



CHAPTER II

THEORY and LITERATURE REVIEW

2.1 Polymerization Techniques

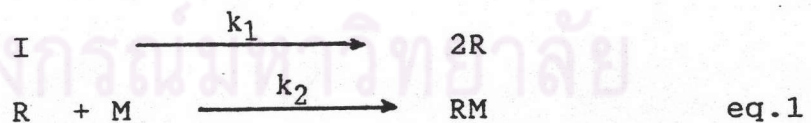
Polymers are macromolecules built up by linking together of large numbers of much smaller chemical units. The small molecules that combine with each other to form polymer molecules are known as monomers, and the reactions by which they combine are termed polymerization. Polymers and their polymerization process or reactions can be classified in two ways. Based on the composition or structure of the polymers, they may be condensation or addition polymers and the corresponding polymerization reactions, step and chain. On the other hand, they can be called sometimes step or chain polymers and the corresponding polymerization reactions (or process), based on the mechanism of the polymerization reactions (2). Since polymers of the same structure can be obtained under different conditions through different mechanisms, the use of these two classifications is not always interchangeable. For polymerization, the classification based on mechanism is natural, therefore polymerization can be either a chain or a step reaction. In general, during a step polymerization the size of the polymer formed grows continuously. During a chain polymerization the amount of polymer increases with time and the

molecular weight of the polymer formed remains constant.

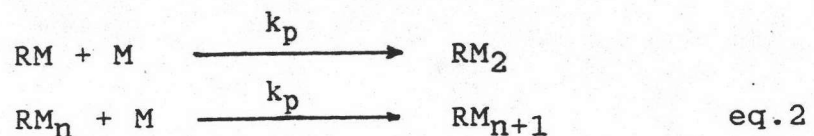
Chain polymerizations can proceed with a mechanism where the reaction center involved is a free radical, a cation, or an anion.

For the purpose of discussions on organic polymerization free radicals can be defined as organic segments containing odd or unpaired electrons (3). Free radical polymerization comprises four main reactions: (i) initiation, in which an initiator, e.g., a peroxide, decomposes to form primary radicals; (ii) propagation, in which a free radical adds monomer molecules in succession to form a large polymeric radical; (iii) termination, in which the polymeric radicals react to form dead polymer; (iv) transfer, in which a polymeric radical abstracts an active hydrogen or halogen from a compound to terminate the growing radical and form a radical which may initiate a new chain reaction. These four main reactions are presented in the following equations (4,5):-

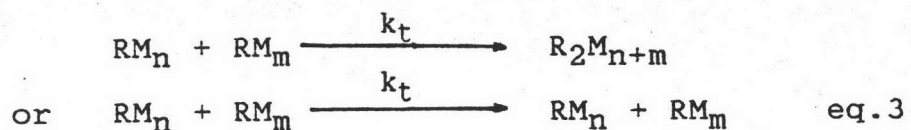
Initiation:



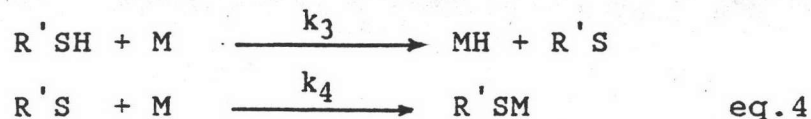
Propagation:



Termination:



Chain transfer:



This type of polymerization may be carried out in bulk e.g., clear, liquid styrene monomer can be polymerized to transparent, hard, rigid polystyrene. However, the polymerization is exothermic, and means must be provided to remove the heat of polymerization. One approach is polymerization in an inert diluent or solvent, e.g., toluene, which is compatible with both styrene and polystyrene; however, the polymer must be separated from the solution after polymerization. Another approach is suspension polymerization, in which fine drops of the monomer are dispersed in water; each monomer drop polymerizes as a small bulk polymerization, and the beads produced can be removed from the water by filtration. Still another approach is emulsion polymerization, in which the monomer is dispersed in water using an oil-in-water emulsifier to form microscopic droplets and polymerized to form a fluid latex comprised submicroscopic polymer spheres. Dispersion polymerization is another method of producing polymer in particles. The monomer is dissolved in a miscible medium which is a nonsolvent for the polymer. The polymerization proceeds like a solution polymerization at beginning. The polymer molecules then precipitate to form particles which are stabilized by the dissolved polymeric surfactant, usually block copolymers.

2.2 Suspension Polymerization

In suspension polymerization a monomer or mixture of monomers is dispersed by strong mechanical agitation into droplets suspended in a second liquid phase in which both monomer and polymer are essentially insoluble. The monomer droplets, which are larger than those in a true emulsion, are then polymerized the dispersion of which is maintained by continuous agitation. To the suspending liquid, which is almost always water, are added suspending agents which hinder the coalescence of the droplets during polymerization, the details of which are presented in the following section. Polymerization initiators or catalysts soluble in the monomer phase are generally used. According to the particular monomer treated, hard or soft spheres, beads, pearls or, less often, irregular granules, which normally separate easily from the aqueous phase when stirring is discontinued, are formed. Aside from cast resins and the synthetic rubbers, suspension polymerization has become the most important commercial method for polymerization of olefinic monomers, Despite the prominent industrial role of the method, relatively few publications have appeared and the scientific aspects have been little explored (6).

Reasons for the industrial development of suspension polymerization are clear. Most important, the large heat of polymerization can be dissipated, and granular, easily filtered products can be obtained directly from many polymers otherwise difficult to break

up from their tough, hard adhesive or rubbery masses. The necessity for coagulation of latex and intensive washing of emulsion polymers is avoided.

Several other types of polymerizations 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 2.1⁶. Suspension polymerization has been little used outside the field of vinyl-type or ethylenic monomers.

2.2.1 The Aqueous Phase and Suspending Agents

The aqueous phase maintains the monomer in the form of droplets and serves as a heat exchange medium. It is the vehicle for monomer and polymer. Water is seldom used alone but is modified by addition of various suspending agents. The most important types of these additives are:

- (a) water-soluble organic polymers (so-called protective colloids), and
- (b) inorganic compounds in the form of water-insoluble powders.

Surface active agents may be added in small concentrations. A survey of the materials used as suspending agents is given in Table 2.2 (7).

