CHAPTER II

THEORETICAL BACKGROUND

2.1 Radical chain polymerization [6]

Polymerization of olefinic compounds, particularly that containing vinyl group in proximity to aromatic or polar groupings, can be converted into high molecular weight substances by chain polymerization. Chain polymerization has at least three basic reaction types occurring simultaneously during polymerization. They are initiation, in which the chain is formed; propagation, in which monomer is added to the growing chain and termination, in which the growth activity of the chain is destroyed, leaving the polymer molecule.

Initiation in radical-chain polymerization is the process by which a monomer molecule acquires an active site for the propagation of the chain reaction, that is, becomes a free radical. The most common form of initiation: the production of a free radical by the thermal decomposition of a relatively unstable initiator molecule, and the subsequent addition of a monomer to this primary radical to form the first chain radical. Among the common initiators for free radical polymerization are peroxides, such as benzoyl peroxide, and azo compounds, such as azobisisobutyronitrile. If we designate such a molecule R:R, where the two dots represent the electrons of the unstable bond, e.g., the O-O bond in benzoyl peroxide, the primary initiation step is the thermal rupture of this bond, one electron remaining with each radical fragment :

$$R\text{-}R \quad \xrightarrow{k_d} \quad 2\,R\cdot \tag{2.1}$$

where the single dot electron represents the unpaired electron characteristic of a free radical and k_d is the rate for thermal decomposition of the initiator. The second step of initiation, in which R· adds to a monomer M, may be represented schematically as

$$R· + M \rightarrow RM· \tag{2.2}$$

As a result of this step, the initiation fragment R is chemically bonded to the growing chain and thus incorporated into the final polymer molecule. If the first step is rate determining, the rate of initiation, R_i, is

$$R_i = 2fk_d[I] \tag{2.3}$$

where f is initiator factor, and [I] is initiator concentration, because all the radicals generated by decomposition of initiator may not be effective in reacting with monomer to produce active chain.

The second step of radical chain polymerization is propagation. The free radical chain formed in the initiation step is capable of adding other monomers in succession:

$$RM· + M \rightarrow RM_2· \tag{2.4}$$

or, in general,

$$RM_x· + M \xrightarrow{k_p} RM_{x+1}· \tag{2.5}$$
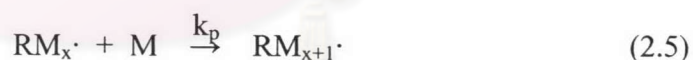
The rate constant for propagation is represented by k_p. We can then write the rate of propagation as

$$R_p = k_p[M][M·] \tag{2.6}$$

where [M·] is the sum of the concentrations of all chain radicals of the type $M_x·$.

The growing chain radicals are extremely reactive toward one another; only their low concentration (typically about 10^{-8} M) prevents their early reaction, pairing the two odd electrons and destroying their activity. Eventually, this bimolecular reaction occurring in one of two possible ways is combination or disproportionation. In term of

molecular structure, in the typical case of a vinyl monomer of the general structure $CH_2=CHX$, where X is hydrogen in ethylene, CH_3 in propylene, Cl in vinyl chloride, etc.,

In case of combination which is the two chains yield a single polymer molecule,

$$-CH_2CHX\cdot + \cdot CHXCH_2- \quad \rightarrow \quad -CH_2CHXCHXCH_2- \qquad (2.7)$$

or disproportionation, which is hydrogen transfer, occurs with the formation of two polymer molecules,

$$-CH_2CHX\cdot + \cdot CHXCH_2- \quad \rightarrow \quad -CH_2CH_2X + HXC=CH- \qquad (2.8)$$

Then we can write the rate of termination is

$$R_t = 2k_t[M\cdot]^2 \qquad (2.9)$$

where $k_t = k_{t,c} + k_{t,d}$, $k_{t,c}$ is the rate constant of termination by combination, $k_{t,d}$ is the rate constant of termination by disproportionation.

The rate of overall polymerization can be written by the steady-state assumption as

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

The rate of polymerization is seen to have the significant conclusion of the dependence of the polymerization rate on the square root of initiation rate. Doubling the rate of initiation does not double the polymerization rate; the polymerization rate is increased only by the factor $\sqrt{2}$. This behavior is a consequence of the bimolecular termination reaction between radicals.

2.2 Chain copolymerization [6]

In the polymerization of a mixture of two or more monomers, the rates at which different monomers add to the growing chain determine the composition and hence the

properties of the resulting copolymer. The order as well as the ratio of amounts in which monomers add is determined by their relative reactivities in the chain-growth step, which in turn are influenced by the nature of the end of the growing chain, depending on which monomer added previously. Among the possibilities are random and regular alternating additions as well as block formation. With two monomers present, there are four possible propagation reactions, assuming that growth is influenced only by the nature of the end of the growing chain and of the monomer:

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1M_1\cdot \qquad (2.11)$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_1M_2\cdot \qquad (2.12)$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_2M_1\cdot \qquad (2.13)$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2M_2\cdot \qquad (2.14)$$

With the definition of reactivity ratio $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and the application of the steady-state assumption, one can derive a copolymer equation relating the instantaneous composition of copolymer being formed, $d[M_1]/d[M_2]$, to the monomer concentration :

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])} \qquad (2.15)$$

A useful approximation to this equation for low conversion, where [M1]/[M2] is constant, is

$$r_2 = r_1H^2/h + H(1-h)/h \qquad (2.16)$$

where $H = [M_1]/[M_2]$ and $h = d[M_1]/d[M_2]$. This equation is used to evaluating r_1 and r_2. The reactivity ratios are ratios of the rate constants for a given radical adding its own monomer to that for its adding the other monomer. A value of $r > 1$ means that the radical prefers to add its own monomer, and vice versa.

