PRECIPITATION POLYMERIZATION OF DIVINYLBENZENE TO MONODISPERSE MICROSPHERES: AN INVESTIGATION OF THE PARTICLE FORMATION MECHANISM

By

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Abstract

This thesis addresses how the interactions between the reaction solvent and the forming polymer affects the morphology of the polymer formed in crosslinking polymerizations. Specifically, the mechanisms of nucleation, stabilization, growth and de-solvation have been studied in the precipitation polymerization of divinylbenzene to monodisperse microspheres. These polymer beads have diameters in the micrometer range and may prove usefully for applications such as the separation of chemical mixtures using porous microspheres.

The nucleation mechanism was found to proceed through transient microgels that are produced both by intermolecular reactions between oligomers and by further propagation. These microgels are transient and disappear from the reaction mixture at the same time as microspheres appear. This suggests that the microgels are the nuclei that grow to become the final microspheres. Internal curing reactions throughout the course of the polymerization transform the soft and deformable microspheres observed early in the reaction, into the rigid microspheres observed at the end of the reaction.

As a result of both the nucleation and growth processes and the solvency of the polymerization medium, the microspheres have a gel surface that is formed *in situ*. When swollen with good solvents this surface gel serves as a steric stabilizer and when collapsed the microspheres flocculate together.

Using a seeded polymerization method, the microspheres were shown to grow by a reactive growth mechanism. Oligomers were captured continuously from solution by radical reactions with existing microspheres. In contrast, microspheres having inert alkyl groups on their surface did not grow. Instead secondary or continuous nucleation was observed to produce new, smaller microspheres with broad size distributions.

The microspheres observed in precipitation polymerization were then related to the morphologies more commonly observed in crosslinking polymerizations: microgels, macrogels, and coagulum. The volume occupied by the polymer was observed to decrease both with decreasing solvency of the continuous phase and with increasing crosslinking monomer concentration. Crosslinking in near *theta*-solvents was determined to be responsible for contraction of the polymer network into dense microspheres. The contraction of the polymer network is likely progressive, supporting the presence of a lightly crosslinked corona around the microspheres that acts as a steric stabilizer.

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I am forever grateful to my parents Clare and Jeannette Downey for their help and support. It is without a doubt that I could not have completed graduate school without you. I would like to thank the rest of my family Kim, Harold, Ryan and Michael DeVries, Edward Downey, Christine Stiles, Carolyn Downey, and Tony Liberati for their support and

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Dedication

I dedicate this thesis to my parents Clare and Jeannette Downey and Wendy McFarlane.

Without You I Could Not Have Done It.

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CHAPTER 1

Introduction to the Particle Formation Mechanisms of Heterogeneous Polymerizations

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1.0 General Introduction

It has been said that Wolfgang Pauli once wrote, "God created the solids, the devil their surfaces" and this statement is especially true when trying to characterize the surface of colloidal particles. By definition, colloids have a least one dimension in the range of 10 nm to 1 μm and as a direct result of this, they have some very interesting and unique properties. Their small size results in an extremely large surface area per unit volume and a low mass per particle. Thus, the intermolecular forces of attraction operating between all matter have a significant impact on the properties of colloidal particles. In the case of larger objects the forces of attraction usually can not overcome the object's inertia, while, in the case of colloidal particles these same forces can lead to aggregation. Hence, for many applications steps must be taken to prevent or control this property of colloidal aggregation.

Recently, in the literature on the preparation of polymer colloids, examples have appeared where aggregation of the forming particles is inherently controlled by the polymerization. These are the so-called precipitation polymerizations and their mechanisms are not understood. It is the purpose of this thesis to gain an understanding of these mechanisms so that they may be used for the development of new materials.

This chapter starts with an introduction to the attractive forces between colloidal particles, followed by methods of preventing aggregation and their use in heterogeneous polymerizations. Emulsion, suspension and dispersion polymerization are discussed since the formation of monodisperse microspheres is better understood for these systems. The nucleation and stabilization mechanisms for the preparation of monodisperse microspheres in precipitation polymerization are investigated in Chapter 2. The growth mechanism for these particles is reported in Chapter 3 and its implications for particle stabilization are considered. The polymer morphology in crosslinking polymerizations and differing solvents is discussed in Chapter 4 and the relationships between microspheres and the more commonly observed structures of microgels, macrogels and coagulum are examined. The thesis is then summarized in Chapter 5 and future directions are recommended.

1.1 The Attractive Forces Between Colloidal Particles

In the late nineteenth century it was recognized that real gases do not always behave as predicted by the ideal gas laws and thus van der Waal proposed a modified set of equations of state to account for these differences. It is now known that this deviation from ideal gas behaviour is caused by three types of intermolecular forces of attraction between adjacent gas molecules: i) permanent dipole - permanent dipole forces, ii) permanent dipole - induced dipole forces, and iii) transitory dipole - transitory dipole forces.

Keesom first described the attractive forces between permanent dipoles in separate molecules.[1] In this model, permanent dipoles that are randomly arranged and mobile have a tendency to orient themselves such that pairs of molecules align their dipoles and produce a maximum attractive effect. A considerable temperature dependence is observed for the

Keesom attraction where increasing the temperature causes the molecules to loose their optimum alignment and hence decreases their attraction.

Debye[2,3] recognized a second source of attraction where one molecule with a permanent dipole moment attracts a second molecule by inducing a dipole moment in it. This effect only shows a temperature dependence if the second molecule has a preferred direction of polarization.

London showed in 1930 that fluctuations of the electronic charge distributions in atoms or molecules is an additional force of attraction and that this force does not require permanent dipole moments.[4,5] If we consider two infinitely separated helium atoms, the positions of their electrons about their nuclei are uncorrelated. However, as these atoms approach one another the spontaneous thermal fluctuations in their electronic distributions become coupled in such a way that an attractive force is generated between them. These correlations of electronic distributions are called transitory dipole - transitory dipole interactions with correlation lifetimes of approximately 0.1 fs. These forces are independent of atomic or molecular orientation and hence are not affected by thermal perturbations.

In the case of condensed matter such as colloids, London forces are solely responsible for long-range attractions. The reason for this is that the underlying quantum mechanical fluctuations of electronic density can be considered additive over a many-bodied system.

The effect of adding all of the possible atomic interactions is a net long range attraction between colloidal particles. This is unlike the Keesom and Debye effects where two dipoles in optimum alignment can not be in optimum alignment for attraction to a third dipole that is randomly positioned in space around them. Thus, within a single colloidal particle the Keesom and Debye effects tend to average to zero and as a result there is no net attraction between particles due to these effects.

London's original treatment of dispersion forces between gaseous atoms was extended to colloidal particles in a vacuum by Hamaker in 1937.[6,7] In his analysis, the attraction V_A between two spheres, each with a radius a, resulted in an expression with the form:

$$V_A = -(A^*/6)G \tag{1.1}$$

where A^* is the effective Hamaker constant which has dimensions of energy, and G is a geometrical expression concerned with the solid geometry of the system in question. If the separation distance between the spheres H_0 is small in comparison to the particle radius a then an approximation of $a/2H_0$ can be used for G, and Equation 1.1 simplifies to

$$V_A \approx -A^* a / 12Ho. \tag{1.2}$$

The importance of the Hamaker method is that it suggests that the attraction between colloidal particles can operate over several tens of nanometers and not just within contact distances of less than 1 nm. Thus, in order to prepare individually dispersed colloidal particles a comparable force of opposite direction and active over a greater distance must be provided to the system. The current methods for achieving these criteria are presented in the following sections.

Hamaker's original calculations are based on several assumptions that are invalid for real colloidal dispersions. He assumed that the particles in question where separated by a vacuum, however, in practice colloidal particles are normally dispersed in liquid media. Also, London's original derivation of the pair-wise attraction between gas molecules was concerned with molecules that are separated by distances comparable to that of the wavelength of the radiation responsible for the coupling of their electronic fields. Thus, only a few neighbouring molecules experience an attractive force of any significant magnitude. On the other hand, Hamaker's approach considers the sum of the attractive force between the individual molecules within a condensed colloid particle as if these molecules were in complete isolation. This is incorrect since each of these molecules is surrounded by many others and this would modify the attractive potential between them. Also, Hamaker's approach does not take into consideration that the molecules within one particle are not separated by vacuum but rather that their electronic coupling must occur through the intervening medium of the particle itself and finally through the dispersing solvent. Hence, the Hamaker approach must be modified to take into account these issues.[8] Nevertheless, calculation of the attractive force using Equation 1.2 is a good first approximation for determining the particle-particle repulsion required to prevent flocculation.

1.2 Current Methods of Repulsion

The force of attraction generated by the pair-wise coupling of the quantum mechanical fluctuations in electron density is of sufficient strength and range to cause the coagulation of naked uncharged colloidal particles. In order to prevent the aggregation of these small particles, a force of at least an equal magnitude and opposite direction, and of sufficiently long range must be generated by some means. Currently, there are only two general methods by which colloidal stability can be introduced to a system: electrostatic stabilization; and steric stabilization. Interestingly, these methods of stabilization can be combined into one system where polyelectrolytes provide electrosteric stabilization.

1.2.1 Electrostatic Stabilization

One method for projecting the repulsion over distances comparable to those of the attraction predicted by Equation 1.2 is to use Coulombic repulsion. This concept is illustrated in Figure 1 where negatively charged particles are dispersed in liquid media. The counterions of the charged particles give rise to the electrical double layers that surround each particle and these "like" charges repel one another on close approach and provide electrostatic stabilization to the colloidal particles.[8-11]

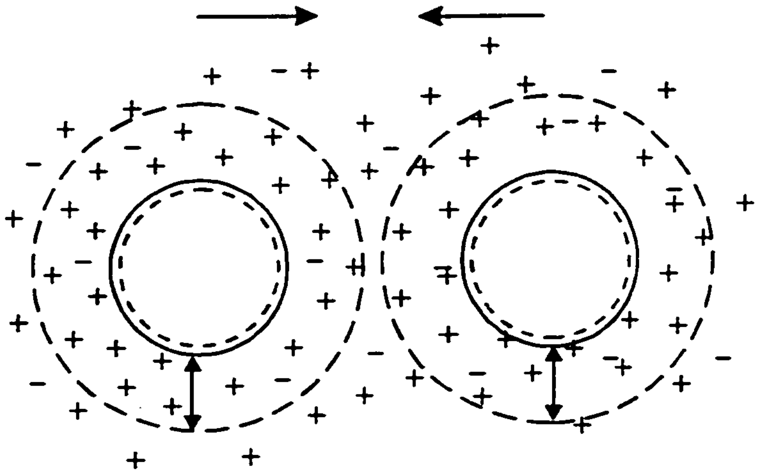


Figure 1. Schematic of the electrical double layers that give rise to electrostatic stabilization. Negatively charged particles are shown with positive counterions in the dispersion medium.[8]

Electrostatic stabilization is important only in high dielectric media, such as water, since the repulsion is generated from the diffuse counterion double layers surrounding the particles. In low dielectric media, such as most organic solvents, the thickness of the double layer is greatly diminished and does not provide sufficient repulsion to overcome the inherent van der Waals attraction between colloidal particles.

1.2.2 Steric Stabilization

A more common and arguably older method of imparting colloidal stability is that of steric stabilization which is effective in both aqueous and non-aqueous environments. Steric stabilization also offers practical advantages over electrostatic stabilization including insensitivity to high electrolyte concentrations, equal efficacy at both high and low solids content, reversibility of flocculation and good freeze-thaw stability.

The concept of steric stabilization is shown in Figure 2. Decreasing the particle separation distance, h, to a distance shorter than twice the stabilizer layer thinkness, δ, causes the surface concentration of stabilizer chains, C, to increase to $2C$ by either inter-penetration or compression. The osmostic diffusion of solvent into this region of high local concentration generates a repulsive force that separates the particles.[8,11]

An alternative approach to understanding steric stabilization is based on the thermodynamics of mixing. In this theory, inter-penetration of the steric layers to form the

$2C$ region would require solvent molecules to be expelled from this region thus breaking stronger solvent-stabilizer contacts in favour of weaker stabilizer-stabilizer contacts. This would lead to an increase in the enthalpy of the system. Also, the entropy of the system would decrease as the concentration of the stabilizer chains is forced to increase to $2C$. Consequently, colloidal particles are sterically stabilized when dispersed in a medium that is a good solvent for their attached stabilizer chains.[8,11]

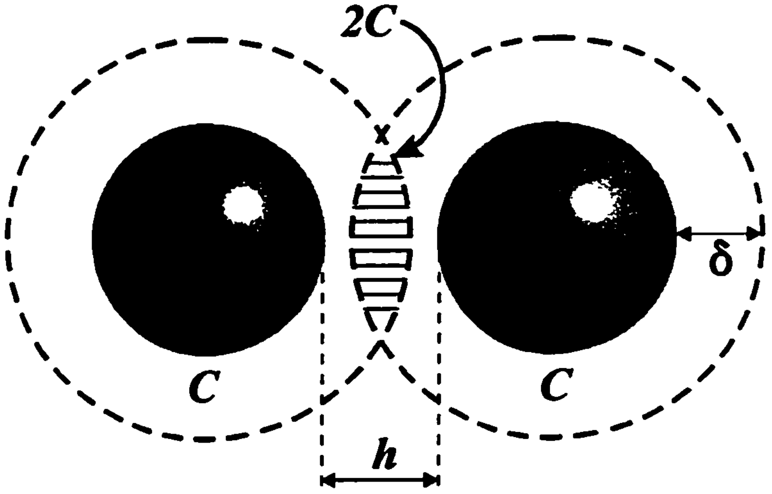


Figure 2. Schematic representation of steric stabilization for the close approach of two colloidal particles with a surface concentration of stabilizer chains *C*, separated by a distance *h*, and a stabilizer layer thickness δ.[11]

Steric stabilization can be achieved only when the stabilizing polymers have an affinity for both the particle and the surrounding media. The polymer can be attached to the particle surface by either physical adsorption or by covalent bonding through copolymerization or grafting reactions.

1.2.2.1 Block Copolymers as Steric Stabilizers

Amphipathic block copolymers where one block is soluble in the dispersion media and the other has no or limited solubility, can be used as steric stabilizers. This concept is shown in Figure 3 where an insoluble block, A, adsorbs to the particle leaving the soluble block, B, freely solvated by the dispersing media and this in turn sterically stabilizes the particle.

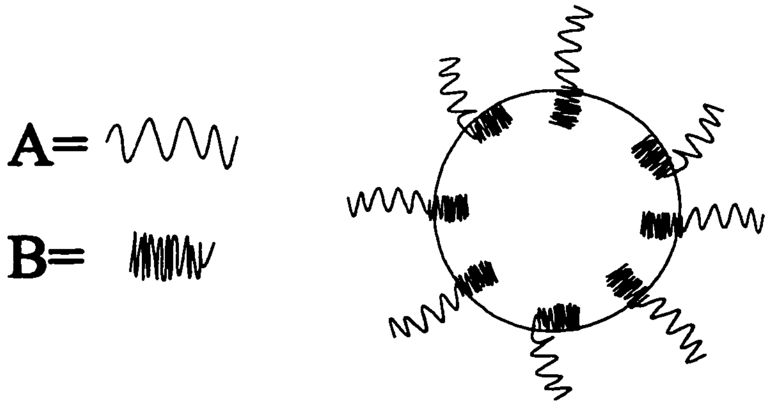


Figure 3. Amphiphilic block copolymers as steric stabilizers.

Several groups have investigated the effect of block copolymer concentration on particle size in heterogeneous polymerizations. It is commonly observed that the particle size obtained in a given system decreases with increasing concentration of the block copolymer. The increased stabilizer concentration means that there are more stabilizing blocks available to the system to form more interfacial surface area and consequently smaller particles are obtained.[12-16]

Winzor *et al.* investigated the effect of stabilizer molecular weight on particle diameter in the polymerization of styrene in methanol using poly(styrene-*b*-ethylene oxide) copolymer stabilizers.[12] The insoluble styrene segment anchors the stabilizer to the particle surface whereas the ethylene oxide fragment is the solubilizing block. Comparing a block copolymer with PS=1840 g/mol and PEO=6 800 g/mol to one with PS=16 000 g/mol and PEO= 56 000 g/mol they observed that much smaller particles were formed using the higher molecular weight stabilizer. These authors and others have indicated that it is primarily the molecular weight of the stabilizing block that is important and not necessarily the total molecular weight of the polymer.[12,13,16]

A distinct advantage of using block copolymers as steric stabilizers is that their structure can be fine tuned. Baines and coworkers investigated the polymerization of styrene in alcoholic media using poly(2-(dimethylamino)ethyl methacrylate-*b*-alkyl methacrylate) copolymers.[13] The alkyl methacrylate block anchored the stabilizing PDMAEMA block to the polystyrene particle surface. The hydrophobicity of the anchoring block was varied by copolymerizing methyl, ethyl, *n*-butyl, and *n*-octyl methacrylate with DMAEMA and all of these block copolymers contained approximately 20 mol% alkyl methacrylate. Stable latexes were produced when the anchoring block consisted of methyl, ethyl or *n*-butyl methacrylate although, in the ethyl and *n*-butyl cases some coagulum was observed. When the anchoring block consisted of *n*-octyl methacrylate stable dispersions could not be obtained. The increase in stabilizer efficiency with decreasing size of the alkyl substituents was attributed to the increasing compatibility of the stabilizer with the polystyrene particle surface.

Although amphiphilic block copolymers are an obvious choice, other copolymer architectures have been investigated for their suitability as steric stabilizers.[14-17]

1.2.2.2 Steric Stabilization using Homopolymers

Soluble homopolymers are a much less obvious way of providing steric stabilization to colloidal dispersions since they do not have a clear method of attaching themselves to the particle surface. Consequently, there has been some controversy about their actual mode of attachment.[18-20] It is now generally accepted that hydrogen abstraction followed by grafting reactions results in the *in situ* formation of amphiphilic copolymers which then adsorb onto and stabilize the forming particles. This is represented schematically in Figure 4.[18,21-27]

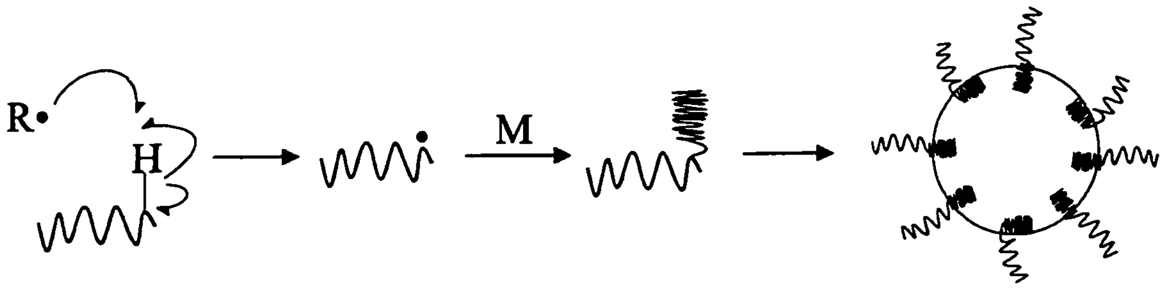


Figure 4. Schematic of the hydrogen abstraction and monomer grafting reactions by which homopolymers become steric stabilizers.

Lok and Ober studied the polymerization of styrene in various solvents using nonionic cellulose derivatives as steric stabilizers.[18] They indicated that radicals formed from decomposition of the initiator first abstract hydrogens from the cellulosic stabilizer, and that these macroradicals then add monomer to form cellulose-*g*-PS copolymers which act as the actual steric stabilizer.

Paine and coworkers have studied the polymerization of styrene in alcoholic media using poly(vinyl pyrollidone), PVP, as steric stabilizer.[19] The stability of the final particles was attributed to the formation of PVP-*g*-PS copolymers formed by abstraction of an *alpha* hydrogen on the pyrollidone moiety, and subsequent graft formation from this site.

Investigating the early stages of the polymerization of methyl methacrylate in methanol using PVP as steric stabilizer, Shen *et al.* suggested that both graft copolymer formation and adsorption of PVP contributed to the stabilization of the forming latex particles.[20]

Kobayashi *et al.* investigated the effect of homopolymer molecular weight in the polymerization of methyl methacrylate using poly((propionylimino) ethylene), PPIE, as steric stabilizer. They observed that the particle size decreased as the molecular weight of the homopolymer stabilizer increased and this is analogous to the case of block copolymer stabilizers.[28]

1.2.2.3 Macromonomers as Steric Stabilizers

As described above, stabilization using block copolymers involves physical adsorption of the stabilizer to the surfaces of the particles. Homopolymers become stabilizers by hydrogen abstraction followed by grafting reactions to form amphiphilic copolymers *in situ*. In both of these cases a considerable amount of stabilizer, typically around 10% by weight based on monomer must be added to the system. In practice it would be preferable if the amount of added stabilizer could be minimized as this would reduce the cost and complexity of the polymer synthesis. Recently, more efficient stabilizers have been developed where the stabilizing moiety is covalently attached to a polymerizable group. This concept is illustrated in Figure 5.

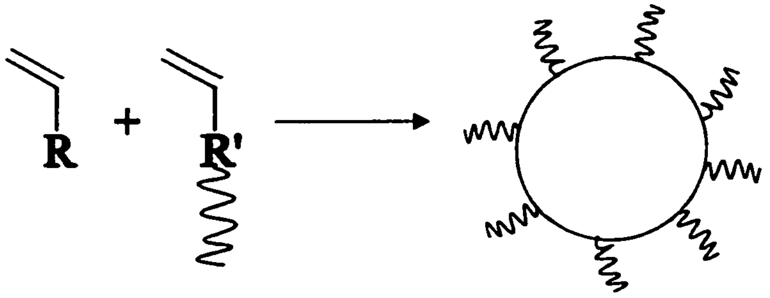
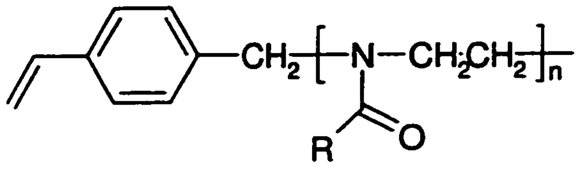


Figure 5. Macromonomer stabilizers copolymerize with the monomer to covalently attach the stabilizing moiety to the particle surface.

Kawaguchi *et al.* investigated the copolymerization of *n*-butyl methacrylate with poly(ethylene oxide) macromonomers in mixtures of methanol-water. They were particularly interested in the effects of structure, molecular weight, and concentration of the macromonomers on particle size.[29] Macromonomers of the general structure $CH_3O\text{-}(EO)_n\text{-}(CH_2)_m\text{-}S$ were used where S is styrene. A decrease in particle size was observed when the length of the alkyl spacers, m, was increased from m=1 to 7. Their explanation for this observation was that the relative reactivity of the C7 macromonomer would be greater since it would tend to adsorb to the surface of the hydrophobic latex, increasing its local concentration. Particles with radii of approximately 112 nm and 89 nm (calculated from Figure 2 in reference) were observed when the length of the poly(ethylene oxide) segments, n, were 53 and 110 respectively. This observed decrease in latex size with increasing stabilizer molecular weight was attributed to the increased surface area occupied by a single PEO chain. Latex size was found to decrease with increasing concentration of all the macromonomers studied and this is in agreement with the observations made for the more common block copolymer stabilizers.[12,13]

Styryl-terminated poly(2-alkyl-2-oxazoline) macromonomers have been investigated as steric stabilizers in the polymerization of *n*-vinylformamide in polar media by Uyama and coworkers.[30] A generalized structure for the stabilizers investigated is shown in Figure 6.