If a layer of water-insoluble liquid monomer is poured over water and then the liquids are stirred, monomer droplets are formed. After the agitation

TABLE 2.1

Polymerization Processes in water

Type of polymerization	Monomer solubility in water	Aqueous phase	Initiators	Phase of initiation of polymerization	Polymer products
					Molecular weight Type of product
Solution polymerization	Water-soluble, e.g., acrylic acid, methacrylic acid and alkali salts; vinyl pyrrolidone	Form homogeneous solution with the monomers	Water soluble, e.g., persulfates, hydrogen peroxide, hydroperoxides	In aqueous solution	Clear, viscous, aqueous solutions
Precipitation polymerization (polymer is not water soluble)	Soluble such as acrylonitrile or less soluble, e.g., acrylic ester, vinyl acetate	Free from emulsifying and dispersing agents	Water soluble, e.g., persulfates, hydrogen peroxide	In aqueous solution	Usually higher than in bulk polymerization Water insoluble; polymer precipitates out or forms a slurry (gel effect)

TABLE 2.1

Polymerization Processes in water

Type of polymerization	Monomer solubility in water	Aqueous phase	Initiators	Phase of initiation of polymerization	Polymer products
Emulsion polymerization	Only slightly soluble, e.g., styrene, acrylic and methacrylic ester	Emulsifying agents- anionic; cationic or non-ionic surfactants	Water soluble peroxides with redox activators	In aqueous solution or in micelle surfaces	Latex of fine dispersion, e.g., 0.2 or lower particle diameter
Dispersion polymerization	Only slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride	High molecular; water-soluble polymers, e.g., poly(vinyl alcohol), poly(acrylic acid salts)	Water soluble peroxides, hydrogen peroxide, redox systems	In aqueous solution or in monomer droplets	Higher than in bulk polymerization larger particles
Pearl or bead polymerization	Most slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride, vinyl acetate	Lower concentrations of above or inorganic pulverulent agents	Monomer soluble, e.g., benzoyl peroxide, azobisisobutyronitrile	In monomer droplets	As in bulk polymerization granules temporarily suspended in water, easily separated

TABLE 2.2

Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
1. Natural polymeric agents	Unsaturated esters of organic acids, such as acrylate esters and vinyl esters
-Carbohydrates: starch, agar, tragacanth, pectin, plant gums such as acacia, sodium alginate	
-Proteinaceous materials: glue, gelatin, isinglass	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.
-Carboxymethyl cellulose sodium salt	Vinyl compounds
-Hydroxyethyl cellulose	Vinyl chloride
3. Synthetic polymeric agents	
(a) Containing carboxyl groups:	
-Salts of polyacrylic acid and of polymethacrylic acid	Acrylic and vinyl esters and homologs
-Above at pH 5.5-8 with buffers	Acrylic compounds
-Na salts of copolymers of	Dichlorostyrene, acrylonitrile

TABLE 2.2 (continued)
Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
methacrylic acid with dichloro- styrene	methylmethacrylate
-Salts of copolymers of maleic acid, crotonic acid, with styrene, vinyl ethers, vinyl acetate, etc.	Unsaturated, polymerizable organic compounds generally
-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
-Na salts of copolymers of 1-alko xybutadiene and maleic acid	Polymerizable vinyl compounds
(b) Containing nitrogen:	
-Poly(vinyl pyrrolidone)	All polymerizable organic compounds
-Polymeric reaction products of methylmethacrylate with ammonia	Acrylic, vinyl esters and mixtures
-Above at pH 5.5-8 with buffers	Acrylic compounds, homologs

TABLE 2.2 (continued)

Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
-Polymethacrylamide with NaH_2PO_4 and Na_2HPO_4 as buffers	Monomers in general
(c) Containing alcoholic OH groups:	
-Poly(vinyl alcohol)	Acrylic and vinyl esters
-Poly(vinyl acetate) partially saponified, mixtures of different mol.wt. and degrees of saponification	Vinyl acetate
(d) containing sulfonic acid groups:	
-Sulfonated polystyrene with 0.15-0.5 SO_3H group per ring	Vinyl chloride with less vinylidene chloride
-Reaction products of poly(vinyl alcohol) with aldehyde sulfonic acids	Polymerizable vinyl compounds
4. Low molecular compounds	
-Ester of organic hydroxyacids, e.g., octyl lactate	Polymerizable vinyl compounds generally
-Aliphatic acid esters of poly(ethylene glycol)	Vinyl chloride
-Partial esters of polyalcohols with fatty acids, e.g., pentaerythrityl laurate	Vinyl chloride, vinylidene chloride and other vinyl compounds

TABLE 2.2 (continued)

Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
-Phthalate esters	Vinyl chloride
5. Condensation polymers	
Urea-formaldehyde	Vinyl chloride, vinylidene chloride, acrylonitrile
Water-soluble phenol-formaldehyde	Vinyl chloride polymers
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 μ	Polymerizable vinyl and vinylidene compounds
-Hydrated complex magnesium silicates	Polymerizable vinyl and vinylidene compounds
-Bentonite (colloidal clay)	Polymerizable vinyl and vinylidene compounds

is stopped, less dense monomer droplets rise, and again unite to form a homogeneous layer. But this coalescence does not occur instantly. Instead the monomer droplets move about among each other for some time, and on collision may rebound like billiard balls. There is a tendency to maintain the original spherical droplet form which results from interfacial tension. The lower the interfacial tension, the more easily are the monomer droplets deformed under the influence of the moving water as judged by the intensity of agitation required for forming lens-shaped or elongated drops. On the other hand, a high surface tension has the effect of greatly increasing the stability of the large spherical drop form. In that case, on collision a deformation of the spherical drop can hardly occur, but instead there is an elastic reaction which leads to rebound. When interfacial tension is low, the tendency to maintain spherical form is comparatively low. A deformed drop on collision will then be further deformed, giving a larger surface area. Thus, low interfacial tension leads, with agitation, to breaking up the monomer into very small droplets; too much surfactant, of course, gives true emulsions.

Under the unique conditions of pearl polymerization the droplets easily blend with one another without change of size. Among good suspending agents are found polymeric substances such as starch, proteinaceous materials and poly(vinyl alcohol), which are only very weak surface active substances. Pronounced surface

active agents such as wetting agents and soaps are not useful alone as suspending agents. However, in certain cases they may be used in combination with other agents for reducing bead size, e.g., along with strongly dissociated inorganic salts which raise the surface tension of the water phase, thus compensating to some extent for the wetting action. The surface activity of salts alone is sufficient in the case of some monomers such as lower acrylic esters for carrying out suspension polymerization. Salt addition is often used also in polymerization in combination with regular suspension stabilizers.

It is easy to understand how the increase of viscosity of the aqueous phase by dissolved organic polymers has a stabilizing action in suspension polymerization. The molecules of water layer which exists between two colliding droplets are easily pushed aside. But, if the thin layer of water contains dissolved polymer such as poly(vinyl alcohol) or protein, imparting increased viscosity, there is substantially more resistance to coalescence of droplets. For this reason it is important that the organic polymers serving as suspension stabilizers be soluble in water but completely insoluble in the monomer phase. The increased viscosity imparted to the aqueous phase is directly important in delaying the process of coalescence.

In the case of the inorganic materials used in fine powder form as outstanding suspension

stabilizers, the viscosity of the aqueous phase is not affected. Powders suspended in water are wetted by the aqueous phase. When two monomer droplets approach each other, their recombination may be prevented by the powder particles which lie between them. This can be observed distinctly under the microscope.

