CHAPTER SEVEN

POLYMER SOLUTIONS

A. CRITERIA FOR POLYMER SOLUBILITY

The Solution Process. Dissolving a polymer is a slow process that occurs in two stages. First, solvent molecules slowly diffuse into the polymer to produce a swollen gel. This may be all that happens—if, for example, the polymer–polymer intermolecular forces are high because of crosslinking, crystallinity, or strong hydrogen bonding. But if these forces can be overcome by the introduction of strong polymer–solvent interactions, the second stage of solution can take place. Here the gel gradually disintegrates into a true solution. Only this stage can be materially speeded by agitation. Even so, the solution process can be quite slow (days or weeks) for materials of very high molecular weight.

Polymer Texture and Solubility. Solubility relations in polymer systems are more complex than those among low-molecular-weight compounds, because of the size differences between polymer and solvent molecules, the viscosity of the system, and the effects of the texture and molecular weight of the polymer. In turn, the presence or absence of solubility as conditions (such as the nature of the solvent, or the temperature) are varied can give much information about the polymer; this is in fact the topic of most of this chapter.

From what has already been said, it is clear that the topology of the polymer is highly important in determining its solubility. Crosslinked polymers do not dissolve, but only swell if indeed they interact with the solvent at all. In part, at least, the degree of this interaction is determined by the extent of crosslinking: Lightly crosslinked rubbers swell extensively in solvents in which the unvulcanized material would dissolve, but hard rubbers, like many thermosetting resins, may not swell appreciably in contact with any solvent.

The absence of solubility does not imply crosslinking, however. Other features may give rise to sufficiently high intermolecular forces to prevent solubility. The presence of crystallinity is the common example. Many crystalline polymers, particularly nonpolar ones, do not dissolve except at temperatures near their crystalline melting points. Because crystallinity decreases as the melting point is approached (Chapter 10) and the melting point is itself depressed by the presence of the solvent, solubility can often be achieved at temperatures significantly below the melting point. Thus linear polyethylene, with crystalline melting point $T_m = 135°\text{C}$, is soluble in many liquids at temperatures above 100°C, while even polytetrafluoroethylene, $T_m = 325°\text{C}$, is soluble in some of the few liquids that exist above 300°C. More polar crystalline polymers, such as 66-nylon, $T_m = 265°\text{C}$, can dissolve at room temperature in solvents that interact strongly with them (for example, to form hydrogen bonds).

There is little quantitative information about the influence of branching on solubility; in general, branched species appear to be more readily soluble than their linear counterparts of the same chemical type and molecular weight.

Of all these systems, the theory of solubility, based on the thermodynamics of polymer solutions, is highly developed only for linear polymers in the absence of crystallinity. This theory is described in Sections *C* and *D*. Here the chemical nature of the polymer is by far the most important determinant of solubility, as is elucidated in the remainder of this section. The influence of molecular weight (within the polymer range) is far less, but it is of great importance to fractionation processes (Sections *D* and *E*), which yield information about the distribution of molecular weights in polymer samples.

Solubility Parameters. Solubility occurs when the free energy of mixing

$$\Delta G = \Delta H - T\Delta S$$

is negative. It was long thought that the entropy of mixing ΔS was always positive, and therefore the sign of ΔG was determined by the sign and magnitude of the heat of mixing ΔH. For reasonably nonpolar molecules and in the absence of hydrogen bonding, ΔH is positive and was assumed to be the same as that derived for the mixing of small molecules. For this case, the heat of mixing per unit volume can be approximated (Hildebrand 1950) as

$$\Delta H = v_1 v_2 (\delta_1 - \delta_2)^2$$

where v is volume fraction and subscripts 1 and 2 refer to solvent and polymer, respectively. The quantity δ^2 is the cohesive energy density or, for small molecules, the energy of vaporization per unit volume. The quantity δ is known as the *solubility parameter*. (This expression for the heat of mixing is one of several alternatives used in theories of the thermodynamics of polymer solutions; in Section *C*, ΔH is written in a different but equivalent way.)

The value of the solubility-parameter approach is that δ can be calculated for both polymer and solvent. As a first approximation, and in the absence of strong interactions such as hydrogen bonding, solubility can be expected if $\delta_1 - \delta_2$ is less than 3.5–4.0, but not if it is appreciably larger.

This approach to polymer solubility, pioneered by Burrell (1955), has been extensively used, particularly in the paint industry. A few typical values of δ_1 and δ_2 are given in Table 7-1; for polymers, they are the square roots of the cohesive-energy densities of Table 1-4. Extensive tabulations have been published (Burrell 1975, Hoy 1970). Perhaps the easiest way to determine δ_2 for a polymer of known structure is by the use of the molar-attraction constants E of Table 7-2,

$$\delta_2 = \frac{\rho \Sigma E}{M}$$

where values of E are summed over the structural configuration of the repeating unit in the polymer chain, with repeat molecular weight M and density ρ.

