

CHAPTER II

THEORY AND LITERATURE REVIEW

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 liquids, which is almost always water, are added suspending agents that 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 (5).

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

rubber 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 1 (6). Suspension polymerization has been little used outside the field of vinyl-type or ethylenic monomers.

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:

- 1.1 water-soluble organic polymers (so-called protective colloids)
- 1.2 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 (6).

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 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 droplets form that 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

Table 1 Polymerization Processes in Water

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

Table 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 group 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 poly(methacrylic acid)	Acrylic and vinyl esters and homopolymers
-Above at pH 5.5-8 with buffers	Acrylic compounds
-Na salts of copolymers of methacrylate acid with dichlorostyrene	Dichlorostyrene, acrylonitrile, methyl methacrylate
-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 esters or vinyl esters	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-alkoxybutadiene and maleic acid	Polymerizable vinyl compounds
(b) Containing nitrogen:	
-Poly(vinyl pyrrolidone)	All polymerizable organic compounds
-Polymeric reaction products of methyl methacrylate with ammonia	Acrylic, vinyl esters and mixtures
-Above at pH 5.5-8 with buffers	Acrylic compounds, homologs

Table 2 Materials Used in Suspension Polymerization (continued)

Suspending agent	Monomer suggested
-Polymethacrylamide with NaH_2PO_4 and Na_2HPO_4 as buffers	Monomers in general
(c) Containing alcoholic OH groups:	Acrylic and vinyl esters
-Poly(vinyl alcohol)	Vinyl acetate
-Poly(vinyl acetate) partially saponified, mixtures of different mol. wt. and degrees of saponification	
(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
-Phthalate esters	Vinyl chloride
5. Condensation polymers	
Urea-formaldehyde	Vinyl chloride, vinylidene chloride,
Water-soluble phenol-formaldehyde	acrylonitrile
	Vinyl chloride polymers
6. Inorganic agents	
-Powder such as kaolin, barium sulfate, talcum, aluminum hydroxide	Polymerizable vinyl and vinylidene compounds
-Addition of powders produced by precipitation together with monomers	Polymerizable vinyl and vinylidene compounds
-Tricalcium phosphate	Polymerizable vinyl and vinylidene compounds
-Difficultly soluble neutral phosphates of 0.2- 0.005 μm	Polymerizable vinyl and vinylidene compounds
-Hydrated complex magnesium silicates	Polymerizable vinyl and vinylidene compounds
-Bentonite (colloidal clay)	Polymerizable vinyl and vinylidene compounds

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.

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.

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 (7) 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.

Sorption - Desorption Kinetics

1. Sorption 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 (8). If the polymer is crosslinked the chains remain linked to each other through chemical bonds. The polymer will swell but not dissolve in

the solvent. The swelling of these materials is determined by the solvent properties of the liquid for the polymer and the degree of crosslinking. The positive entropy of mixing of the polymer and the solvent enhances swelling. The heat of mixing may enhance (if negative) or retard (if positive) swelling. The tension set up in the polymer subchains resists swelling. A "good" solvent will give a high degree of swelling. A lightly crosslinked polymer will give a high degree of swelling, a heavily crosslinked a smaller degree of swelling.

Tanaka and Fillmore (9) characterized the swelling of spherical gels in liquids as a relaxation process. They defined the diffusion coefficient of the gel in the liquid by:

$$D = [(4u/3) + K] / f \quad (1)$$

where u is the shear of polymer network alone

K is the bulk modulus of polymer network alone

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

A characteristic swelling time τ was defined by:

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

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

$$\ln (\Delta a_t / \Delta a_0) = \text{const.} \cdot -t/\tau \quad (3)$$

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

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

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

2. Desorption Kinetics

By bringing the swollen gel into contact with a substrate and separated from the bulk of the swelling liquid, the imbibed solvent may be released. If the substrate competes favorably for the solvent the desorption will be effective, if the substrate competes poorly the desorption will be incomplete. A rapid sorption by the substrate makes the desorption from the bead rapid. A slow sorption by the substrate makes the desorption slow. The diffusion of solvent into substrate has been shown to follow the Rideal-Washburn equation (2), which describes the penetration of a liquid into capillary pores:

$$I^2 = rt \gamma \cos \theta / 2\eta = Kt \gamma \cos \theta / 2 \quad (4)$$

where I is the depth of penetration

r is the radius of the cylindrical capillaries

t is the time of penetration

η is the viscosity of the liquid

γ is the surface tension of the liquid

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

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

Crosslink Density

One of the most important structural parameters characterizing crosslinked polymers is \bar{M}_c , the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of \bar{M}_c significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine \bar{M}_c . Early research by Flory and Rehner laid the foundations for the analysis of equilibrium swelling. According to the theory of Flory and Rehner (10), for a perfect network,

$$\bar{M}_c = -V_1\rho_p \frac{(\phi_p^{1/3} - \phi_p/2)}{[\ln(1 - \phi_p) + \phi_p + \chi_1\phi_p^2]} \quad (5)$$