2.3 Suspension polymerization [7]

Suspension polymerization, sometimes called pearl or bead polymerization, can be considered to be bulk polymerization carried out with the monomer dispersed in small droplets, typically 10-1000 micrometers in diameter. The droplets are suspended in a medium in which the monomer is essentially insoluble (usually water) by means of carefully controlled agitation and with the aid of a dispersant or protective colloid. If the agitation is stopped, the phases often separate the less dense rising to the top of the reactor. This is usually a water-soluble polymer such as poly(vinyl alcohol) or methyl cellulose in the aqueous phase, but an oil-soluble dispersant may also be added to the monomer phase. The dispersant prevents the aggregation of partially polymerized monomer particles at the stage when they are quite sticky. The polymerization takes place entirely in the monomer phase. No mass transfer occurs between the monomer and the aqueous phase. Monomer-soluble initiators are used in suspension polymerization. The basic polymerization mixture consists of monomer, initiator, dispersant and suspending medium.

Suspension polymerization is, like emulsion polymerization, a reaction which proceeds in the disperse medium. When using a stabilizer in suspension polymerization, the monomer is emulsified by vigorous stirring into the aqueous phase. The polymerization starts, as with homogeneous polymerization, where an oil-soluble initiator decomposes into initiating radicals. Initiation, propagation and termination proceed in monomer droplets, obeying the laws of block radical polymerization. The stabilizer is a decisive factor, affecting the dispersion of monomer in water, particle formation and the stability of the polymer suspension (as in emulsion polymerization). After dispersing the monomer phase in water, the stabilizer is absorbed and spread over the particle surface. It creates a protective membrane which prevents coalescence of the particles during collision. In this situation, the polymer particles do not coalesce if the repulsive forces prevail over the attractive forces. Collision of these stable particles are accompanied only by overlap of their surface layers; in the zone of mutual overlap the osmotic pressure increases (owing to the flow of water into these regions), which gradually separated the particles one from another. The rate of separation of the suspension particles, whose

surface layers mutually overlap after collision, is not only a function of the osmotic pressure but also of the forces of mutual interaction of the stabilizer molecules and of interactions between the stabilizer molecules and polymer or monomer

Colloidal stability is important in suspension polymerization. For colloidal suspension to be stable, it is essential to provide a repulsive barrier between the particles so that the London and van der Waals attractive energies do not exceed the energy of thermal motion. Suspensions of neutral colloidal particles flocculate rapidly as a result of the long-range attractive forces. In particle suspensions, the total potential is the sum of the energies of attraction and repulsion. When the potential energy maximum is quite large as compared to the thermal energy, then the corresponding suspensions show long-term stability.

In order to achieve a potential energy maximum, it is necessary to provide a repulsive potential energy between the particles. In suspension polymerization, this is achieved mainly by steric stabilization. If the stabilizer has ionic groups, then electrostatic stabilization can take place.

Interparticle repulsion due to Coulombic forces between two particles is a function of the dielectric constant of the continuous medium. The surface potential develops by adsorption of the relevant ions. If the particles approach a point where the attractive forces overcome the electrostatic forces, then flocculation will occur.

The emulsified monomer droplets function as small block reactors, in which the polymerization takes place via radical homogenous polymerization with the difference that the removal of heat is easily controlled and does not influence the course of polymerization even at high conversions. The aqueous phase surrounding the polymer particles effectively removes the heat of reaction and keeps the temperature constant in the critical phases of the polymerization. The advantages of suspension polymerization also include the low viscosity of the final dispersion over the range of conversions and the use of the cheap nontoxic continuous reaction phase. However, the process has a disadvantage, namely contamination of the final polymer with the stabilizer which, after evaporation, becomes a component of the polymer and adversely affects the product quality. Purification of the product to remove the stabilizer is energetically costly and involves washing of the products with water, organic solvents and drying.

At low conversions, the monomer particles are subject to coalescence, their reverse dispersion into smaller particle size and distribution at this point and finally also the properties of the polymer suspension. The stage of medium conversion is characterized by increased stickiness of the polymer particles and their greater tendency to coalesce. The coalescence of these particles is irreversible: neither addition of extra stabilizer nor more vigorous stirring lead to dispersion of the associates. As the reaction reaches higher conversions, the polymer particles lose their stickiness and are no longer vulnerable to coalescence.

The course of suspension polymerization and the properties of polymer suspension are controlled by the character and intensity of stirring; this affects the average particle size and size distribution and the surface properties of the particles. The rate and duration of stirring enable the preparation of monomer particle size. After the completion of stirring, the particles (in the absence of the stabilizer) rapidly associate into the separating oil phase. Addition of the stabilizer suppresses association of the particles and lowers the rate of coalescence. The size of the final polymer particles depends on the size of the monomer droplet formed by dispersing the oil phase in water in the presence of the stabilizer. The influence of stirring on the mechanism for the formation and stability of the polymer dispersion is rather complex. At lower stirring rates, an increase in the intensity of stirring usually leads to a decrease of the average size of the polymer particles. On exceeding a certain critical rate of stirring, no further increase in the number of particles is observed, but the association of the particles is initiated which causes an increase in particle size. Under these conditions, a large number of smaller particles with a much greater surface area are produced: a higher concentration of stabilizer is needed to stabilize them. If the system does not contain the required amount of stabilizer, the particles coagulate and dispersion is formed with a larger particle size.

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.

Suspension or bead polymerization give relatively large particles of better purity which are simply isolated, e.g., directly by centrifuging or filtering. These suspension polymers find wide application in molding plastics, ion exchange resins, and as flocculating agents.

2.4 Polymer Solubility and Solutions [8]

2.4.1 Typical phase behavior in polymer-solvent systems

At low temperatures, a two-phase system is formed. The dotted tie lines connect the compositions of phase in equilibrium, a solvent-rich (dilute-solution) phase on the left and a polymer-rich (swollen-polymer or gel) phase on the right. As the temperature is raised, the compositions of the phases become more nearly alike, until at the upper critical solution temperature (UCST) they are identical. Above the USCT, the system forms homogeneous (single-phase) solutions across the entire composition range. The location of the phase boundary depends on the molecular weight of the polymer and the interaction between the polymer and solvent.