The original solubility-parameter approach was developed for nonpolar systems. Modifications to include polarity and hydrogen bonding have led to three-dimensional solubility-parameter schemes, which lack the simplicity of the single-parameter method but are more widely applicable. Despite its shortcomings, the concept is nevertheless still extremely useful and should not be abandoned without test.

In contrast to the above considerations of the thermodynamics of dissolution of polymers, the rate of this step depends primarily on how rapidly the polymer and the solvent diffuse into one another (Ueberreiter 1962, Asmussen 1962). Solvents that promote rapid solubility are usually small, compact molecules, but these kinetically good solvents need not be thermodynamically good as well. Mixtures of a kinetically good and a thermodynamically good liquid are often very powerful and rapid polymer solvents.

TABLE 7-1. Typical Values of the Solubility Parameter δ for Some Common Polymers and Solvents[a]

Solvent	$\delta_1[(\mathrm{J/cm^3})^{1/2}]$	Polymer	$\delta_2[(\mathrm{J/cm^3})^{1/2}]$
n-Hexane	14.8	Polytetrafluoroethylene	12.7
Carbon tetrachloride	17.6	Poly(dimethyl siloxane)	14.9
		Polyethylene	16.2
Toluene	18.3	Polypropylene	16.6
2-Butanone	18.5	Polybutadiene	17.6
Benzene	18.7	Polystyrene	17.6
Cyclohexanone	19.0	Poly(methyl methacrylate)	18.6
Styrene	19.0	Poly(vinyl chloride)	19.4
Chlorobenzene	19.4	Poly(vinyl acetate)	21.7
Acetone	19.9	Poly(ethylene terephthalate)	21.9
Tetrahydrofuran	20.3		
Methanol	29.7	66-Nylon	27.8
Water	47.9	Polyacrylonitrile	31.5

[a] Collins (1973).

TABLE 7-2. Molar Attraction Constants E^a

Group	E [(J-cm^3)$^{1/2}$/mole]	Group	E [(J-cm^3)$^{1/2}$/mole]
$—CH_3$	303	NH_2	463
$—CH_2—$	269	—NH—	368
$>$CH—	176	—N—	125
$>$C$<$	65	C≡N	725
$CH_2=$	259	NCO	733
—CH=	249	—S—	429
$>$C=	173	Cl_2	701
—CH=aromatic	239	Cl primary	419
$>$C=aromatic	200	Cl secondary	425
—O—ether, acetal	235	Cl aromatic	329
—O—epoxide	360	F	84
—COO—	668	Conjugation	47
$>$C=O	538	cis	−14
—CHO	599	trans	−28
$(CO)_2O$	1159	Six-membered ring	−48
—OH→	462	ortho	−19
OH aromatic	350	meta	−13
—H acidic dimer	−103	para	−82

[a] Hoy (1970).

GENERAL REFERENCES

Hildebrand 1950; Gardon 1965; Hoy 1970; ASTM D3132; Burrell 1975; Morawetz 1975, Chapter 2; Olabisi 1979, Chapter 2.3; Snyder 1980.

B. CONFORMATIONS OF DISSOLVED POLYMER CHAINS

As specified in Chapter 1, those arrangements of the polymer chain differing by reason of rotations about single bonds are termed *conformations*.† In solution, a polymer molecule is a randomly coiling mass most of whose conformations occupy many times the volume of its segments alone. The average density of segments within a dissolved polymer molecule is of the order of 10^{-4}–10^{-5} g/cm^3. The size of the molecular coil is very much influenced by the polymer–solvent interaction forces. In a thermodynamically "good" solvent, where polymer–solvent contacts

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†Here we differ from some authorities, notably Flory (1969), who prefers the use, well established in statistical mechanics, of the term *configuration* here. We follow the convention of organic chemistry in which configuration designates stereochemical arrangement (see Chapter 10A).

solvent: A solvent for which α is large is said to be a thermodynamically "good" solvent for that polymer, and vice versa.

In a sufficiently poor solvent, or at a sufficiently low temperature (since solvent power and α vary with the temperature), it is possible to achieve the condition $\alpha = 1$, where the chain attains its unperturbed dimensions. This special point is called the *Flory temperature* Θ; a solvent used at $T = \Theta$ is called a Θ *solvent*. The calculation of α and Θ and their relation to thermodynamic quantities is treated in Section *C*.