Additions of surface active agents to the aqueous phase have great influence along with powders as suspending agents, because of the reduction of surface tension. Very small additions of such surface active agents can promote the fine dispersion of the insoluble powder without changing the surface tension of the water very much. If these wetting agents are only used in extremely small concentration, they are adsorbed practically completely upon the powder surface, so that few freely diffusing wetting molecules are present in the aqueous phase. Because of the better dispersion of the suspending powder, smaller polymer granules are formed.

The suspension stabilizers must perform their function during the whole course of the polymerization. The most critical phase of each polymerization, however, is that when the droplets contain enough dissolved polymer to become syrupy, and because of their higher viscosity they can no longer be broken up as readily by the agitation as when they were mobile pure monomers. At this stage also, the droplets are not yet sufficiently solidified to prevent sticking together on collision. It is possible that this critical

phase is also influenced by the changes in interfacial tension between the aqueous and organic phases occurring during the progress of polymerization. The monomer and the polymeric product may possess widely different values of surface tension. When the polymer is insoluble in the monomer, as in the case of vinyl chloride, of course no sticky, viscous condition can cause coalescence.

2.2.2 The Monomer Phase

Generally, those monomers which are insoluble or only slightly soluble in water are polymerized by suspension processes. However, where the solubility of the monomers or the products is too great, electrolytes such as alkali salts of strong acids, which have a salting-out effect, may be added. Mixtures of different monomers also may be copolymerized in suspension where a difficulty soluble monomer acts as an extracting agent for a second more soluble monomer. In this way copolymer pearls from relatively water-soluble monomers may be obtained, especially in the presence of salts. Similar action can be exerted by plasticizers which occasionally have been added initially to the monomers in order to facilitate uniform pearl formation.

In pearl or bead polymerization the monomer phase usually contains the dissolved polymerization initiator or catalyst. Practically the same initiators are used as in ordinary bulk and solution polymerization of unsaturated monomers, i.e., organic peroxides, and less frequently azo compounds.

2.3 Seeded Suspension Polymerization

Polymer beads produced by this method usually have diameters in the range of 0.1 mm to about 1 mm, depending on the condition of agitation, monomer-water ratio, and concentration of suspending agent. Large drops are subjective to shear distortion and may even break up during the early stages of polymerization. Generally, under the conditions of the combination of agitation and suspending agent in a conventional suspension polymerization, beads of diameter larger than 2 mm are difficult to obtain.

Seeded emulsion polymerization has been widely studied. Recently the production of large-particle-size monodisperse latexes in microgravity (8) was developed. On the other hand, seeded suspension polymerization remains a new technology in industrial polymerization. To prepare large imbibed beads of 3-5 mm for special applications, seeded suspension polymerization is proved useful. Seeded suspension polymerization is the polymerization of seed beads swollen with the monomer solution to effect the final bead composition. A major difference between this process and seeded emulsion polymerization is that in seeded emulsion polymerization the polymer particles absorb monomer through the water phase medium, while in seeded suspension polymerization the excess monomer may be directly added to the neat seed beads. The imbibed monomer solution is polymerized within the swollen network of the crosslinked seed beads. The replacement of

the dispersion operation by swollen of the seed beads, and the easier maintenance of suspension, due to the higher rigidity of the swollen beads compared to liquid droplets, facilitate better stabilization and therefore easier scale-up.

2.4 Sorption-Desorption 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 (9). 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.

By bringing the swollen gel into contact with a substrate and separated from the bulk of the swelling liquid, the imbibed solvent may be released. If the

substrate competes favorably for the solvent the desorption will be more, 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.

These phenomena are important in the application of polymers as imbibers beads, liquid agent carrier for its dissemination, or in the "swelling-controlled" systems of controlled release devices (10). The traditional application of imbibers beads is to soak up oil spill. In this case, normally only the sorption process is a concern. The solubility parameter of these beads is adjusted to maximize to release the solvent unless they are placed in contact with a substrate of even more closely matched solubility parameter. In separation science, e.g., chromatography and ion-exchange (11), the degree of swelling of the beads is important in determining the efficiency of separation. In the areas of pharmaceutical and agricultural preparations the kinetics of both sorption and desorption processes may be fundamentally important in the development of release devices. The driving force of sorption and desorption depends on the competition of the interaction between the solvent and the polymer network, and the interaction between the solvent and the substrate. Therefore if the polymer is used as a carrier in the dissemination of a functional liquid, these interactions must be balanced so that the polymer can imbibe a large

amount of the agent and yet release it as completely as possible when brought into contact with the target substrate.

The conventional approach to characterizing the swelling of a crosslinked polymer in a solvent is the solubility parameter concept. The original solubility parameter concept (12,13) was solely based on the thermodynamic heat of mixing of a solute, such as a polymer, and a solvent. This concept predicts that the closer the match between the solubility parameters of the polymer and solvent, the "better" the solvent for the polymer and the higher the degree of the swelling of the crosslinked polymer. The interaction between polymers and solvents, however, cannot be described completely by heat of mixing; other interactions such as acid-base interactions and hydrogen bonding also influence the polymer-solvent interaction. The most useful modification of the solubility parameter concept to take into account these other interactions is the three-dimensional scheme in which the solubility parameter comprises contributions from dispersion forces (i.e., heat of mixing), polar interactions, and hydrogen bonding interactions (14). This modification has been successful in explaining most of the polymer-solvent interactions (15).

2.5 Thermodynamics of Solutions

Two substances mix when the free energy of mixing is negative. This quantity should strictly be calculated from the partition function of the mixture, but this is

impracticable, and approximate methods must be used.

Huggins has given an equation for the free energy of mixing a linear, liquid, homogeneous polymer and a solvent, equivalent to

$$\Delta G_{\text{cm}^3} = \frac{RT}{V_s} (\phi_s \ln \phi_s + \frac{\phi_p}{m} \ln \phi_p + \mu \phi_s \phi_p) \quad \text{eq.5}$$

where ΔG_{cm^3} is the free energy/cm³. of mixture, ϕ is the volume fraction (subscripts s and p refer to solvent and polymer respectively) and V_s is the molar volume of solvent; m is the ratio of molar volumes of polymer solvent, so that mV_s is the molar volume of the polymer. The constant μ is the sum of two parts,

$$\mu = \mu_z + V_s k / RT \quad \text{eq.6}$$

where μ_z is a small constant (empirically 0.2-0.3) depending upon the co-ordination number of the quasi-lattice assumed in the entropy calculation, and k is a heat of mixing constant for the system concerned defined by

$$\Delta H_{\text{cm}} = k \phi_s \phi_p \quad \text{eq.7}$$

where ΔH_{cm} is the heat of mixing/cm³. of mixture. From [eq.6], it is clearly seen that the value of μ depends largely on the value of k , which will be further described below.

