

## CHAPTER II

### THEORETICAL BACKGROUND

#### 2.1 Free-Radical Polymerization [4, 5]

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  $\gamma$ -radiation. The initiation step composes of two reactions including (a) the production of primary radicals (Eq. 2.1a) and (b) the addition of primary radicals produced to the first monomer molecule to obtain the initiating species  $M_1^\bullet$  (Eq. 2.1b). The initiator ( $I$ ) is usually homolytically dissociated to yield a pair of radicals  $R^\bullet$



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 number of monomer molecules. Each addition creates a new radical which has the same identity as the one previously mentioned, except that it is larger by one additional monomer unit. This step can be presented in a general term 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  $10^{-3}$  sec. 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 chain 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 radical centers to form one long chain; and the disproportionation which a hydrogen atom in *beta* position of one radical center is abstracted by another radical center to give a saturated and an unsaturated polymer chain. One or both

reactions may be active in any system depending on the monomer and polymerizing condition. The general term expressing the termination step is



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

## 2.2 Suspension Polymerization [6, 7]

The term suspension polymerization refers to a polymerizing system in which monomer(s) is suspended as the discontinuous phase of droplets with steric stabilizers and vigorous stirring (which is maintained during polymerization) in a continuous phase. The reactor product is a slurry of suspended polymer particles. The monomers suitable for suspension polymerization usually can be polymerized by free-radical mechanisms. The continuous phase is usually water, as most monomer are relatively insoluble in water. Polymerization initiators or catalysts soluble in the monomer phase are generally used 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 the droplets during the polymerization process. The interfacial tension, the degree of agitation, and the design of stirrer/reactor system govern the dispersion of monomer droplets. The presence of suspending agents (e.g., stabilizer) hinders 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 a spherical form in which the monomer was dispersed in the aqueous phase.

Several characteristics of the suspension polymerization method are common to most systems. The volume ratio of the continuous aqueous phase to the dispersed organic phase varies from 1:1 to 6:1. Higher ratios are required in rapid polymerizations, where heat is removed in a short time [7]. The bulk viscosity of the slurry is near that of water during most of the polymerizations. The low bulk fluid viscosity allows good mixing of the reactor contents at modest energy inputs and can improve heat transfer in the polymerization reactor. Water is a good medium for removing heat from polymerizing droplets because it has both a high heat capacity and a high thermal conductivity. However, suspension polymers must be separated and dried from the water phase. Suspension droplets are not thermodynamically stable, and their coalescence is controlled by balancing the agitation system and the suspending agents. A survey of the materials used as suspending agents is given in Table 2.1 [8].

The reactor vessel is usually a stirrer tank. The monomer phase is subjected to either turbulent pressure fluctuations or viscous 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. Individual drops do not retain their unique identity but undergo continuous breakup and coalescence instead. In some cases, an appropriate dispersant can be used to induce the formation of a protective film on the

Table 2.1 Materials used in suspension polymerization [8]

Suspending agents	Monomers suggested
1 Natural polymeric agents	
- Carbohydrates: starch, agar, tragacanth, pectin, plant gums such as acacia, sodium alginate	Unsaturated esters of organic acid, such as acrylate esters and vinyl esters
- Proteinaceous materials : glue, gelatin	Vinyl esters, vinyl chloride, etc.
- Alginic acid and salts	Methyl methacrylate
- Starch with buffer	Vinyl acetate
2 Modified natural polymeric agents	
- Methyl cellulose	Acrylic and vinyl esters
- Methyl hydroxypropyl cellulose with 0.05-0.2 hydroxypropyl gr per C6 unit	Vinyl compound: vinylidene chloride, vinyl chloride, acrylonitrile, etc.
- Carboxyethyl cellulose sodium salt	Vinyl chloride
- Hydroxyethyl cellose	Vinyl chloride
3 Synthetic polymeric agents	
(a) Containing carboxyl groups:	
- Salts of poly(acrylic acid) and of poly(methacrylic acid)	Acrylic and vinyl esters and homologs
- Above at pH 5.5-8 with buffers	Acrylic compounds
- Sodium salts of copolymers of methacrylic acid with dichloro-styrene	Dichlorostyrene, acrylonitrile, methyl methacrylate
- Salts of copolymers of maleic acid, crotonic acid, with styrene, vinyl ethers, vinyl acetate, etc.	Unsaturated, polymerizable organic compounds generally

Table 2.1 Materials used in suspension polymerization (continued)

Suspending agents	Monomers suggested
- Salts of acrylic acid copolymers with acrylic ester or vinyl ester	Vinyl chloride, etc.
- Copolymers of maleic acid, maleic anhydride with vinyl acetate	Vinyl halides and comonomers
- Copolymers of vinyl methyl ether and maleic anhydride	Vinyl halides and comonomers
- Polymers of itaconic, fumaric, maleic, citraconic, aconitic acids also partial esters or their salt	Vinyl compounds including Acrylic compounds
- Sodium 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 $\text{Na}_2\text{HPO}_4$ and $\text{Na}_2\text{HPO}_4$ as buffers	Monomers in general
(c) Containing alcoholic OH groups:	
- Poly(vinyl alcohol)	Acrylic and vinyl esters