R = Me	M_w=4800
R = Et	M_w=3500
R = *iso*-Pr	M_w=4200

Figure 6. General structure for the styryl terminated poly(2-alkyl-2-oxazoline) macromonomers used as steric stabilizers in the polymerization of *n*-vinylformamide in alcoholic media.

While studying the effect of the structure of the alkyl substituents on particle size and size distribution it was observed that monodisperse beads with diameters of 1.2 µm were obtained for the methyl-substituted macromonomer whereas at the same macromonomer concentration of 0.5 wt%, the ethyl- and *iso*-propyl-substituted species lead to polydisperse particles with average diameters of approximately 0.6 µm. The ethyl and *iso*-propyl substituted macromonomers were too hydrophobic to act as efficient stabilizers. Also, their results were compared to those obtained for a poly(2-ethyl-2-oxazoline) homopolymer with a molecular weight similar to those of the macromonomer stabilizers. Monodisperse particles with diameters of 1.7 µm were observed using 10 wt% of the homopolymer stabilizer whereas using only 0.5 wt% of the methyl substituted macromonomer particles with diameters of 1.2 µm were obtained. Thus, the authors have suggested that the efficiency of the macromonomer stabilizers is much increased over that of the homopolymer stabilizer.

1.2.3 Electrosteric Stabilization

Electrosteric stabilization combines the concepts of electrostatic and steric stabilization where polyelectrolytes are used to stabilize the colloidal particles and this is shown in Figure 7. This hybrid system has the distinct advantage that stabilization can be achieved in both organic solvents and in aqueous media.[8,11]

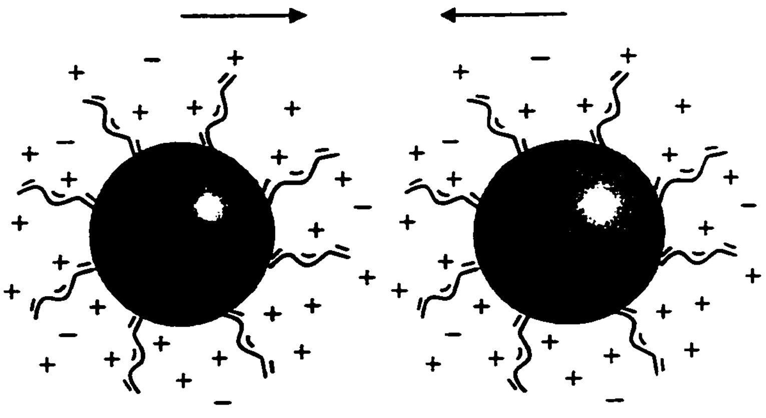


Figure 7. Schematic of the close approach of two colloidal particles electrosterically stabilized by polyelectrolytes.[8]

1.3 Heterogeneous Polymerizations

In solution polymerization monomers are dissolved in the continuous phase which can be an organic diluent or the monomer itself. As polymerization proceeds and more, or higher molecular weight, polymers are formed the solution viscosity increases significantly and this makes processing on an industrial scale both difficult and costly. Also, polymerization is typically an exothermic process and at higher monomer concentrations the increasing viscosity can lead to a significant gel effect where termination reactions are essentially shut off. This in turn produces more heat which further accelerates the rate of polymerization. If the heat is not removed as fast as it is produced then the reaction can run away. Not only does this pose obvious safety concerns, but it can also lead to a degradation of the polymer properties. In addition, many organic solvents suitable for polymerizations have been identified as toxic or environmentally unfriendly and as a result the polymerization medium of choice is water. However, most organic polymers are insoluble in water. The heterogeneous polymerization techniques which include emulsion, suspension, dispersion and precipitation polymerization have been developed to overcome the aforementioned issues.

1.3.1 Emulsion Polymerization

Emulsion polymerization has become the most important method of industrial polymer synthesis and as a result a considerable amount of work has been published in this field.[31-41]

Typically, these polymerization are conducted by emulsifying an organic monomer in water with the help of an electrostatic stabilizer. The structures that form are shown in Figure 8. The initiator is chosen so that it is located in the continuous aqueous phase. The bulk of the monomer is located in large droplets while some of it partitions into the aqueous media and from there into the micelles. The distribution of the monomer between these three sites depends on its solubility in water. For example, styrene has a solubility of only 0.25 g/L at 70 °C in water and thus is located primarily in droplets and swollen micelles.

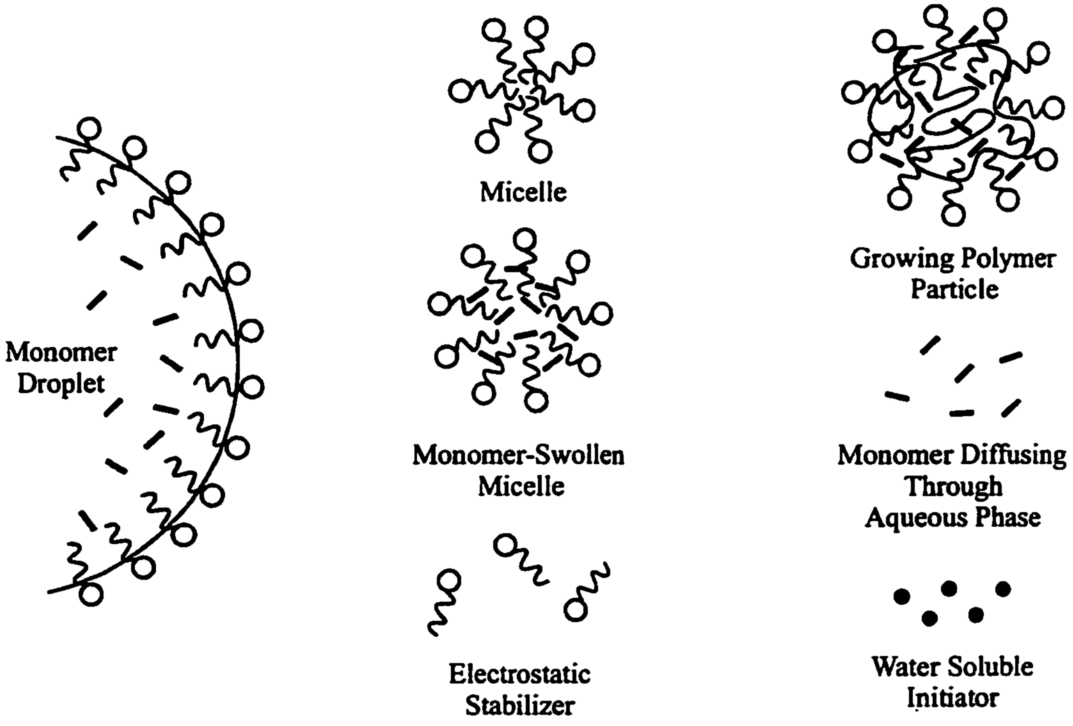


Figure 8. The structures observed in emulsion polymerization.

Polymerization begins in the aqueous phase since the monomer has slight water solubility and the free radical initiator is present only in this phase. The hydrophobicity of the growing chains increase with each monomer added and particle nucleation occurs when a growing chain enters into the hydrophobic interior of a micelle. Considering that there are several orders of magnitude more micelles present than monomer droplets it has been reasoned that statistically a diffusing chain will encounter a micelle before it encounters a monomer droplet. Once nucleation has occurred the interior of the micelles become the primary locus of polymerization. Nucleation stops when there are no more original micelles. The monomer droplets continually re-supply the aqueous phase with monomer that has been consumed by the polymerization.

1.3.1.1 Effect of Stabilizer Concentration

The size of the monomer droplets has no direct effect on the size of the particles formed and the reason for this is that polymerization occurs inside the micelles. However, parameters that directly effect the number of micelles produced will ultimately change the number of particles formed and their size. Increasing the concentration of the stabilizer increases the number of micelles formed. Since nucleation occurs by primary chains entering into the micelles it is expected that the number of particles formed would also increase. A general relationship of $N \propto S^{0.6}$ has been determined for emulsion polymerizations where N is the number of particles formed and S is the concentration of the surfactant. This relationship has been observed for a wide range of emulsion polymerization systems.[31]

1.3.1.2 Effect of Initiator Concentration

The initiator is only present in the aqueous phase and this is where polymerization begins. Nucleation occurs when the growing chains enter into the micelles and therefore it is expected that the initiator concentration should affect the number of particles produced in emulsion polymerization. Zimehl and coworkers studied the effect of potassium peroxodisulphate concentration on the polymerization of styrene in aqueous media using sodium dodecyl sulphate stabilizer.[42] The particle size decreased from greater than 500 nm to 100 nm and the size distribution narrowed as the concentration of the initiator increased from 0.50 g to 1.00 g for every 25 mL of styrene. This effect has been observed for other systems, as well.[31,33,41,43]

Increasing the initiator concentration increases the rate of initiation of polymer chains and subsequently the number of micelles which are entered would increase as well. Since a greater number of nuclei are formed the final particle size decreases.

1.3.1.3 Effect of Temperature

It is expected that the nucleation mechanism outlined above should be influenced by parameters that effect the reaction kinetics. The effect of reaction temperature on particle size has been studied by Bagchi *et al.* for the polymerization of vinyl toluene in aqueous media using sodium dodecyl sulphate stabilizer and initiated with potassium persulphate.[43] It was observed that the latex size decreased from 80 nm at 23 °C to 40 nm at 80 °C.

Increasing the reaction temperature has an effect similar to that of increasing the initiator concentration in that the number of radicals produced in the aqueous phase per given time interval would increase at higher temperatures and consequently a greater number of nuclei are formed.[31]

1.3.1.4 Effect of Monomer Solubility

The mechanism of emulsion polymerization is dependent on the partial solubility of the monomer in water since this determines both the concentration of monomer in the same phase as the initiator, as well as the rate of partitioning of the monomer from droplets to nuclei. Ultimately, this affects both the nucleation mechanism and the kinetics of the reaction. A great deal of work has been conducted in this area and recently it has been reviewed.[41]

1.3.1.5 Emulsifier-free Emulsion Polymerization

An interesting variation of emulsion polymerization is the so called emulsifier-free emulsion polymerization where stable latex particles are prepared in the absence of an added electrostatic stabilizer. Reactions of this type are initiated with an ionic species such as potassium persulphate and as a result all chains will have an ionic end group. It has been estimated that growing chains containing 3-7 repeat units aggregate into micellar structures and subsequently polymerization proceeds by the typical emulsion polymerization mechanism.[44] Recently, Thomson *et al.* have shown experimentally that the size of these initial chains is 8-9 repeat units in the polymerization of methyl methacrylate.[45]

1.3.2 Suspension Polymerization

The primary difference between an emulsion and suspension polymerization is the choice of initiator. In suspension polymerizations, the initiator is dissolved in the organic monomer and these two are insoluble in the aqueous phase. Mechanical mixing of this system causes the formation of droplets which are then stabilized by either an electostatic or steric stabilizer. Polymerization converts these droplets directly into microbeads. Thus, suspension polymerization can be considered a microbulk, or if the monomer droplets are diluted with an inert solvent, a microsolution polymerization.

1.3.2.1 Particle Size Control

The final particle size in suspension polymerization is determined by the size of the monomer droplets from which they are derived. The droplet size is determined by two competing processes: i) mechanical stirring that continually decreases droplet size, and ii) coalescences that continually increases droplet size. As a result, a range of droplets sizes are observed and hence the final particle size distributions are broad.[46-48] Reaction parameters such as stabilizer concentration, ratio of aqueous to organic phases, and the viscosities of both phases can influence the equilibrium droplet size and consequently, affect the final particle size.[46-52]

1.3.2.2 Internal Morphology of Suspension Polymerization Beads

An important feature of suspension polymerization is the ability to control the internal morphology of the polymer particles and it is for this reason that they have found wide-spread use as separation media for chromatographic applications. The beads can be made porous by diluting the monomer phase with organic solvents and the volume and size of the pores is dependent on the interaction between the diluent and the forming polymer. A useful method for estimating these interactions is based on the Hildebrand solubility parameters which are derived from the heat of mixing, ΔH_m,

$$\Delta H_m / V = \phi_1 \phi_2 [\delta_1 - \delta_2]^2 \qquad (1.3)$$

where V is the total volume of the mixture, ϕ_i is the volume fraction and δ_i is the solubility parameter of the i component, respectively. The solubility parameters are theoretically defined as $\delta_i = (c_i w_{ii}/2 v_i)^{1/2}$ where c_i is the number of contacts one molecule can make with other molecules, w_{ii} is the interaction energy of the different molecular contacts and v_i is the molar volume. In practice, solubility parameters can be determined from the energy required to vaporize a volatile liquid since the molecules are taken from their equilibrium distance to an infinite separation in the vapour phase where all of the c_i contacts with w_{ii} energy are broken. Therefore the solubility parameter can be estimated from the cohesive energy density, *CED*,

$$\delta = CED^{1/2} = (\Delta E / V)^{1/2} \qquad (1.4)$$

where ΔE is the energy required to vaporize a liquid of volume V. Thus, for small molecules the solubility parameters can be determined in a straightforward manner, however, in the case of polymers, which are not vaporizable, the solubility parameter must be estimated. This is typically done by assigning it the solubility parameter of the small molecule that swells a lightly crosslinked version of the polymer the greatest, or alternatively, that of the molecule which produces the highest intrinsic viscosity of the polymer in solution. Polymer dissolution occurs when $\Delta G_m=\Delta H_m-T\Delta S_m$ is negative, where ΔG_m is the free energy of mixing, ΔH_m is the heat of mixing, T is the absolute temperature and ΔS_m is the entropy of mixing. For ideal solutions the entropy of mixing is always positive and thus to ensure dissolution of the polymer ΔH must be near zero or negative. Therefore, from Equation 1.3 it can be seen that this condition can be met when $\delta_1=\delta_2$. Experimentally it is observed that polymers usually dissolve when the difference between the solubility parameters of the polymer and the solvent is less than approximately 2(cal/cm^3)$^{1/2}$. However, it is sometimes observed that polymers dissolve even though their solubility parameters are considerably different. To explain this Hansen has divided the single solubility parameter into a three dimensional solubility parameter comprised of a H-bonding term, a dipolar term and a dispersion term. For many polymer-solvent systems where H-bonding and dipolar interactions are dominant, this method is much more accurate for predicting solubility.[53]

The effective solubility parameter for a mixture of solvents, δ_m, can be estimated from,

$$\delta_m = \phi_A\,\delta_A + \phi_B\delta_B \tag{1.5}$$

where ϕ_A, ϕ_B and δ_A, δ_B are the volume fractions and the solubility parameters of the solvents

A and B, respectively.[9,11] Consequently, dissolution of a polymer may be observed in a mixture of solvents where the individual solvents alone would not dissolve the polymer.

Several groups have used mixed solvent systems to control the internal morphology of suspension polymerization particles.[48-50,53-63] In general, the monomer is diluted with either a good solvent, a poor solvent or a mixture of both, for the forming polymer. The solvency of the mixture can be calculated as shown in Equation 1.5. Crosslinking monomers are added to the mixture to increase particle integrity and this is important for chromatographic applications where the solvents used would otherwise dissolve the polymer. In the presence of good solvents and a crosslinking monomer the forming polymer phase separates late in the reaction and particles with either no permanent pores[57] or with small pores are observed.[50] On the other hand, large pores are formed in poor solvents since the polymer phase separates early in the reaction to form globular structures which then aggregate and further crosslink to form the final particles.[50,54,57,64-66]

The internal morphology of suspension polymer beads has been investigated using electron microscopy by both Guyot and Horák.[54,57] Guyot studied the polymerization of styrene whereas Horák investigated acrylate derivatives. In both cases, the interior of the suspension beads was observed to consist of spheres ranging in size from several hundred nanometers to several micrometers. These primary structures are formed by phase separation and crosslinking of the forming polymer and at later stages of the reaction they overlap but can not coalesce since they are crosslinked. Further crosslinking between these primary structures leads to the final particles.

As mentioned earlier, suspension polymerization can be considered as a microsolution or a microbulk polymerization, however, this author suggests that considering the conditions used for the preparation of macroporous resins above, suspension polymerization could also be considered as a microprecipitation polymerization. From this perspective Chapters 2, 3 and 4 of this thesis could be considered an investigation of the mechanisms leading to the primary structures observed in suspension polymerization where overlap and crosslinking between the primary structures is prevented by the low monomer loadings.

1.3.3 Dispersion Polymerization

Dispersion polymerization has been developed largely by the coatings industry in response to the limitations of both solution and emulsion polymerization. The viscosity of a polymer solution rises sharply with increasing concentration and molecular weight of the polymer and thus low solids formulations with low molecular weights must be used for spray or brush application. The limitation of emulsion polymerization for the preparation of coatings is that imposed by the continuous aqueous media. Water has a much higher latent heat of evaporation (2.3 kJ/g) compared to most organic solvents (<0.4 kJ/g) and in coating applications a significantly higher heat input is required for evaporation and film formation.

Also, water has a relatively high freezing temperature in comparison to many organic solvents and this can complicate the storage and use of polymer emulsions in cold conditions. In addition, the dispersants used to stabilize the emulsion particles introduce a residual water sensitivity to the final film which decreases performance. Since its original development dispersion polymerization has become an increasingly important process for the production of adhesives, cosmetics, lubricants, encapsulated pigments, polishes, rubbers, textile treatments, polymeric supports, and many others. Barrett has described dispersion polymerization as a special case of precipitation polymerization, where flocculation is prevented and particle size is controlled.[11]

1.3.3.1 Mechanism of Particle Formation

The mechanism of dispersion polymerization has been investigated by several groups in an attempt to understand and further control the polymers produced.[18,20,21,24,67,68]

In a dispersion polymerization, the monomer, initiator and dispersant are dissolved in an organic solvent that is a poor solvent for the forming polymer. Typical examples include the polymerization of styrene or methyl methacrylate using AIBN in ethanol with PVP as stabilizer. The mechanism of dispersion polymerization is shown in Figure 9. Initially, oligomers are formed in solution and as they grow they eventually reach the limit of their solubility and collapse upon themselves. Being colloidally unstable, they then aggregate to form precursors. Simultaneous to the formation and aggregation of the precursors is their adsorption of the amphiphilic steric stabilizers. Eventually the precursors become covered with stabilizer and their aggregation with similar sized species (homocoagulation) ceases because they are now sterically stabilized. The resulting species are called particle nuclei. Monodisperse final particles are observed when all particle nuclei are formed within a short period of time. Nuclei grow by continuous diffusional capture of precursors (heterocoagulation) and propagation within the particles. Final particles tend to be monodisperse and may have sizes ranging from 1-20 μm.[67]

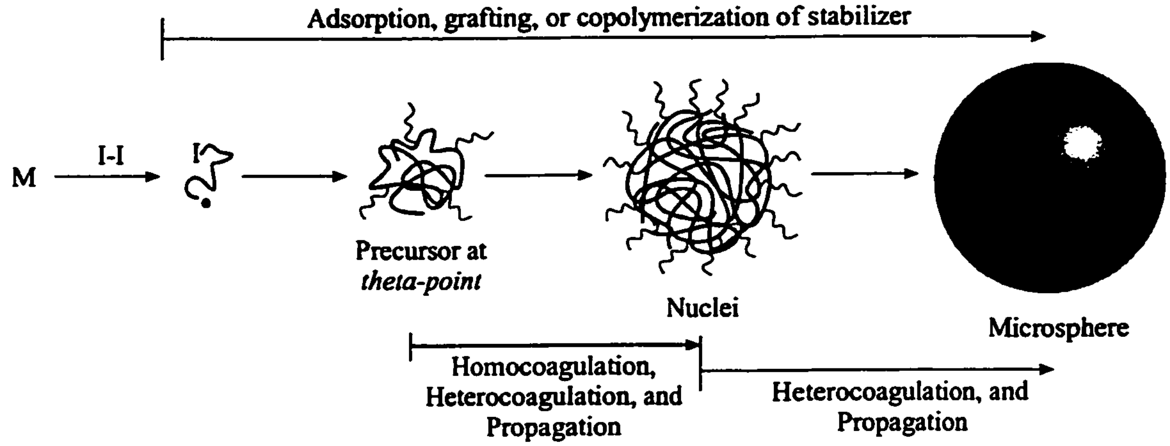


Figure 9. The mechanism of dispersion polymerization.[67]

1.3.3.2 Effect of Initiator Concentration

Since increasing the initiator concentration was found to decrease the size of latex particles prepared by emulsion polymerization, several groups have investigated its effect on particle size in dispersion polymerization to see if similar control can be obtained. Thomson *et al.* observed that the average particle diameter increased from 3.6 μm at 1.0 wt% AIBN to 6.5 μm at 3.0 wt% AIBN in the polymerization of styrene.[69] This effect is opposite to that observed in emulsion polymerization and a similar effect has been observed by others.[19,28,67,70] Paine and coworkers suggested that increasing the initiator concentration decreases the molecular weight of the polystyrene graft and as a result the PVP-*g*-PS has less amphiphilic nature and therefore is less efficient as a stabilizer.[19] Kobayashi *et al.* attributed the increasing particle size to an increase in the number of chain transfer to initiator reactions which they claim would lead to the formation of fewer particle nuclei and hence larger particles.[28] Lok and Ober on the other hand, observed an increase in particle size with decreasing initiator concentration in the dispersion polymerization of styrene using cellulosic stabilizers.[18] Thus, the mechanism by which initiator concentration affects particle size is still not completely understood.

1.3.3.3 Effect of Temperature

The effect of temperature in dispersion polymerizations has not received a great deal of attention. The reason for this is that it affects both the rate of free radical formation and the solubility of the polymer formed. The particle size was observed to increase with increasing temperature in the polymerization of styrene using benzoyl peroxide initiator and hydroxypropyl cellulose stabilizer. This effect was attributed to the formation of more soluble, lower molecular weight polymers at higher temperatures, and hence these soluble polymers would have less tendency to aggregate and form nuclei. This would in turn lead to an increase in the final particle size.[71] Similar observations have been made in the dispersion polymerization of methyl methacrylate using PVP stabilizer and initiated with AIBN.[20]

1.3.3.4 Effect of Solvency

The choice of solvents for a dispersion polymerization affects several aspects of the reaction including the rate and locus of polymerization, monomer partitioning and stabilizer efficiency.