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

V_1 is the molar volume of the solvent

ρ_p is the polymer density

ϕ_p is the volume fraction of polymer in the swollen gel

χ_1 is the Flory-Huggins interaction parameter between solvent and polymer

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

$$q = \frac{M_o}{\bar{M}_c} \quad (6)$$

where M_o is the molecular weight of polymer repeat unit. We defined q in eq. (6) in order to simplify direct comparison with the mole fraction of divinyl monomers in copolymerization.

BET Method for Determination of Surface Area

The Brunauer Emmett Teller (BET) gas adsorption method has become the most widely used standard procedure for the determination of the surface area of finely-divided and porous materials, in spite of the oversimplification of the model on which the theory is based. It is customary to apply the BET equation in the linear form (11)

$$\frac{p}{n^a (p^o - p)} = \frac{1}{n_m^a C} + \frac{(C-1)p}{n_m^a C p^o} \quad (7)$$

where n^a is the amount adsorbed at the relative pressure p/p^o

n_m^a is the monolayer capacity

According to the BET theory C is related exponentially to the enthalpy (heat) of adsorption in the first adsorbed layer. It is now generally recognised, however, that although the value of C may be used to characterise the shape of the isotherm in the BET range it does not provide a quantitative measure of enthalpy of adsorption but merely gives an indication of the magnitude of the adsorbent-adsorbate interaction energy. Thus, in reporting BET data, it is recommended that C values are stated, but not converted to enthalpies of adsorption.

The application of the BET method is the calculation of the surface area (often termed the BET area) from the monolayer capacity. This requires a knowledge of the average area, a_m (molecular cross-sectional area), occupied by the adsorbate molecule in the complete monolayer. Thus

$$A_s(\text{BET}) = n_m^a L a_m \quad (8)$$

and

$$a_s(\text{BET}) = A_s(\text{BET})/m \quad (9)$$

where $A_s(\text{BET})$ is the total surface areas of the adsorbent

$a_s(\text{BET})$ is specific surface areas of the adsorbent (of mass m)

L is the Avogadro's constant.

At the present time, nitrogen is generally considered to be the most suitable adsorptive for surface area determination and it is usually assumed that the BET monolayer is close-packed, giving $a_m(\text{N}_2) = 0.162 \text{ nm}^2$ at $-196 \text{ }^\circ\text{C}$ (77 K).

Literature Review

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

M.H.J. Kang (2) prepared large polymer beads of 3-5 mm by seeded suspension polymerization starting with seed beads of poly(*t*-butylstyrene) crosslinked with divinylbenzene. The suspending agents were HPMC with HEC, the temperature and time schedule for polymerization was $70 \text{ }^\circ\text{C}$ -4 hr+ $90 \text{ }^\circ\text{C}$ - 2 hr and that of seeded suspension polymerization was $70 \text{ }^\circ\text{C}$ -4 hr+ $90 \text{ }^\circ\text{C}$ -8 hr. The maximum absorption of large imbibed bead was 17.1 times its own dimension.

P. Asawaworarith (3) synthesized poly(styrene-co-divinylbenzene) by suspension polymerization using the mixture of 0.4 % HPMC and 0.076 % HEC as suspending agents and BPO as an initiator. The time schedule for polymerization was 70 °C - 4 hr + 90 °C - 2 hr and seeded suspension polymerization was 70 °C-10 hr+90 °C -2 hr. The properties of copolymer beads are: specific surface area 0.1-0.8 m²/g, density 1.05 g/cm³, maximum absorption at 13.2 times its own dimension and complete desorption time of absorbed toluene at 23 hr.

T. Karoowanchareern (4) studied effect of such influential parameters as monomer fraction, temperature and time schedule, concentrations of diluent and inhibitor on absorption properties. The beads synthesized had the following properties: pore volume 0.28 cm³/g, specific surface area 94.4 m²/g, density 0.618 g/cm³, and swelling ratio 17.7 within 20 hr.