Table 2.1 Materials used in suspension polymerization (continued)

Suspending agents	Monomers suggested
- 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 <sub>3</sub> H 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 weight 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 polyalcohols with fatty acids, e.g., penta-erythrityl 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 agents	Monomers suggested
6 Inorganic agents	
- Powders 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 $\mu\text{m}$	Polymerizable vinyl and vinylidene compounds
- Hydrated complex magnesium silicates	Polymerizable vinyl and vinylidene compounds
- Bentonite (colloidal clay)	Polymerizable vinyl and vinylidene compounds

droplet surface. As a result, pairs of clusters of drops that tend to coalesce are broken up by the action of the stirrer before the critical coalescence period elapses. A stable state is ultimately reached in which individual drops maintain their identities over prolonged periods of time.

In the case of a polymer that is miscible in all proportions with its monomer (e.g. styrene and methyl methacrylate), a very variation of range of the dispersed phase viscosity is observed during the course of polymerization. The initially low-viscosity liquid monomer is transformed gradually into an increasingly viscous



polymer in monomer solution, and as conversion increases, the dispersed phase acquires the characteristics of a solid particle. Particularly in the “tacky” intermediate stage, individual polymer particles tend to form incompletely fused clumps. Agglomeration at this critical stage of conversion is somewhat inhibited by the action of the dispersant, but other effective measures to reduce coalescence may also be taken, including adjusting the densities of the two phases to make them more similar or increasing the viscosity of the aqueous continuous phase. Rapid polymerization during the sticky stage minimizes the number of effective collisions among polymer particles and thus should reduce coagulation.

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 depends 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.

Several other types of polymerization are carried out in aqueous medium. These must be distinguished from suspension and pearl polymerization, and they give different types of end products. An outline of these processes of polymerization is presented in Table 2.2 [8]. Suspension polymerization has been used little outside the field of vinyl-type or ethylenic monomers.

Table 2.2 Polymerization processes in water [8]

Type of polymerization	Monomer solubility in water	Aqueous phase	Initiators	Place of initiator of polymerization	Polymer product	
					Molecular weight	Type of product
Solution polymerization	Water-soluble, e.g., acrylic acid, methacrylic acid and alkali salts; vinyl pyrrolidone	Forms homogeneous solutions with monomers	Water-soluble, e.g., persulfates, hydrogen peroxide, hydroperoxides	In aqueous solution	Lower than in bulk polymerization	Clear, viscous, aqueous solution
Precipitation polymerization (polymer is not water soluble)	Soluble, such as acrylonitrile or less soluble, e.g., acrylic esters, vinyl acetate	Free from emulsifying and dispersing agents	Water-soluble, e.g., persulfates, hydrogen peroxide, hydroperoxides	In aqueous solution	Usually higher than in bulk polymerization (gel effect)	Water-insoluble; polymer precipitates out or forms a slurry
Emulsion polymerization	Only slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride	Emulsifying agents anionic; cationic or nonionic surfactants less common (generally 1% or more)	Water-soluble, e.g., persulfates and peroxides; organic peroxides with redox systems	In aqueous solution or in micelle surface	Higher than in bulk polymerization	Latex of fine dispersion, e.g., 0.2 $\mu$ or lower particle diameters or lower particle diameter
Dispersion polymerization	Only slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride and especially vinyl acetate	High molecular, water-soluble polymers, e.g., poly (vinyl alcohol), poly (acrylic acid and salts)	Water-soluble persulfates, hydrogen peroxide, redox systems	In aqueous solution or in monomer droplets	Higher than in bulk polymerization when gel effect occurs	So-called polymer "emulsions", larger particle than in true latex
Pearl or bead polymerization	Most slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride and especially vinyl acetate	Lower concentrations of above or inorganic pulverulent agents	Monomer-soluble, e.g., benzoyl peroxide, azobisbutylonitrile	In monomer droplets	As in bulk polymerization	Spheres or granules temporarily suspended in water, easily separated

Suspension polymerization has the following advantages compared with the other polymerization processes (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 a 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.

## **2.3 Polymer Solubility**

### **2.3.1 General Rules for Polymer Solubility [7, 9]**

A polymer solution refers to a uniform molecular dispersion of a macromolecular solute in a solvent usually of much lower molecular weight. The solubility is the measure of the extent to which the two pure components can be mixed homogeneously.