In the dispersion polymerization of methyl methacrylate it was found that changing the ratio of water:methanol from 80:20 to 0:100, respectively changed the rate of polymerization, with higher rates observed at higher water concentrations.[28] In neat methanol, polymerization occurs primarily in the continuous phase whereas in the aqueous mixture the MMA partitions into the disperse phase where polymerization occurs under gel effect conditions. This was confirmed by molecular weight measurements where M_w for the polymer prepared in 20:80 water:methanol was 1.1×10^5 g/mol compared to 11×10^5 g/mol for the 80:20 sample, respectively. Also, the average particle diameter was observed to decrease with increasing volume fractions of water. A possible explanation is that the degree of polymerization at which oligomers form nuclei decreases with increasing water content and as a result a greater number of nuclei are formed and correspondingly smaller particles are observed.[28]

Ober and Lok investigated the effect of solvency in the dispersion copolymerization of styrene and *n*-butyl methacrylate at 15% total monomer loading in ethanol:water mixtures, using poly(acrylic acid) as steric stabilizer and benzoyl peroxide as initiator.[23] The volume percent of water in the ethanol:water mixture was varied from 6.3% to 9.8% which corresponds to solubility parameters ranging from 13.1 to 13.7 $(cal/cm^3)^{1/2}$, respectively. The observed average particle diameter decreased from 13.5 μm at 6.3 vol% water to 2.41 μm at 9.8 vol %. In the range of 7.0 to 7.7 vol% water, monodisperse particles were formed, while outside of this range the distribution broadened. Increasing the water concentration decreases the solubility of the forming polymer and promotes nucleation by aggregation. The result of this effect is a decrease in the final particle size. Also, the rate of polymerization was observed to increase since the monomer partitions into the particle phase where polymerization proceeds under gel-effect conditions.

1.3.3.4 Effect of Monomer Concentration

The monomers in a dispersion polymerization are an integral part of the initial solvent mixture. The effect of initial methyl methacrylate concentration on particle size and size distribution has been investigated by Kobayashi and coworkers.[28] Varying the initial monomer concentration from 5 to 30 wt% of the reaction mixture, it was observed that the average particle diameter increased from 2.1 μm at 5 wt% to 6 μm at 30 wt%. However, monodisperse particles were observed only between 5 to 10 wt% while above this range the particle size distribution broadened. It has been established that increasing the solvency of the continuous phase increases the particle size observed in dispersion polymerizations.[19] Since most monomers are good solvents for their polymers it is reasonable that increased monomer concentration would also lead to an increase in particle size. Another effect of increasing monomer loading is that the solvency of the reaction mixture changes as monomer is consumed, and in some cases this may lead to coagulation late in the reaction.[67]

1.3.3.5 Effect of Crosslinking Monomers

Certain applications for polymer particles require them to retain their integrity under many different conditions one of which is in the presence of good solvents. Since, dispersion polymer particles are aggregates of linear chains they will dissolve in good solvents. Several groups have investigated copolymerization with crosslinking monomers to increase the stability of dispersion particles in good solvents. It has been observed that crosslinking monomer levels of as little as 1% lead to coagulation.[19-21,26,69,72] These results suggest that at higher crosslinking monomer concentrations the stabilizers become buried within the particle because of crosslinks, and can not migrate to the surface.

Studying the dispersion copolymerization of technical grade divinylbenzene, Li and coworkers observed that at effective crosslinker concentrations of 50% to 55% and PVP concentrations of 16 g/L, narrow disperse highly crosslinked microspheres could be prepared. This high amount of stabilizer compensates for the stabilizer chains that become buried within the particles during the polymerization.[70]

1.3.4 Precipitation Polymerization

Precipitation polymerization is a modified solution polymerization where the polymerization is conducted in a non-solvent for the resulting polymer. Therefore as the reaction proceeds the forming polymer precipitates from solution. Stabilizers are not added to the reaction mixture and as a result the precipitating polymers rapidly aggregate to form particles with ill-defined shapes and sizes. It is interesting to note that Barrett has referred to dispersion polymerization as a precipitation polymerization where aggregation is controlled by adding steric stabilizers.[11]

1.3.4.1 Mechanism of Particle Formation

Precipitation polymerizations begin as homogeneous solutions were the monomers and initiator are dissolved in the continuous phase which could be either aqueous or non-aqueous. In certain cases the monomer itself can be the continuous phase and examples are the bulk polymerizations of both vinyl chloride and acrylonitrile.[48] The unique aspect of precipitation polymerization that separates it from the other heterogeneous processes is that surface stabilizers are absent from the reaction mixture. Initiation and polymerization occur in the continuous solution and eventually the growing polymer chains reach the limit of their solubility and precipitate from solution. The point at which the polymer precipitates is dependent on the solubility of the polymer. In good solvents, the polymer is freely soluble and does not become insoluble unless a crosslinking monomer is added to the reaction mixture. This decreases the swellability of the polymer by decreasing the entropy of mixing. In poor solvents, the enthalpy of mixing of the solvent and polymer is positive and as a result they phase separate. At this point, polymerization can occur in the continuous phase, the polymer rich phase, or both. Thus, the locus of polymerization depends largely on the partitioning of the monomer and initiator between the different phases.

1.3.4.2 Particle Size Control

Bamford and coworkers reported the synthesis of polymeric supports by precipitation copolymerizations of either styrene, methyl methacrylate or 2-hydroxy ethyl methacrylate with divinylbenzene, using AIBN as initiator in mixtures of benzene and hexane.[73] The particles obtained in all cases were irregular shaped and polydisperse, with sizes ranging from 25 to 100 mesh. The average particle could be decreased by increasing the rate of stirring, however, they were unable to obtain fine control of the particle size and size distribution.

Kawaguchi *et al.* have reported the preparation of monodisperse microspheres by precipitation copolymerization of acrylamide (AAm), methylene-bisacrylamide (MBAM) and methacrylic acid (MAA) in methanol, ethanol and 1-propanol.[74] Coarse and polydisperse particles were observed for the polymerization of acrylamide and this was independent of the type of alcohol solvent used and also independent of MBAM concentration. Narrow or monodisperse microspheres were observed for the terpolymerization of AAm, MBAM and MAA when the ratio of monomers was between 2/1/1 to 5/1/1, respectively. Increasing the relative amount of MAA resulted in a decrease in particle size corresponding to an increase in the total particle surface area. This result suggests that MAA serves as a steric stabilizer for the particles because of its amphiphilic properties. Electrosteric effects may contribute, also, to stabilization in alcoholic solvents.

Naka and coworkers studied the polymerization of diethylene glycol dimethacrylate (DEGMA) initiated by γ-rays.[75,76,19] Microspheres were observed when the polymerization of 10 vol% DEGMA was conducted at 25 °C in ethyl acetate which is a good solvent for the polymer. Monomer conversion and particle size were observed to increase with increasing irradiation time. Naka suggested that since discrete microspheres were formed in good solvents, there must be a driving force causing the collapse of the network. Specifically, crosslinking is thought to be responsible for collapse of the polymer into dense particles since microspheres are observed only in the presence of the crosslinking monomer. Thus, microsphere formation could be a special case in the polymerization of crosslinking monomers, where morphologies such as microgels and macrogels are more commonly observed.

Li and coworkers reported the preparation of monodisperse microspheres in the precipitation polymerization of divinylbenzene at monomer loadings of 5 vol% and below.[70,77] The polymerization solvent was found to be critical since monodisperse microspheres were observed only, in acetonitrile and mixtures of acetonitrile containing up to 40 vol% toluene. Diluting DVB-55 or DVB-80 with 4-methyl styrene, they were able to investigate the effect of crosslinker concentration over the range of 0% to 80%. It was observed that a high concentration of crosslinking monomer was required to produce microspheres. More recent experiments have indicated that microspheres can be prepared by this method using as little as 5% DVB.[78] Originally, it was suggested that their crosslinked structure along with their surface roughness was responsible for their colloidal stability. Varying the initiator concentration between 1 wt% and 6 wt% was found to slightly increase the size of the final particles, in accordance with higher monomer conversions..

1.4 Preparation of Microgels by Solution Polymerization

Although not usually recognized as a heterogeneous polymerization, colloidal sized microgel particles can be prepared by solution polymerization of crosslinking monomers at either low monomer loadings or at low conversions in bulk systems.[79-90] Microgels are defined as intramolecularly crosslinked macromolecules that have sizes in the nanometer range and are able to swell in good solvents.[81]

Both methods of preparation mentioned above, produce microgel particles that have heterogenous structures where a highly crosslinked core is surrounded by a more weakly crosslinked matrix. Cyclization reactions[91] early in the polymerization along with local inhomogeneities caused by crosslinking[92] and the preferential consumption of divinyl monomers[81] all contribute to the heterogeneous structure of microgels.

Microgels are observed to be colloidally stable in good solvents for their linear analogs. Transferring them into a poor solvent causes the microgel network to collapse and aggregate. Graham and Hayes suggested that copolymer microgels prepared from 95% methyl methacrylate and 5% diethylene glycol dimethacrylate in a range of ketone solvents are inherently sterically stabilized as a result of uncrosslinked chains on their exterior. Furthermore, they have suggested that this effect favoured intra-particle rather than inter-particle reactions and was responsible for the postponement of macrogelation.[88]

1.5 Theses Objectives

Typically precipitation polymerizations lead to particles with ill-defined shapes and sizes, however, more recently, cases have been found where monodisperse microspheres can be prepared by this method. Precipitation polymerization is unique among the heterogeneous polymerizations methods in that stabilizers are absent from the reaction mixture. Consequently, the mechanisms of emulsion, suspension and dispersion polymerization do not apply in this case. Hence, the mechanism of monodisperse microsphere formation in precipitation polymerization is unknown.

Arguably the most important aspect in the preparation of polymer colloids is their stabilization and since stabilizers are not added to a precipitation polymerization they must be formed *in situ*. Hence, it is hypothesized that the mechanisms of nucleation and growth produce structures that stabilize the particles throughout the reaction and these processes are investigated in Chapters 2 and 3, respectively.

Two interesting aspects in precipitation polymerization to monodisperse microspheres are the following: i) a crosslinking monomer is required for their preparation, and ii) the solvency of the continuous medium must be better than that used in a typical precipitation polymerization. Chapter 4 investigates the effects of crosslinking monomer concentration and solvency of the continuous medium on the morphology of the polymer formed.

Thus, it is the objective of this thesis to determine the effect of the crosslinking monomer and the effect of the solvency of the continuous phase on the mechanisms of nucleation, growth and ultimately stabilization. A sound understanding of these processes is important in explaining the different morphologies observed in crosslinking polymerization in organic solvents and in turn, may prove to be useful in the preparation of new materials.

1.5.1 Contributions to this Thesis by Others

Geoff McIsaac worked as a undergraduate thesis student and later as a research assistant in our laboratory where I co-supervised his work on the synthesis of polymer microgels. In this time period he helped me confirm some of the experiments that I had conducted to determine the nucleation mechanism in Chapter 2 and he also aided in carrying out some of the experiments used to prepare the morphology map in Chapter 4.

Randy Frank and myself have worked closely throughout our graduate studies. He has contributed significantly to my thesis by helping me work through experimental difficulties.

Wen-Hui Li conducted a significant amount of work on developing a seeded growth method for the preparation of large particles by precipitation polymerization. She recommended the seeded polymerization recipe I used in Chapter 3, to investigate the growth mechanism for precipitation polymerization.

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CHAPTER 2

Nucleation and Stabilization Mechanisms of Polydivinylbenzene Microspheres in Precipitation Polymerization

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2.0 Abstract

The nucleation mechanism in the precipitation copolymerization of divinylbenzene-55 to monodisperse microspheres was found to proceed through transient microgels that serve as the nuclei of the resulting particles. Low molecular weight polymer formed in solution and having pendent vinyl bonds, react together and also undergo further propagation to form microgels. These microgels disappear from the reaction mixture at the same time as microspheres appear as an insoluble fraction. These microspheres then crosslink internally and this transforms them from gel like structures observed early in the reaction, to the more rigid final particles.

The reaction medium was determined to be a better than *theta*-solvent for the forming polymer. Following polymerization, the microspheres could be flocculated by transferring them into non-solvents. Thus, in was concluded that the microspheres are sterically stabilized by their solvent swollen surfaces that form *in situ* as a result of the nucleation and growth mechanisms.

2.1 Introduction

The nucleation stage of heterogeneous polymerizations determines the number of particles produced, and ultimately their size and size distribution.[1-4] A considerable amount of work has gone into the preparation of monodisperse colloids since these are most desirable for applications such as chromatography.[5-7] La Mer first described the prerequisites for the preparation of monodisperse inorganic colloids. A typical LaMer diagram is shown in Figure 1. A gradual and continuous increase in the concentration of a material, either molecules or ions, must be brought about by some means. Precipitation does not occur until a certain level of super-saturation has been obtained since there is no template for the material to build upon. The formation of tiny nuclei which eventually grow to become the final particles is a spontaneous process once the nucleation concentration is achieved. These nuclei grow very quickly by scavenging further material from solution and this effectively reduces the concentration of the molecules or ions in solution. If a method is found which maintains the concentration of the molecules or ions above the saturation concentration then the nuclei continue to grow in size. Monodisperse colloids are formed when all nuclei are formed at exactly the same time (t_n approaches 0) and secondary nucleation and particle-particle coalescence are avoided. Secondary nucleation will only occur if the concentration of the soluble fraction is allowed to increase to a level greater than the nucleation concentration. Coalescence is avoided if the particles are adequately stabilized.

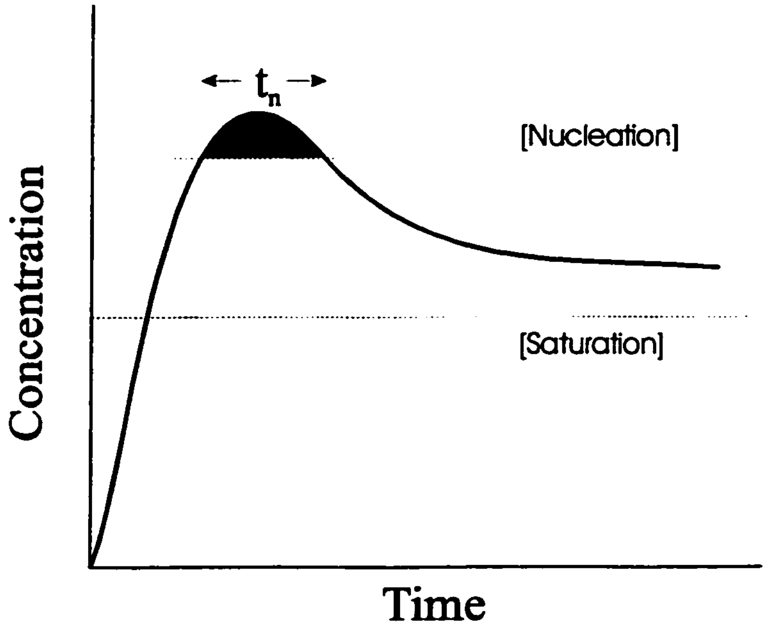

Figure 1. A typical La Mer diagram for the preparation of monodisperse inorganic colloids. For the preparation of monodisperse colloids the nucleation period t_n should approach zero.

Many of these concepts also apply to the preparation of organic polymers by heterogeneous polymerizations, and emulsion and dispersion polymerizations are widely studied examples of these. Monomer droplets continuously renew the monomer consumed in emulsion polymerization and this is one of the reasons that monodisperse particles can be prepared by this method. Monodisperse microspheres can be prepared by dispersion polymerization since the steric stabilizer prevents homocoagulation of like-sized species and continuous heterocoagulation ensures that secondary nucleation does not occur.[4,8-11]

During the 1990's the methods available for the preparation of monodisperse microspheres was expanded to include precipitation polymerization.[12-22] The mechanisms of this type of reaction are not well understood. The starting conditions for precipitation polymerization are similar to those of dispersion polymerization, however, steric stabilizers are absent from the reaction mixture and yet monodisperse microspheres are prepared. It is hypothesized that steric stabilizers are produced *in situ* in precipitation polymerization. In comparison, it is well known that electrostatic stabilizers are produced during the reaction, in surfactant-free emulsion polymerizations.[23-25]

The goal of this chapter is to determine the nucleation mechanism to mono-disperse microspheres in the precipitation copolymerization of divinylbenzene in mixtures of methyl ethyl ketone and heptane. This information will help in the design and synthesis of new materials for advanced applications such as chromatography and microencapsulation.

2.2 Experimental

2.2.1 Materials

Technical grade divinylbenzene, DVB-55, containing 55% divinyl isomers and 45% ethylvinyl isomers was purchased from Aldrich Chemical Company. The composition was verified by gas chromatography and the monomer was used without purification. The radical initiator 2,2'-azobis-(2-methylpropionitrile) (AIBN) was received from DuPont and recrystallized from methanol prior to use. The polymerization solvents, HPLC grade methyl ethyl ketone and heptane, were purchased from Caledon Chemical Company and were used as received. The solvent used for separating the soluble polymer from the insoluble fraction was HPLC grade tetrahydrofuran, THF, and it was purchased from Caledon Chemical Company and used without further purification.

2.2.2 Sample Preparation

A large scale polymerization was conducted at 15 vol% monomer loading to ensure sufficient sample for molecular weight analysis of the soluble polymer obtained at low conversion. Precipitation polymerization of DVB-55 at this high monomer loading produces microspheres in the early stages of the reaction, that coagulate later in the reaction because of their high collision frequency.[15] A 2L, 3-neck round bottom flask was fitted with an overhead stirrer, a nitrogen bubbler and a rubber septum through which samples could be removed and the entire apparatus was partially immersed in a water bath. A charge containing 170 mL methyl ethyl ketone, MEK, and 680 mL heptane, Hep, were added to the reactor and allowed to equilibrate to the reaction temperature of 70°C. After this time, a

150mL aliquot of DVB-55 containing 2.74g, 16.7mmol, of AIBN was added quickly to the polymerization solvent. The entire reaction mixture was stirred very gently to ensure thermal homogeneity without providing excessive collisional energy to the microspheres that would form. Aliquots of 100 mL were removed from the reaction vessel at timed intervals through a large bore needle attached to a syringe and injected into 100 mL of THF containing 0.28g of 4-*tert*-butyl catechol, a free radical inhibitor, to terminate the active radicals. This step ensured the polymers could be re-dissolved following isolation.[26]

The teminated polymers were concentrated by rotary evaporation under reduced pressure and then precipitated into a 15 fold excess of methanol. The polymer was dried under vacuum for 48 hours and the yield was measured gravimetrically.

Small scale reactions at 4 vol% monomer loading were performed to obtain samples for particle size analysis. A masterbatch of monomer and initiator was prepared just prior to polymerization, consisting of 20.0mL DVB-55, and 1.82g, 11.1mmol, AIBN. Individual 0.80mL aliquots of this masterbatch mixture were then added to 4.80mL of MEK and 14.4mL of heptane in 20mL Wheaton scintillation vials. The samples were vigorously shaken for approximately 2 minutes and then placed in a constant temperature reactor set to 70 °C where they were agitated by rolling them horizontally at 4 revolutions per minute. This procedure ensures thermal homogeneity of the reaction mixture and prevents the forming microspheres from settling. The samples were removed from the reactor at timed intervals and the polymerization was terminated by adding 4-*tert*-butylcatechol to the reaction mixture. The polymer was then isolated in the same manner as in large scale polymerizations.

2.2.4 Turbidity

The turbidity of the samples as a function of the polymerization time was observed visually with the aid of a He-Ne laser (λ=633 nm). Light scattering was observed by illuminating the samples contained within 20mL scintillation vials with the laser and observing the samples visually at an angle approaching 90 degrees. Turbidity was noted when the light path through the sample first created a diffuse scattering band.

2.2.5 Particle Size Measurements

Particles with sizes greater than 1μm were measured using a Coulter Multisizer fitted with a 50μm aperture. Approximately, $12\text{x}10^3$ particles were counted in a period of 30 seconds to ensure both good statistics and a low coincidence count. Particles with diameters in the range of 0.04μm to 1μm were measured by a Polarization Intensity Diffraction System (PIDS) using a Coulter LS-230. The solvent for the analysis was neat MEK and earlier experiments determined that the samples could be analysed without prior workup. Also, the particles were analyzed in the dry state using a Philips ElectroScan 2020 Environmental Scanning Electron Microscope (ESEM). The samples were dispersed onto a glass cover slide attached to an aluminum stub and sputter coated with 15nm of gold. The particle diameters were determined by manually averaging the sizes of 50 to 100 microspheres. When the size permitted, an Olympus BH-2 optical microscope was used to verify the particle sizes measured by the other techniques.

2.2.6 Molecular Weight

The molecular weight of the soluble fractions was determined by Gel Permeation Chromatography using Ultrastyragel columns attached to a Waters 440 pump that was programmed to have an elution rate of 1 mL/min. The solvent for the analysis was HPLC grade THF and the instrument was calibrated using nine narrow-disperse linear polystyrene standards having molecular weights in the range of 580 to 514 000 g/mol. In cases were the sample contained an insoluble fraction, it was separated from the soluble polymer prior to molecular weight analysis by centrifuging the reaction mixture at 8000 rpm for 30 minutes and extracting only the soluble fraction. THF was then added to the insoluble fraction and this centrifugation procedure was repeated for a total of 3 times for each sample.

2.2.7 Observation of Particle Swelling by Optical Microscopy

Photomicrographs of the particles were taken both in THF, and dried from THF, using an Olympus BH-2 optical microscope with a Minolta *HT si Plus* 35 mm SLR camera attached using a phototube. Multiple micrographs were taken directly following dispersion of the particles onto glass slides, until the THF had completely evaporated. The pictures were then developed at a photo-lab and converted into digital form using a Logitech Colour PageScan optical scanner.

2.2.8 Swelling Measurements using the Coulter Multisizer

Swelling measurements were conducted using a variation of the Coulter Multisizer particle sizing method. The setup is shown in Figure 2. A layer of *p*-xylene was dispensed onto the top of the Isoton II electrolyte solution and care was taken to prevent the formation of an emulsion. This mixture was stirred gently for 30 minutes to allow the concentration of *p*-xylene in the electrolyte solution to equilibrate. The particles were then injected directly into the Isoton II layer and the particle size measured periodically over several hours. The initial measurement was found to correspond to the size of the microspheres measured in the absence of *p*-xylene. Subsequent measurements were taken until the particle size no longer increased. This typically took 1 to 1.5 hours. The samples were continuously and gently stirred during this time to prevent settling.