Neutron-scattering experiments (Chapter 8*C*) show that the above considerations apply as well to chain conformations in the melt and the glassy state.

Nonlinear Chains. A branched molecule occupies a smaller volume than a linear one with the same number of segments, that is, the same molecular weight. It is convenient to express this diminution of size as a factor $g = \overline{s^2}$ (branched)/$\overline{s^2}$ (linear), which can be calculated statistically for various degrees and types of branching (Zimm 1949). For random branching, five trifunctional branch points per molecule reduce g to about 0.70. The change in size is the basis of a method to measure branching (Chapter 8*E*).

Billmeyer (1972, 1977) has used a "pop-it" bead model to illustrate the dimensions of polymer chains.

GENERAL REFERENCES

Flory 1953, 1969; Volkenstein 1963; Birshtein 1966; Bovey 1969, 1979, Chapter 3.9; Lowry 1970; Hopfinger 1973; Vollmert 1973, Chapter 32; Morawetz 1975, Chapter 3; Elias 1977, Chapter 4; de Gennes 1979, Chapter 1.

C. THERMODYNAMICS OF POLYMER SOLUTIONS†

The behavior of polymers toward solvents is characteristic and different from that of low-molecular-weight substances. The size and conformations of dissolved polymer molecules require special theoretical treatment to explain their solution properties. Conversely, it is possible to obtain information about the size and shape of polymer molecules from studies of their solution properties.

The first group of properties of interest includes those depending upon equilibrium between two phases, one or both of which is a solution of the polymer. In this section we discuss situations in which one phase is pure solvent, and in Section *D* solubility phenomena in which both phases contain polymer.

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†For reviews of thermodynamics as background to this subject see Hildebrand (1950) and Lewis (1961).

Thermodynamics of Simple Liquid Mixtures

From the condition for equilibrium between two phases may be derived relations such as that for the free energy of dilution of a solution:

$$\Delta G_A = kT \ln \left(\frac{p_A}{p_A{}^0}\right) \tag{7-1}$$

where ΔG is the free energy of dilution resulting from the transfer of one molecule of liquid A from the pure liquid state with vapor pressure $p_A{}^0$ to a large amount of solution with vapor pressure p_A. This expression is written in terms of one of the *colligative properties* of solutions: vapor-pressure lowering, freezing-point depression, boiling-point elevation, and osmotic pressure. The values of these properties cannot be related to the composition of the system by pure thermodynamic reasoning. It is necessary to know the type of variation of one property with concentration; the variation of the others may then be deduced.

Ideal Solutions. In the simplest type of mixing, the molecules of components A and B have roughly the same size and shape and similar force fields. They may then form an *ideal solution*, defined as one in which Raoult's law is obeyed. This law states that the partial vapor pressure of each component in the mixture is proportional to its mole fraction. Therefore

$$p_A = p_A{}^0 \frac{N_A}{N_A + N_B} = p_A{}^0 n_A \tag{7-2}$$

where n denotes mole fraction, and Eq. 7-1, for example, becomes

$$\Delta G_A = kT \ln n_A \tag{7-3}$$

The total free energy of mixing is

$$\begin{aligned} \Delta G &= N_A \, \Delta G_A + N_B \, \Delta G_B \\ &= kT(N_A \ln n_A + N_B \ln n_B) \end{aligned} \tag{7-4}$$

The conditions for ideal mixing imply that the heat of mixing $\Delta H = 0$; that is, the components mix without change in enthalpy. Since $\Delta G = \Delta H - T\,\Delta S$, the entropy of mixing is given by

$$\Delta S = -k(N_A \ln n_A + N_B \ln n_B) \tag{7-5}$$

which is positive for all compositions, so that, by the second law, spontaneous mixing occurs in all proportions.

Other Types of Mixing. In practice, few liquid mixtures obey Raoult's law. Three types of deviations are distinguished:

- a. "Athermal" solutions, in which $\Delta H = 0$ but ΔS is no longer given by Eq. 7-5.
- b. "Regular" solutions, in which ΔS has the ideal value but ΔH is finite.
- c. "Irregular" solutions, in which both ΔH and ΔS deviate from the ideal values.