The process of dissolving a pure polymer begins with solvent molecules permeating bulk polymer. The polymer near the surface swells to accommodate incoming molecules of solvent whereas individual long-chain molecules may be freed from near the surface and diffuse into the solvent phase. If the solubility limit is not exceeded, the system eventually becomes homogeneous. The extent to which the solution process can occur depends especially on the temperature, the chemical nature

of the solute and solvent, the molecular weight of the polymer, and on the degree of crystallinity for semicrystalline polymers. Highly cross-linked polymers can imbibe solvent and swell, forming a saturated polymer gel. Solvent added beyond this point remains as a second phase.

Generally, polymers are less soluble than are their low molecular weight analogs; the solubility of most polymers decreases as their molecular weight is increased. Temperature-*vs*-weight fraction phase diagrams showing the solubility of amorphous polymers are skewed; the region of limited miscibility typically occurs at low concentrations of polymer rather than near the middle of the phase diagram. Consequently, mixing polymer with “poor” solvent sometimes leads to a swollen polymer phase in equilibrium with almost pure solvent. As with mixtures of low molecular weight liquids, the solubility of polymers in most cases increases with increasing temperature.

The saying “Like dissolves like” applies to polymer solutions as well as to mixtures of small molecules. Also, solution is favored when specific interactions such as hydrogen bonding are formed between solvent and polymer.

Some general qualitative observations on the distribution 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, poly(vinyl alcohol) dissolves in water and polystyrene in toluene but toluene does not dissolve poly(vinyl alcohol) and water does not dissolve polystyrene, either.

2. In a given solvent at a particular temperature, the solubility of a polymer decreases 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.

### 2.3.2 The Thermodynamic Basis of Polymer Solubility [7]

Some relationships from the thermodynamics of mixing are important for understanding polymer solubility. The free energy change  $\Delta G$  for mixing two pure substances at temperature  $T$  is given by the familiar equation

$$\Delta G = \Delta H - T\Delta S \quad (2.4)$$

The heat of mixing  $\Delta H$  is a positive quantity for most solutions, i.e., the formation of polymer solutions is usually an endothermic process. The entropy of mixing  $\Delta S$  is positive owing to the more random nature of solutions compared to that of the unmixed components. Both  $\Delta H$  and  $\Delta S$  vary with temperature and

concentration. A necessary condition for the formation of a thermodynamically stable solution is that  $\Delta G \leq 0$ .

### 2.3.3 The Flory-Huggins Theory [7]

Mathematical models of polymer solutions have increased our understanding of how various factors affect polymer solubility. The Flory-Huggins theory for noncrystalline polymers is valuable in this capacity. An algebraic expression for  $\Delta G$  derived from the model can be combined with general thermodynamic relationships for calculating the phase behavior of polymer solutions.

The Flory-Huggins model uses a combinatorial analysis to estimate the increase in configurations available to the system when a flexible polymer in a disordered state is mixed with a solvent. The result leads to a predicted increase in entropy of

$$\Delta S = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (2.5)$$

where  $n_1$  and  $n_2$  = the number of moles of solvent and polymer, respectively;

$\phi_1$  and  $\phi_2$  = the volume fraction of solvent and polymer, respectively;

and  $R$  = the gas constant

In almost all polymer solutions this increase in entropy is the principal driving force for the mixing process.

The heat of mixing in the Flory-Huggins theory is the van Laar heat:

$$\Delta H = z \Delta \varepsilon n_1 \phi_2 \quad (2.6)$$

In this equation  $z$  is the coordination number for the solvent molecule, i.e., the average number of solvent molecules and solvent-sized segments of polymer in contact with one molecule of solvent. The energy  $\Delta\varepsilon$  is the difference between the intermolecular contact energy between a segment of the polymer and a solvent molecule and the average interaction for a pair of polymer segments and a pair of solvent molecules. Usually  $\Delta\varepsilon$  is positive corresponding to endothermic mixing; however, it is negative in the unusual instances of exothermic mixing.

The ratio  $z\Delta\varepsilon/RT$  is generally written as the unitless Flory-Huggins interaction parameter  $\chi$ :

$$\chi = z \Delta\varepsilon / RT \quad (2.7)$$

The Flory-Huggins equation for the free energy of mixing becomes

$$\Delta G = RT (n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2) \quad (2.8)$$

The smaller that  $\chi$  is, the more stable is the solution relative to the pure components and the more likely that the system is miscible over a wide (or the entire) range of concentrations. Values of  $\chi$  are typically in the range 0.2-0.9. For most systems  $\chi$  decrease with increasing temperature and increases with increasing concentration of polymer.

The Flory-Huggins theory is applicable to amorphous polymers. Crystalline polymers require an additional energy, namely, the heat of fusion, in order to mix with solvent and therefore tend to have lower solubilities than their amorphous counterparts. For systems in which there are strong specific interactions between

solvent and solute, such as hydrogen bonding, mixing can be exothermic and/or can occur with an entropy change that differs markedly from that predicted by Flory and Huggins.