2.5.1 Heat of Mixing

The molar cohesive energy of a liquid is defined as the energy necessary to break all the intermolecular contacts in a mole of the liquid; it is thus equal to the internal energy of vaporization to a

perfect gas, provided that the intramolecular contacts are similar in the gas state and the liquid state; this provision may fail for long flexible organic molecules which can coil up in the gas phase.

Since perfect gases mix without heat change, if the cohesive energy of a liquid mixture is greater than the sum of the cohesive energies of the component liquids, heat is liberated and ΔH is negative; since the entropy is always positive mixing will then occur. In the opposite case, ΔH may be so positive as to outweigh the mixing entropy, so that the free energy is positive. Such a solution, if formed, will unmix. In the polymer field, such unstable solutions do actually occur; an example is a polymer containing an excess of an incompletely compatible plasticizer (which has been rolled in hot); the plasticizer often exudes. Because of the slowness of diffusion through polymers, the unmixing process may be quite slow, and observable.

The heat of mixing thus depends upon the difference of cohesive energies of solution and unmixed components. When the cohesion is due to dispersion forces, the energies of a pair of dissimilar molecules is approximately the geometric mean of the energies of the corresponding pairs of similar molecules. Scatchard(16) proposed a semi-empirical relation for this case

$$\Delta H_{cm}^3 = \phi_1 \phi_2 [(E_1/V_1)^{1/2} - (E_2/V_2)^{1/2}]^2 \quad \text{eq. 8}$$

where E and V are the molar cohesive energies and

molar volumes; this gives for the k of [eq.7]

$$k = [(E_s/V_s)^{1/2} - (E_p/V_p)^{1/2}]^2 = (\delta_s - \delta_p)^2 \quad \text{eq.9}$$

where $\delta = \sqrt{E/V}$.

The quantities E/V and δ are called respectively the 'cohesive energy density' (c.e.d.) and the 'solubility parameter'.

2.5.2 Calculation of Cohesive Energy Densities

Since c.e.d.s. are important in controlling solubility, methods of estimating them are important.

For non-polymeric liquids, this is comparatively easy. The molar cohesive energy is given by

$$E = \Delta U_{\text{vap}} + \int_{v=\text{vap}}^{v=\infty} \left(\frac{\partial U}{\partial V} \right)_T dv = \Delta H_{\text{vap}} - RT \quad \text{eq.10}$$

where U is the internal energy. The integral is the correction for the imperfection of the vapour; this is small when the vapour pressure is low (of the order 2% at 1 atm.) and thus E is approximately the internal energy of vaporization. This may be calculated from calorimetric or vapour-pressure data; when these are lacking, various empirical correlations are available.

This method can obviously not be applied to polymers. The c.e.d. of a polymer can be estimated by determining the equilibrium swelling of a slightly cross-linked analogue in various solvents and correlating with the c.e.d. of the solvent; the swelling is a maximum in solvents of the same c.e.d. Another method would be to

determine μ from a plot of reduced osmotic pressure versus concentration in various solvents, and plot μ against the c.e.d. of the solvent; it would be a minimum in solvents of the same c.e.d. Both these methods are laborious and time-consuming.

The Scatchard [eq.8] is equivalent to the statement that the cohesive energy E of a mixture of n_1 moles of a liquid 1 with cohesive energy E_1 and molar volume V_1 with n_2 moles of liquid 2, is given by

$$E^{1/2} (n_1 V_1 + n_2 V_2)^{1/2} = n_1 (E_1 V_1)^{1/2} + n_2 (E_2 V_2)^{1/2} \quad \text{eq.11}$$

That is, $(EV)^{1/2}$ is an additive property. The author considered it reasonable that it might add, in compounds, on an atomic and constitutive basis. Scatchard has shown that in several homologous series $(EV)^{1/2}$ is linear with the number of carbon atoms.

It proved possible to find a set of additive constants for the common groups in organic molecules, which allow the calculation of $(EV)^{1/2}$. These are called molar-attraction constants, and are denoted by the symbol F .

Then ΣF summed over the groups present gives the value of $(EV)^{1/2}$ for one mole of the substance concerned; the molar cohesive energy E , c.e.d. and solubility parameter are then given by

$$E = \frac{(\Sigma F)^2}{V} ; \text{ c.e.d.} = \frac{\Sigma F}{V} ; \delta = \frac{\Sigma F}{V} \quad \text{eq.12}$$

These values, given in Table 2.3, have

TABLE 2.3
Molar-Attraction Constants, 25°C(17)

Group	F, cal ^{1/2} c.c. ^{1/2}	Group	F, cal ^{1/2} c.c. ^{1/2}
CH ₃	214	H(variable)	80-100
CH ₂ single bonded	133	O ethers	70
$\begin{array}{c} \\ -CH \\ \end{array}$ single bonded	28	CO ketones	275
$\begin{array}{c} \\ -C- \\ \end{array}$ single bonded	-93	COO esters,	310
CH ₂ = double bonded	190	CN	410
-CH= double bonded	111	Cl(mean)	260
>C= double bonded	19	Cl single	270
CH≡C-	285	Cl twinned as in >CCl ₂	260
-C≡C-	222	Cl triple as in -CCl ₃	250
Phenyl	735	Br single	340
Phenylene(o,m,p)	658	I single	425
Naphthyl	1146	CF ₂ n-fluorocarbons only	150
Ring, 5-membered	105-115	CF ₃ n-fluorocarbons only	274
Ring, 6-membered	95-105	S sulphides	225
Conjugation	20-30	SH thiols	315
		O NO ₂ nitrates	~440
		NO ₂ (aliphatic nitro compounds)	~440
		PO ₄ (organic phosphates)	~500

been estimated from the available vapour-pressure and heat of vaporization data in the literature; all compounds such as hydroxyl compounds, amines, amides, and carboxylic acids, in which hydrogen bonding occurs, have been excluded. It has been assumed that for the classes of compounds considered the dipole-interaction energy is negligible; the only compounds for which this seems to be possibly in error are the lower esters and ketones, and in these cases data for the higher members of the series have been used where possible. All the values given refer to 25°C.