When we talk about a polymer being soluble in particular solvent, we generally mean that the system lies between it's a lower critical solution temperature (LCST) and USCT; that is, it forms homogeneous solutions over the entire composition range. Keep in mind, however, that homogeneous solutions can still be formed the extremes of the composition range below the UCST and above the LCST.
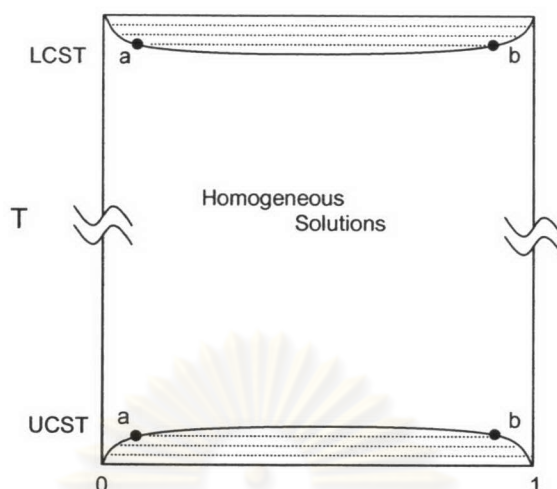
Figure 2.1 Schematic phase diagram for polymer-solvent system: (a) dilute solution phase; (b) swollen polymer or "gel" phase. UCST, upper critical solution temperature; LCST, lower critical solution temperature.[8]

2.4.2 General rules for polymer solubility

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

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 in some cases it has 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 (at least in principle), while item 4 is a rate phenomenon and is governed by the rates of diffusion of polymer and solvent.

2.4.3 The thermodynamic basic of polymer solubility

Consider the process of mixing a pure polymer and a pure solvent at constant pressure and temperature to form a solution:

$$\Delta G = \Delta H - T\Delta S, \qquad (2.17)$$

where
ΔG = the change in Gibbs free energy

ΔH = the change in enthalpy

T = the absolute temperature

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 than in the solid (this might not always be the case with lyotropic liquid-crystal material). The positive product is preceded by a negative sign. Thus, the third ($-T\Delta S$) term in Equation 2.17 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.

One of the things that make polymers unusual is that the entropy change in forming a polymer solution is generally much smaller than that which occurs on dissolution of equivalent masses or volumes of low molecular weight solutes. The reasons for this are illustrated qualitatively on a two-dimensional lattice model in Figure 2.2.

solubility parameters. The value of the solvent at which maximum swelling is observed is taken as the solubility parameter of the polymer (Fig 2.3)

Solubility parameters of solvent mixtures can be readily calculated from

$$\delta_{mix} = \frac{\sum \gamma_i \upsilon_i \delta_i}{\sum \gamma_i \upsilon_i} = \sum \phi_i \delta_i \qquad (2.21)$$

Where γ_i = mole fraction of component i

υ_i = molar volume of component i

ϕ_i = volume fraction of component i

δ_i = solubility parameter of component i

Equation 2.21 has often been used to prepare a series of mixed solvents for establishing the solubility parameter of a polymer as described above. Care must be exercised in this application, however, because what winds up inside the swollen polymer is not necessarily what you mixed up. In general, the crosslinked polymer will preferentially absorb the better (closer δ) solvent component, a phenomenon known as coacervation.

In the absence of specific data on solvents, a group-contribution method is available for estimating both the solubility parameters and molar volumes of liquids.

While the solubility-parameter concept has proved useful, there are unfortunately many exceptions to Equation 2.19. First, regular solution theory which leads to Equation 2.17 has some shortcomings in practice. Second, polymer solubility is too complex for a phenomenon to be described quantitatively with a single parameter. Several techniques have been proposed that supplement solubility parameters with quantitative information on hydrogen bonding and dipole moments. One of the simplest methods is to of these classify solvents into three categories according to their hydrogen-bonding ability (poor, moderate, strong). Three different δ ranges are then listed for each polymer, one for each solvent category. Presumably, a solvent that falls within the δ range for its hydrogen-bonding category will dissolve the polymer.

2.4.5 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:

$$\Delta E_v = \Delta E_d + \Delta E_p + \Delta E_h \tag{2.22}$$

Dividing by the molar volume v gives

$$\frac{\Delta E_v}{v} = \frac{\Delta E_d}{v} + \frac{\Delta E_p}{v} + \frac{\Delta E_h}{v} \tag{2.23}$$

or

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2.24}$$

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

Thus, the solubility parameter δ may be thought of as a vector in a three-dimensional d, p, and h space. Equation 2.23 gives the magnitude of the vector in terms of its components. A solvent, therefore, with given values of $\delta_{p1}, \delta_{d1}, \delta_{h1}$ is represented as a point in space, with δ being the vector from the origin to this point.

A polymer is also characterized by $\delta_{p2}, \delta_{d2}, \delta_{h2}$. 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 $\left(\delta_{p2}, \delta_{d2}, \delta_{h2}\right)$.

Solubility judgments for the determination of R are usually based on visual observation of 0.5 g polymer in 5 cm^3 of solvent at room temperature. Given the concentration and temperature dependence of the phase boundaries in Fig 2.3, this is somewhat arbitrary, but it seems to work out pretty well in practice, probably because the boundaries are fairly "flat" for polymers of reasonable molecular weight.
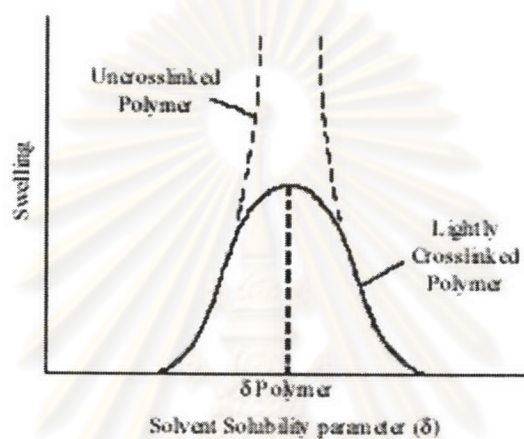

Figure 2.3 Determination of polymer solubility parameter by swelling lightly crosslinked samples in a series of solvent. [8]

The three-dimensional equivalent of Equation 2.20 is obtained by calculating the magnitude of the vector from the center of the polymer sphere $(\delta_{p2}, \delta_{d2}, \delta_{h2})$ to the point representing the solvent $(\delta_{p1}, \delta_{d1}, \delta_{h1})$. If this is less then R, the polymer is deemed soluble:

$$4\left[\left(\delta_{p1} - \delta_{p2}\right)^2 + \left(\delta_{h1} - \delta_{h2}\right)^2 + 4\left(\delta_{d1} - \delta_{d2}\right)^2\right]^{1/2} \langle R \quad \text{for solubility} \tag{2.25}$$