### 2.3.4 The Solubility Parameter [9]

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

$$\Delta H \approx \Delta E = \phi_1\phi_2(\delta_1 - \delta_2)^2 \quad [=] \text{ cal / cm}^3 \text{ soln} \quad (2.9)$$

where  $\Delta E$  = the change in internal energy per unit volume of solution

$\phi_i$  = volume fractions

$\delta_i$  = solubility parameters

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

$$\delta = (\text{CED})^{1/2} = (\Delta E_v / \nu)^{1/2} \quad (2.10)$$

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

$\Delta E_v$  = molar change in internal energy on vaporization

$\nu$  = 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 hildebrand =  $0.4889 (\text{MPa})^{1/2}$ ).

For a process that occurs at constant volume and 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. 2.4 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  $\delta_1$  and  $\delta_2$  (they must be positive), the predicted  $\Delta H$  is always positive, because Eq. 2.4 applies only in the absence of the specific interactions that lead to negative  $\Delta H$ 's. Inspection of Eq. 2.4 also reveals that  $\Delta H$  is minimized, and the tendency toward solubility is therefore maximized by matching the solubility parameters as possible. As a very rough rule-of thumb,

$$|\delta_1 - \delta_2| < 1 (\text{cal}/\text{cm}^3)^{1/2} \text{ for solubility} \quad (2.11)$$

Measuring the solubility parameter of a low molecular weight solvent is not a problem. Polymers, on the other hand, degrade long before reaching their vaporization temperatures, making it impossible to evaluate  $\Delta E_v$  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 which maximum swelling is observed is taken as the solubility parameter of polymer (Figure 2.1).

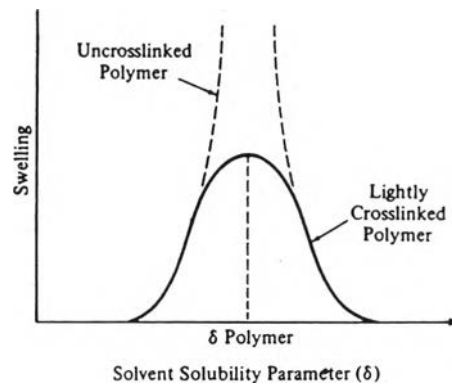


Figure 2.1 Determination of polymer solubility parameter by swelling a lightly crosslinked polymer in a series of solvents [9].

Solubility parameters of solvent mixtures can be readily calculated from

$$\delta_{mix} = \frac{\sum y_i v_i \delta_i}{\sum y_i v_i} = \sum \phi_i \delta_i \quad (2.12)$$

where  $y_i$  = mole fraction of component  $i$

$v_i$  = molar fraction of component  $i$

$\phi_i$  = volume fraction of component  $i$

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

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

### 2.3.5 Hansen's Three-Dimensional Solubility Parameter [9, 11]

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

$$\Delta E_v = \Delta E_d + \Delta E_f + \Delta E_h \quad (2.13)$$

Dividing by the molar volume  $\nu$  gives

$$\frac{\Delta E_\nu}{\nu} = \frac{\Delta E_d}{\nu} + \frac{\Delta E_p}{\nu} + \frac{\Delta E_h}{\nu} \quad (2.14)$$

$$\text{or } \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.15)$$

$$\text{where } \delta_j = \left( \frac{\Delta E_j}{\nu} \right)^{1/2} \quad j = d, p, h$$

Thus, the solubility parameter  $\delta$  may be thought of as a vector in a three-dimensional  $d, p, h$  space. Equation 2.15 gives the magnitude of the vector in terms of its components. A solvent, therefore, with given values of  $\delta_{d1}$ ,  $\delta_{p1}$ , and  $\delta_{h1}$  is represented as a point in space, with  $\delta$  being the vector from the origin to this point.

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

The three-dimensional equivalent of Eq. 2.11 is obtained by calculating the magnitude of the vector from the center of the polymer sphere ( $\delta_{d2}$ ,  $\delta_{p2}$ , and  $\delta_{h2}$ ) to the point representing the solvent ( $\delta_{d1}$ ,  $\delta_{p1}$ , and  $\delta_{h1}$ ). If this is less than  $R$ , the polymer is deemed soluble:

$$\left[ (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 + 4(\delta_{d1} - \delta_{d2})^2 \right]^{1/2} < R \text{ for solubility} \quad (2.16)$$

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

Table 2.4 Hildebrand solubility parameters, coordinates of three-dimensional solubility parameters  $\delta_i$  ( $\delta_d$ ,  $\delta_p$ , and  $\delta_h$ ) [10]

DILUENT	$\delta$ (MPa) <sup>1/2</sup>	$\delta_i$ (MPa) <sup>1/2</sup>		
		$\delta_d$	$\delta_p$	$\delta_h$
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
Diocetyl 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>i</i> -AmAc)	16.0	15.3	3.1	7.0
Isoamyl alcohol ( <i>i</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

Table 2.5 Classification of the solvating power of the diluents according to diluent-polymer distances ( $R$ ) in a three-dimensional  $\delta_d, \delta_p$ , and  $\delta_h$  [10]

DILUENT	$R$ (MPa) <sup>1/2</sup>	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 Solvents $10.0 < R < 12.7$
EtAc	11.4	
BuAc	11.4	
MIBK	12.0	
<i>i</i> -AmAc	12.4	
Hep	14.0	Poor Solvents $R > 12.7$
<i>i</i> -AmA	14.4	

### 2.3.6 Properties of Diluent Solutions [9]

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).