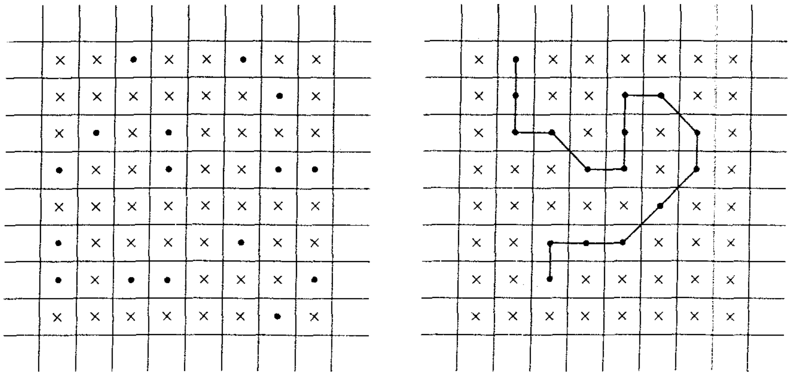
It is usually found in systems of similar-sized molecules that ΔS is nearly ideal when $\Delta H = 0$; therefore athermal solutions are nearly ideal. Many mixtures are found for which ΔH is finite, however. Such cases arise when the intermolecular force fields around the two types of molecule are different. Expressions for the heat of mixing may be derived in terms of the cohesive-energy density of these force fields (Section *A*).

Entropy and Heat of Mixing of Polymer Solutions

Deviations From Ideal Behavior. Polymer solutions invariably exhibit large deviations from Raoult's law, except at extreme dilutions, where ideal behavior is approached as an asymptotic limit. At concentrations above a few percent, deviations from ideality are so great that the ideal law is of little value for predicting or correlating the thermodynamic properties of polymer solutions. Even if the mole fraction is replaced with the volume fraction, in view of the different sizes of the polymer and solvent molecules, there is not a good correlation with the experimental results.

Entropy of Mixing. Deviations from ideality in polymer solutions arise largely from small entropies of mixing. These are not abnormal, but are the natural result of the large difference in molecular size between the two components. They can be interpreted in terms of a simple molecular model. The molecules in the pure liquids and the mixture are assumed to be representable without serious error by a lattice. A two-dimensional representation of such an arrangement for nonpolymer liquids is shown in Fig. 7-5*a*. Whereas the molecules of a pure component can be arranged in only one way on such a lattice, assuming that they cannot be distinguished from one another, the molecules of a mixture of two components can be arranged on a lattice in a large but calculable number of ways, *W*. By the Boltzmann relation, the entropy of mixing $\Delta S = k \ln W$. Equation 7-5 results for the case of molecules that can replace one another indiscriminately on the lattice.

It is assumed that the polymer molecules consist of a large number x of chain segments of equal length, flexibly joined together. Each link occupies one lattice site, giving the arrangement of Fig. 7-5*b*. The solution is assumed to be concentrated enough that the occupied lattice sites are distributed at random rather than lying in well-separated regions of x occupied sites each. It can now be seen qualitatively



(a) (b)

FIG. 7-5. Two-dimensional representation of (a) nonpolymer liquids and (b) a polymer molecule located in the liquid lattice.

why the entropy of mixing of polymer solutions is small compared to that with normal solutes. There are fewer ways in which the same number of lattice sites can be occupied by polymer segments: Fixing one segment at a lattice point severely limits the number of sites available for the adjacent segment. The approximate calculation of W for such a model is due separately to Flory (1942) and Huggins (1942*a,b,c*); their results (which differ only in minor detail) are known as the *Flory–Huggins theory* of polymer solutions. The entropy of mixing is analogous to that given in Eq. 7-5 for simple liquids: For polymer solutions

$$\Delta S = -k(N_1 \ln v_1 + N_2 \ln v_2) \tag{7-6}$$

where subscript 1 denotes the solvent and 2 the polymer, and v_1 and v_2 are *volume fractions* defined as

$$\begin{aligned} v_1 &= \frac{N_1}{N_1 + xN_2} \\ v_2 &= \frac{xN_2}{N_1 + xN_2} \end{aligned} \tag{7-7}$$

Heat and Free Energy of Mixing. The heat of mixing of polymer solutions is analogous to that of ordinary solutions:†

$$\Delta H = \chi_1 kTN_1v_2 \tag{7-8}$$

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†The nomenclature of Flory is used throughout. Huggins writes $\mu_h{}^0$ instead of χ_1, and Hildebrand expresses ΔH in terms of the solubility parameter, as in Section A.

where χ_1 characterizes the interaction energy per solvent molecule divided by kT. Combining Eqs. 7-6 and 7-8 gives the Flory–Huggins expression for the free energy of mixing of a polymer solution with normal heat of mixing:

$$\Delta G = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \tag{7-9}$$

From this expression may be derived many useful relations involving experimentally obtainable quantities. For example, the partial molar free energy of mixing is

$$\Delta \bar{G}_1 = kT\left[\ln(1 - v_2) + \left(1 - \frac{1}{x}\right)v_2 + \chi_1 v_2^2\right] \tag{7-10}$$

and from it is obtained the osmotic pressure

$$\pi = -\frac{kT}{V_1}\left[\ln(1 - v_2) + \left(1 - \frac{1}{x}\right)v_2 + \chi_1 v_2^2\right] \tag{7-11}$$

where V_1 is the molecular volume of the solvent. If the logarithmic term in Eq. 7-11 is expanded and only low powers of v_2 are retained, the following equation for the osmotic pressure is obtained:

$$\pi = \frac{kT}{V_1}\left(\frac{v_2}{x} + (\tfrac{1}{2} - \chi_1)v_2^2 + \cdots\right) \tag{7-12}$$