(The factor of 4 arises from the empirical need to double the δ_d scale to achieve a spherical solubility region)
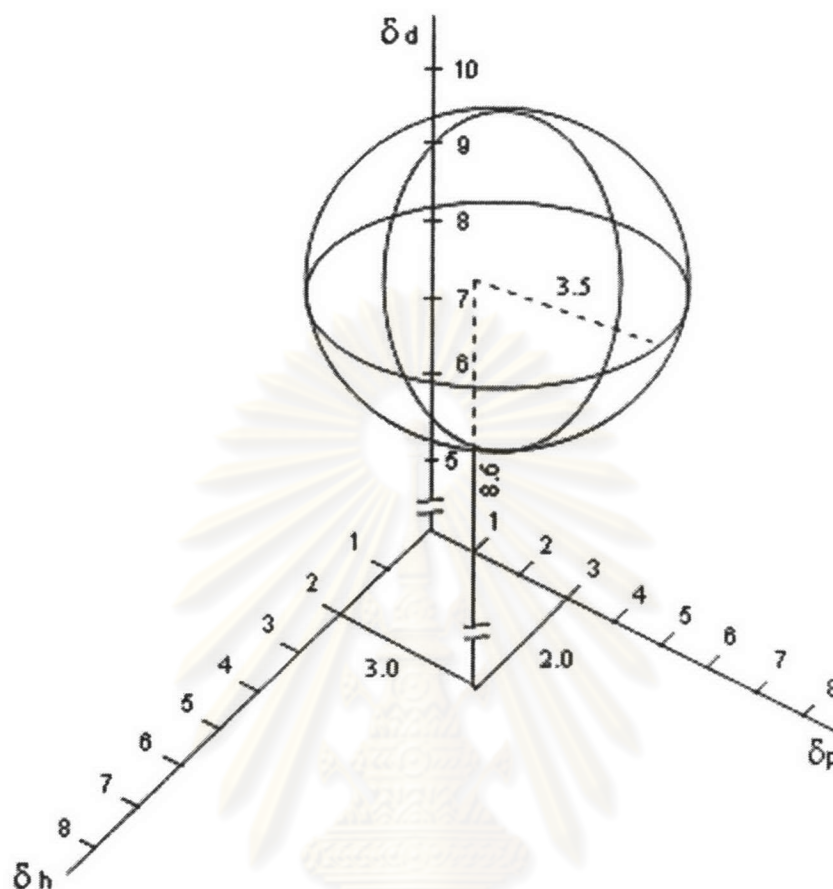
Figure 2.4 The Hansen solubility sphere for polystyrene ($\delta_d = 8.6$, $\delta_p = 3.0$, $\delta_h = 2.0$, R = 3.5). [8]

Figure 2.4 shows the solubility sphere for polystyrene ($\delta_d = 8.6$, $\delta_p = 3.0$, $\delta_h = 2.0$, R = 3.5, all in Hildebrands). Note that parts of the polystyrene sphere lie outside the first octant. The physical significance of these areas is questionable, at best.

The range of δ_d's spanned by typical polymers and solvents is rather small. In practice, therefore, the three-dimensional scheme is often reduced to two dimensions, with polymers and solvents represented on $\delta_h - \delta_p$ coordinates with a polymer solubility circle of radius R.

Values of the individual components δ_h, δ_p and δ_d have been developed from measured δ values, theoretical calculations, studies on model compounds, and plenty of

computer fitting. They are extensively tabulated for solvents. They, along with R, are less readily available for polymers, but have been published. Mixed solvents are handled by weighting the individual δ_j components according to Equation 2.21.

Despites its semi-empirical nature, the three-dimensional solubility parameter has proved of great practical utility, particularly in the paint industry, where the choice of solvents to meet economic, ecological, and safety constraints is of critical importance. It is capable of explaining those cases in which solvent and polymer δ's are almost perfectly matched, yet the polymer won't dissolve (the δ vectors have the same magnitudes, but different directions), or where two nonsolvents can be mixed to form a solvent (the solvent component lie on opposite sides outside the sphere, the mixture within). Inorganic pigments may also be characterized by δ vectors. Pigments whose δ vectors closely match those of a solvent tend to from stable suspensions in that solvent.

2.4.6 The Flory-Huggins theory

Theoretical treatment of polymer solutions was initiated independently and essentially simultaneously by Flory and Huggins in 1942. The Flory-Huggins theory is based on the lattice model shown in Figure 2.2. In the case of the low molecular weight solute, Fig 2.2a, it is assumed that the solute and solvent molecules have roughly the same volumes; each occupies one lattice site. With the polymeric solute, Fig. 2.2b, a segment of the polymer molecule (which corresponds roughly but not necessarily exactly to a repeating unit) has the same volume as a solvent molecule and also occupies one lattice site.

By statistically evaluating the number of arrangements possible on the lattice, Flory and Huggins obtained an expression for the (extensive) configurational entropy change (that due to geometry alone), ΔS^* in forming a solution from n_1 moles of solvent and n_2 moles of solute:

$$\Delta S^* = -R\left(n_1 \ln \phi_1 + n_2 \ln \phi_2\right) \tag{2.26}$$

where the ϕ's are volume fractions,

$$\phi_1 = \frac{x_1 n_1}{x_1 n_1 + x_2 n_2} \qquad (2.27)$$

$$\phi_2 = \frac{x_2 n_2}{x_1 n_1 + x_2 n_2} \qquad (2.28)$$

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 Equation 2.25 for each individual species in the distribution, but x2 is usually taken as $\overline{x_n}$, the number-average degree of polymerization, with little error. (Writing the volume fractions in terms of moles implies equal molar segmental volumes.) Note that while ϕ_1, ϕ_2, and n_1 are the same in Figures. 2.2a and 2.2b, $n_2 = 20$ molecules for the monomeric solute, but only 1 molecule for the polymeric solute.