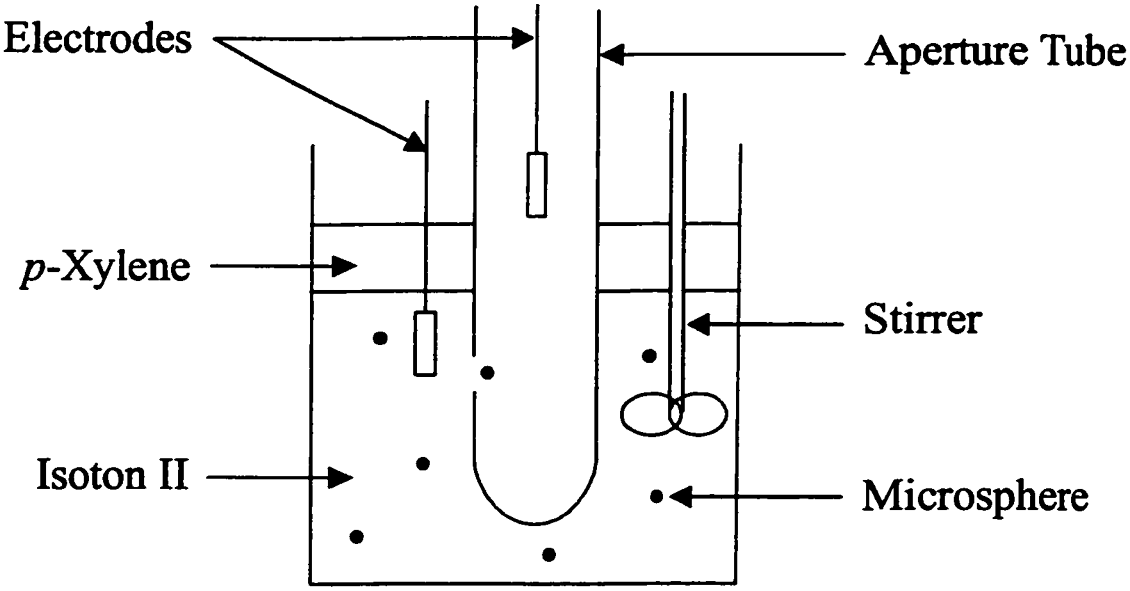

Figure 2. Experimental setup used for measuring particle swelling using the Coulter Multisizer.

2.2.9 *Theta*-Composition Measurements

Theta-compositions for poly(4-methyl styrene) were determined in mixtures of MEK:Heptane and THF:Water by the Elias cloud point titration method.[27] Poly(4-methyl styrene) samples were dissolved in either MEK or THF at several concentrations ranging from 1.0×10^{-3} g/mL to 2.5×10^{-2} g/mL. The dissolved polymer was then slowly titrated at 25 °C in 100 mL covered beakers with the precipitating solvent until a strong cloud point was observed. This was detected by holding dark printed text of 12 point font behind the beaker and titrating until the text could no longer be read through the mixture.[27]

2.2.10 Flocculation Experiments

Samples were prepared consisting of 50 mg of 3.4 μm monodisperse microspheres dispersed into vials containing from 5 mL to 20 mL of THF in 1 mL increments. These vials were then placed into an ultrasonic bath for 30 seconds to ensure the particles were individually dispersed and this was checked using the Coulter Multisizer. The concentration of particles was chosen to give subsequent flocculation half-lives of several hours according to Smoluchowski kinetics. The samples were further diluted to a total volume of 20 mL with HPLC grade water. The vials were then gently rolled horizontally at 4 rpm for 24 hours at room temperature. After this time the particle or aggregate size was measured using the Coulter Multisizer as indicated in Section 2.2.5.

2.3 Results and Discussion

2.3.1 Change in Particle Structure with Reaction Time

DVB-55 microspheres have been prepared by precipitation polymerization in a range of solvents including acetonitrile, mixtures of acetonitrile and toluene and mixtures of methyl ethyl ketone and heptane. Figure 3 shows electron micrographs of DVB-55 particles obtained (A) after 2 hours 45 minutes, and (B) after 24 hours of polymerization in acetonitrile. The particles are soft and deformable early in the reaction, and more rigid later in the reaction. The microspheres apparently form initially as a swollen gel which then grows and cures through internal crosslinking to form the more rigid structures shown in Figure 3B. Both of these samples readily de-colourize bromine solution indicating that they contain residual double bonds capable of internal crosslinking. Naka and Yamamoto have observed a decrease in the IR adsorption bands of the pendent vinyl bonds in precipitation polymerization of diethylene glycol dimethacrylate and they have attributed this to an increase in the internal crosslinking of the poly(DEGMA) microspheres.[19] Funke[28,29] and others,[30,31] have suggested a heterogeneous structure for polymer microgels as a result of internal crosslinking. In these cases, the core of the microgels is surrounded by a more lightly crosslinked corona.

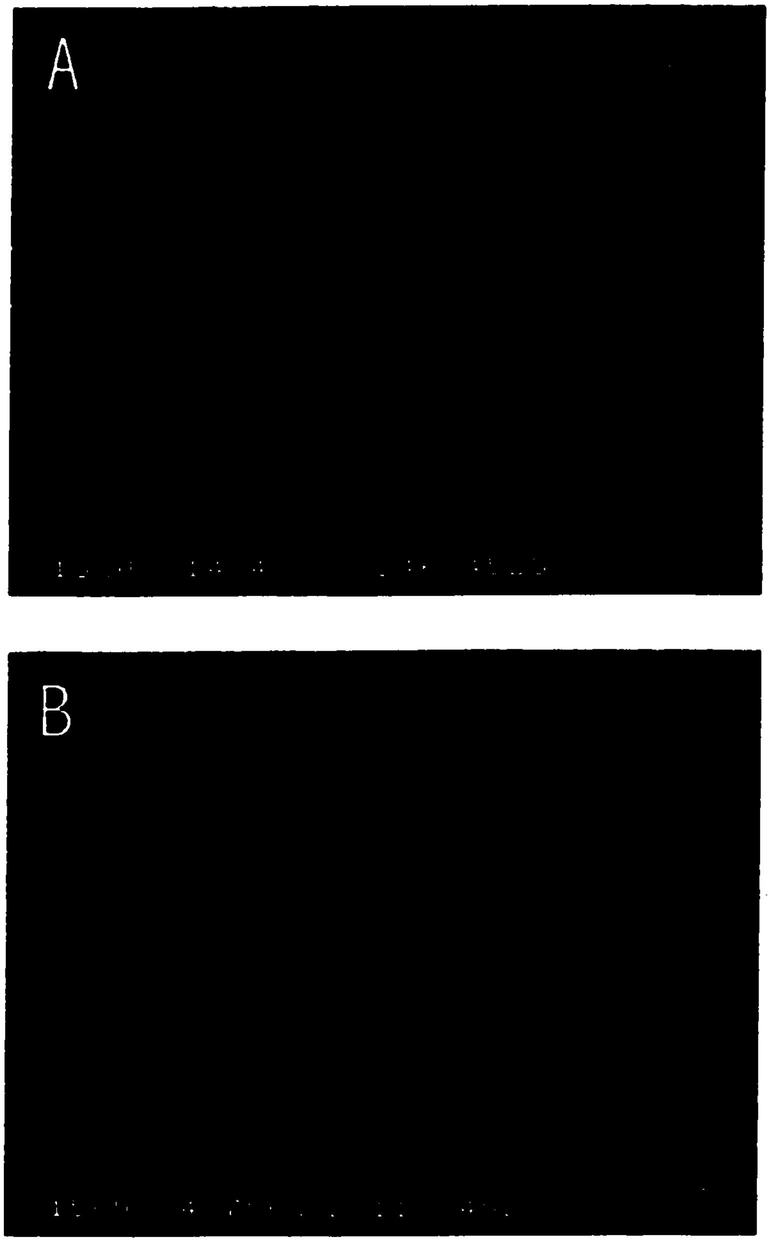

Figure 3. DVB-55 microspheres formed by precipitation polymerization in acetonitrile after (A) 2 hours 45 minutes, and (B) 24 hours of reaction.

2.3.2 Turbidity

A series of vials indicating the increasing turbidity as a function of reaction time are shown in Figure 4. Initially, only the physical appearance of these samples will be addressed. In subsequent sections, the molecular weight of the soluble polymer, monomer conversion, particle size, and particle size distribution will be discussed.

The appearance of the initial reaction mixture is shown by sample A, while the appearance after 130 minutes of reaction is shown by sample B. Both of these reaction mixtures were transparent. A cloudy mixture was observed when sample B was added drop-wise into methanol indicating that it contained polymer. Observation of this sample by optical and electron microscopy failed to reveal microspheres thus it was concluded that it contained only soluble polymer. Sample C, taken after 145 minutes of polymerization, showed the first appearance of turbidity. Microspheres were observed in this sample by optical microscopy. Thus, it is only after the appearance of turbidity that microspheres can be observed. The turbidity continues to increase at longer reaction times and this is shown in sample D (150 minutes) and sample E (155 minutes). Eventually, the reaction mixture becomes completely opaque as indicated by sample F (200 minutes). Qualitative examination by optical and electron microscopy indicated that the size of the microspheres increased with increasing polymerization time until sample G taken after 24 hours

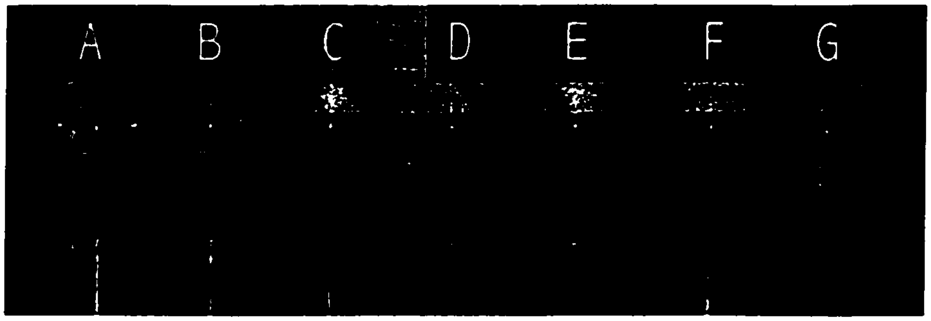

Figure 4. The polymerization of DVB-55 in 25% MEK and 75% heptane begins as a homogeneous solution and as the reaction proceeds at 70°C it becomes increasingly turbid. The samples were taken after A=0, B=130, C=145, D=150, E=155, F=200, and G=1440 minutes. Microspheres were first observed in C following the appearance of turbidity.

The onset of turbidity was observed to vary by as much as 10 minutes between replicate samples and thus the series of samples presented in Figure 4 was used as a guide to determine when samples should be taken from the reaction mixture for molecular weight analysis. Since microspheres could only be observed after the reaction mixture became turbid, the particle nucleation stage of the reaction must take place at or prior to this time.

2.3.3 Molecular Weight Analysis

Investigations by Funke[28,29] and by Antonietti[32,33] have indicated that in polymerizations that undergo macrogelation, microgels are formed first and then react together to form the larger macrogel. Naka has suggested that microspheres are a special morphology formed in gelling reactions.[18-20] Chapter 4 investigates the relationships between the different morphologies of microgels, macrogels and microspheres. Microgels could be precursors to microspheres and in order to investigate this hypothesis the molecular weight of polyDVB-55 as a function of reaction time and conversion was measured.

A plot of polymer molecular weight at varying reaction times is presented in Figure 5. Early in the reaction only low molecular weight polymer is formed and this is shown in sample (a) at 115 minutes and at a corresponding monomer conversion of 3.0%. The molecular weight for this samples was M_n=1.2x10^4 g/mol. Radical termination using 4-*tert*-butyl catechol dissolved in THF ensured that the polymers could be re-dissolved following isolation.[26] In earlier experiments, methanol was used as the solvent for this step and it was found that once the polymer collapsed it could not be re-dissolved. Antonietti made similar observations and hydrosilylated the residual double bonds to prevent further crosslinking.[26]

Sample (b) was taken after 125 minutes and at a conversion of 4.1%. In this sample, a low molecular weight fraction remains however a higher molecular weight shoulder is now observed and this is reflected in the overall M_n of $1.7\text{x}10^4$ g/mol. Sample (c) was removed after 135 minutes which corresponds to a conversion of 5.6%. In this sample the low molecular weight fraction at approximately $1\text{x}10^4$g/mol, is still observed. However, the high molecular weight shoulder now extends to approximately $1\text{x}10^6$ g/mol which is near the exclusion limit of the GPC columns used. Sample (d) was taken at 145 minutes and the high molecular weight shoulder has disappeared. The total conversion in this sample was 7.2% and it consisted of both a soluble fraction (4.0%) and an insoluble fraction (3.2%). The molecular weight of the soluble fraction was $M_n=7.3\text{x}10^4$ g/mol and the insoluble fraction consisted of microspheres observed by optical microscopy. At all later reaction times, the soluble fraction contained only low molecular weight polymer. Therefore, the mechanism responsible for the formation of the high molecular weight soluble fraction observed in sample (c) was shut-off after 145 minutes.

The reproducibility of the molecular weight analysis as discussed above was determined for 5 parallel reactions. A higher molecular weight shoulder as shown in Figure 5c was observed in all cases, however, the molecular weight that it extended to was observed to vary from reaction to reaction. This is a result of both the transient nature of the higher molecular weight fraction, and also of the fluctuations in time (approximately 10 minutes) at which events occur during the polymerization.

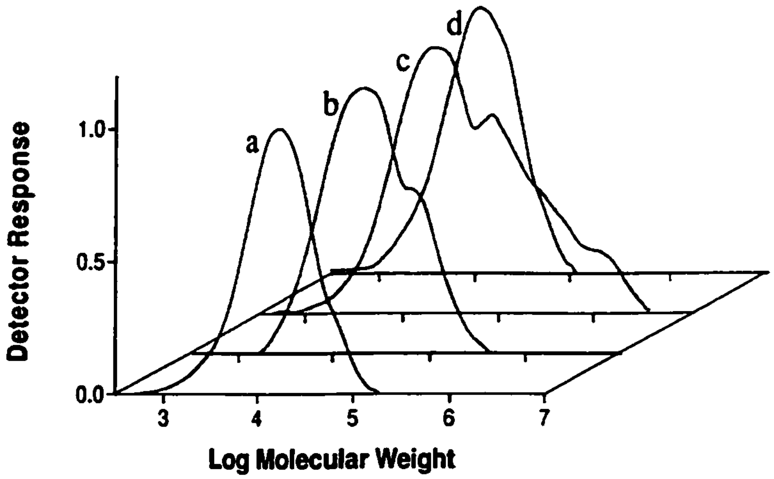

Figure 5. Molecular weight evolution in the polymerization of 15vol% DVB-55 in a mixture of 20% MEK and 80% Heptane. The reaction times and total conversions are (a)=115 min and 3.0%; (b)=125 min and 4.1%; (c)==135 min and 5.6%; and (d)=145 min and 7.2%, respectively.

The high molecular weight polymer observed in sample (c) would have a microgel structure that would be swollen with solvent. The structure of polymer microgels prepared by solution polymerization of crosslinking monomers has been reviewed by Funke,[29] and their synthesis is analogous to the preparation methods used in this study. Since the microgels disappear from the soluble fraction at approximately the same time that microspheres appear it was concluded that the microgels are the nuclei of the microspheres.

2.3.4 Post Nucleation Microsphere Growth

Microsphere volume as a function of monomer conversion is shown in Figure 6 for samples prepared using 4 vol% DVB-55 in 25% MEK and 75% heptane. The linear relationship indicates that nucleation shuts-off after the first burst of nucleation, and that no new particles are formed subsequently. Continuous nucleation would result in the formation of new, smaller particles and consequently the slope of the conversion versus volume plot would decrease with increasing conversion. Also, a narrow size distribution was observed by optical microscopy for all samples, indicating only a single batch of particles was present in all samples. Particle-particle coalescence was not observed during the polymerization since this would have the effect of rapidly increasing the microsphere volume without a corresponding change in monomer conversion. Thus, coagulation of like-sized particles, homocoagulation, was also shut-off following nucleation indicating that the particles were colloidally stable throughout the reaction.[4,8,9,11,15,34]

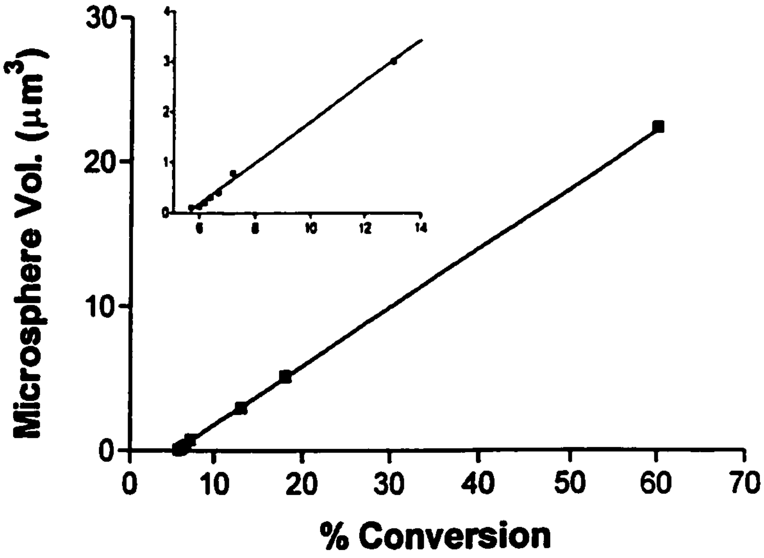

Figure 6. The change in microsphere volume as a function of monomer conversion. Inset is an expansion of the low conversion area.

The yields of soluble polymer in samples (a) through (d) described in Figure 5 are shown with respect to reaction time in Figure 7 in form of a *"pseudo"*-La Mer diagram. The y-axis shows the concentration of soluble polymer. In a typical La Mer diagram the y-axis has units of mol/L and represents a single species with a specific molecular weight. In this case, the soluble polymers have a range of molecular weights, discussed earlier in Figure 5, and thus it is more appropriate to represent the concentration in terms of monomer equivalents or weight % relative to original monomer. The first sample removed from the reaction vessel at 115 minutes had a conversion of 3.0% and this increased to 4.1% and then to 5.6% after 125 and 135 minutes, respectively. Following the sample taken at 135 minutes the reaction mixture became turbid and the next sample taken at 145 minutes contained both a soluble and an insoluble fraction which could be separated by centrifugation. The total conversion for this sample was 7.2%. The insoluble fraction (3.2%) was observed to contain microspheres while the soluble fraction (4.0%) was low molecular weight polymer. At all subsequently longer reaction times the conversion to soluble fraction was approximately 3% while the insoluble material continued to increase.

The shape of the curve shown in Figure 7 was reproducible when the high molecular weight shoulder shown in Figure 5c extended to molecular weights that approached the exclusion limits of the GPC columns. In this case, the maximum amount of the transient microgel could be isolated from the reaction mixture. When the higher molecular weight shoulder did not extend as far, then the "snapshots" taken to construct a similar Figure 7 did not reveal a significant maxima.

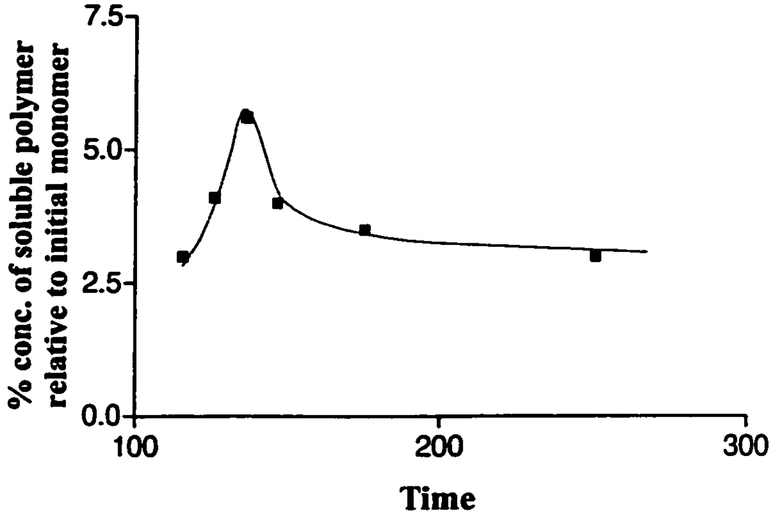

Figure 7. Monomer conversion to soluble polymer as a function of reaction time.

2.3.5 Nucleation Mechanism

The proposed nucleation mechanism for the precipitation polymerization of divinylbenzene to mono-disperse microspheres is shown in Figure 8. Polymerization begins in solution to form low molecular weight polymer. This process continues throughout the reaction and for this reason it was termed the oligomer pipeline. These oligomers readily decolourize bromine solution and this indicates they have pendent vinyl groups. In the early stages of the reaction, oligomers are supplied by this pipeline until they have built up a high enough concentration to allow intermolecular reactions between them. These intermolecular reactions between oligomers and oligoradicals, and also further propagation, would lead to the formation of the microgel fraction. This microgel disappears from the soluble fraction just as the reaction mixture becomes turbid and microspheres are observed. Therefore it was concluded that the microgels serve as the nuclei of the microspheres. The microgels grow by continuously capturing the oligomers supplied by the pipeline. This growth mechanism is investigated in Chapter 3. Concurrent to growth, the microgels undergo internal desolvation and collapse, and this is investigated in Chapter 4. Monodisperse microspheres are formed by this mechanism when two conditions are met: i) all nuclei are formed in a short period of time, and ii) following nucleation all oligomers supplied by the pipeline are captured by existing particles. Once microspheres are formed they must have some mechanism of maintaining colloidal stability since particle-particle coalescence is not observed. This is investigated in the following sections.

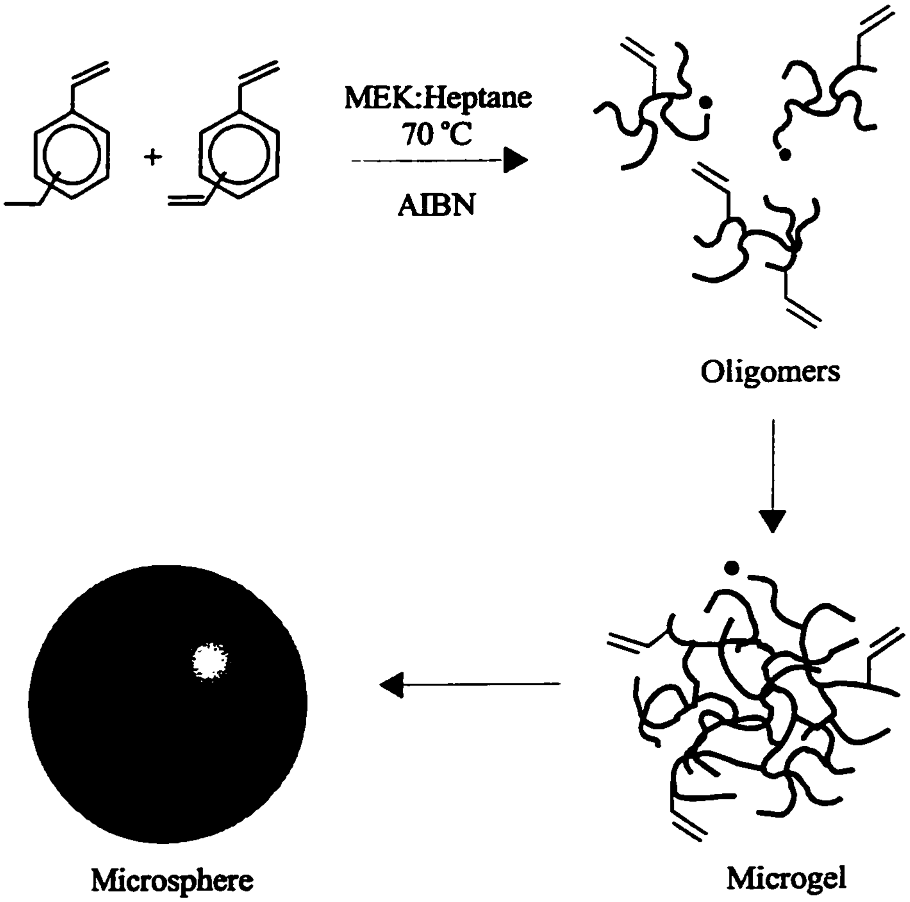

Figure 8. The mechanism of nucleation in the preparation of monodisperse microspheres by precipitation polymerization.