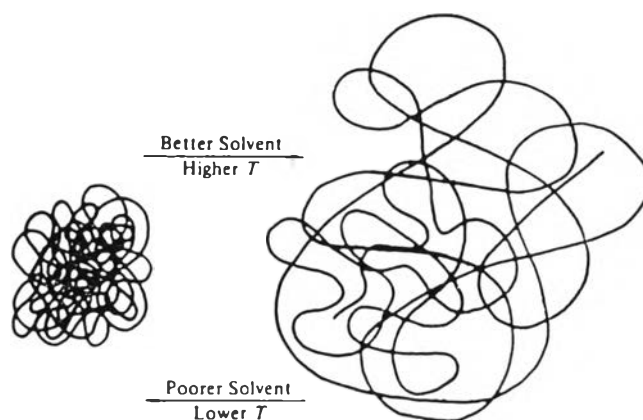


Figure 2.2 The effects of solvent power and temperature on a polymer molecule in solution [9].

## 2.4 Crosslinked Polymers [12]

When long polymer molecules are chemically linked together to form a three dimensional network, the resulting material exhibits a unique set of properties that have come to be referred to as “rubber-like”. Among these are large deformation elasticity which has important consequences for mechanical behavior and resistance to solvent attack. As for the latter, when solvent molecules penetrate into the polymer, it undergoes swelling rather than dissolution, and the diluted network is referred to as a chemically crosslinked gel. While there are several structures that exhibit gel-link behavior, e.g., (1) covalent networks of long chain molecules, (2) physical networks formed by aggregation of polymer chains (gelatin, agarose), (3) lamellar, fibrillar or reticular systems exhibiting partially ordered structures (clays, surfactants, etc.), the

focus of this work is solely on elastomeric polymer networks containing a three-dimensional permanent structure of high molecular weight chain molecules swollen in a low molecular weight diluent as depicted in Figure 2.3.

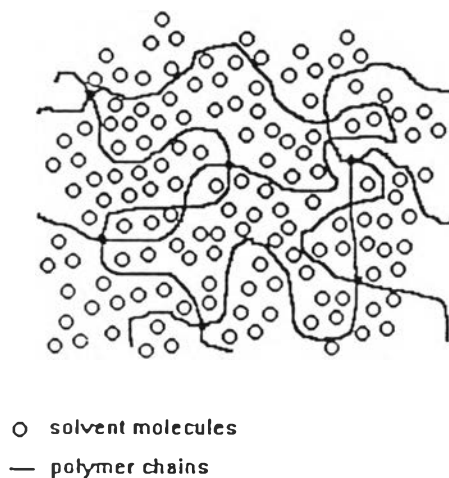


Figure 2.3 Schematic representation of a chemically crosslinked polymer network swollen by a low molecular weight solvent [12].

#### 2.4.1 Chemical Crosslinking [13]

The most severe mechanism for decreasing molecular freedom is chemical crosslinking-linking the polymer chains together through covalent or ionic bonds to form a network. Occasionally the term curing is used to denote crosslinking. There are a number of ways crosslinking can be brought about, but basically they fall into two categories: (1) crosslinking during polymerization by use of polyfunctional instead of difunctional monomers, and (2) crosslinking in a separate processing step after the linear (or branched) polymer is formed. The crosslinks may contain the same structural features as the main chains, which is usually the case with the former, or



they may have an entirely different structure, which is more characteristic of the latter.

A number of extreme changes accompany crosslinking. If previously soluble, the polymer will no longer dissolve (except in the case of some ionically crosslinked polymers). In the presence of solvent, a crosslinked polymer swells as solvent molecules penetrate the network. The degree of swelling depends on the affinity of solvent and polymer for one another, as well as on the level of crosslinking. It may be recalled that a solvent-swollen crosslinked polymer is called a gel. Covalently crosslinked polymer also lose their flow properties. They may still undergo deformation, but the deformation will be reversible; that is, the polymer will exhibit elastic properties. Ionically crosslinked polymers will flow at elevated temperatures, however.

With network polymers it is common to speak of the crosslink density, that is, the number of crosslinked monomer units per main chain. The higher the crosslink density, the more rigid the polymer. Very high crosslink densities lead to embrittlement. Because crosslinking reduces segmental motion, it is frequently employed to increase the glass temperature.