In expansions of this type the coefficient of v_2^2 is known as the *second virial coefficient* A_2 (see also Chapter 8*B*). Here it is defined as

$$A_2 = \frac{\bar{v}_2^2}{N_0 V_1}(\tfrac{1}{2} - \chi_1) \tag{7-13}$$

where $\bar{v}_2$ is the specific volume of the polymer. This simple treatment does not describe the temperature and molecular-weight dependence of A_2 in good agreement with experiment.

Experimental Results With Polymer Solutions

The first system for which accurate experimental results were compared with the Flory–Huggins theories was that of rubber in benzene (Gee 1946, 1947). Free energies for the system were calculated from vapor-pressure measurements by Eq. 7-1, and heats of solution were measured in a calorimeter. The predicted concentration dependence of the partial molar heat of dilution

$$\Delta \bar{H}_1 = kT\chi_1 v_2^2 \tag{7-14}$$

E. FRACTIONATION OF POLYMERS BY SOLUBILITY

In this section are discussed only the most important and widely practiced techniques for fractionating polymers by solubility differences. Many variations and less useful techniques exist and are reviewed by Hall (1959), Guzmán (1961), and Cantow (1967).

Bulk Fractionation by Nonsolvent Addition

Fractional precipitation in bulk (Kotera 1967) is carried out by adding the nonsolvent to a dilute solution of the polymer until a slight turbidity develops at the temperature of fractionation. To ensure the establishment of equilibrium the mixture may be warmed until it is homogeneous and allowed to cool slowly back to the required temperature, which should thereafter be carefully maintained. The precipitated phase is allowed to settle to a coherent layer, and the supernatant phase is removed. A further increment of precipitant is added and the process repeated. The polymer is isolated from the precipitated phase, which may still be relatively dilute (perhaps 10% polymer).

Refractionation is often used to achieve better separation. A more efficient procedure is to restrict the initial experiments to very dilute solutions, or to refine each initial fraction by a single reprecipitation at higher dilution, returning the unprecipitated polymer from this separation to the main solution before the next fraction is removed.

The solvent and the precipitant should be chosen so that precipitation occurs over a relatively wide range of solvent composition yet is complete before too high a ratio of precipitant to solvent is reached. Other important considerations are the stability and volatility of the liquids and their ability to form a highly swollen, mobile gel phase. Relatively simple equipment, for example, a three-neck flask of several liters capacity (Fig. 7-16), is adequate for bulk precipitation fractionation.

Column Elution

Solvent–Gradient Elution. In elution methods (Elliott 1967), polymer is placed in contact with a series of liquids of gradually increasing solvent power. Species of lowest molecular weight, and thus highest solubility, dissolve in the first liquid, and successively higher molecular-weight fractions in subsequent liquids. To ensure rapid equilibration, the polymer must be present as a very thin film. For convenience, the polymer is often applied to a finely divided substrate such as sand or glass beads, which is subsequently used to pack a column. By the use of mixing vessels, a continuous gradient of solvent–nonsolvent composition can be produced and eluted through the column.

Thermal-Gradient Elution. A modification of the solvent–gradient method utilizes a small temperature gradient from one end to the other of the column, in addition to the gradient of solvent composition (Baker 1956, Porter 1967). The

Techniques of Polymerization

For laboratory and industrial purposes, polymerization is practised by a variety of approaches and techniques that require different design considerations with respect to recipe of polymerization and with respect to physical conditions for the process and process equipment. Generally, polymerizations are studied and practised by four different techniques:

1. Bulk or Mass Polymerization
2. Solution Polymerization
3. Suspension Polymerization and
4. Emulsion Polymerization

Of the four techniques, the last two are essentially heterogeneous polymerization systems containing a large proportion of a non-solvent, usually water, acting as a dispersion medium for the immiscible liquid monomer. Bulk and solution polymerization may be either homogeneous all the way or homogeneous to begin with, but becoming heterogeneous with progress of polymerization due to the polymer formed being insoluble in its monomer (for bulk polymerization) or in the solvent used to dilute the monomer (for solution polymerization). Polymerization of monomers used in the gaseous phase, to begin with, also usually ends up in a heterogeneous system. Most condensation polymerizations are conveniently done by employing bulk or the solution techniques.