2.3.6 Particle Swelling

Earlier investigations of the precipitation copolymerization of DVB-55 suggested that the microspheres prepared by this technique were completely rigid structures due to the high concentration of crosslinker in the monomer mixture.[14-16] If this were the case and if we consider that electrostatic or steric stabilizers are absent from the reaction mixture, then the particles should coagulate since there would be no method for overcoming the van der Waals attraction between particles. However, it is observed that the particles do not coagulate in the presence of good solvents. Therefore, it is hypothesized that the particles have a heterogeneous structure where the interior is highly crosslinked and the outer surface is more gel-like. This surface gel would sterically stabilize the particles. In this case, the particles should swell to some extent in good solvents and this will be tested in the section below. The methods available to measure the swelling of particles in the micrometer range are limited. The methods include the following techniques:

i) Dynamic Light Scattering has been used to measure the change in particle size as a function of changing solvency conditions.[35] This technique is most suited to the measurement of sub-micrometer particles since de-convolution of the auto-correlation function becomes ambiguous as a result of multiple scattering from larger particles. In precipitation copolymerization with DVB the average particle size is much larger than 1 μm and as a result this technique would not be of use.

ii) The degree of swelling of polymeric materials can be calculated by simply measuring the change in their dimensions between the swollen and dry states using a ruler.[36] However, to conduct these measurements on microspheres they should have a close-packed arrangement in a suitable container. In practice, ensuring that the entire sample has such a packing arrangement would be difficult. Besides, swelling microspheres in a confined vessel produces an additional force opposing particle swelling.

iii) Direct Polarization Magic Angle Spinning NMR techniques have been used to measure the degree of swelling of crosslinked polystyrene gels where the percentage of crosslinking monomer available to the reaction is typically below 1%.[37] In the DVB case, 55% of the monomer is *meta-* and *para-*divinylbenzene and 45% of it is *meta-* and *para-*ethyl vinylbenzene. This high crosslinker content leads to broad ^{1}H and ^{13}C peaks and thus the signals from the poly(DVB-55) samples were extremely weak.

2.3.6.1 Microscopy Observation

An attempt to measure the swelling of individual particles in THF using optical microscopy was made, however, the diffraction of light at the particle edges made it difficult to carry out this measurement and introduced significant error. An attempt to overcome this problem was made by taking measurements from one end to the other of a row of particles and averaged over the number of particles in the row. This somewhat improved the measurements.

A more comprehensive method using optical micrographs followed by image analysis was then attempted. Images were taken continuously as THF evaporated from a large area of particles dispersed onto glass microscope slides. Figure 9a shows this layer before THF has evaporated and 9b shows the same area following complete evaporation of THF. The dry sample has a "mud-cracked" appearance. Mud-cracking is commonly observed in clay soils which have shrunk from their swollen state following evaporation of water.[38] In the DVB-55 case, it was concluded that this "mud-cracking" was a result of the microspheres shrinking as the solvent evaporated. Calculations of the degree of swelling varied widely (5 to 15%) and a possible reason for these variations is that the particles rearrange themselves upon drying. Further evidence that the particles are swollen in THF is that the particles become out of focus as they dry because they shrink below the locked focal plane of the microscope. This indicates shrinking in the third, z, dimension.

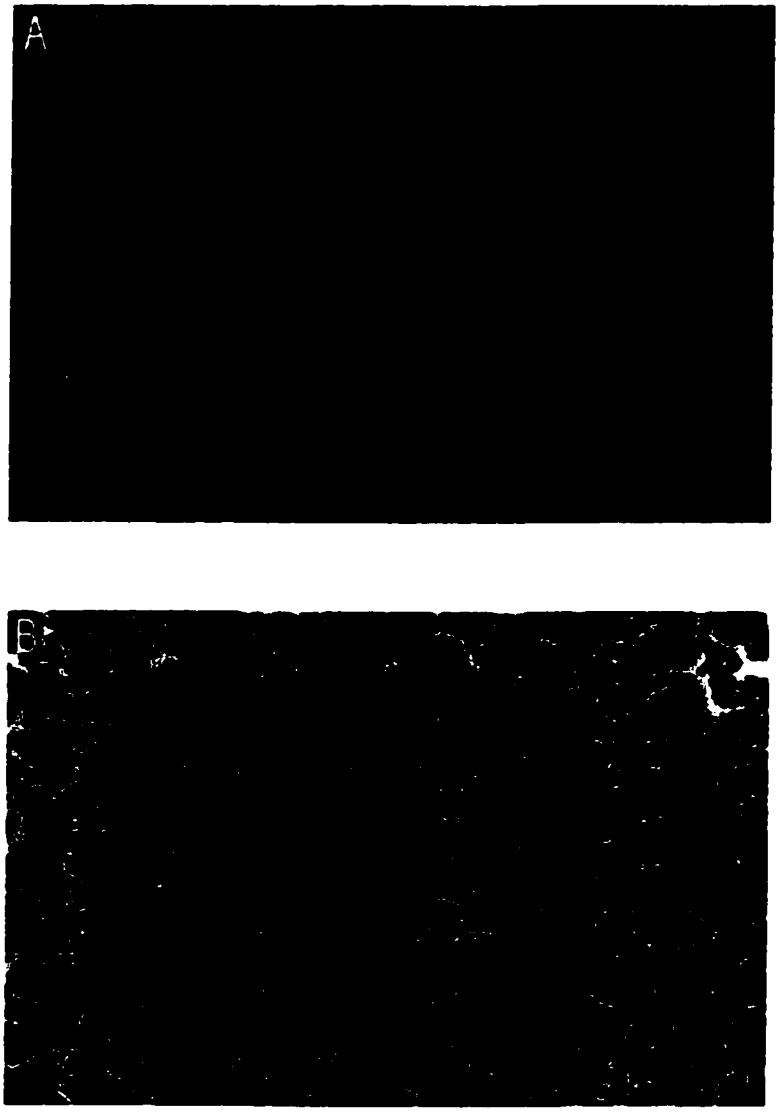

Figure 9. Optical micrographs of a layer of precipitation polymerization microspheres swollen with THF (a), and the same layer of microspheres after evaporation of THF (b).

2.3.6.2 Particle Swelling Measured by Coulter Multisizer

A variation of the particle sizing method was used to measure particle swelling with the Coulter Multisizer. In this case a layer of *p*-xylene was dispensed on top of the electrolyte solution. Para-xylene was chosen because its water solubility is only 0.18 g/L. This low concentration of organic solvent does not significantly change the conductivity of the electrolyte solution and hence would not change the size of the particles reported by the Coulter Multisizer. Once the particles are dispersed in the Isoton II solution they act as micro-sponges absorbing *p*-xylene and in the process they swell. The layer of *p*-xylene on top of the electrolyte solution continuously replenishes the *p*-xylene that has partitioned into the particles.

The swelling ratio, V_S/V_0, for microspheres prepared using 4% of DVB-20, DVB-30, DVB-40 and DVB-55 in a mixture of 20% MEK and 80% heptane, are shown in Table 1. The diameter of the dry particles is D_0 and the diameter of the swollen particles is D_S and their corresponding volumes are V_0 and V_S, respectively. Particle swelling increases as the concentration of DVB in the monomer feed decreases. This is to be expected since reducing the DVB concentration decreases the number of potential crosslinking sites along the polymer chains. What is interesting about this result is that even the particles prepared using as high as 55% DVB may swell as much as 100 nm in diameter. The experimental technique used for this investigation involved measuring the change in position of a column shaped particle size distribution. Although the particles used were not monodisperse the position of the particle size "column" was found to be highly reproducible. Thus, the shift of this "column" to larger sizes in the presence of *p*-xylene was used as a measure of microsphere swelling and the uncertainties listed in Table 1 represent the channel spacings in the Coulter Multisizer.

A solvated surface gel layer of these dimensions should provide more than enough repulsion to sterically stabilize the particles.[39] Polymer molecules of molecular weights greater than 10 000 g/mol have spatial extensions comparable to, or greater than, the range of the London attraction between colloidal particles. A crude measure of the diameter of a polymer molecule is the rms end-to-end distance and is given by $\langle r^2\rangle^{0.5}/\text{nm} \approx 0.06M^{0.5}$ and thus the diameter of a 10 000 g/mol polymer would be in the order of 6 nm.

Table 1. The degree of swelling for samples prepared using DVB-20, DVB-30, DVB-40 and DVB-55. Monomer concentration was 4 vol% and the solvent was 20:80 MEK:Heptane respectively.

% DVB	D_0 *(μm)*	D_S *(μm)*	V_0 *(μm³)*	V_S *(μm³)*	V_S/V_0
55	4.87±0.03	4.97±0.03	60±1	64±1	1.06±0.04
40	4.51±0.03	4.64±0.03	48±1	52±1	1.09±0.04
30	4.42±0.03	4.61±0.03	45±1	51±1	1.13±0.05
20	4.19±0.03	4.48±0.03	39±1	47±1	1.21±0.05

2.3.7 Particle Swelling Observed by Atomic Force Microscopy

The development of tapping mode Atomic Force Microscopy, AFM, has allowed soft materials such as polymer gels to be imaged at high spatial resolution. Instead of simply dragging the AFM tip across the sample and measuring its deflection, the tip oscillates at frequencies of 20 to 30 KHz in the vertical direction as it is scanned across the sample. This minimizes sample deformation and permits imaging of soft materials.

The submicron structure of poly(*N*-isopropyl acylamide) gel surfaces in water and their response to external stimuli have been investigated using tapping mode AFM.[40] In this study the authors observed structural changes of the gel in response to changing either solvency or temperature.

The goal was to use this technique to directly observe swelling and contraction of the poly(DVB) particle surface upon changing from a good solvent to a poor solvent. Figure 10 shows an AFM image of a dry DVB-55 microsphere mounted on a glass slide using Crystalbond® thermal plastic adhesive to prevent the particle from moving. The particle diameter was 3.4 μm which approaches the length of the AFM tip (approximately 5 μm) and thus the particle had to be held in place to prevent the tip from pushing it around the surface. Several factors prevented imaging of the particles in the presence of organic solvents. First, organic solvents attacked the Crystalbond and weaken the attachment of the particle. Second, both the AFM cantilever and the particle should be submersed in the solvent to prevent artifacts from arising as the tip goes in and out of the liquid phase. Third, the organic solvents of interest for this study have low surface energies and thus tend to wet the glass surface instead of forming a droplet around the particle to be imaged. In order to continue with this study these problems need to be addressed. A suitable container should be built which allows a pool of solvent to submerse both the tip and the particle. Also, this would ensure that the particle does not dry out during analysis because of evaporation. A crosslinking adhesive must be found which is not attacked by organic solvents. Also, micro-manipulators would allow the particle to be positioned into the adhesive so that the surface to be imaged was not contaminated with adhesive.

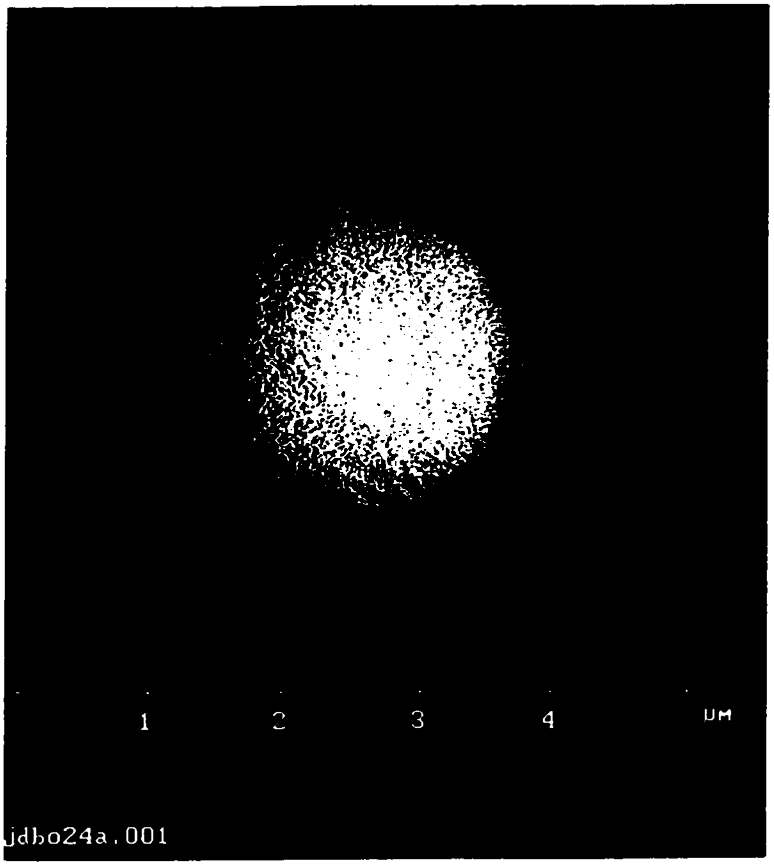

Figure 10. Tapping mode Atomic Force Microscope image of the dry surface of a DVB-55 microsphere.

2.3.8 *Theta*-Point Measurements

Optical microscopy and Coulter Multisizer measurements indicated that the particles swell in good solvents such as THF and *p*-xylene. However, the question remains whether or not the polymer is swollen in the reaction solvent. *Theta*-point measurements were conducted using linear poly(4-methyl styrene) as a model polymer for the particle surface. Microspheres can be prepared using DVB-20, made by diluting DVB-55 with 4-methyl styrene, in MEK and heptane. Thus, the microsphere surface should have solubility properties intermediate between poly(4-ethyl styrene) and poly(4-methyl styrene).

Figure 11 shows the cloud point measurements conducted to determine the *theta*-composition for a 10 000 g/mol sample of poly(4-methyl styrene) in a mixture of MEK and heptane at 25 °C. The cloud points are plotted against the volume fraction of heptane required to precipitate the polymer, and the *theta*-composition is determined by extrapolating to pure polymer. The *theta*-composition for poly(4-methyl styrene) is 20% MEK and 80% heptane at 25°C. Determination of the *theta*-composition at the reaction temperature of 70°C was attempted, however, the polymer would not precipitate. It was later found that at this temperature poly(4-methyl styrene) was completely soluble in neat heptane. Measurements were conducted at a lower temperature of 50 °C and again a strong cloud point,[27] which is required for *theta*-point determination, could not be detected. Microspheres are prepared in the range between 20 MEK:80 Heptane and 33 MEK:67 Heptane using DVB-20 to DVB-55 and at reaction temperatures of 70°C (See Morphology Map Chapter 4). Thus, the reaction conditions required for the preparation of microspheres are well above the *theta*-composition predicted using poly(4-methyl styrene). These results suggest that the particles could be sterically stabilized during their preparation by their solvent swollen surfaces.

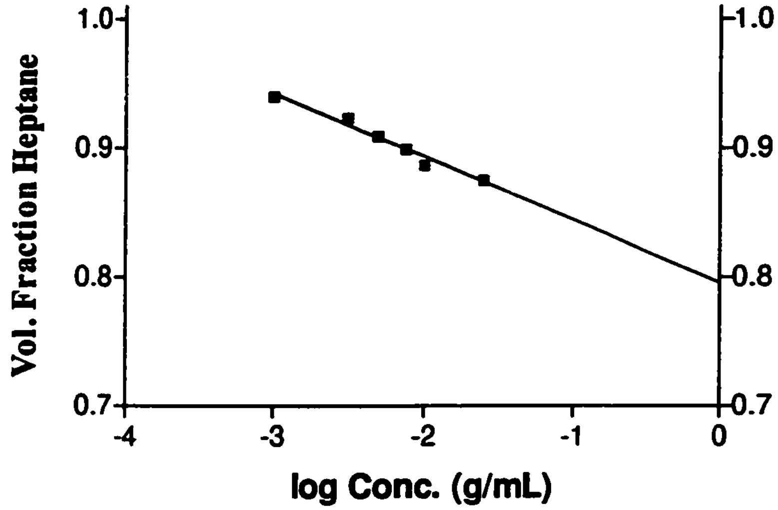

Figure 11. *Theta*-composition determined by cloud point titration for linear 10 000 g/mol PDI=1.02 poly(4-methyl styrene) at 25 °C in MEK and heptane.

The true test of steric stabilization is to decrease the solvency of the dispersing media and observe flocculation by measuring the change in particle or aggregate size as a function of the solvency.[39,41,42] Flocculation experiments were conducted using THF as a dispersing solvent and water as a strong precipitant. These solvents were chosen since the Coulter Multisizer was used to measure particle/aggregate size and both solvents must be compatible with Isoton II. First, the *theta*-compositions of the model polymers were determined in mixtures of THF:water using the Elias cloud point titration method.[27]

The *theta-* composition was determined for both a 10 000 g/mol PDI=1.02 and a 10 000 g/mol PDI=5, poly(4-methyl styrene) sample and this is shown in Figure 12. The θ-composition was determined to be 92% THF and 8% water at a temperature of 25 °C for both of these polymers. This is to be expected since the *theta*-state is a segmental property of a macromolecule that depends on the nature of the segment/solvent interactions. Accordingly, the *theta*-point is independent of molecular weight of the polymer provided its molecular weight is sufficiently high.[43]

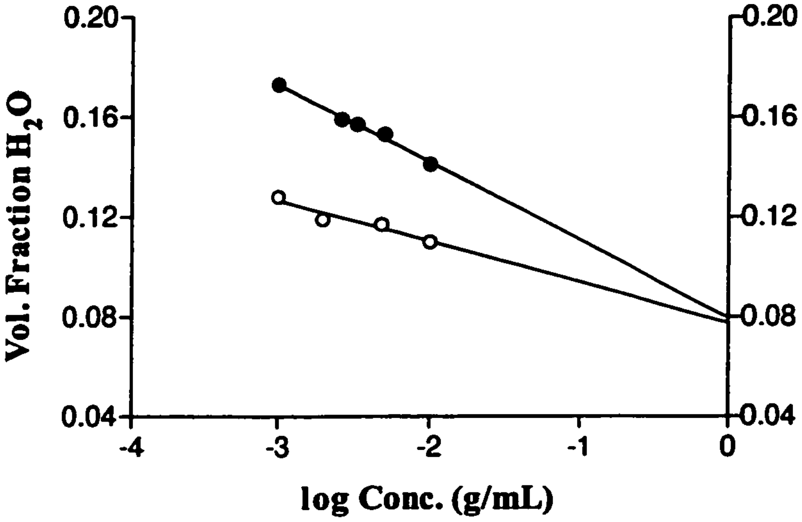

Figure 12. *Theta*-composition as determined by cloud point titration for linear 10 000 g/mol, PDI=1.02 (•) and 10 000 g/mol, PDI=5 (○) poly(4-methyl styrene) at 25°C in THF/water mixtures.

2.3.9 Particle Flocculation

If polymers are to act as steric stabilizers they must be solvated.[39] Therefore a convenient test to determine if steric stabilization is operative is to decrease the solvency of the continuous media and observe flocculation. In a good solvent the polymer remains solvated and thus stabilizes the particles whereas in a poor solvent the polymer collapses and the particles flocculate.

Figure 13 shows the particle/aggregate sizes measured by Coulter Multisizer for 3.4 μm particles dispersed in mixtures of THF:water where the composition was varied from 100:0 to 5:95, respectively. Narrow-disperse particles were observed when the dispersing solvent was neat THF. Increasing the water content causes the particles to flocculate and this is observed by the appearance of doublets at 4.3 μm and triplets at 4.9 μm. The Coulter Multisizer measures the change in resistance as particles pass through an aperture and this is proportional to the particle's volume. It then calculates the average particle diameter. The Multisizer "*sees*" a doublet of 3.4 μm particles as a single particle having a volume of 41.2 μm^3 (each 3.4 μm particle has a volume of 20.6 μm^3) and then calculates the diameter of this "single" particle to be 4.3 μm. Similarly, it "*sees*" the diameter of a triplet of 3.4 μm particles as a single particle with a diameter of 4.9 μm. Peaks assigned to doublets and triplets are readily observed in Figure 13. Microspheres dispersed in more then 50% water could not be measured using the 50 μm aperture tube since the large aggregates in these samples would continually plug it. Above 50% water, flocculation can be seen with the eye by a decrease in the turbidity of the sample and the formation of large flocs. Flocculation of these samples was reversible by either submersing the flocculated samples into an ultrasonic bath for 10 to 15 seconds or by adding excess amounts of THF.

The *theta*-point predicted using the poly(4-methyl styrene) model polymer was predicted to be 92 % THF and 8% water. Some flocculation of the particles was observed at 10% water, however, extensive flocculation was not observed until the water content was greater than 20%. The *theta*-point of the polymer attached to the surface of the particles may be significantly different from that of the freely soluble polymer. The *theta*-point is dependent on the structure of the polymer and thus the branched and crosslinked polymer of the particle surface may have a different *theta*-point. The solution properties of 3 to 12 armed star-branched polymers have been investigated as models for random branched polymers. It is commonly observed that the *theta*-temperature in a particular solvent decreases as the number of arms increases since the polymer chains are unable to coil due to the high chain density near the branch points.[44-47] When the molecular weight of the star branched polymers is high the *theta*-temperature approaches that of the linear polymer.[48,49] Therefore, the highly branched polymer of the particle surface may reach *theta*-state at greater than the 8% water predicted using linear poly(4-methyl styrene). Nevertheless, flocculation was observed at high water concentrations.

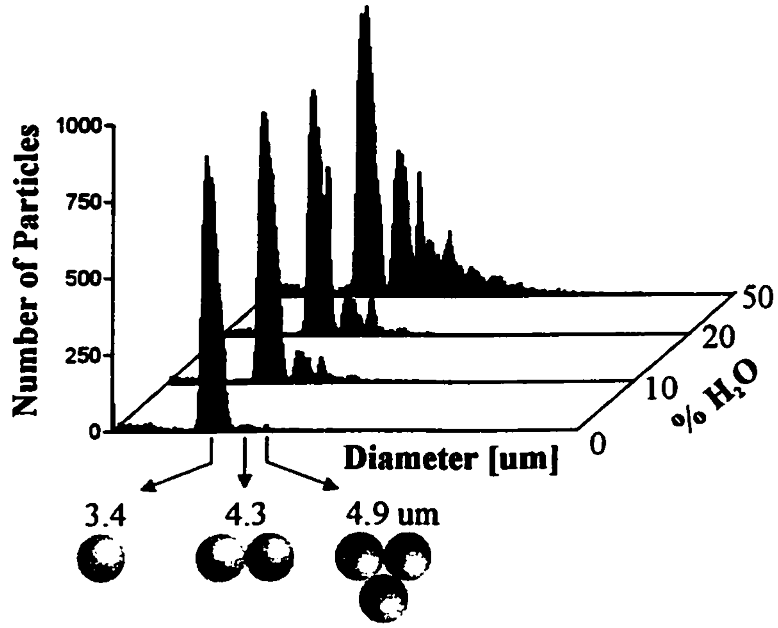

Figure 13. Particle size measured as a function of dispersing solvent composition. The solvent composition was varied from neat THF to 5:95 THF:water.