An expression for the (extensive) enthalpy of mixing, ΔH was obtained by considering the change in adjacent-neighbor (molecules or segments) interactions on the lattice, specifically the replacement of [1, 1] and [2, 2] interactions with [1, 2] interactions upon mixing:

$$\Delta H = RT \chi \phi_2 n_1 x_1 \qquad (2.29)$$

where χ is the Flory-Huggins interaction parameter. Initially, χ was interpreted as the enthalpy of interaction per mole of solvent divided by RT. By equating (2.15) and (2.28) (keeping in mind that the enthalpy in (2.15) is based on a unit volume of solution, while that in (2.28) is an extensive quantity) and making use of (2.27a), it may be shown that the Flory-Huggins parameter and solubility parameters are related by

$$\chi = \frac{v(\delta_1 - \delta_2)^2}{RT} \qquad (2.30)$$

where v is the molar segmental volume of species 1 and 2 (assumed to be the same). For the dissolution of a polymer in a monomeric solvent, v is taken as the molar

volume of the solvent, v_1. From our knowledge of solubility parameters, we see that Equation 2.29 predicts $\chi \geq 0$. Actually, negative values have been observed.

If it is assumed that the entropy of solution is entirely configurational, substitution of Equations 2.27 and 2.28 into Equation 2.16 gives

$$\Delta G = RT\left(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi \phi_2 n_1 x_1\right) \tag{2.31}$$

Again, for the usual monomeric solvent, $x_1 = 1$. For a polydisperse solute, the middle term in the right side of Equation 2.30 must be replaced by a summation over all the solute species; however, treatment as a single solute with $x_2 = \overline{x_n}$ usually suffices.

In term of the Flory-Huggins theory, the criterion for complete solubility of a high molecular weight polymer across the composition range is

$$\chi \leq 0.5 \quad \text{for solubility} \tag{2.32}$$

It is now recognized that there is an interactive as well as a configurational contribution to the entropy of solution. That is also included in the χ term, so χ is now considered to be a ΔG (rather then strictly a ΔH) of interaction per mole of solvent divided by RT. The first two terms on the right of Equation 2.30 therefore represent the configurational entropy contribution to ΔG, while the third term is the interaction contribution and includes both enthalpy and entropy effects.

The Flory-Huggins theory has been used extensively to describe phase equilibria in polymer system. It can, for example, qualitatively describe the lower phase boundary (UCST) in Fig. 2.1, though it rarely gives a good quantitative fit of experimental data. Partial differentiation of Equation 2.31 with respect to n_1 (keeping in mind that ϕ_1 and ϕ_2 are functions of n_1) gives the chemical potential of solvent. This is, of course, a key quantity in phase equilibrium, and also makes χ experimentally accessible. Further development is beyond the scope of this chapter, but the subject is well treated in standard works on polymer solutions.

The limitations of the Flory-Huggins theory have been recognized for a long time. It can not predict an LCST (Fig. 2.1). It is perhaps not surprising that χ depends on temperature, but it unfortunately turns out to be a function of concentration and molecular weight as well, limiting practical application of the theory. These deficiencies are thought to arise because the theory assumes no volume change upon mixing and the statistical analysis on which it is based is not valid for very dilute solutions, particularly in poor solvents. There has been considerable subsequent work done to correct these deficiencies and extend lattice-type theories.

Experimental values for χ have been tabulated for a number of polymer-solvent systems, both single values and even as a function of composition. They may be used with Equation 2.31 to predict solubility.

2.5 The Flory-Rehner equation [8]

The equilibrium swelling theory of Flory and Rehner treats simple polymer networks in the presence of small molecules. The theory considers forces arising from three sources:

1. The entropy change caused by mixing polymer and solvent. The entropy change from this source is positive and favors swelling.

2. The entropy change caused by reduction in numbers of possible chain conformations on swelling. The entropy change from this source is negative and opposes swelling.

3. The heat of mixing of polymer and solvent, which may be positive, negative, or zero. Usually, it is slightly positive, opposing mixing.

The Flory-Rehner equation may be written

$$-\left[\ln(1-v_2) + v_2 + \chi_1 v_2^2\right] = V_1 n \left[v_2^{1/3} - \frac{v_2}{2}\right] \tag{2.33}$$

where v_2 is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent, and χ_1 is the Flory-Huggins polymer-solvent dimensionless

interaction term. This theory, of course, is also related to the thermodynamics of solutions. As a rubber elasticity phenomenon, it is an extension in three dimensions.

The value of equation (2.32) here lies in its complementary determination of the quantity n. This equation determines the number of elastically active chains per unit volume. By measuring the equilibrium swelling behavior of an elastomer, its modulus may be predicted. Vice versa, by measuring its modulus, the swelling behavior in any solvent may be predicted.

Generally, values from modulus determinations are somewhat higher, because physical cross-links tend to count more in the generally less relaxed mechanical measurements than in the closer-to-equilibrium swelling data. However, agreement is usually within a factor of 2, providing significant interplay between swelling and modulus calculations.

Simple elastomers may swell a factor of 4 or 5 or so, leading to a quantitative determination of n. However, several factors need to be considered before the final numerical result is accepted:

1. The front-factor, not explicitly stated in the Flory-Rehner equation, may be significantly different from unity.

2. While step polymerization methods lead to more or less statistical networks and good agreement with theory, addition polymerization and vulcanization non-uniformities lead to networks that may swell as much as 20% less than theoretically predicted.

2.6 Cross-links in gels [10]

Let us consider a polymeric network that contains solvent, usually called a polymeric gel. There are several types of gels. A previously cross-linked polymer subsequently swollen in a solvent follows the Flory-Rehner equation. If the network was formed in the solvent so that the chains are relaxed, the Flory-Rehner equation will not be followed, but rubber elasticity theory can still be used to count the active network segments.

Gels may be prepared using either chemical or physical cross-links. Physical crosslinks in gels may involve dipole-dipole interactions, traces of crystallinity, multiple

helices; and so on and thus vary greatly with the number and strength of the bonds. The number of physical crosslinks present in a given system depends on time, pressure, and temperature. Many such gels are thermoreversible; that is, the bonds break at elevated temperature and reform at lower temperatures.