J.R. Millar, D.G. Smith, W.E. Marr, and T.R.E. Kressman (12) yielded bead copolymers with modified properties by polymerization of styrene-divinylbenzene-solvent mixtures in suspension. Depending on the proportion of solvent and of crosslink agent, a gradation in properties from those of an expanded network to those of a macroporous material is obtained, with swelling properties which can be predicted from the starting conditions. Some properties, of these disentangled copolymers are compared with those of corresponding conventional copolymers. Their structure is discussed and shown to persist in the derived ion-exchange resins.

F.M.B. Coutinho, and R.C.A. Cid (13) prepared styrene-divinylbenzene copolymers with porous structures by suspension polymerization using diluents during polymerization. These diluents, having different affinities for the copolymers, produced changes in their morphology. Various diluent compositions were employed in order to discover their influence on the porous structure of the copolymers. The proportion and type of diluents were varied. n-Heptane was used as a precipitant in association with

isoamyl acetate and ethyl acetate. The morphological changes were evaluated by apparent density, specific area and porosity. A study was also made of the influence of the divinylbenzene content in the synthesis of the copolymers on their morphological characteristics.

F.M.B. Coutinho, and D. Rabelo (14) synthesized styrene-divinylbenzene copolymers by suspension polymerization in the presence of toluene and heptane as diluents for the monomers. The effects of toluene/heptane ratio, degree of dilution of the monomers and divinylbenzene (DVB) content on the surface formation of the copolymer beads were examined by scanning electron microscopy. The sizes of the aggregates and macropores increased with increase of the nonsolvating diluent content and by the degree of dilution of the monomers. The effect of the DVB content was generally the same as that of the diluent for the monomers.

C.M. Cheng, F.J. Micale, J.W. Vanderhoff, and M.S. El-Aasser (15) prepared monodisperse porous polymer particles in the size range of 10 μm in diameter via seeded emulsion polymerization. Linear polymer (polystyrene seed) or a mixture of linear polymer and solvent or nonsolvent were used as inert diluents. The pore diameters of these porous polymer particles were on the order of 1000 \AA with pore volumes up to 0.9 cm^3/g and specific surface areas up to 200 m^2/g . The physical features of the porous polymer particles depended on the diluent type and the crosslinker content, as well as the molecular weight of polymer seed particles. By varying the molecular weight of the linear polymer, monodisperse porous polymer particles with different pore size distribution could be synthesized. Polymer seed with a low degree of crosslinking instead of linear polymer could also be used to prepare monodisperse porous polymer particles with smaller pore volume and pore size.

C.M. Cheng, J.W. Vanderhoff, and M.S. El-Aasser (16) prepared monodisperse porous polymer particles via seeded emulsion polymerization using a mixture of linear polymer (polystyrene seed) and nonsolvent as inert

diluent. Experimental evidence was presented to describe the mechanism of formation of porous polymer particles during the copolymerization and solvent extraction stages, in which porosity was a consequence of phase separation in the presence of diluents. Pore structure formation was investigated by changes in copolymerization kinetics, gel content, crosslinking density, particle morphology, surface area, pore volume, and pore size distribution.

C.M. Cheng, F.J. Micale, J.W. Vanderhoff, and M.S. El-Aasser (17) used monodisperse polystyrene latex particles with molecular weight on the order of 10^6 as inert diluents for the preparation of monodisperse porous styrene-divinylbenzene copolymer particles via seeded emulsion polymerization techniques. Mercury porosimetry and nitrogen adsorption-desorption isotherms were used to assess pore structure and pore size distribution. Pore size distribution was very sensitive to the molecular weight of the polystyrene latex particles used as inert diluent. Scanning electron microscope results indicated the existence of void between the microspheres and their agglomerates within the porous polymer particle, and nitrogen adsorption isotherms confirmed that the pores were due to interstices between these crosslinked microspheres and agglomerates.

Q.C. Wang, K. Hosoya, F. Svec, and J.M.J. Fréchet (18) developed a novel approach to monosized macroporous polymeric separation media with vastly enhanced pore size distributions and chromatographic properties. Key to this approach is the combined use of monodispersed polymeric particles and suitable solvents as porogens in the copolymerization of styrene and divinylbenzene. Following polymerization, the polymeric porogen is dissolved, leaving behind the monosized beads with a controlled pore structure. The exact pore size and pore size distribution of the final beads are largely controlled by the amount of soluble polymer in the polymerizing mixture: the larger the proportion of soluble polymer in the system, the larger the pores.