2.3.10 Mechanism of Particle Stabilization

The mechanism of particle stabilization is shown in Figure 14. In good solvents the surfaces of the polymer particles are swollen with solvent and this would sterically stabilize the particles against flocculation. Decreasing the solvency of the dispersing medium collapses the surface gel and as a result the particles are no longer stabilized and flocculation ensues. This stabilizing surface gel is prepared *in situ* in the precipitation polymerization of DVB-55. Fitch has described a related stabilization method where highly crosslinked organosols are prepared by precipitation polymerization in poor solvents and then transferred to good solvents which swell their surfaces and impart colloidal stability.[41] Graham *et al.* have referred to the *in situ* steric stabilization observed in the preparation of microgel particles as auto-steric stabilization.[31] Thus, it was concluded that an auto-steric stabilization mechanism is also operative in the preparation of monodisperse microspheres by precipitation polymerization.

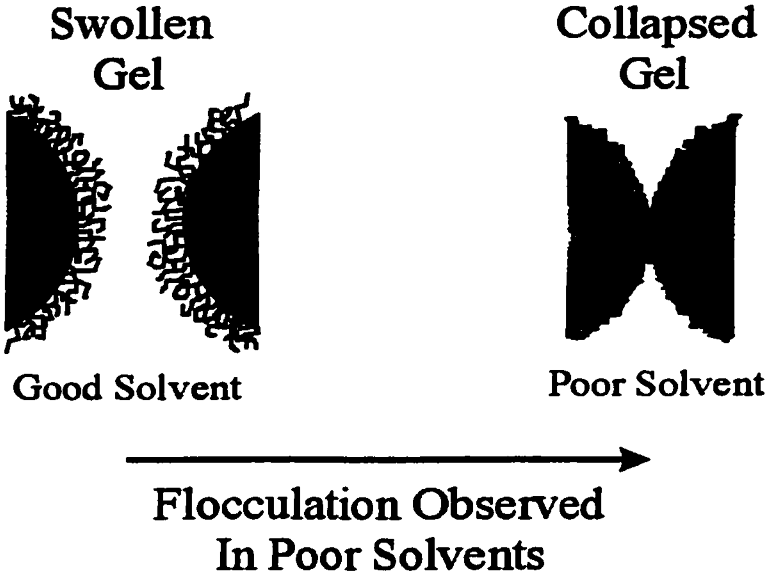

Figure 14. Mechanism of particle stabilization in the precipitation polymerization of DVB.

2.4 Conclusions

The nucleation of polymer microspheres in the precipitation polymerization of divinylbenzene is characterized by the onset of turbidity. The initially homogeneous reaction mixture becomes turbid as a result of both crosslinking, and solvency induced phase separation. In the early stages of the polymerization only low molecular weight polymer is formed, and as the reaction proceeds, intermolecular reactions between oligomeric species along with further propagation lead to the formation of polymer microgel. This microgel fraction appears just prior to and then disappears at the first observation of microspheres which indicates that they are the nuclei of the resulting polymer particles.

The microspheres are sterically stabilized by a surface gel layer formed *in situ* and swollen by the reaction solvent during polymerization. The particles could be de-stabilized by decreasing the solvency of the dispersing media below the *theta*-point of the stabilizing gel which then collapses and flocculation ensues.

2.5 Acknowledgements

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CHAPTER 3

Growth Mechanism of Poly(Divinylbenzene) Microspheres in Precipitation Polymerization

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3.0 Abstract

The residual surface vinyl groups in poly(divinylbenzene) microspheres prepared by precipitation polymerization in acetonitrile, were converted to hexyl groups by treatment with *n*-butyl lithium, and to ethyl groups by catalytic hydrogenation in the presence of Wilkinson's catalyst. These modified particles, as well as the original, unmodified particles, were used as seeds in separate precipitation polymerizations of divinylbenzene in acetonitrile, under identical conditions. Only the original unmodified seeds were able to capture the oligomers formed and grow without secondary initiation. Both the butylated and the hydrogenated seed particles showed extensive secondary initiation instead of seed particle growth. These results demonstrate that precipitation polymerization of divinylbenzene in near-*theta* solvents is an entropic precipitation, involving radical reactions between the macromonomer particles and newly formed oligomers. These results further imply that the growing particles are auto-stabilized by the transient solvent-swollen gel layer on their surfaces, formed by recently captured oligomer.

3.1 Introduction

The wide range of commercial applications for polymer microspheres has encouraged much recent research in this field. In particular, microspheres of uniform size and shape are being used as functional supports,[1] chromatographic separation media,[2,3] and in other areas.[4-6]

The polymerization methods available to prepare monodisperse microspheres, such as water-based emulsions, seeded suspension polymerizations, non-aqueous dispersion polymerizations and precipitation polymerizations, have been reviewed recently.[6-8 9]

Precipitation polymerizations are unique within this group in that they can lead to monodisperse microspheres free of any added surfactant or stabilizer.[10-17] This chapter addresses the mechanisms of microsphere growth and colloidal stabilization during the precipitation polymerization of divinylbenzene in organic solvents.

Precipitation polymerizations start as homogeneous mixtures of monomer, initiator, and optionally, solvents.[11,14-16,18] During polymerization, the growing polymer chains phase-separate from the continuous medium by *enthalpic* precipitation, in cases of unfavourable polymer-solvent interactions, or *entropic* precipitation, in cases where cross linking prevents the polymer and solvent from freely mixing.[19] The bulk polymerizations of vinyl chloride and acrylonitrile are classic examples of enthalpic precipitation polymerizations where the propagating chains grow beyond their solubility limit in the organic medium, which may be the monomer itself, and precipitate. The resulting nuclei typically aggregate into larger, polydisperse particles that continue to grow by capturing other particles, newly formed polymer chains, or by absorption and polymerization of monomer.

This chapter is particularly interested in entropic precipitation polymerizations, i.e., those carried out in the presence of both a crosslinker and a solvent for the polymer. In good solvents, these polymerizations will often produce turbid macroscopic or microscopic gels, depending largely on the original monomer concentration.[20-28] In poorer solvents, precipitation polymerization normally produces micrometer-sized particles.[10-16,18] Their size distribution is often broad due to a lack of colloidal stability.[6]

Recently, our group reported on the formation of monodisperse poly(divinylbenzene) microspheres by precipitation polymerization of divinylbenzene in acetonitrile in the presence of AIBN, a radical initiator.[11] Similar but porous monodisperse microspheres were formed by polymerization in a mixture of acetonitrile and toluene.[12] The narrow particle size distributions observed resemble those found in dispersion polymerizations, suggesting the particles become colloidally stable early on in the polymerization. Previous reports on the use of precipitation polymerization to prepare monodisperse spherical particles are limited. Naka and coworkers reported on both the AIBN and the ^{60}Co γ-ray initiated polymerizations of diethylene glycol dimethacrylate (DEGMA) in a variety of organic solvents.[13] Monodisperse particles were obtained only using γ-ray initiation, while AIBN initiation yielded particles with broad size distributions. In both the divinylbenzene and the DEGMA systems, the mechanism of particle growth and colloidal stabilization in the absence of an added stabilizer remained unclear, although Naka suggested the DEGMA polymer microspheres grow by reacting with a portion of the oligomer formed in solution, and with monomer. However, the DEGMA microspheres were formed in good solvents, suggesting entropic precipitation, while the polymerization of DVB-55 in good solvents such as toluene leads to microgels and space filling gels only.[28] Near *theta*-solvents such as acetonitrile[11] or acetonitrile/toluene mixtures[12] are required to form distinct poly(DVB) microspheres with average diameters of 2-5 μm. The fact that both DEGMA and DVB systems require cross linking monomer to form microspheres, does indicate a critical role for the cross linker, in both growth and stabilization.

Dispersion polymerization is closely related to precipitation polymerization, however, steric stabilizers are added to the dispersion system to control the size, and to narrow the size distribution of the particles.[4] As well, presence of as little as 0.3 % to 0.7 % cross linker relative to monomer in a dispersion polymerization leads to broad size distributions, since the grafted stabilizer becomes buried within the particle.[29-32]

Hence, monodisperse styrenic microspheres may be prepared by several techniques, two of which are: i) dispersion polymerization, in the presence of added steric stabilizer but without significant amounts of cross linker and ii) precipitation polymerization, in the presence of cross linker but without added steric stabilizer. These criteria clearly indicate that the mechanisms of particle growth and stabilization in precipitation polymerization differ considerably from those active in the more established dispersion polymerization.

In this chapter, the critical role of residual surface vinyl groups in the growth process was examined. Precipitation polymerizations involving microspheres with and without surface vinyl groups as seed particles, were studied.

3.2 Experimental

3.2.1 Materials

Technical grade divinylbenzene (DVB-55), containing 55 % of the *para-* and *meta-*divinyl isomers and 45 % of the *para-* and *meta-*ethyl vinyl isomers, was obtained from Aldrich Chemical Company. HPLC grade acetonitrile, toluene and tetrahydrofuran (THF) were purchased from Caledon Chemical, and used as received. 2,2'-Azobis-(2-methylpropionitrile) (AIBN) was purchased from DuPont and recrystallized from methanol prior to use. Wilkinson's catalyst (*tris*-triphenyl phosphine rhodium chloride) and *n*-butyllithium (1.6 molar in hexane), both from Aldrich Chemical Co., were used for particle modification.

3.2.2 Microsphere Preparation

DVB-55 (36.0 mL, 251 mmol), acetonitrile (900 mL), and AIBN (0.657 g, 4.00 mmol) were placed within a one litre polyethylene bottle and shaken vigorously for several minutes to ensure complete dissolution of the initiator. The polymerizations were conducted by placing the bottles within a reactor connected to a programmable temperature controller capable of maintaining the set temperature to within ±1 °C. The reactor gently agitates the sample by rolling the bottles in a horizontal position at approximately 4 revolutions per minute. The temperature profile used for the polymerizations started with a one hour ramp from room temperature to 60 °C followed by a one hour and 40 minute ramp to 70 °C. Once at 70 °C, the reactions were continued for 24 hours. The highly cross linked particles were isolated by vacuum filtration over a 0.5 μm membrane filter with three subsequent washings with tetrahydrofuran (THF). The washed microspheres were dried at room temperature under vacuum for 24 hours. The particles were then analyzed by Fourier Transform Infrared (FT-IR) spectroscopy, Coulter Multisizer and by Environmental Scanning Electron Microscopy (ESEM).

3.2.3 Butylation Reaction

A 250 mL, 3-neck, round-bottom flask was evacuated, flame dried, and purged with dry nitrogen. With nitrogen flowing through the apparatus, a charge of unmodified particles (5.08 g) was placed within the flask. The system was repeatedly evacuated and purged with dry nitrogen. Toluene (200 mL) and THF (20 mL) were added to disperse the particles, and the mixture was stirred magnetically. A solution of *n*-butyllithium in hexanes (30 mL, 48 mmol) was added quickly to the dispersion, producing an orange-red mixture. The reaction was allowed to proceed for 12 hours at room temperature and was then quenched by addition of methanol. The particles were isolated from the reaction mixture by vacuum filtration over a 0.5 μm membrane filter. They were washed with methanol and THF to remove lithium methoxide, and dried for 24 hours under vacuum to yield 5g of white particles. These butylated particles were analyzed by FT-IR, Coulter Multisizer and ESEM.

3.2.4 Catalytic Hydrogenation

Unmodified particles (10.0 g), toluene (100 mL) and *tris*-triphenylphosphine rhodium chloride (0.100 g, 0.108 mmol) where placed within a Parr shaker apparatus which was subsequently charged with 2.5 atmospheres of hydrogen pressure.[33] The reaction was allowed to proceed at room temperature with shaking for 3 days. The resulting hydrogenated microspheres were isolated by vacuum filtration, and washed with toluene and THF to remove catalyst residues. The washed particles were dried under vacuum at room temperature, and were analyzed by FT-IR, Coulter Multisizer and ESEM.

3.2.5 Particle Growth Experiments

Identical growth procedures were used for all three types of seed particles. In each case, the seed particles (0.200 g), DVB-55 (0.6 mL, 4 mmol), acetonitrile (29.4 mL), and AIBN (0.01094 g, 0.0667 mmol) were placed in 30 mL wide mouth polyethylene bottles. The reaction mixtures were vigorously agitated for several minutes in order to disperse the particles and to dissolve the initiator. The bottles were then placed in the polymerization reactor described above, using the same temperature profile. Each reaction was carried out in triplicate. Following polymerization, aliquots of the microspheres were taken from the reaction mixtures, washed with THF and centrifuged repeatedly. These samples were used for particle size determination by Coulter Multisizer, and for ESEM.

3.2.6 Particle Size Analysis

The particle sizes and size distributions were determined using a 256-channel Coulter Multisizer interfaced with a computer. A 30 μm aperture tube was chosen to accommodate the particle size range of 1 to 10 micrometers. A small sample of particles, dispersed in acetone, was added to 25 mL of Coulter Isoton II electrolyte solution and placed in an ultrasonic bath for 10 seconds. The Coulter Multisizer measurements were confirmed using a Phillips ElectroScan 2020 Environmental Scanning Electron Microscope (ESEM).

3.2.7 FT-IR Analysis

Fourier Transform Infrared analysis was performed on a Bio-Rad FTS-40 FT-IR spectrometer. All samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15,000 psi. The spectra were scanned over the range 4 000 to 400 cm^{-1}, in the transmission mode.

3.3 Results and Discussion

The first step in determining the particle growth mechanism was to establish whether polymerization proceeded within the continuous phase as a solution polymerization, or within the precipitated polymeric phase as a micro-bulk polymerization. An auto-acceleration in the reaction rate would be expected if the polymerization were to occur primarily within the polymer rich phase.[5]

Figure 1 shows the conversion of DVB-55 to total polymer, and to polymer microspheres for a polymerization carried out at 4% monomer loading in acetonitrile. The difference between the two conversion curves reflects the presence of a soluble oligomer fraction having an apparent molecular weight of approximately 2 600 g/mol, as measured by size exclusion chromatography using linear polystyrene standards.[12] An auto-acceleration in the rate of monomer consumption was not observed. Instead, the conversion asymptotically approaches a plateau, characteristic of a solution polymerization where the locus of polymerization is primarily within the continuous phase and not within the precipitated polymeric phase. This is in agreement with earlier observations by Li *et al.*[34]

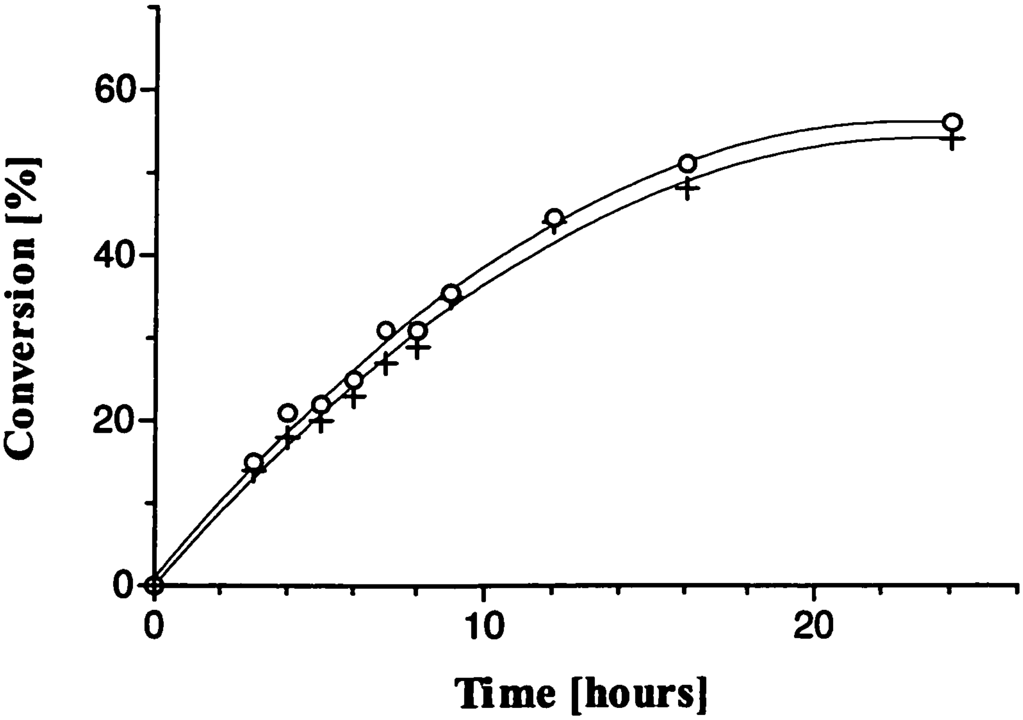


Figure 1. Conversion of monomer to particles (○) and to total polymer (+). The difference between the conversion to particles, and conversion to total polymer, corresponds to the soluble polymer fraction.

3.3.1 Particle Preparation

The second step was to establish how the polymer formed in the continuous phase adds to the particle surface. The key question was whether the microspheres grow by enthalpic precipitation of oligomers grown beyond their solubility limit, or by entropic precipitation where oligomers captured through radical reactions desolvate upon further cross linking to the particle surface. In the latter case, removal of the residual vinyl groups from the surface of the seed particles should prevent their growth in subsequent precipitation polymerizations.

First, a master batch of seed particles was prepared by precipitation polymerization. These particles had a number average particle diameter, $\bar{D}_n$, of 3.8 μm and a coefficient of variation, *c.v.*, of 19 % as measured by Coulter Multisizer, Figure 2. An electron micrograph of these particles is shown in Figure 3a. This master batch was divided into three equal portions. Two of the portions were subjected to butylation or hydrogenation, respectively, in order to convert their residual surface vinyl groups into hexyl or ethyl groups.

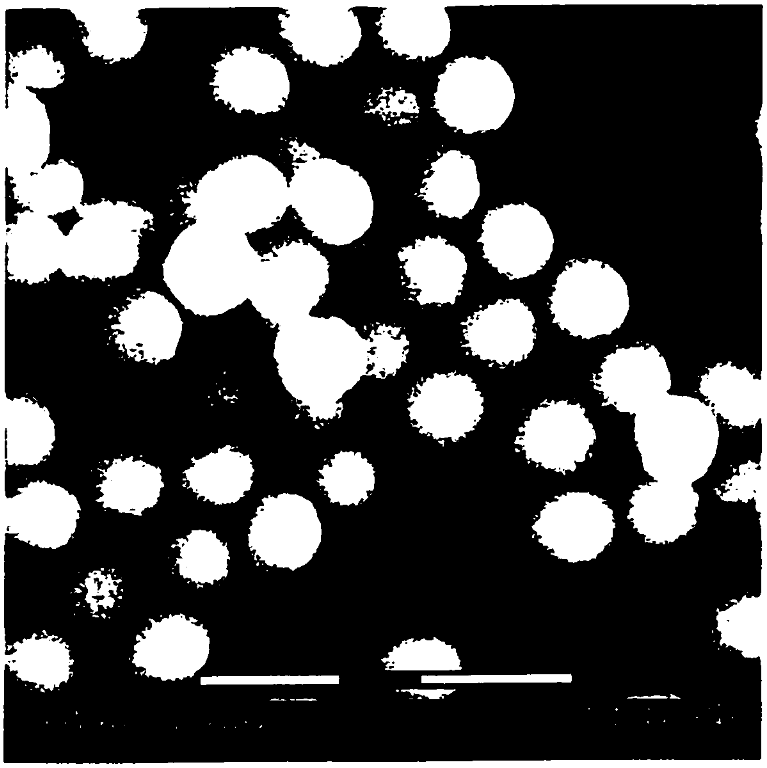


Figure 2. Scanning electron micrograph of the unmodified poly(divinylbenzene) particles used for the butylation and hydrogenation reactions.

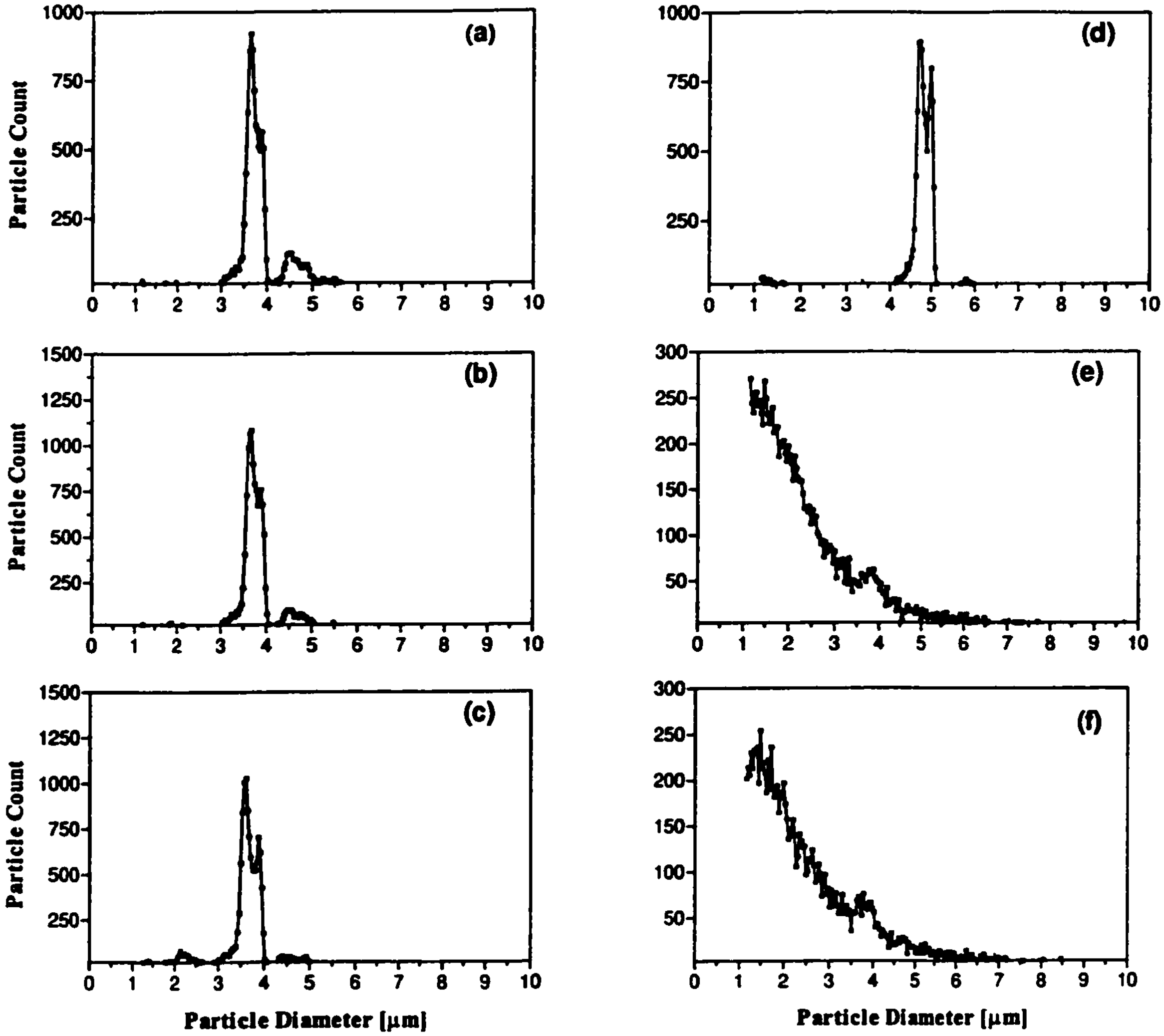


Figure 3. Particle diameters measured by Coulter Multisizer analysis using a 30 μm aperture: a) unmodified seed particles, b) butylated seed particles, c) hydrogenated seed particles, d) after seeded polymerization using unmodified particles as seeds, e) after seeded polymerization using butylated seeds, f) after seeded polymerization using hydrogenated seeds.