Thermoreversible gels may be bonded at single points, called point crosslinks; junction zones, where the chains interact over a portion of their length, in the from of fringe micelles (see Figure 2.5)

Gelatin has the junction zone type of cross-links, where the chains form multiple helices. Natural collagen is in the form of a triple helix. In hot aqueous solution, the denatured protein forms random coils. The helix–coil transition is at about 40°C at about 0.5% concentration, as commonly in foods. Under these conditions, gelatin forms either double or triple helices, a subject of current research. The critical nucleation length is about 20-50 peptide (mer) units, the most important interactions being among praline, hydroxyproline, and glycine.
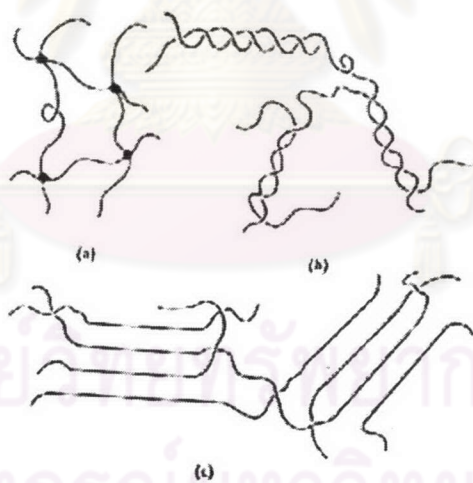

Figure 2.5 Type of thermoreversible cross-links: (a) point cross-links, (b) junction zones and (c) fringed micelles. [10]

Gels sometimes undergo the phenomenon known as syneresis, where the solvent is exuded from the gel. Two types of syneresis are distinguishable: the χ-type, where the polymer phase separates from the solvent due to poor thermodynamics of mixing.

Spinodal decomposition is common in such circumstances. Such gels may be turbid in appearance. The *n*-type, which exudes solvent because of increasing cross-link density. The polymeric gel still forms one phase with the solvent, but its equilibrium swelling level decreases. Such gels remain clear. In both cases, various amounts of fluid surround the gel.

2.7 Fickian diffusion [9]

Diffusion is the process by which concentration gradients in a solution spontaneously decrease until a uniform, homogenous distribution is obtained.

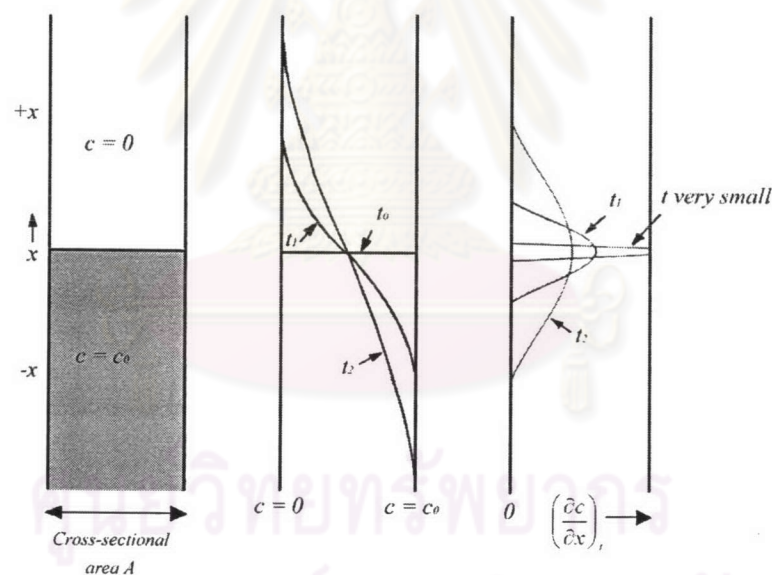Imagine a container with a solution in the lower region and the pure solvent on top, as shown in Figure 2.6.

Figure 2.6 Imagine a container with a solution in the lower region and the pure solvent on top (a) diffusion of a solute from a cell of uniform cross section into the pure solvent component. (b) Plots of versus x. At t = 0 (the t0 curve), the boundary between the solution and solvent component is infinitely sharp. (c) Plots of concentration gradient $(\partial c / \partial x)_t$ versus x at various times t after diffusion have begun. At t = 0, the gradient is a vertical line of infinite height and centered at x = 0. [9]

Initially, there is a sharp boundary between the solution and the solvent. As time progresses, solute molecules gradually move upward by diffusion. This process continues until the entire system becomes homogeneous. In 1855, Fick studied the diffusion phenomenon and found that the flux (J), that is, the net amount of solute that diffuses through unit area per unit time, is proportional to the concentration gradient. Expressing this mathematically in one dimension along the x axis, we write

$$J \propto -\left(\frac{\partial c}{\partial x}\right)_t \qquad (2.34)$$

$$= -D\left(\frac{\partial c}{\partial x}\right)_t \qquad (2.35)$$

Equation 2.35 is known as *Fick's first law of diffusion* in one dimension. The quantity $(\partial c / \partial x)_t$ is the concentration gradient of the diffusing substance (c in mol liter^{-1}) after time t of diffusion, and D is the diffusion coefficient of the diffusing substance in the medium concerned. The negative sign indicates that the diffusion proceeds from higher to lower concentration since the concentration gradient is negative in the direction of diffusion. Thus the flux is a positive quantity. The units of D are cm^{2}S^{-1} (CGS units) or m^{2}s^{-1} (SI units).