The additivity of $(EV)^{1/2}$ is well established for hydrocarbons. Thus the value of $(EV)^{1/2}$ calculated for 72 hydrocarbons (paraffins and olefins) from the additive constants given was compared with values derived from the National Bureau of Standards data; the root mean square deviation was only 0.8% of the mean for the set. For other classes of organic compound there is no comparable set of data, and the evidence of additivity is not so strong. In particular, packing several large groups round a central atom results in a real lowering of the F constant; this effect is taken into account in the values for the hydrocarbon groups, but it is impracticable to give a complete analysis for all substituents. For instance, calculating $(EV)^{1/2}$ for carbon tetrachloride from single Cl 987 cal.^{1/2}c.c.^{1/2} is obtained, whereas the observed value is 835. This effect is always in the same direction and is to be

TABLE 2.4
 Calculated and Observed Solubility Parameters
 of Polymers (δ in cal.^{1/2}/c.c.^{1/2})

Polymer	δ (calc.)	δ (obs.)
Polytetrafluoroethylene	6.2	
Polyisobutylene	7.70	8.05
Natural rubber	8.15	7.9-8.35
Polybutadiene	8.38	8.4-8.6
Butadiene/styrene 85:15	8.48	8.5
Butadiene/styrene 75:25	8.54	8.6
Butadiene/styrene 60:40	8.65	8.67
Polystyrene	9.12	9.1
Polystyrene/divinylbenzene		9.1
Buna N (butadiene 75) (acrylonitrile 25)	9.25	9.38 9.5
Poly(methyl methacrylate)	9.25	9-9.5
Neoprene GN	9.38	9.25
Poly(vinyl acetate)	9.4	
Poly(vinyl chloride)	9.55	9.48
Poly(vinyl bromide)	9.6	9.5
Poly(methyl chloroacrylate)	10.1	
Cellulose dinitrate	10.48	10.56
Cellulose diacetate	11.35	10.9
Polyacrylonitrile	12.75	

expected for steric reasons. There are other effects such as conjugation, as in styrene or butadiene, and ring-closure, which result in a change of F , in these cases the value are increased: analogous effects are found in molecular refraction and the parachor. The ring increment varies with ring size, and increases somewhat with degree of substitution on the ring.

Table 2.4 gives some values of the solubility parameter calculated from the constants of Table 2.3, and experimental values from the literature, mostly obtained by swelling experiments; the agreement is quite satisfactory. In calculating the values for cellulose diacetate and dinitrate a value of 170 was assigned to the OH group, the sum of 100 for the hydrogen and 70 for the ether oxygen atoms. This is rather arbitrary, but the contribution of the OH group to F for the molecule is only some 10%, so that small errors in the value used will not be serious.

2.6 BET Technique for Assessment of Surface Area

Since almost all practically important adsorbents are porous solids a key parameter which is required to characterize an adsorbent is the specific surface area. The specific areas of microporous solids are very large, and values of several hundred square meters/gram are not uncommon. Accurate measurement of the surface area of a microporous solid presented a significant problem in early studies of adsorption and catalysis.

It is evident that if the physical adsorption capacity were limited to a close-packed monolayer, determination of the saturation limit from an experimental isotherm with a molecule of known size would provide a simple and straightforward method of estimating the specific area. The main difficulty is that in chemisorption the sites are usually widely spaced so that the saturation limit bears no obvious relationship to specific surface area while physical adsorption generally involves multilayer adsorption. The formation of the second and subsequent molecular layers commences at pressure well below that required for completion of the monolayer so it is not immediately obvious how to extract the monolayer capacity from the experimental isotherm. This problem was first solved by Brunauer, Emmett, and Teller (BET) (18) who developed a simple model isotherm to account for multilayer adsorption and surface area. A number of refinements to the BET model and to the experimental method have been developed more recently but the basic BET method remains the most widely used technique for measurement of specific surface area.

An exact theoretical treatment of multilayer adsorption presents formidable problems since it is necessary to take account not only of the interactions between sorbate molecules and the adsorbent surface but also of the sorbate-sorbate interactions which are often of comparable magnitude. The BET model is based on a

number of rather serious idealizations which can at best be no more than a first approximation. Each molecule in the first adsorbed layer is considered to provide one "site" for the second and subsequent layers. The molecules in the second and subsequent layers, which are in contact with other sorbate molecules rather than with the surface of the adsorbent, are considered to behave essentially as the saturated liquid while the equilibrium constant for the first layer of molecules in contact with the surface of the adsorbent is different. The expression for the BET isotherm may be derived from these assumptions, either by an extension of the simple kinetic argument put forward above for the monolayer case or by a more refined thermodynamic argument. The resulting equation for the BET equilibrium isotherm is

$$\frac{q}{q_m} = \frac{b(p/p_s)}{(1 - p/p_s)(1 - p/p_s + b p/p_s)} \quad \text{eq.13}$$

in which p_s represents the saturation vapor pressure of the saturated liquid sorbate at the relevant temperature.

Knowing the saturation vapor pressure and the equilibrium uptake at several pressures within the prescribed range, q_s , the sorbate concentration corresponding to a close-packed monolayer, may be easily found from a plot of $p/q(p_s - p)$ versus p/p_s . In order to translate the monolayer coverage into a specific

area, knowledge of the size of the sorbate molecule is required. Close packing of spherical molecules of diameter equal to the van der Waals diameter is generally assumed.

It is evident that in order to make measurements within the required range of relative pressures at conveniently measurable absolute pressures, The temperature of the measurements should be carefully selected. Measurements are commonly made using nitrogen as the sorbate at liquid nitrogen temperatures but other small molecules may also be employed. Some indication of the accuracy of the BET model as the method for determination of surface area may be obtained from a comparison of data obtained with different sorbates on the same porous material. Some representative data obtained with a microporous NH_3 synthesis catalyst are summarized in Table 2.5.

TABLE 2.5

Comparison of BET Area of NH_3 Synthesis Catalyst Determined with Different Sorbates

Sorbate	T (K)	Area (m^2/g)
N_2	77	580
Br_2	352	470
CO_2	195	460
CO	90	550

These data suggest that absolute area may be determined to within about 20-25% by this method. Relative areas may be determined with somewhat greater accuracy by comparing the uptake by different adsorbents over the same relative pressure range.

2.7 Pore-Size distribution of Porous Materials

2.7.1 Capillary Condensation: The Kelvin equation

In a porous adsorbent there is a continuous progression from multilayer adsorption to capillary condensation in which the smaller pores become completely filled with liquid sorbate. This occurs because the saturation vapor pressure in a small pore is reduced, in accordance with the Kelvin equation, by the effect of surface tension.

The Kelvin equation may be derived from simple thermodynamic considerations. We consider a straight cylindrical pore (radius r) containing liquid adsorbate, as sketched in Figure 2.1. Suppose that n moles of liquid ($n = \pi r^2 dl / V_m$) are evaporated from the pore under the equilibrium vapor pressure P_s , the saturation vapor pressure for the pure liquid at the same temperature. The work done against surface tension is exactly equal to the free energy difference:

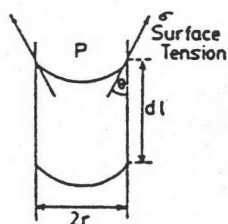


FIGURE 2.1 Derivation of Kelvin equation.