D. Rabelo, and F.M.B. Coutinho (19) developed a simple method of porous volume determination for styrene-divinylbenzene copolymers. This method is based on water uptake measurements after surface treatment with methanol in order to reduce the characteristic water repellance of the copolymer beads. The porous volume determined by water uptake is in good agreement with mercury porosimetry measurements.

M. Hattori, E.D. Sudol, and M.S. El-Aasser (20) prepared monodisperse poly(divinylbenzene) and poly(styrene-co-divinylbenzene) particles in the 0.4-3 μm size range by dispersion polymerization in methanol and methanol/co-solvent mixtures. The effects of polymerization parameters, such as the crosslinking monomer concentration, the co-solvent, and presence of oxygen were studied. For good colloidal stability, it was necessary to use a relatively large fraction of crosslinking monomers. The initial presence of oxygen was also found to play an important role in determining the colloidal stability during the polymerization.

S. Omi, K. Katami, A. Yamamoto, and M. Iso (21) obtained relatively uniform polymeric microspheres, the coefficients of variation being close to 10 % by the BPO-initiated suspension polymerization of styrenic monomers. Unlike the conventional stirred-tank system, a particular microporous glass membrane provided uniform monomer droplets continuously when monomer was allowed to permeate through the micropores. The monomer droplets were suspended in an aqueous solution containing the stabilizing agents, transferred to a stirred vessel, and polymerized. Crosslinked polystyrene spheres were also synthesized in the presence of various low-molecular-weight diluents. While a good solvent, toluene, was not so effective; poor solvents, n-hexane and n-heptane, easily yielded the microporous structure, the specific surface area being as high as 160 m^2/g .

D. Rabelo, and F.M.B. Coutinho (22) investigated the effect of the solvating power of pure diluents on the porous structure and swelling properties of styrene-divinylbenzene copolymers. The Hildebrand solubility parameter (δ) and the three-dimensional solubility parameter (δ_T) were used to predict the diluent-polymer affinity. In a general way, δ_T was a better predictor than δ . It was found that the accessibility of polymer surfaces depends not only on the fixed pore volume but also on the elasticity of internuclear chains.

D. Rabelo, and F.M.B. Coutinho (23) investigated the influence of binary mixtures of heptane with different diluents on the porous structure of styrene-divinylbenzene copolymers. It was found that the porosity produced by the diluent mixtures depends not only on the affinity of each diluent for the copolymer but also on the interaction of the diluent molecules with themselves. In this work it was observed that some polar aromatic solvents when mixed with heptane presented cosolvency effects. In general, the accessible pore volumes were higher than the fixed pore ones, indicating the formation of elastic internuclear chains.

D. Rabelo, and F.M.B. Coutinho (24) investigated the influence of binary mixtures of alcohols with different diluents on the porous structure of styrene-divinylbenzene copolymers. Two series of binary mixtures were tested: one with isoamyl alcohol (i-AmA) and another with benzyl alcohol (BA). For systems containing i-AmA, the hydrogen bonding between alcohol and polar solvent molecules exert strong precipitating effects. Copolymers prepared with polar solvent/i-AmA presented higher porosities than copolymers obtained in presence of nonpolar solvent/i-AmA. Binary mixtures with i-AmA produced more porous and rigid networks than with BA.

Q.C. Wang, K. Hosoya, F. Svec, and J.M.J. Fréchet (25) controlled the porous structure of monodisperse macroporous beads by using soluble polymers with well-defined structural characteristics as part of the porogenic mixture. In general, the use of linear polystyrene as a porogen in the

preparation of poly(styrene-co-divinylbenzene) beads shifts the pore size distribution towards larger pores. While a direct correlation between pore size and molecular weight of the poregen has been established, the chemical composition of the polymer porogen has no effect on the porous and chromatographic properties of the beads. These findings suggest that the average molar volume of the porogenic system is important while the miscibility of the polymer porogen with the crosslinked polymer that is formed is of little relevance.

M. Gallia, F. Svec, and J.M.J. Fréchet (26) studied the effect of concentration of divinylbenzene on pore size distribution and surface areas of micropores, mesopores, and macropores in uniformly sized porous poly(styrene-co-divinylbenzene) beads prepared in the presence of linear polystyrene as a component of the porogenic mixture has been studied. While the total specific surface area was clearly determined by the content of divinylbenzene, the sum of pore volumes for mesopores and macropores as well as their size distribution does not change within a broad range of DVB concentrations. Consequently, the size exclusion chromatography calibration curves are almost identical for all the beads prepared with different percentages of crosslinking monomer. However, the more crosslinked beads have better mechanical and hydrodynamic properties.