Let us investigate the diffusion process in a little more detail. A question of importance is: What is the change of concentration with time at a given point along the *x*-axis? Consider a volume element *Adx* (where *A* is the area of cross section) shown in Figure 2.7.
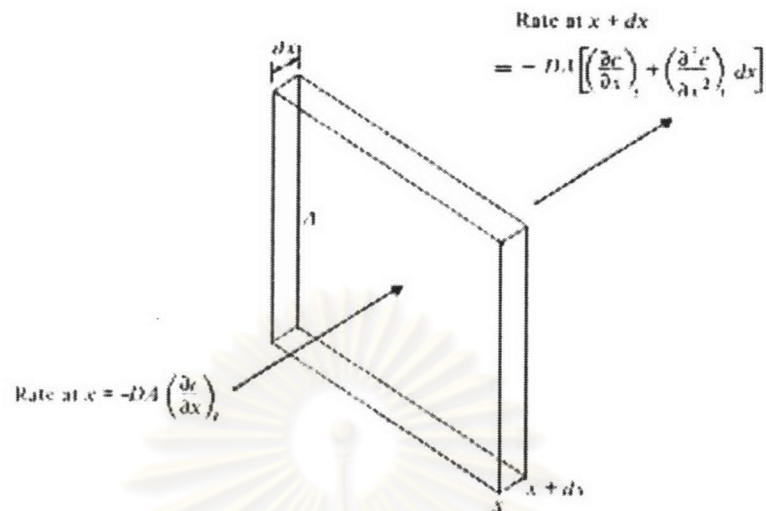
Figure 2.7 Rate of accumulation of solute in a volume element Adx during a diffusion processes. [9]

At distance x measured from the original boundary, the rate of solute molecules entering the volume element is $-DA(\partial c/\partial x)_t$. Since the rate at which the concentration gradient changes with x is given by

$$\frac{\partial}{\partial x}\left(\frac{\partial c}{\partial x}\right)_t = \left(\frac{\partial^2 c}{\partial x^2}\right)_t \quad (2.36)$$

The rate of solute molecules leaving the volume element, after having traveled distance dx, is

$$-DA\left(\frac{\partial c}{\partial x}\right)_t - DA\left(\frac{\partial^2 c}{\partial x^2}\right)_t dx = -DA\left[\left(\frac{\partial c}{\partial x}\right)_t + \left(\frac{\partial^2 c}{\partial x^2}\right)_t dx\right] \quad (2.37)$$

Thus the rate of accumulation of solute in the volume element is the difference of the foregoing two quantities:

Rate of accumulation of solute in the volume element = Rate of solute entering the volume element – Rate of solute leaving the volume element

$$= -DA\left(\frac{\partial c}{\partial x}\right)_t + DA\left[\left(\frac{\partial c}{\partial x}\right)_t + \left(\frac{\partial^2 c}{\partial x^2}\right)_t dx\right]$$

$$= DA\left(\frac{\partial^2 c}{\partial x^2}\right)_t dx$$

Now, there is another way of arriving at an expression for the rate of accumulation. As time goes on, the concentration of solute in the volume element is steadily increasing as a result of diffusion. The rate of this increase is given by the product of the volume element and the change of concentration with time, that is, $(\partial c / \partial t)_x (Adx)$. Equating these two rates of solute accumulation, we obtain

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t \qquad (2.38)$$

This equation is known as *Fick's second law of diffusion*. It says that the change of concentration with time at a certain distance x from the original is equal to the product of diffusion coefficient and the change of concentration gradient in the direction of x at time t.

2.8 Literature Review

The crosslinked copolymer has been developed in many chemical classes such as poly(styrene-co-divinylbenzene), poly(isobutyl methacrylate) and poly(styrene-co-acrylate). The functional polymer as acrylate or methacrylate is interesting because it has many useful applications in many fields. Many researchers tried to develop this type of materials as shown below:

Rabelo and Coutinho [11] studied the effect of the solvent power of pure diluents on the porous structure and swelling properties of styrene-divinylbenzene copolymer. In a general way, the three-dimensional solubility parameter was a better predictor than the Hildebrand solubility parameter. It was found that the accessibility of polymer surfaces

depended not only on the fixed pore volume but also on the elasticity of internuclear chains.

Rabelo and Coutinho [12] investigated the influence of binary mixtures of heptane with different diluent on the porous structure of styrene-divinylbenzene (Sty-DVB) copolymers. It was found that the porosity produced by the diluent mixtures depended not only on the affinity of each diluent for the copolymer but also on the interaction of the diluent molecules with themselves. 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 chains.

Rabelo and Coutinho [13] investigated the influence of binary mixtures of alcohols with different diluents on the porous structure of styrene-divinylbenzene (Sty-DVB) copolymers. Two series of binary mixtures were tested: one with isoamyl alcohol and another with benzyl alcohol. For the systems containing isoamyl alcohol, the hydrogen bonds between alcohol and polar solvent molecules exerted strong precipitating effects. Copolymers prepared with the polar solvent and isoamyl alcohol presented higher porosities than the copolymers obtained in presence of the nonpolar solvent and isoamyl alcohol. Binary mixtures with isoamyl alcohol produced more porous and rigid networks than with benzyl alcohol.

Kiatkamjornwong, et al [1] studied the effect of diluent and nitrogen gas flowrate on organic solvent absorption and desorption properties of styrene-divinylbenzene beads. Large polymer beads could be prepared by a new technique of seeded suspension polymerization. It was found that the beads prepared with toluene as a good solvent had larger pore sizes than those from a nonsolvent such as heptane, which produced many tiny pores. The nitrogen gas flowrate affected the beads properties, when increasing the nitrogen gas flowrate for the good solvent medium (toluene), the swelling ratio decreases, but swelling ratio increases in the poor solvent medium (heptane). The flow of nitrogen gas helps material circulation when the viscosity of the medium is low. When the viscosity is high at the gel point, the nitrogen gas is trapped within the bead. The more the gas is trapped, the higher the porosity.

Kuroda and Osawa [2] carried out the suspension polymerization of glycidyl methacrylate (GMA) with divinylbenzene (DVB) in the presence of various diluents to act as precipitants. The macroporous copolymer beads which have large specific surface area and pore volume could be prepared in the presence of an alcohol such as 4-methyl-2-pentanol as a diluent. While many cracks were formed in the copolymer beads when a conventional plasticizer for polymers was used and smooth skin layers were formed on the surface of the beads in the presence of a hydrocarbon. It was found that the skin layer was formed when the interfacial tension between diluent and continuous phase is large than that between monomers and continuous phase.

Jang and Kim [3] synthesized the copolymer of styrene with 2-ethylhexyl (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA) and stearyl acrylate (SA) by suspension polymerization. The styrene-acrylate (EHA, LA, LMA and SA) copolymers were synthesized with and without a crosslinking agent of divinylbenzene. The glass transition temperature (Tg) of the styrene-acrylate copolymers could be controlled by crosslinking density. At a low crosslinking, Tg was increased due to reduced segmental mobility. At a high crosslinking, the T_g was increased due to changing of chemical structure to network structure. Acrylate monomers often introduced branching or crosslinking to the copolymer.