1. Bulk Polymerization

Polymerization in bulk, i.e. of undiluted monomer is apparently the most obvious if not the most simple method or technique of polymer synthesis. In terms of polymerization recipe, this obviously provides the most simple system, requiring the use of a very low concentration of an initiator as the only additive in the monomer and that again decomposes and reaches almost a vanishing concentration at the end of the polymerization process. For uncatalyzed vinyl polymerization (using no catalyst or initiator) done thermally, photochemically or otherwise, the polymer produced would be the most pure, free from any (additive) contaminants except probably traces of unreacted monomer.

Vinyl polymerizations are highly exothermic. Again, to obtain polymer at convenient rates, temperature in the range 80–200°C is needed. For dissipation of the heat liberated with progress of polymerization, continuous stirring of the monomer–polymer mixture is essential. But the stirring process and heat dissipation become progressively difficult with conversion due to gain in the medium viscosity due to solubilization or precipitation of polymer in the monomer, more so in the high conversion zones. The autoacceleration or gel effect often makes the problem more acute. If left uncontrolled, excessive rise of temperature at local points known as "hot spots" may lead to discolouration, thermal degradation, branching, development of chain unsaturation or even cross-linking, thus giving rise to irreproducible and often inferior product quality. Because of these problems and disadvantages, bulk polymerization technique finds rather limited use in commercial production of vinyl polymers, e.g. in the production of poly-(methyl methacrylate) as acrylic castings (sheets), and in the making of certain grades of polystyrene, poly (vinyl chloride) and (low density) polyethylenes. The heat dissipation problem in such cases is kept to a minimum and within tolerable limits by two approaches: (i) by carrying out the polymerization to low conversions as in high pressure polymerization of ethylene using narrow but long tubular reactor at temperatures far higher than the melting temperature of the polymer; and (ii) by accomplishing the polymerization in stages—first up to about 20–30% conversion in a stirred reactor at 80–100°C and subsequently allowing the monomer–polymer syrup (viscous mass) poured in an appropriate mould assembly to polymerize to (near) completion at progressively higher temperatures in stages (e.g. preparations of acrylic castings from methyl methacrylate monomer) or allowing the monomer–polymer syrup, called the prepolymer to flow under gravity aided by some positive pressure down a vertical tower reactor with appropriate design for heat transfer or heat dissipation and having a temperature gradient with increasing temperature zones downward for the reaction mixture till it reaches a stage of near-complete conversion (manufacture of polystyrene from styrene monomer).

2. Solution Polymerization

Solution polymerization, i.e. polymerization of a monomer in the presence of a diluent miscible in all proportions with the monomer and usually with the ability to dissolve the polymer is conceived as a means to overcome much of the problems and disadvantages of the bulk method. The solvent reduces the viscosity gain with conversion, allows more efficient agitation or stirring of the medium, thus effecting better heat transfer and heat dissipation and minimization or avoidance of local overheating or heat accumulation. Although the solution technique allows much better control of the process, it has its own demerits. The solution method often requires handling of flammable or hazardous solvents and removal or recovery of the solvent to isolate the polymer after the polymerization is over. Chain transfer to solvent may also pose a problem and purity of the polymer may suffer due to retention of last traces of solvent in the isolated product. Solution polymerization is, however, advantageous if the polymer formed is to be applied in solution by brushing or spraying as in the case of making of coating (lacquer) grade poly (methyl methacrylate) resins from methyl methacrylate and related monomers. In certain cases, the solvents generally used may not be able to dissolve the polymer being formed and so, the system becomes heterogeneous in character with polymer formation (polymerization of acrylonitrile in water or in some common organic solvents).

3. Suspension Polymerization

This is a case of heterogeneous polymerization right from the beginning. This technique is designed to combine the advantages of both the bulk and solution techniques, and it is one of the extensively employed techniques in the mass production of vinyl and related polymers. This technique primarily involves breaking down or dispersion of the liquid monomer mass into separate tiny droplets in a large continuous mass of a nonsolvent commonly referred to as the dispersion or suspension medium, by efficient agitation. Water is invariably used as the suspension medium for all water insoluble monomers because of many advantages that go with it, viz. ready availability at low cost, non-toxic nature, ease of storage and handling without the necessity of recovery, etc. Moreover, the boiling temperature of water is a convenient upper limit for radical vinyl polymerization and in aqueous suspension system the rise in temperature in any location due to exothermic nature of polymerization cannot go beyond the boiling temperature of the medium.