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$$n\Delta G = (2 \pi r dl) \gamma \cos\theta = nRT \ln \frac{(P_S)}{(P)} = \frac{\pi r^2 dl RT}{V_m} \ln \frac{(P_S)}{(P)}$$

eq.14

$$\frac{P}{P_S} = \exp \left(\frac{-2 \gamma V_m \cos\theta}{rRT} \right) \quad (\text{Kelvin equation})$$

eq.15

If the restriction to cylindrical pore geometry is relaxed, the same argument leads to the more general relationship:

$$\frac{dV}{dA} = - \frac{V_m \gamma \cos\theta}{RT \ln(P/P_S)} \quad \text{eq.16}$$

where dV/dA is simply the rate of change of pore volume with surface area which, for a cylindrical pore, corresponds to $r/2$.

Taking benzene at 20°C as an example ($\gamma \approx 29$ mN/m, $V_m \approx 89$ cm³/mole, $\theta \approx 0$) we note that in cylindrical pores of 50 Å capillary condensation will occur at relative pressure of P/P_S 0.67 whereas in pores of 500 Å the relative pressure will be 0.96. It is evident that the capillary effect is significant only in quite small pores.

In the capillary condensation region the isotherm generally shows hysteresis so that the apparent equilibrium pressures observed in adsorption and desorption experiments are different. Several plausible explanations for this effect have been put forward.

During adsorption multilayers build up on the capillary walls but a complete meniscus is not formed until saturation is reached at which all pores are filled. The relationship between pressure and adsorbed phase concentration along the adsorption branch of the isotherm will therefore be governed by an appropriate multilayer isotherm analogous to the BET equation. (Note that the BET equation itself is not applicable in this region since its range of validity is limited to relative pressures of less than about 0.35.) Once the saturation limited for capillaries of a particular size has been reached desorption will occur from a curved meniscus and the equilibrium pressure will be governed by the Kelvin equation. According to this theory the adsorbed film formed during adsorption is in a metastable state, the true equilibrium state being represented by the capillary condensed liquid. The apparent stability of the multilayer film depends on the absence of nuclei to allow condensation to the bulk liquid (19)

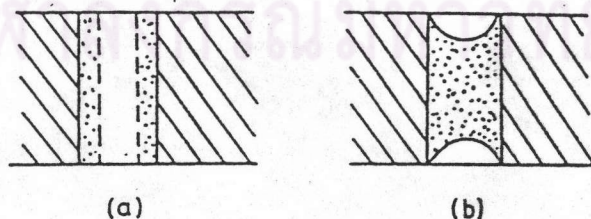


FIGURE 2.2 (a) Radial filling of pores during adsorption
(b) evaporation from filled pores with hemispherical meniscus during desorption.

An alternative view was suggested that capillary condensation occurs along both adsorption and desorption branches of the isotherm, the difference being due to a difference in the shape of the meniscus. During adsorption the pore fills radially and a cylindrical meniscus is formed as sketched in Figure 2.2 (a).

Under these conditions $dv/ds = r$ (rather than $r/2$ as assumed in the Kelvin equation) and with $\theta = 0$:

$$\frac{P}{P_S} = \exp \left(\frac{-6V_m}{rRT} \right) \quad \text{eq.17}$$

During desorption the meniscus is hemispherical and the Kelvin equation [eq.15] applies. It follows that

$$\frac{P_a^2}{P_S} = \frac{P_d}{P_S} \quad \text{eq.18}$$

Where P_a and P_d represent the apparent equilibrium pressures on the adsorption and desorption branches of the isotherm at a given loading. Many experimental isotherms show approximate agreement with this equation but the agreement is by no means quantitative and universal. Deviation may be explained as arising from deviations in the shape of the pores from simple cylindrical geometry or alternatively such deviations can be taken as evidence against Cohan's mechanism.

Measurement of an isotherm under

conditions of capillary condensation provide a simple means of determining the pore size distribution of the adsorbent. Applying the Kelvin equation to the desorption branch of the isotherm gives the value of r' corresponding to a known relative pressure (P'/P_0) and the corresponding adsorption loading (q'). If adsorption on the pore walls is neglected, q'/ρ would correspond to the total pore volume made up of pores of radius less than or equal to r' . A plot of q'/ρ versus r thus gives the cumulative pore size distribution from which the frequency distribution may be readily determined by differentiation. If an accurate determination of the pore size distribution is required it is necessary to correct for adsorption on the pore walls. This correction may be found from measurement of the equilibrium isotherm for the same sorbate on a large pore adsorbent under conditions such that there is no capillary condensation. A representative example of the pore size distribution calculated in this way is shown in Figure 2.3

2.7.2 Mercury Porosimetry

If the contact angle between liquid and solid is greater than 90° , then at equilibrium the pressure on the convex side of the meniscus must be greater than on the concave side. Thus if the porous solid is immersed in a nonwetting liquid such as mercury there will be no penetration of the pores until the applied pressure reaches the equilibrium value. The

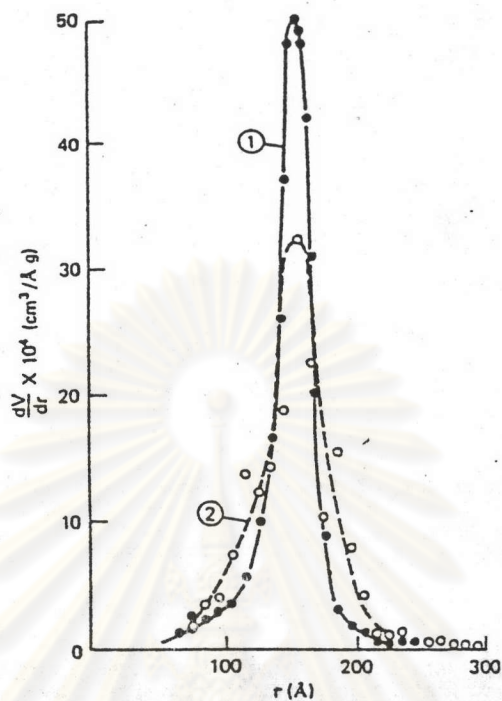


FIGURE 2.3 Comparison of pore size distribution for $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalyst measured by mercury penetration and from the nitrogen desorption isotherm. (1) Pore size distribution from N_2 desorption isotherm. (2) Pore size distribution from mercury penetration.

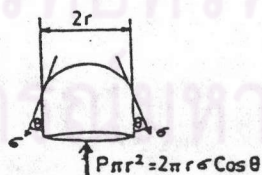


FIGURE 2.4 Force balance for mercury penetrometer.

equilibrium pressure and pore radius are related through a simple force balance as illustrated in Figure 2.4

Some values of P and r for mercury ($\theta \approx 40^\circ$, $\sigma \sim 480$ mN/m) are summarized in Table 2.6. It is evident that penetration of the smaller pores characteristic of microporous adsorbents is achieved only at very high pressures.

