kinetic model for the post-gelation period of free-radical monovinyl-divinyl monomer copolymerization reactions. The model involved the moment equations of both the primary and the branched molecules in the sol, and predicted the vinyl-group conversions, the number of crosslinks and the chain-length averages as a function of the reaction time. Formulae for the weight fraction and cycle-rank density of the gel and its equilibrium degree of swelling were derived. The predictions were found to be in good agreement with experimental data on the copolymerization of styrene with m- divinylbenzene. The reaction time for incipient phase separation during styrene-divinylbenzene copolymerization in the presence of a solvent and the threshold concentration of the divinylbenzene for the formation of heterogeneous structures were also calculated.

Sajjadi et al. [22] studied the crosslinking copolymerization of styrene with a mixture of para- and meta-divinylbenzenes. The crosslinking copolymerization, initiated with benzoyl peroxide, was performed at temperatures of 70, 80 and 90°C. The mole ratio of divinylbenzenes to styrene was kept small, i.e. within 4-8%. At various stages of the polymerization the overall conversion of the monomers to sol and gel were measured by gravimetry. The sol and gel formations with time were also measured. The gels were characterized by equilibrium swelling measurements as a function of the overall degree of conversion. The experimental data were then incorporated into the kinetic model developed by Tobita and Hamielec. The kinetic parameters involved in the crosslinking

copolymerization of styrene/divinylbenzenes were also estimated. The model was observed.



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