The size of the monomer droplets usually range between 0.1–5 mm in diameter. Continuous agitation is allowed to prevent coalescence of the droplets. Low concentrations of suitable water-soluble polymers such as carboxymethyl cellulose (CMC) or methyl cellulose, poly(vinyl alcohol) (PVA), gelatin, etc., are used to raise the medium viscosity and they play the role of suspension stabilizers particularly in the intermediate stages of conversion when the tendency of the suspended droplets to coalesce together becomes high as the polymer beads become sticky. The water-soluble polymeric stabilizers form a thin layer on the monomer–polymer droplets and stabilization is effected due to repulsion between like charges thus gathered on different droplets. Finely divided suspended clay particles such as kaolin or china clay in small amounts is sometimes used to interfere mechanically with the agglomeration of beads. In suspension polymerization, oil-soluble initiators such as organic peroxides, hydroperoxides or azocompounds are used and thus, each tiny droplet behaves as a miniature bulk polymerization system. At the end of the process, polymers appear in the form of tiny beads or pearls and hence, the process is also known as bead or pearl polymerization. The polymers are filtered, washed profusely with water to remove the water soluble stabilizer as far as practicable, and dried. They, however, usually retain traces of stabilizers besides the residual initiator as contaminants. A typical recipe for suspension polymerization is given in Table 4.6.

Table 4.6. A typical recipe for suspension polymerization of a vinyl monomer

Ingredients	Parts by Weight
Monomer	100
Water	200–400
Initiator (peroxides, azo compounds)	0.2–0.5
Stabilizers (CMC, PVA, gelatin, etc.)	0.02–1.5

4. Emulsion polymerization

a. ***Description of the System*** The use of water as a medium of polymerization by the solution and suspension techniques has been described and discussed above. A special feature about water is that it provides us with a medium characterized by zero chain transfer constant.[27] Another polymerization technique, in which water is used as the medium, is the "emulsion polymerization". Polymers from water-insoluble monomers are usually obtained at faster rates in the aqueous medium by the emulsion technique using water soluble initiators. For efficient making of an emulsion, it is necessary to agitate the monomer–water mixture in presence of a measured dose of an emulsifying agent, i.e. a soap or a detergent. To minimize fluctuations in surface tension of the emulsion as polymerization progresses, small proportion of a surface tension regulator (usually a long chain fatty alcohol such as cetyl alcohol) is used. Small volume of a selected buffer solution is added to minimize or eliminate variations of *pH* of the system due to hydrolysis or other reactions. A chain length regulator or chain transfer agent of high transfer constant, such as dodecyl mercaptan is often used in low concentrations to permit optimum control of polymer chain length. A selected inhibitor, known as a short-stop may be added in small amounts late into the system in order to stop the reaction at a desired extent of polymerization.

A low concentration of a water-soluble polymer such as carboxymethyl cellulose (CMC), poly(vinyl alcohol) (PVA), gelatin, dextrin, etc. is normally used in the emulsion polymerization system not to control the polymerization process with respect to rate or degree of polymerization but with the purpose of obtaining stable emulsion and to prevent emulsion break-down with progress of polymerization; this ingredient is commonly called a protective colloid or (emulsion) stabilizer.

In principle and practice, and as a physical system, emulsion polymerization is distinctly different from suspension polymerization. It is associated with almost all the advantages of suspension polymerization and moreover, using selected efficient redox initiator systems, emulsion polymerization is conveniently accomplished at ambient or slightly elevated temperatures giving very high rates and degrees of polymerization at the same time. The rate and degree of polymerization in the emulsion system can be varied in a large measure independently of each other. The emulsion technique is extensively employed for the polymerization of dienes such as isoprene and butadiene, and vinyl compounds such as vinyl chloride, vinyl acetate, styrene, various acrylates and methacrylates and for making various copolymers of these and other related monomers. A typical recipe for emulsion polymerization of a vinyl monomer is shown in Table 4.7.

Table 4.7. A typical recipe for emulsion polymerization of a vinyl monomer

Component	Parts by Weight
Monomer	100
Water	180–200
Surfactant/Emulsifier (soap/detergent)	4–8
Initiator: (i) $K_2S_2O_8$	0.1–0.25
(ii) $NaHSO_3$	0.1–0.2
Surface tension regulator (octanol/lauryl alcohol)	0.5
Emulsion stabilizer (CMC/PVA, etc.)	0.5–1.5
Buffer solution	5–10
Chain length regulator (a mercaptan)	0.3–0.8