Jang and Kim [4] synthesized the copolymer of styrene with 2-ethylhexyl (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA) and stearyl acrylate (SA) by suspension polymerization. Crosslinked copolymers were evaluated by swelling properties for oil-absorbency application. The oil absorbency was influenced mainly by the degree of crosslinking and hydrophobicity of the copolymer unit. The copolymer with a longer alkyl acrylate had higher oil absorbency in the order of stearyl acrylate (SA) > lauryl acrylate (LA) > 2-ethylhexyl acrylate (EHA). The oil absorbency of the lauryl methacrylate (LMA) copolymer was higher than that of the LA copolymer.

Zhou et al [5] prepared the oil-absorptivity of crosslinked polymers containing stearyl methacrylate, 4-t-butylstyrene (tBS), and divinylbenzene. The oil-absorptivity of the crosslinked polymer poly[(stearyl methacrylate)-co-divinylbenzene] [CP(SMA-co-DVB)] and CP(SMA-co-DVB)/poly(t-butylstyrene-co-divinylbenzene) IPN decreased with increasing concentrations of DVB and tBS, respectively. The highest oil-

absorptivity of CP(SMA-co-DVB) and the IPN(PtBS : 25%) were 615 % and 330%, respectively. The toluene absorptivity of the synthesized polymers decreased in following order: CP(tBS-co-DVB) > CP(SMA-co-DVB) > IPN(PtBS : 25%) > IPN(PtBS : 50%) > IPN(PtBS : 75%) at immersion above 60 min.

Okubo *et al* [14] studied the suspension polymerizations of divinylbenzene/toluene droplets dissolved in different kinds of methacrylate and acrylate homopolymers. Hollow polymer particles were produced not by high polarity polymers but with low polarity polymers. The result indicated that the preferential adsorption of the homopolymers having high polarity at the interface of the droplets depressed the formation of the hollow structure. A minimum polymer concentration was necessary to produce hollow particles.

Aykurt *et al* [15] prepared copolymer beads of methyl methacrylate(MMA) and ethylene glycol dimethacrylate(EGDMA) by suspension polymerization. A mixed solvent, composed of two different solvents, namely toluene and cyclohexane, was used as the diluent in the polymerization medium. The porosity and pore size increased gradually with the increase of cyclohexane content. Cyclohexane, the bad solvent for copolymer, in the polymerization medium caused to form greater pores due to the phase separation between the copolymer and the diluent. If the solvent used to extract the residual monomer and diluent from the pores is the good solvent for the copolymer, it may cause the walls of the pore to collapse.

Kangwansupamonkon *et al* [16] studied the effect of the third acrylated vinyl comonomer on absorption and desorption properties of styrene-divinylbenzene-alkyl acrylate terpolymers, imbibing solvent on a water surface. The third copolymers used in this work are n-butyl acrylate and 2-ethyl hexyl acrylate. The porous structure increased with increasing acrylated vinyl comonomer content. The beads can absorb organic solvents having solubility parameters of 14.9-20.9 $(MPa)^{1/2}$ and can be also used to absorb many mixed solvents or petroleum on a water surface. The beads could be used to absorb and desorb a Tol/Hep mixture for many cycles. Increase in the number of carbon atoms of the acrylated vinyl monomer enhances the absorption of the aliphatic hydrocarbon solvents of hexane, heptane and cyclohexane.

Ishiza and Shiratori [17] synthesized the polymer microspheres by dispersion copolymerization of divinylbenzene with vinylbenzyl-terminated poly(t-butyl methacrylate) macromonomers in the nonaqueous media (methanol and acetonitrile). The particle diameter increased gradually with an increase of the DVB concentration in methanol or acetonitrile. The particle size distribution was very narrow. The PBMA similar to the macromonomer acted not only as a comonomer but also as a stabilizer. The particle diameters obtained in acetonitrile were smaller than those obtained in methanol. Thus, we observed a tendency in which the more the solubility of the PBMA macromonomer in the media became, the smaller the particle size was obtained.

Bodugoz and Guven [18] synthesized the nonporous poly(isobutyl methacrylate) microspheres by suspension polymerization technique and investigated their swelling properties. Swelling behaviors and network properties were found to be dependent on the diameter, crosslinking density of the sphere, and crosslinking agent and solvent. The results of this study indicate that the crosslinked PiBMA microsphere can swell in gasoline very well and retains a high ratio (1500% of its volume) of gasoline in their structure.

Kangwansupamonkon et al [19] studied the effects of the crosslinking agent and diluents on bead properties of styrene-divinylbenzene copolymer by suspension polymerization. It was found that at a concentration divinylbenzene of the range of 3-15 wt% was used to produce spherical imbiber beads. When the divinylbenzene concentration was increased, the average size decreased slightly and the particle shape was unchanged. A mixture of the good and poor solvent was used to control the phase separation and the pore formation in the beads. The imbiber beads obtained in the range of 940-1050 kg m^{-3} and the diffusion coefficient in the range of 2.9×10^{-6} to 4.52×10^{-5} cm^{2}s^{-1}, yielding bead swelling ratios 4 to 12.3.

Kiatkamjornwong et al [20] studied and synthesized acrylate core/shell imbiber beads by seed suspension copolymerization. In the one-stage suspension copolymerization, the polymer beads had a heterogeneous structure without a specific morphology, whereas the polymer beads from the seeded suspension polymerization distinguished the shell separated from the core of corresponding polymers. The more hydrophilic polymer is distributed preferentially in the shell, while the more hydrophobic

ones reside in the core. The beads of PS/PMMA, PMMA/PS and P(2-EHA)-PS were able to absorb aromatic hydrocarbon solvents better then aliphatic hydrocarbon solvents.

Gawdzik and Maciejewska [21] studied the influence of diluent composition on the porous structure of methacrylate copolymers by suspension polymerization. The results indicate that the increase of good solvent (toluene) concentration has a similar impact on the porous structure of copolymers obtained from two tetra-functional monomers (DMGE-DVB and PDM-DVB) and quite a different influence on the structure of the ST-DVB copolymer synthesized from two- and tetra-functional monomers.