TABLE 2.6
Pore Radius for Mercury Penetration
as Function of Pressure

P (atm)	r (A)
10	22000
10^2	2200
10^3	220
10^4	22

The mercury porosimeter is simply an instrument designed to apply a controlled mercury pressure to the adsorbent and record the volume of mercury penetrating the pore structure. Because of practical limitations on the maximum pressure, the minimum pore radius which can be measured by this method is about 50-100 A. The method is however more suitable

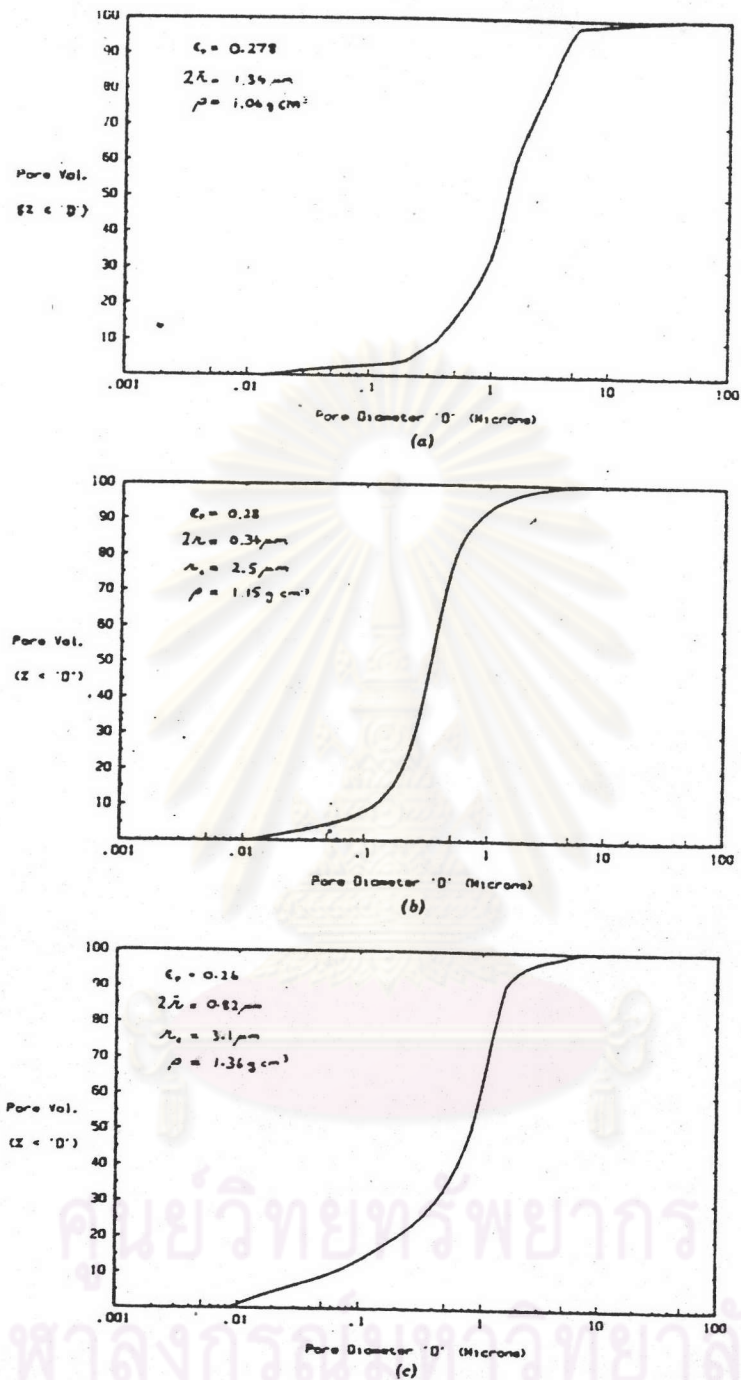


FIGURE 2.5 Macropore size distribution determined from mercury penetration measurements for (a) carbon molecular sieve, (b) Linde 5A (extrudates), and (c) H-Zeolon (H-mordenite).

for measurement of larger pores in the range 1000-10,000 Å. Some examples of pore size distribution curves measured by mercury penetration are given in Figure 2.5.

Since pore size distribution may also be measured by gas adsorption, as discussed above, a comparison of the two methods is possible. Such a comparison was made for a $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalyst with a mean pore radius of about 150 Å. The results of the two methods showed good agreement as may be seen from Figure 2.3. However, since mercury penetration measures in effect the pore volume accessible through openings of a given diameter, agreement with the results of gas adsorption measurements can be expected only when the pore shape is reasonable regular. If the pore mouths are constricted ("ink bottle pores") the apparent pore diameters derived from mercury penetration will be too low. It is therefore possible, in principle, to obtain some information about the macropore structure from a comparison of results obtained by the two methods. Other methods of characterizing in detail the structure of porous materials have been discussed.

2.8 Literature Survey

So far the synthesis of the porous polystyrene crosslinked with divinylbenzene for the use as raw materials for ion exchanges, functionalized copolymers, or as polymeric supports in chromatography and absorption has been the matters of a large number of published papers. Recent works on the study of the porous copolymer

by suspension polymerization are listed below.

G.J. Howard and C.A. Midgley (20) prepared porous polymers by suspension copolymerization of styrene/divinylbenzene in various ratios together with various quantities of diluents, both solvating and nonsolvating. Parallel bulk polymerizations were made to detect the onset of gelation and phase separation. The dry polymeric beads were examined by a range of techniques: apparent densities; mercury porosimetry; nitrogen sorption/desorption isotherms, vapor sorption, equilibrium swelling, and electron microscopy. The properties of the porous polymers are discussed in terms of phase separation during polymerization consequent on either an unfavorable polymer-solvent interaction or a microsineresis.

Ignat Poinescu, et al. (21) studied the copolymerization of styrene with divinylbenzene in the presence of tri-n-butylphosphate or a mixture of di-2-ethylhexylphosphoric acid and chlorobenzene in order to perform porous networks, solvent impregnated copolymer, etc. The diluents behave as strong precipitants allowing to prepare permanent porous copolymers having low contents of the crosslinking agent.

The effect of dilution, crosslinking degree, and nature of diluent on the porosity as well as on the uptake coefficients, the specific surface area, and the average pore diameter, were studied to elucidate the manner in which such inert compounds contribute to the

formation of porous networks.

O. Okay, et al. (22) investigated phase separation by suspension copolymerization of styrene/divinylbenzene with di-2-ethylhexyl phthalate(DOP) as diluent using equilibrium swelling, swelling rate, apparent densities, and mercury porosimetry. The copolmer prepared in the absence of DOP is heterogeneous, showing that a phase separation exists in the polymerization system, and, in the presence of DOP, the propagating copolymer separates earlier. Furthermore, with increasing amounts of divinylbenzene, phase separation occurs earlier than gelation, which causes a sudden increase in the amount of pores about 200-500 A in diameter corresponding to the interstices between the microspheres.