b. ***Principle and Theory*** The surfactant or the emulsifier plays an important role. When soap or detergent is taken in an aqueous system in excess of a low critical concentration, micellar or layered aggregates consisting of 50, 100 or even more soap/detergent molecules are formed. They may be lamellar micelles or spherical micelles with their polar ends (heads) facing water remaining in the outer surface and the long hydrophobic hydrocarbon 'tails' meeting at the central or interior part of the micelle[28,29]. The diameter or thickness of the initial micelles approximates twice the length of the soap/detergent molecules (40–80 Å). When water insoluble monomer is present, part of it gets "solubilized" and finds room within the micelles, presumably among the hydrophobic tails of the soap/detergent molecules forming the micellar aggregates. The solubilization leads to some swelling of the initial micelles. A major part of the monomer taken, however, remains initially in macroscopic droplets. The micelles offer a far greater total surface area than the droplets, even though the total volume of the micelles is significantly lower than that of the monomer droplets. A schematic representation of micelles with or without solubilized monomer, surfactant molecules or ions in aqueous solution and monomer droplets is given in Fig. 4.6.

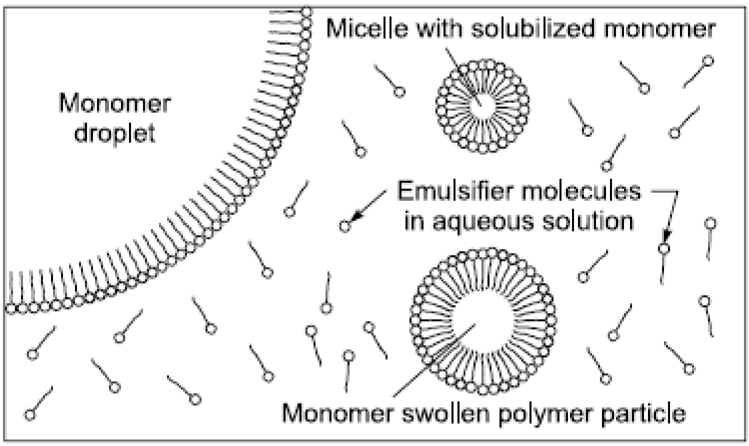

Figure 4.6. Schematic representation of an emulsion system in an emulsion polymerization

Experiments clearly demonstrate that polymer is not formed in the monomer droplets. This leaves the aqueous phase and the micelles as the locus of polymerization in the emulsion system. Aqueous polymerization can be readily effected without the use of an emulsifier and without having excess monomer as droplets (i.e. using the monomer within its solubility limit in water), though at much lower rates. But this alone is far insufficient to account for the bulk of the polymer formed in a typical emulsion system. In presence of a surfactant, the polymerization rate increases with surfactant concentration.

Polymerization begins in the aqueous phase as that is where the initiators occur and react or decompose into radicals. The primary radicals immediately pick up monomers dissolved in water to bring about chain initiation. With very low concentration of monomer in the aqueous phase, chain growth at relatively low rates proceeds till the radicals enter micelles which are present abundantly in the system. It is also not altogether unlikely that the primary radicals would find straight entry into the micelles being attracted by their high monomer reserve. Within the micelles, polymerization or chain growth takes place much rapidly in view of high monomer concentration due to accumulation of solubilized monomer there. As polymer is formed due to monomer depletion in the micelles, more monomer is transferred to the micelles from the reservoirs of monomer droplets. The former expands at the expense of the latter.

Soon after a low conversion stage (a few per cent) in the emulsion system, the low surface tension of the initial emulsion rises quite sharply evidently as a consequence of a fall in surfactant concentration in the aqueous phase of the emulsion, leading to breakdown or disruption of the micelles and consequent instability of the monomer droplets. Micelles give way to numerous polymer particles which at this stage average to not more than 200–400 Å in diameter. Nearly all of the surfactant used get adsorbed on the surfaces of the polymer particles. A redistribution of surfactant in favour of polymer particles makes the monomer droplets unstable at this stage. If agitation is discontinued, the monomer droplets cluster together into a continuous phase with zero polymer content. Monomer is now fed to the growing polymer particles by diffusion through the aqueous medium. As polymerization proceeds further, the polymer particles swell and grow in size even though they remain sensibly constant in their number. The rate of polymerization is practically constant over most part till about 60–80% conversion, excepting the initial zone up to several per cent. From the stage the monomer droplets completely disappear, the rate follows a fast decreasing trend with further conversion. In the final analysis, the emulsified polymer particles grow to a size in the range 500–1500 Å in diameter which is much larger than the size range of micelles initially formed but much smaller than the size of initially formed monomer droplets (> 10,000 Å). After polymerization to optimum conversion, appropriate dose of a short-stop or inhibitor is added to stop further conversion. The polymer is isolated by breaking the emulsion using salt or acid, coagulating, filtering, washing and drying.