#### **2.4.2 Physical Crosslinking [13]**

When polymer chemists use the term crosslinking, they invariably mean covalent chemical crosslinking. Covalent crosslinking has certain disadvantages, however. Once crosslinked, a polymer cannot be dissolved or molded. One approach has been to investigate thermally labile crosslinks, that is, chemical crosslinks that break apart on heating and reform on cooling. Ionic crosslinks fall into this category.

The other approach has been to introduce strong secondary bonding attraction between polymer chains such that the polymer exhibits properties of a thermosetting material while remaining thermoplastic. Crystalline polymers fit into this category. Because of the very strong secondary forces arising from close chain packing, many of the mechanical and solution properties of crystalline polymers resemble those of crosslinked amorphous polymers. Certain materials intermolecularly associated through hydrogen bonds also behave like crosslinked polymers.

In recent years the technology of block copolymers has been applied to the area of physical crosslinking. The method involves synthesis of block copolymers of the ABA type in which the A and B blocks differ substantially in structure. Consider, for example, a long-chain “flexible” polymer such as polybutadiene, capped at each chain end with short blocks of a “rigid” polymer such as polystyrene. Because polybutadiene and polystyrene are inherently immiscible (incompatible), the

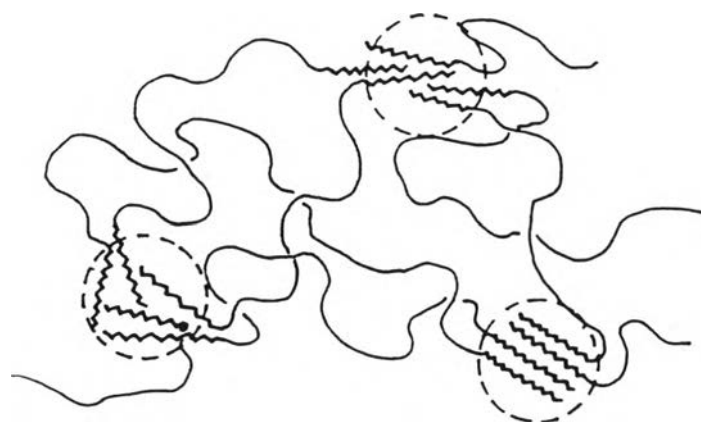


Figure 2.4 Representation of aggregation in an ABA block thermoplastic elastomer ( $\text{~~~~~}$  represents end blocks,  $\text{⊙}$  represents microdomains) [13].

polystyrene blocks tend to aggregate and form separate phases (microdomains) within the polymer matrix, as shown in Figure 2.4. If the structure of the end blocks is stereoregular, the aggregations may form crystalline microdomains. The aggregations impart a significant degree of elastic behavior, yet the copolymers still exhibit the flow properties of thermoplastics.

### 2.4.3 Crosslink Density [14]

One of the most important structural parameters characterizing crosslinked polymers is  $\overline{M}_c$ , the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of  $\overline{M}_c$  significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine  $\overline{M}_c$ . Early research by Flory and Rehner laid the foundations for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, for a perfect network,

$$\overline{M}_c = -V_1 \rho_p \frac{(\phi_p^{1/3} - \phi_p/2)}{[\ln(1 - \phi_p) + \phi_p + \chi_{12} \phi_p^2]} \quad (2.17)$$

where  $\overline{M}_c$  is the number average molecular weight of the polymer between crosslinks

$V_1$  is the molar volume of the solvent

$\rho_p$  is the polymer density

$\phi_p$  is the volume fraction of polymer in the swollen gel

$\chi_{12}$  is the Flory-Huggins interaction parameter between solvent and polymer

The swelling ratio,  $S$ , is equal to  $1/\phi_p$ . Here, the crosslink density,  $q$ , is defined as the mole fraction of crosslinked units.

$$q = \frac{M_o}{M_c} \quad (2.18)$$

where  $M_o$  is the molecular weight of polymer repeat unit. We defined  $q$  in Eq. (2.18) in order to simplify direct comparison with the mole fraction of divinyl monomers in copolymerization.