O.Okay and T.I.Balkas (23) compared the pore structure of styrene/divinylbenzene copolymers formed by phase separation before or after gelation using apparent densities and mercury porosimetry. The copolymers were prepared with di-2-ethylhexyl phthalate(DOP) as diluent. The pore structure of copolymers formed in homogeneous gelation can collapse upon drying in the rubbery state. The collapsed pores have a mean diameter of about 100-200 A corresponding to the interstices between the microspheres. The collapsed microspheres reexpand again during the sulfonation or chloromethylation reactions, or during the solvent exchange. The pore structure of styrene/divinylbenzene networks formed in heterogeneous gelation do not collapse on drying in the swollen state,

this being a stable and permanent porosity. The critical crosslink density for transition from homogeneous to the heterogeneous gelation represents a borderline between stable and unstable porosity. The drastic change of swelling and porosity values at the critical crosslink density is due to the collapse of unstable pores.

O. Okay, et al. (24) investigated the change in the porosity of styrene/divinylbenzene copolymers during drying as a function of the quality of the diluent and of the divinylbenzene concentration after drying the networks from water (maximum porosity) and from toluene (stable porosity). Two different diluents, namely toluene and cyclohexanol, were used in the polymerization system at a fixed volume fraction of the organic phase (0.50). The phase separation in toluene is accompanied by a slight deswelling of the network phase, whereas that in cyclohexanol leads to largely unswollen network phase. The stable porosity increases abruptly over a narrow range of the divinylbenzene concentrations, i.e., between 40 and 50% divinylbenzene in toluene and between 15 and 25% divinylbenzene in cyclohexanol. The maximum porosity increases almost linearly with increasing divinylbenzene concentration up to a certain value, and then remains constant. The results indicate that the two main factors which determine the physical state of the swollen heterogeneous styrene/divinylbenzene copolymers, as well as the stability of the porous structures, are:

- (1) the critical conversion at the incipient phase

separation and (2) the degree of the in homogeneity in crosslink distribution.

L.A. Errede (25) demonstrated that swelling of crosslinked polymers can be monitored much more conveniently and reproducibly after that polymer has been comminuted to a fine powder, and then fabricated mechanically into a tough microporous composite film consisting of the particulate matter (>80%) enmeshed in polytetrafluoroethylene [PTFE; <20%]. The latter component provides the physical integrity that affords ease of handling and ensures permanent entrapment of the particles even after 100 cycles of swelling and desiccation to the original dry state. The PTFE microfiber network, however, does not affect adversely either the physiochemical properties of the particles or the permeability to fluids. Kinetic studies in 10 replicates have shown that the void space (0.3 to 0.6 ml/g of composite) is filled by capillary action within the first few minutes of contact with the liquid, and the swelling to the equilibrium state (2 to 90 ml/g of composite) usually occurs within 0.5 to 2 hours thereafter, depending primarily upon the surface-to-volume ratio of the particles. The magnitude of swelling at equilibrium, however, is dependent only on the thermodynamic state of the gelled polymer in excess liquid, and is reproducible usually within 0.2%.

L.A. Errede (26) developed a very convenient and reliable gravimetric method for measuring swelling of

styrene/divinylbenzene copolymer in particulate form. The method is based on the gravimetric procedure reported earlier for monitoring liquid uptake by thin (<0.3 mm) microporous composite films, consisting of swellable particulate (80% by weight) enmeshed in polytetrafluoroethylene microfibers (20%). The swellability S (in milliliter of liquid absorbed per gram of polymer in equilibrium with excess liquid) for six styrene/divinylbenzene copolymers with crosslink densities \bar{x} ranging from 0.01 to 0.12 was measured in 19 organic liquids. In each study of S as a function of \bar{x} the relationship was given by

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) = C(\bar{x}^{-1/3} - \bar{x}_0^{-1/3}) \quad \text{eq.19}$$

where $\lambda = 1/\bar{x}$ is the average number of carbon atoms in the "backbone" of the polystyrene segments between crosslink junctions, C is the relative swelling power of the liquid, and $\bar{x} = 1/\lambda_0$ is the critical crosslink density above which S is equal to zero.

L.A. Errede (27) reexamined the styrene/divinylbenzene copolymer swelling studies which were reported years ago by Staudinger, Boyer, and Rempp, so as to test the validity of the observation made recently that swelling, S , of such polymers is given in terms of crosslink density, \bar{x}_0 , by the general equation:

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) = C(\bar{x}^{-1/3} - \bar{x}_0^{-1/3})$$

where $\lambda = 1/\bar{x}$ is the average number of carbon atoms in

the "backbone" of the polystyrene segments between crosslink junction;

C is a constant characteristic of the swelling power of the liquid for the kind of polymer being investigated at temperature T;

λ_0 is the critical crosslink density of the polymer at or above which $S=0$.

In every reexamination, S , obtained from the reported swelling data, was a linear function of $\lambda^{1/3}$, calculated from the corresponding reported polymer molecular weight data, but the constants C and $\lambda_0^{1/3}$ depended upon the conditions of copolymerization that affect the λ -distribution. Similar linear relationships appear to obtain for swelling studies of "macronet" crosslinked polyesters reported by Takahashi and perhaps for water-swellaible "macronet" crosslinked polyacrylates reported by Refojo. It is concluded that the above linear relationship may be generalized for crosslinked polymer networks and it is therefore useful to the planning of future studies aimed at a better understanding of polymer swelling in terms of the molecular structures of the polymer and the swelling liquid.

L.A. Errede (28) studied the swellability, S , of styrene-co-divinylbenzene polymers in 20 aromatic and 24 aliphatic liquids as a function of crosslink density, λ^{-1} , from $\lambda^{-1} = 0.01$ to $\lambda^{-1} = 0.12$. In every study the relationship was given by:

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) \quad \text{eq. 20}$$

where λ is the average number of carbon atoms in the "backbone" of the polystyrene segments between crosslink junctions, C is the relative swelling power of the liquid, and λ_0^{-1} is the critical crosslink density, above which $S=0$. The observed C was correlated with the corresponding known Hildebrand solubility parameter, δ , for five liquid classifications. The solubility parameter of the polymer, δ_{sty} , determined thereby was 9.5 for substituted benzenes, 9.1 for ketone, 8.4 for ester and 7.3 for ethers. This set of observed δ_{sw} spans the range reported by earlier investigators, i.e., $\delta_{sw} = 8.6-9.7$. The plot of C as functions of the corresponding $(\delta_{sty} - \delta_{liq})^2$ for the homologous series of liquids $Z(CH_2)_nH$, where $n < 5$, are almost parallel lines given approximately by $C = A - 0.60(\delta_{sty} - \delta_{liq})^2$, where A is 2.19 for $Z = Ph$, 1.48 for $Z = RCO_2$, 1.42 for $Z = RCO$, and 0.64 for $Z = RO$. Apparently, the major factor that determines swelling power is the relative affinity of Z for the polymer. The cumulative contribution to swelling power owing to the $(CH_2)_nH$ group is only a mitigating factor superimposed on the former.