The FT-IR spectrum of the unmodified particles was measured for comparison with those for the modified particles. In the unmodified particles, the band at 2924 cm^{-1} results from the asymmetrical stretching of methylene groups while the band at 1603 cm^{-1} originates from the asymmetrical stretching of conjugated double bonds. The band at 990 cm^{-1} is associated with the CH out-of-plane deformation in mono-substituted vinyl compounds, representing residual vinyl groups.[35]

Table 1 compares the peak area ratios for the 2924 cm^{-1}, 1603 cm^{-1}, and 990 cm^{-1} bands, for all particles studied. In the case of the unmodified particles, the relative area ratios are 3.7, 7.1, and 0.51 for the 2924 cm^{-1}/1603 cm^{-1}, 2924 cm^{-1}/990 cm^{-1} and 990 cm^{-1}/1603 cm^{-1} bands, respectively. These relative areas were used as a baseline for comparison with the butylated and hydrogenated particles.

Table 1. Area ratios of key FT-IR bands in the unmodified seed particles, the butylated seed particles, and the hydrogenated seed particles.

Seed Particles	**FT-IR Bands (Intensity Ratios)**		
	2924 cm^{-1}/1603 cm^{-1}	**2924 cm^{-1}/990 cm^{-1}**	**990 cm^{-1}/1603 cm^{-1}**
Unmodified	3.7	7.1	0.51
Butylated	4.2	9.1	0.46
Hydrogenated	4.8	10	0.48

3.3.2 Seeded Polymerization using Unmodified Seed Particles

The unmodified 3.8 µm particles were used as seeds for the preparation of larger particles by seeded precipitation polymerization. The reaction conditions were the same as those used to prepare the original particles, except for the presence of 0.2g of seed particles having an average diameter 3.8 µm. During this growth reaction, the original seed particles increased in size to an average diameter of 4.6 µm, with a *C.V.* of 16 % (Figure 3d). This particle growth was confirmed by electron microscopy (Figure 4). The two smaller particles visible in this micrograph are likely particles that were initially smaller than the 3.8 µm seed particles, and as such have not grown to as large a diameter. It appears therefore, that during the polymerization in presence of unmodified seeds, particle growth occurs exclusively on the surface of the seed particles and secondary initiation is not observed.

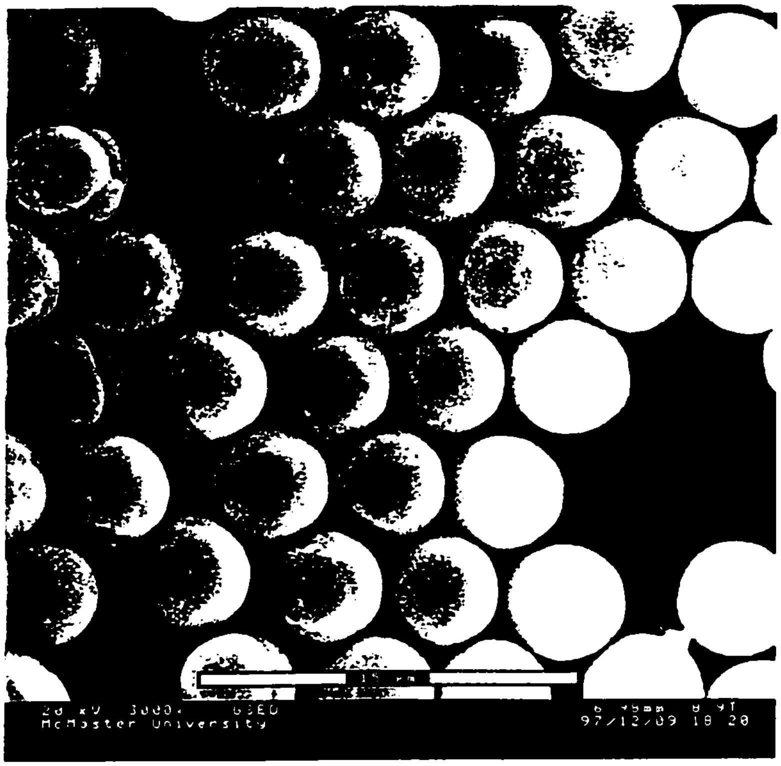


Figure 4. **Scanning electron micrograph of the microspheres produced when unmodified particles were used during seeded polymerization.**

The particle growth mechanism for this seeded reaction should be identical to the growth mechanism during the post-nucleation stage of a non-seeded precipitation polymerization, since particle loading, reagent concentrations and temperature all reflect those used during the initial microsphere preparation.

3.3.3 Seeded Polymerization Using *n*-Butyl Modified Seed Particles

A sample of the unmodified 3.8 μm particles was treated with excess *n*-butyl lithium in a mixture of 10:1 toluene:THF, respectively, to convert the residual surface vinyl groups into unreactive hexyl groups. This reaction mixture turned orange-red, due to formation of benzylic anions, and returned to white after quenching with methanol. It is expected that alkylation took place only at the surface of the particles, as diffusion of the solvated butyl lithium reagent into the microspheres would be a slow process. Indeed, the butylated particles slowly decolorized bromine, likely due to reaction with residual internal vinyl groups. As well, FT-IR of the butylated particles showed only a small reduction in the level of vinyl groups. In comparison to the unmodified particles, FT-IR of the butylated particles showed an increase in the intensity of the asymmetrical methylene stretch, 2924 cm^{-1}, relative to both the asymmetrical conjugated double bond stretch, 1603 cm^{-1}, and the CH out-of-plane deformation of mono-substituted vinyl groups, 990 cm^{-1} (Table 1). These changes are in agreement with butylation of the surface vinyl groups. No change in average particle diameter was observed during the butylation reaction (Figure 3b).

Subsequently, seeded precipitation polymerizations were performed using the *n*-butylated microspheres as seed particles, under reaction conditions identical to those described for the unmodified seeds. Figure 3e indicates the particle size distributions obtained after the reaction. New generations of particles have formed by extensive secondary initiation, resulting in a broad final size distribution. The electron micrograph shown in Figure 5 indicates that the new generations range in diameter from several hundred nanometers to more than 7 μm. Particles with diameters of 4 μm and larger may either be a component of the new generation, or may result from the growth of some of the seed particles.

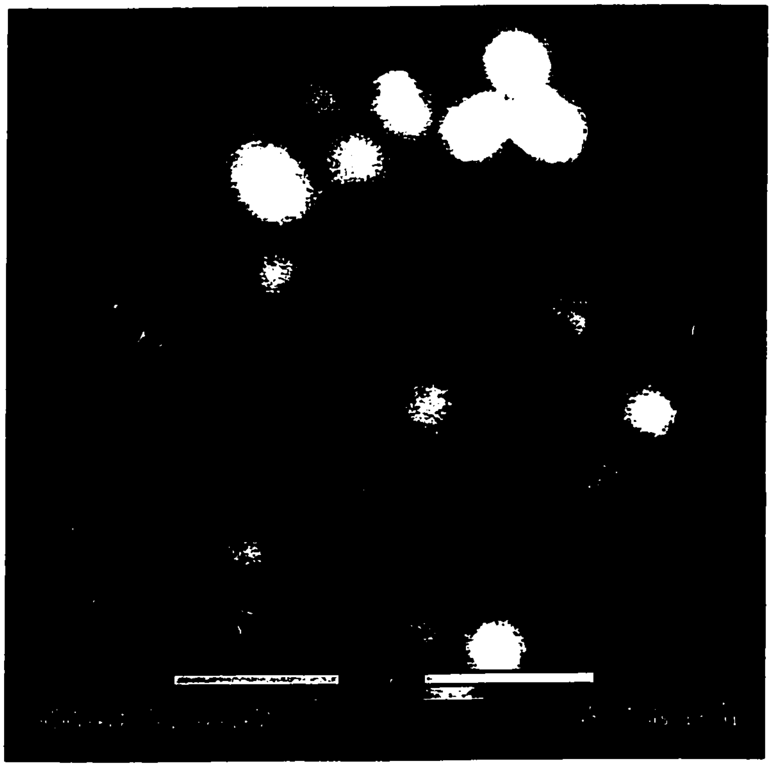


Figure 5. Scanning electron micrograph of the microspheres produced when butylated particles were used during seeded polymerization.

Clearly, butylation substantially interferes with deposition of new oligomer during the seeded polymerization. It is possible that not all accessible vinyl groups were butylated, and hence some of the 3.8 μm particles could grow to diameters greater than 4 μm.

Reaction of the residual vinyl bonds with *n*-butyllithium results in the formation of pendant hexyl groups. It was found previously that aliphatic co-monomers such as butylmethacrylate or dodecylmethacrylate do not interfere with particle formation and growth.[36] Nevertheless, it was decided that a second method of modification that would alter the particle surface to a lesser degree should be investigated.

3.3.4 Seeded Polymerization using Hydrogenated Seed Particles

Hydrogenation of the particles was used to convert their pendant vinyl groups into ethyl groups. The DVB-55 used for the preparation of the original microspheres already contains 45 % ethyl vinylbenzene. Therefore, hydrogenation would be a subtle method to eliminate surface vinyl groups, and to study particle growth in the absence of an entropic precipitation mechanism.

Heterogeneous hydrogenation catalysts such as platinum or palladium supported on an inert surface, are commonly used for the hydrogenation of alkenes. However, a homogeneous catalyst is required for the hydrogenation of solid polymer particles. Wilkinson's catalyst, *tris* triphenylphosphine rhodium chloride, a soluble catalyst commonly used for homogeneous hydrogenations,[33] should be well suited to the reduction of vinyl groups on a particulate surface. The hydrogenation reaction was followed by FT-IR, and the relative areas of the key bands are shown in Table 1. The asymmetrical methylene stretch, 2924 cm^{-1}, increased with respect to the asymmetrical conjugated double bond stretch, 1603 cm^{-1}, and to the CH out-of-plane deformation of mono-substituted vinyl groups, 990 cm^{-1}. These changes are consistent with reduction of some of the vinyl groups at the surface. The particles did not change in size as a result of the hydrogenation reaction (Figure 3c).

Subsequently, a seeded polymerization was conducted using the hydrogenated microspheres as seed particles. Again, these particles easily dispersed in acetonitrile. The size and size distribution of the particles isolated from this seeded polymerization are shown in Figure 3f. As in the case of the butylated seed particles, the electron micrograph shown in Figure 6 indicates that new generations of particles had formed, with diameters ranging from several hundred nanometers to more than 7 μm. A band between 3 μm and 4 μm that remains visible in the final particle size plot corresponds to the original seed microspheres. These observations are consistent with the results of the polymerization using the butylated seed particles.

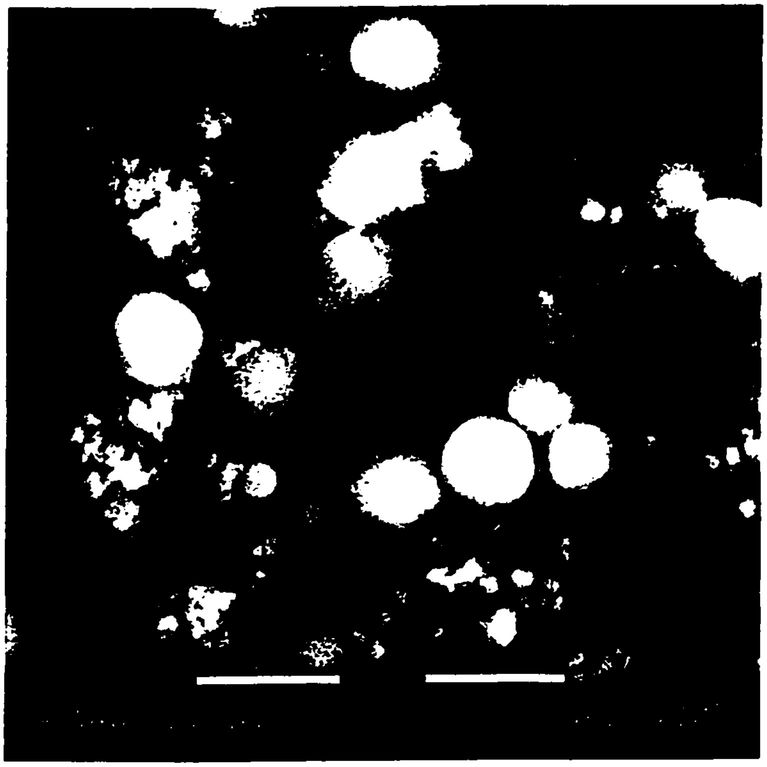
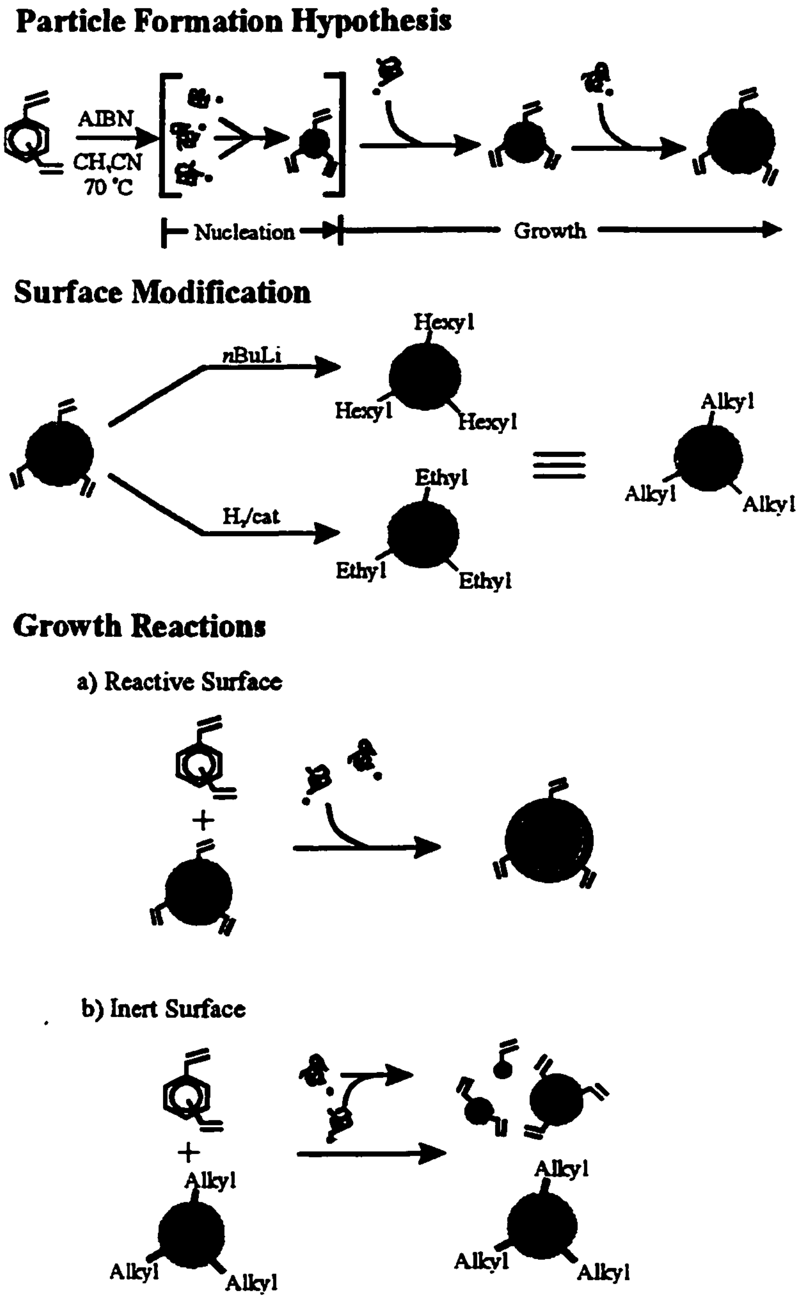


Figure 6. Scanning electron micrograph of the microspheres produced when hydrogenated particles were used during seeded polymerization.

3.3.5 Interpretation of Growth Mechanism

Scheme 1 outlines the investigation of the particle formation process. It includes the particle surface modifications and subsequent reactions designed to test the growth hypothesis.



Particle Formation Hypothesis

Surface Modification

Growth Reactions

Scheme 1. The proposed particle formation process has two stages and they are nucleation and growth. The growth stage involves the reactive or entropic capture of soluble oligomers by surface vinyl groups, followed by de-solvation. This growth hypothesis was tested by converting surface vinyl groups to inert alkyl groups by i) alkylation and ii) hydrogenation. In subsequent seeded growth reactions, only the reactive seed particles grew uniformly, by capturing oligomers (a). Under the same conditions, the modified, inert seed particles did not grow. Rather, in these reactions the oligomers formed, aggregated into poly-disperse secondary particles (b).

The hypothesis for the particle formation consists of two stages: nucleation and growth. Nucleation starts by aggregation and reaction of soluble oligomers to form swollen microgels, that subsequently de-solvate to form the particle nuclei. This stage of particle formation has been described in Chapter 2.

The particle growth hypothesis is that throughout the polymerization, soluble oligomer radicals are captured from solution by reaction with the vinyl groups on the particle surface. In particular, a reactive, entropic capture mechanism is proposed. This is different than the capture mechanism of dispersion polymerization which is solely driven by enthalpic de-solvation and deposition of the forming polymer onto the particle surface.

The reactive growth hypothesis implies that the captured oligomers form the new surface of the particles, and hence even the final particles should contain surface vinyl groups. This allows us to test the overall hypothesis, by removing the vinyl groups from the surface of model seed particles, and comparing their ability to grow during subsequent polymerizations, with that of unmodified particles.

To this end, a master batch of seed particles was prepared by precipitation polymerization of DVB-55. This batch of particles was then divided into three parts, two of which were modified, one by reaction with *n*-butyl lithium, and one by hydrogenation using Wilkinson's catalyst, (Surface Modification, Scheme 1).

In subsequent identical growth reactions, only the unmodified particles, containing reactive surface vinyl groups, grew to larger diameters in a uniform fashion, without secondary particle initiation.

In contrast, neither the butylated nor the hydrogenated microspheres were able to grow, since their unreactive surfaces prevented oligomer capture. Instead, extended secondary nucleation was observed in their presence, leading to the broad final size distributions indicated in Scheme 1. This finding indicates that the presence of surface vinyl groups is essential for particle growth in this process, and supports the hypothesis that particle growth is an entropic precipitation driven by radical reactions. In effect, the poly(divinylbenzene) particles do not merely provide an inert surface onto which oligomers, grown above their solubility limit, deposit by desolvation. Rather, they act as macromonomers during particle growth.

It was unclear why the secondary particles formed in the presence of the inert seed particles, have a wide size distribution. Conducting the equivalent polymerization in the absence of any seed particles normally produces microspheres with narrow size distributions. It is likely, though that the inert seed particles interfere with oligomer capture by the new generation of particles, and thus promote continuing secondary initiation.

The oligomers involved in particle growth probably resemble the soluble polymer fraction having an apparent number average molecular weight of 2 600 g/mol that was isolated at the end of the polymerizations. These oligomers would correspond to the low molecular weight fraction of the branched polymers formed by polymerization of DVB in benzene.[22]

The growth reaction involving the unmodified seed particles produces a core-shell morphology. In the present case, the core and shell both consist of DVB-55, and the experiment serves primarily as a control experiment. In an upcoming paper, the formation of core-shell particles having functional shells will be described.[37]

3.3.6 Implications for Particle Stabilization

As a consequence of the particle growth mechanism described above, the surface of the microspheres continuously captures soluble or highly swollen oligomers from the reaction medium. Accordingly, the particle surface at any instant during the polymerization must be a solvent-swollen, partially cross linked gel. Considering the narrow particle size distribution observed without any added steric or ionic stabilizers, it is proposed that this surface gel sterically stabilizes the particles, preventing homocoagulation that would otherwise lead to broad size distributions.

Polymer colloids, stabilized only by solvent swollen surfaces, have been known for some time. An early example are the solvent swollen microgels first prepared by Staudinger and Huseman,[38] and more recently studied by Funke,[25] Burchard[39] and Antonietti.[22] These microgels are formed by polymerizing cross linking monomers at low monomer loadings or low conversions in good solvents.

During precipitation polymerizations carried out in a marginal, near-*theta* solvent such as acetonitrile, the transient gel surface of the particles continuously de-solvates and collapses, even while newly formed oligomer is captured.[11,12] This de-solvation likely occurs by a spinodal decomposition that is both driven and frozen by cross linking, similar to the analogous process discussed by Antonietti for small polymer microgels.[23] It can be described as a polymerization-induced-phase-separation (PIPS)[40] taking place first within the initially formed gel particles, and subsequently within the transient gel on the surface of the growing microspheres.

Related surface-swollen polymer particles have been prepared earlier by a very different approach. Fitch has reviewed highly cross linked organosols originally prepared by precipitation polymerization in poor solvent, and subsequently transferred to a good solvent which swells the outer surface to the limit allowed by the cross linking. The solvent-swollen surface gel layer obtained by this approach stabilized these organosols against aggregation.[19]

Graham and Mao have used the term auto-steric stabilization to describe the mechanism by which their polyurethane microgels avoid aggregation. Here, hydroxy-terminated poly(ethyleneglycol) chains added to the polymerization are anchored on the surface of the microgels, and provide steric stabilization.[41]

Naka and Yamamoto have studied the precipitation polymerization of DEGMA in the presence of good solvents which are capable of swelling the outer surface of the microspheres. Presumably, these particles are also auto-sterically stabilized by solvated polymer chains and gel anchored to the surface of the microspheres.[42]

Therefore, the mono-disperse microspheres prepared by precipitation polymerization of divinylbenzene in acetonitrile could be called: a one-step organosol preparation, where the surface swollen particles are prepared *in situ*; a polymer microgel with internal desolvation; or preferably a precipitation polymer particle auto-sterically stabilized during growth by the transient gel layer on its surface.

3.4 Conclusions

These experimental results indicate that particle growth during precipitation polymerization of divinylbenzene occurs by an entropic precipitation mechanism where soluble oligomeric species are captured from solution by reaction with vinyl groups on the particle surface. This is in contrast to the enthalpic precipitation mechanism commonly observed for dispersion polymerization, where polymer grown above its solubility limit phase separates from solution and deposits onto the surface of existing particles.

Continuous capture of oligomeric species from solution suggests that the particle surface is swollen with solvent. This transient surface gel layer stabilizes the particles during their growth stage, by a process termed auto-steric stabilization. Thus narrow particle size distributions, similar to those obtained in dispersion polymerizations, can be achieved by precipitation polymerization in the absence of added stabilizers.