## 2.5 Absorption-Desorption Kinetics

### 2.5.1 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. 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 [15] characterized the swelling of spherical gels in liquid as a relaxation process. They defined the diffusion coefficient of the gel in the liquid by:

$$D = \frac{(4U/3) + K}{f} \quad (2.19)$$

where  $U$  is the shear of polymer network alone

$K$  is the bulk modulus of polymer network alone

$f$  is the frictional coefficient between the network and fluid medium

A characteristic swelling time  $\tau$  was defined by:

$$\tau = a^2 / D \quad (2.20)$$

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

$$\ln \left( \frac{\Delta a_t}{\Delta a_o} \right) = \text{const} - t/\tau \quad (2.21)$$

where  $\Delta a_t$  is the difference between the size at time  $t$  and that at saturation swelling

$\Delta a_o$  is the total change in radius throughout the entire swelling process

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

### 2.5.2 Desorption Kinetics

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:

$$l^2 = \frac{rt\gamma \cos\theta}{2\eta} = Kt\gamma \cos\frac{\theta}{2} \quad (2.22)$$

where  $l$  is the depth of penetration

$r$  is the radius of the cylindrical capillaries

$t$  is the time of penetration

$\eta$  is the viscosity of the liquid

$\gamma$  is the surface tension of the liquid

$\theta$  is the contact angle of the liquid on the capillary walls

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

## 2.6 Literature Review

So far the synthesis of the porous polystyrene crosslinked with divinylbenzene for the use as raw materials for ion exchange, functionalized copolymers, or as polymeric supports in chromatography and absorption has been the matter of a large number of published papers. Recent works on the study of the styrene-divinylbenzene copolymers are listed below.

Poinescu, et al. [16] studied the formation of the permanent porosity in the classical matrix, styrene-divinylbenzene copolymers, using cyclohexane, cyclohexanol, or cyclohexanone as diluent. The data concerning porous networks were corroborated with the solvent-polymer interaction factor and the cohesive energy density which are important in the prediction of copolymer porosity. Between diluents there are noticeable differences, though the diluent volume and the divinylbenzene percent strong influence the porous structure of the network. Cyclohexanol was the most efficient diluent for building up the highest porosity even at low percents of divinylbenzene.

Coutinho and Cid [17] prepared the porous structure of styrene-divinylbenzene copolymers by suspension polymerization using diluents during polymerization. These diluents, having different affinities for the copolymers, produced changes in their morphology. Various diluent compositions were employed in order to discover their influence on the porous structure of the copolymers. The proportion and type of diluents were varied. *n*-Heptane was used as a precipitant in association with isoamyl acetate and ethyl acetate. The morphological changes were evaluated by apparent density, specific area and porosity. A study was also made of

the influence of the divinylbenzene content in the synthesis of the copolymers on their morphological characteristics.

Coutinho and Rabelo [18] synthesized styrene-divinylbenzene copolymers by suspension polymerization in the presence of toluene and heptane as diluents for the monomers. The effects of toluene/heptane ratio, degree of dilution of the monomers and divinylbenzene (DVB) content on the surface formation of the copolymer beads were examined by scanning electron microscopy. The sizes of the aggregates and macropores increased with increase of the nonsolvating diluent content and by the degree or dilution of the monomers. The effect of the DVB content was generally the same as that of the diluent for the monomers.

Kiatkamjornwong and Asawaworarith [19] 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 m<sup>2</sup>/g, density of 1.05 g/cm<sup>3</sup>, maximum absorption at 13.2 times its own dimension and complete desorption time of absorbed toluene at 23 hr.

Kiatkamjornwong, et al [20] studied effect of such influential parameters as monomer fraction, temperature and time schedule, concentrations of diluent and inhibitor on absorption properties. The beads synthesized had the following properties: pore volume 0.28 cm<sup>3</sup>/g, specific surface area 94.4 m<sup>2</sup>/g, density 0.618 g/cm<sup>3</sup>, and swelling ratio 17.7 within 20 hr.

Rabelo and Coutinho [21] synthesized styrene-divinylbenzene copolymers by suspension polymerization in the presence of toluene (Tol) and heptane (Hep) as diluents for the monomers. The effects of Tol/Hep ratio, dilution of the monomers and



divinylbenzene (DVB) content on the porous structure formation and swelling properties of the copolymers were investigated. Each system presented critical concentrations of diluent and DVB for the production of macroporous copolymers. The lower the solvating power of the diluent mixture the lower were the critical concentrations to ensure the formation of fixed pores. Toluene uptakes of macroporous copolymers were considered as a result of three contributions: filling of the fixed pores, expansion of the fixed pores and swelling of the polymeric nuclei. The expansion of the fixed pores produced an increasing of the volume of the copolymer beads. The kinetic data of heptane uptakes, permitted a classification of the porous structures as: gel type, collapsed, macroporous/collapsed and macroporous. The difference between Tol uptake and Hep uptake was a good measure of swelling of polymer nuclei of copolymers with different porous structures.

Rabelo and Coutinho [10] investigated the effects of the solvating power of pure diluents on the porous structure and swelling properties of styrene-divinylbenzene (sty-DVB) copolymers. The Hildebrand solubility parameter ( $\delta$ ) and the three-dimensional solubility parameter ( $\delta_T$ ) were used to predict the diluent-polymer affinity. In a general way,  $\delta_T$  was a better predictor than  $\delta$ . It was found that accessibility of polymer surface depends not only on the fixed pore volume but also on the elasticity of internuclear chains.

Rabelo and Coutinho [22] investigated the influence of binary mixtures of heptane with different diluents on the porous structure of styrene-divinylbenzene copolymers. It was found that the porosity produced by the diluent mixtures depends not only on the affinity of each diluent for the copolymer but also on the interaction of the diluent molecules with themselves. In this work it was observed that some polar

aromatic solvents when mixed with heptane presented cosolvency effects. In general, the accessible pore volumes were higher than the fixed pore ones, indicating the formation of elastic internuclear chain.

Rabelo and Coutinho [23] investigated the influence of binary mixtures of alcohols with different diluents on the porous structure of styrene-divinylbenzene copolymers. Two series of binary mixtures were tested: one with isoamyl alcohol (*i*-AmA) and another with benzoyl alcohol (BA). For systems containing *i*-AmA, the hydrogen bonding between alcohol and polar solvent molecules exert strong precipitating effects. Copolymers prepared with polar solvent/*i*-AmA presented higher porosities than copolymers obtained in presence of nonpolar solvent/*i*-AmA. Binary mixtures with *i*-AmA produced more porous and rigid networks than with BA.

Wojaczynska and Kolarz [24] prepared structures of copolymers of styrene and divinylbenzene (50 % crosslinking degree) in suspension polymerization in the presence of mixtures of *nonsol* (heptane or decane) and *sol* (toluene or tetralin) diluents were investigated. The studies showed that the diluents enriched with nonsol solvents resulted in an increase of pore volumes and porosities for the prepared copolymers. The sol diluents affected mainly the gel regions of the polymer matrices. Isotropic swelling of the matrices prepared in the presence of toluene is the opposite of the effect observed for tetralin family copolymers. The virtual difference of both kinds of matrices was demonstrated in the sorption of phenol. The tetralin family copolymers were characterized by a prolonged time for column breakthrough.

Coutinho, et al. [1] synthesized styrene-divinylbenzene copolymers by suspension polymerization in the presence of bis-2-diethylhexylphosphoric acid (DEHPA) and methyl ethyl ketone (MEK) as diluents for the monomers. The

influence of DEHPA/MEK ratio and dilution degree for the formation of porous structure of the copolymers was investigated by surface area, pore volume, pore size distribution and apparent density. It was found that 50 % DEHPA in the diluent mixture always leads to macroporous sorbents whatever the MEK content.

Iayadene, et al. [25] studied the copolymerization of styrene with divinylbenzene in the presence of a mixture of *n*-heptane and ethyl-hexanol in order to prepare porous beads. The effect of *n*-heptane/ethyl-hexanol ratio, dilution and crosslinking degree, on porosity, pore volume, apparent density, as well as uptake coefficients, was studied and correlated with the solubility parameters of the components.

Coutinho, et al. [2] synthesized small spherical particles of styrene-divinylbenzene copolymers by modified suspension polymerization. The effects of divinylbenzene (DVB) contents, dilution degree of the monomers and diluent composition on the porous structure and swelling properties of the copolymers were investigated. Toluene uptakes of macroporous copolymers were considered as a result of three contributions: filling of the fixed pores, expansion of the fixed or collapsed pores, and nuclei swelling and heptane uptakes as a result of the two first contributions. The increase of DVB content in the copolymers synthesized in the presence of a solvating diluent (toluene) provoked a decrease on the nuclei swelling. The increase of dilution degree with solvating diluents changed the toluene and heptane uptakes, and when the diluent-copolymer affinity was reduced, the fixed pore volume increased.

Coutinho, et al. [26] synthesized a series of styrene-divinylbenzene copolymers by suspension polymerization using two types of diluent systems:

diethylphthalate (DEP)/*n*-heptane (Hep) and diethylphthalate (DEP)/isoamylacetate (*i*-AmAc). The influence of DEP/*i*-AmAc ratio on the formation of the porous structure and swelling of the copolymers were investigated. The mixtures of these diluents produced copolymers with lower pore volumes than those produced with the pure diluents, these results were attributed to the cosolvency effect provoked by the interaction and association between the components of the diluent systems.

Guttaf, et al. [11] prepared porous styrene/divinylbenzene/methylmethacrylate terpolymers by radical suspension polymerization. Mixtures of two pore forming agents, *n*-heptane and 2-ethyl hexanol, were used to generate various STY/DVB/MMA networks. The morphological changes were made apparent by porous volume, porosity, apparent density, volume fraction of polymer in the swollen gel, toluene/cyclohexane uptake and scanning electron microscopy. These properties were correlated with the diluent-polymer ( $R_{ij}$ ) in three-dimensional  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  space solubility parameters.

Kiatkamjornwong, et al. [27] studied the effect 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 of 139.87 m<sup>2</sup>/g, pore volume of 0.12 cm<sup>3</sup>/g, density of 0.9667 g/cm<sup>3</sup>, swelling ratio of 16.4 with 50 min.