3.5 Acknowledgements

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CHAPTER 4

Poly(Divinylbenzene) Microspheres as an Intermediate Morphology Between Microgel, Macrogel and Coagulum in Crosslinking Precipitation Polymerization

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4.0 Abstract

Precipitation copolymerizations of divinylbenzene (DVB) and 4-methylstyrene were conducted in solvent mixtures comprised of methyl ethyl ketone and heptane at monomer loadings of 4 vol%. In this investigation DVB content was varied from 0 to 55% and the solvent mixture varied from neat MEK to neat heptane. Four distinct polymer morphologies including microspheres, microgels (and soluble polymer), macrogel and coagulum were observed and have been reported in the form of a morphology map. The structure of these polymer architectures is described and the effect of both, DVB concentration and solvency on the transitions between morphologies are discussed.

The volume occupied by the polymer formed decreases with both decreasing solvency and increasing DVB concentration. These results indicate that the microspheres are formed, in part, by an internal contraction which is caused by both the marginal solvency of the continuous phase and crosslinking of the polymer network. This contraction is likely progressive, supporting the presence of a lightly crosslinked corona around the microspheres which acts as a steric stabilizer.

4.1 Introduction

The precise control of polymeric architecture has led to many applications for materials such as microspheres, microgels and macrogels. Crosslinked microspheres serve as key components in Merrifield's polymer-supported peptide synthesis,[1] and as stationary phases in chromatography.[2-5] Microgels have been used both as coatings[6] and as substrates for biomedical and diagnostic purposes.[7] Macrogels have been used as stationary phases in monolithic chromatography columns,[8,9] and as molecularly imprinted polymers, using template molecules, for high affinity separation resins.[10]

Microspheres, microgels, and macrogels, all of which can be prepared by free-radical copolymerization of monovinyl and divinyl monomers in suitable solvents, are expected to have some similarities in their formation mechanisms. This chapter describes the formation of crosslinked poly(divinylbenzene) microspheres, microgels and macrogels under conditions varying only in solvent composition and crosslinker concentration, focussing on the fundamental connections between these important network morphologies.

The preparation of functionalized, porous, or even core-shell microspheres by precipitation polymerization has been an interest in this laboratory for several years. This method is particularly interesting because monodisperse particles can be synthesized without adding steric or ionic stabilizers to the reaction mixture.[11-14] Thus, the particle formation mechanisms are fundamentally different from those of the other heterogeneous polymerization techniques namely, dispersion, emulsion and suspension.[15] The formation processes of particular interest are nucleation, growth, desolvation and stabilization.

Chapter 3 examined the particle growth mechanism in the precipitation copolymerization of divinylbenzene (DVB). In this system, DVB-55 is polymerized at monomer loadings below 5 vol% in acetonitrile, or mixtures of acetonitrile and toluene, by free radical polymerization using AIBN as an initiator.[11,13,14] It was found that the particles increase in size by a reactive growth mechanism where oligomeric radicals are captured from solution by reaction with surface double bonds on existing particles. Thus, their surfaces are continuously renewed with soluble species and at any given point these surfaces should resemble a solvent-swollen polymer gel. Concurrent with the ongoing capture of oligomeric species on the surface, there is an internal de-solvation of this gel to form the dense, final microspheres.[16] It is proposed that the most important role of this surface gel is to act as a steric stabilizing layer which prevents the particles from coagulating.

Microgels are defined as intramolecularly crosslinked macromolecules that have sizes in the nanometer range and are able to swell in good solvents. They can be prepared by polymerizing crosslinking monomers in moderately dilute solution in good solvents. In this case, intramolecular reactions are favoured due to radical chain ends having a higher local concentration of pendent reactive groups from their own chain in comparison to those from other macromolecules.[20] Thus, below a critical threshold of monomer loading macrogelation is avoided.[21] The classic example is the synthesis of styrene-DVB microgels first prepared by Staudinger and Husemann. Polymerizing DVB in benzene at concentrations of less than 8 vol% monomer produced only microgel whereas at higher concentrations macrogelation was observed.[21]

Microgel particles prepared by the aforementioned technique have an inhomogeneous structure, consisting of a strongly crosslinked core embedded in a lightly crosslinked corona.[20] There are several reasons for this inhomogeneity: i) divinyl monomers are often more reactive than their monovinyl counterparts, and therefore, are incorporated into the structure at an earlier stage of the reaction; ii) the microgel core is older than the outer surface, and thus, has more time to crosslink.[20] Graham *et al.* have suggested that the lightly crosslinked outer surface of microgels, acts as a steric stabilizing layer in the presence of better than "*theta*" solvents and in turn prevents aggregation of the colloidal sized gels.[22,23]

In the past, much of the research on macrogels has focussed on predicting when macrogelation occurs during the polymerization of crosslinking monomers. Renewed interest in this morphology has developed as a result of the synthesis of one step chromatographic column packings. Sellergren has reported the preparation of molecularly imprinted polymers (MIPS) were ethylene glycol dimethylacrylate, acrylic acid, a diluent and a template molecule are mixed within glass tubes which upon polymerization form space-filling macrogels that can be attached to an HPLC for evaluation of their ability to recognize the template molecule.[24]

The purpose of this article is to define how microspheres produced in crosslinking precipitation polymerizations are related to the more common and competing morphologies of microgel, macrogel and coagulum. For a constant monomer loading of 4 vol%, both solvency of the continuous media and concentration of the crosslinking monomer are expected to influence the polymer morphology. The effects of these two parameters on microsphere formation are reported here.

4.2 Experimental

4.2.1 Materials

Divinylbenzene-55 was obtained as a technical grade mixture containing 55% of the *para-* and *meta-*divinyl isomers and 45% of the *para-* and *meta-*ethylvinyl isomers. The composition of this mixture was confirmed by gas chromatography prior to use. DVB-55 and the comonomer 4-methylstyrene were purchased from Aldrich Chemical Company and used as recieved. In earlier experiments the inhibitor, 4-*tert*-butyl catechol, was removed from the monomers by passing them through silica columns and it was determined that this had little effect on the polymerizations. The initiator 2,2'-azobis-(2-methylpropionitrile) (AIBN) was purchased from DuPont and recrystallized from methanol prior to use. The solvents for the polymerizations, methyl ethyl ketone (MEK) and heptane (HEP), were purchased from Caledon Chemical and they were used as received.

4.2.2 Sample Preparation

In addition to commercial DVB-55, samples of DVB-50, 45, 40, 35, 30, 25, 20, 15, 10, where the number represents the percentage of crosslinking monomer in the mixture, were prepared by diluting DVB-55 with 4-methylstyrene. Master batches of these monomer mixtures were prepared according to the following equation:

$$V_{DVB55} = xV_T / 55 \qquad (1)$$

were V_{DVB55} is the volume of DVB-55 to be diluted, x is the desired crosslinker content of the monomer mixture (ie. DVB-x) and V_T is the total volume of the masterbatch. The volume of 4-methyl styrene, V_{4MeS}, added to dilute the DVB-55 was then calculated as follows,

$$V_{4MeS} = V_T - V_{DVB55}. \tag{2}$$

For example, a 100 mL masterbatch of DVB-40 would contain 72.7 mL of DVB-55 and 27.3 mL of 4-methyl styrene. AIBN, 1.824 g (111.1 mmol) was added to each monomer masterbatch just prior to dispensing to the polymerization vials. All samples were prepared in 20 mL Wheaton scintillation vials. For each sample, a 0.80 mL aliquot of the monomer mixture was diluted to a total volume of 20 mL using MEK and heptane. The ratio of MEK to heptane was varied from neat MEK to neat heptane. The polymerizations were conducted at a constant temperature of 70 °C in a reactor that provided gentle agitation by rolling the scintillation vials horizontally at 4 revolutions per minute. All samples reported here correspond to 24 hours of polymerization.

4.2.3 Polymer Characterization

Following polymerization, the soluble polymer was separated from the insoluble fraction by vacuum filtration and the insoluble residue was washed extensively with THF. Excess solvent was removed from the soluble polymer by rotatory evaporation under reduced pressure. Both fractions were then dried under vacuum at room temperature for 48 hours. The molecular weights of both the linear and microgel polymers were characterized using a Waters 590 programmable pump connected to Ultrastryragel columns using a Waters 410 differential refractometer as a detector, tetrahydrofuran as solvent at a flow rate of 1 mL/min, and narrow disperse polystyrene as standards. The morphologies of the microspheres, macrogels and particles were examined using a Phillips ElectroScan 2020 Environmental Scanning Electron Microscope (ESEM). The average diameters of the microspheres were measured using a Coulter Multisizer II fitted with a 50 µm aperture tube and Isoton II as the conductive electrolyte solution. The sizes of polymer microgels were measured using a Polarization Intensity Diffraction System (PIDS) (Coulter LS230) where THF was used as the dispersing solvent.

Macrogels were placed in large containers filled with THF to separate any soluble polymers from the insoluble macrogel. The wash solvent was changed three times during the course of one week. At which point, the volumes of the THF swollen macrogel cylinders were calculated by measuring their dimensions. The macrogels were then allowed to dry to constant weight and their new dry volumes recorded. Particles and microspheres were resuspended in THF, in 20 mL scintillation vials, and then allowed to settle over the course of one week, at which point, the volume of the layer of settled particles was measured.

4.3 Results and Discussion

4.3.1 Polymer Morphology Map

Four distinct morphologies were observed in the crosslinking copolymerization of DVB and 4-methylstyrene conducted in different solvent compositions and at low monomer loadings. Figure 1 indicates both the solvency and crosslinking requirements for the preparation of soluble polymers (including microgels), macrogels, microspheres, and coagulum and each of these architectures will be discussed in detail in the following sections. These morphologies all correspond to samples obtained after 24 hours of polymerization.

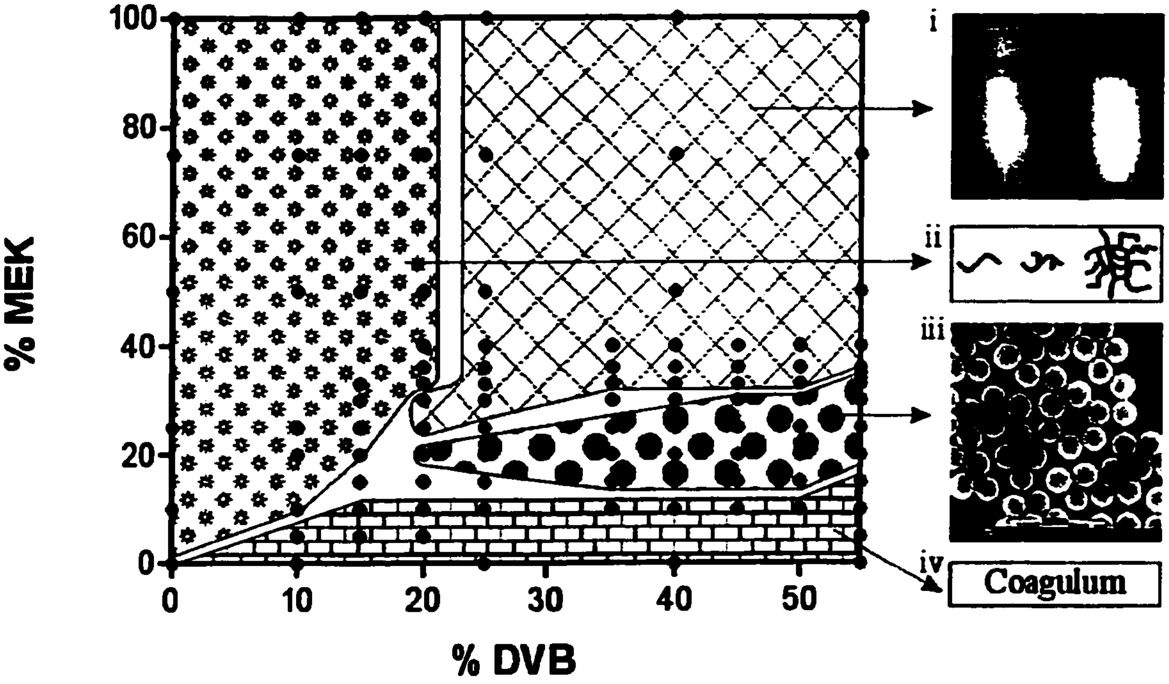

Figure 1. Morphology map for the polymerizations reported here. The 4 vol% monomer feed contained from 0 to 55% DVB. The solvent compositions for the polymerizations were varied from neat MEK to neat heptane. Four distinct morphologies are represented: i) space-filling macrogels; ii) soluble polymer which includes linear, branched and microgel structures; iii) microspheres; iv) coagulum. The morphologies shown here correspond to samples obtained after 24 hours of polymerization.

4.3.2 Effect of Solvent Composition on Poly(DVB-*x*) Morphology

First, we will consider the changes in the poly(DVB-*x*) structure observed as a result of varying the solvent composition from neat MEK, a good solvent, to neat heptane, a poor solvent.

Space-filling macrogels are obtained at high MEK and high DVB levels. Under these conditions the polymer network forms in a swollen state and thus fills the entire reaction volume. Polymerizing DVB-55 in neat MEK produces an opaque space-filling macrogel that is smooth to the limits of resolution by electron microscopy. Decreasing the solvency of the continuous phase to 36 vol % MEK by dilution with heptane still produces an opaque space-filling macrogel, but scanning electron microscopy of this macrogel in the dry state indicates a heterogeneous structure comprised of small interconnected nodules of approximately 100 to 200 nm (Figure 2).

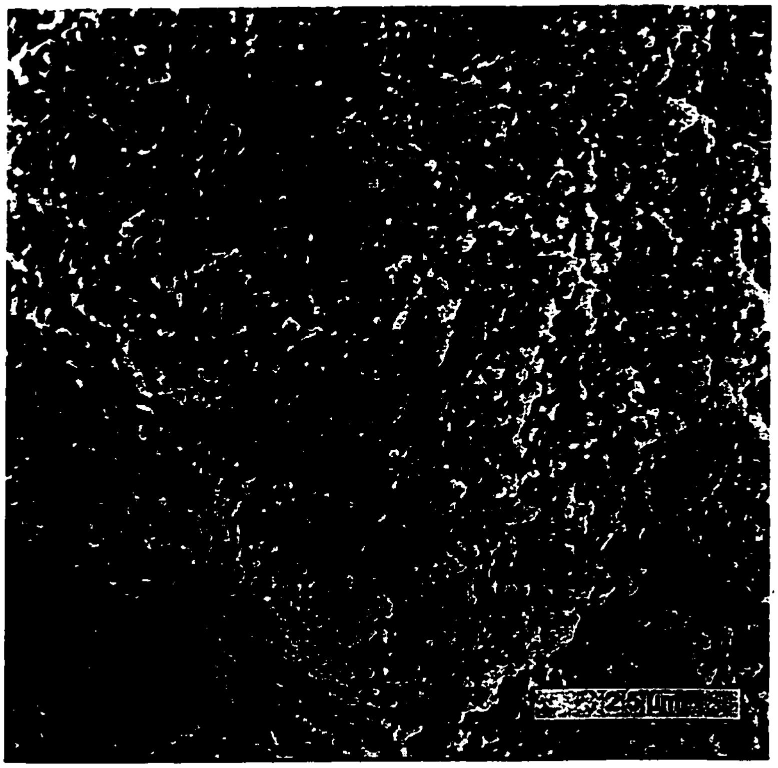

Figure 2. Electron micrograph of a space-filling macrogel in the dry state prepared from 4 vol% DVB-55 in a mixture of 40:60 MEK:heptane.

Transmission electron microscopy of sections microtomed from the same macrogel, swollen and embedded in low viscosity epoxy resin, showed similar nodules of 100 to 200 nm. No connecting "fibrils" or gel bridges were observed, likely due to their low contrast with the epoxy. Hence, this macrogel, formed near the morphology transition to microspheres, is comprised of strongly crosslinked, non-swellable nodules interconnected by regions of lower crosslink density. In good solvents, the nodules do not change their size significantly whereas the interconnecting fibrils are able to swell and extend.

In polymerizations carried out at 35 and 34% MEK, scanning electron microscopy images revealed rough particles of irregular shapes with dry diameters of 200 - 400nm. (Figure 3).

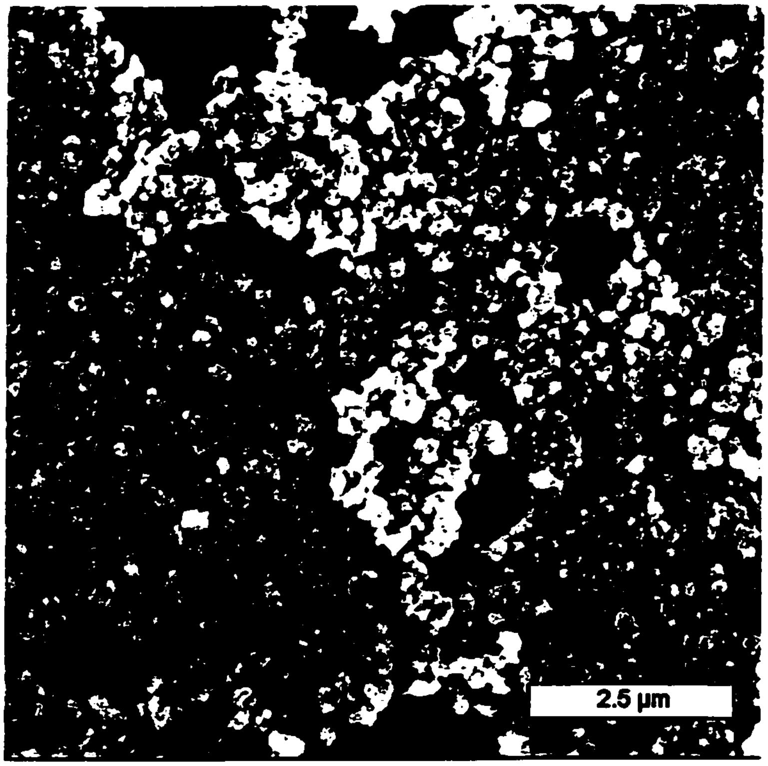

Figure 3. Electron micrograph of irregular shaped particles in the dry state prepared from 4 vol% DVB-55 in a mixture of 35:65 MEK:heptane.

In the range of 33 vol% to 20 vol% MEK, discrete microspheres were formed. Figure 4 shows the microspheres prepared with 33 vol% MEK. They have rough surfaces and average diameters of 1.8 ± 0.5 μm, and their interstitial volume contains polymer that could not be removed even after successive centrifugation from tetrahydrofuran. It was concluded that this was a lightly crosslinked polymer gel covalently bonded to the surface of the particles and that this surface gel prevents particle aggregation by an auto-steric stabilization mechanism.

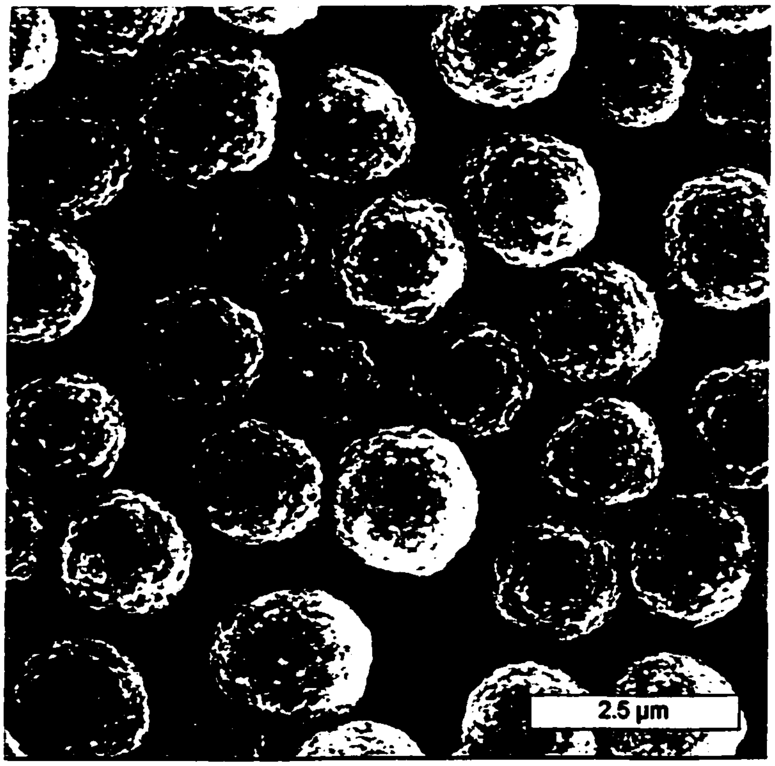

Figure 4. Electron micrograph of microspheres in the dry state prepared from 4 vol% DVB-55 in a mixture of 33:67 MEK:heptane.

Decreasing the concentration of MEK to 25 vol% led to an increase in the size of the microspheres to 3.8 ± 0.3 μm and a decrease in the roughness of the particle surface (Figure 5). At 20 vol% MEK the average particle diameter increased further to 4.6 ± 0.4 μm (Figure 6).

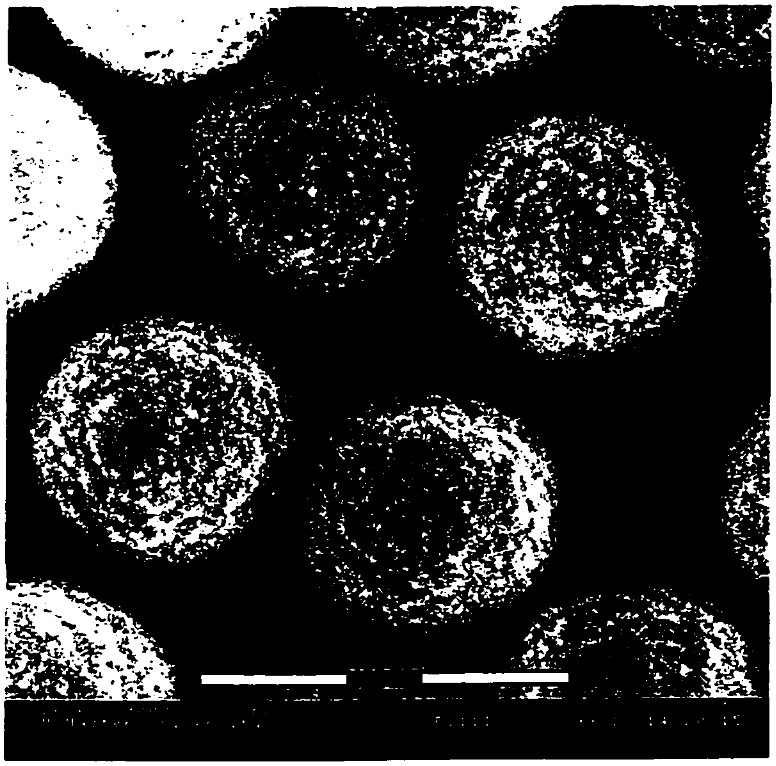

Figure 5. Electron micrograph of microspheres in the dry state prepared from 4 vol% DVB-55 in a mixture of 25:75 MEK:heptane. The scale bar is 5 µm in length.

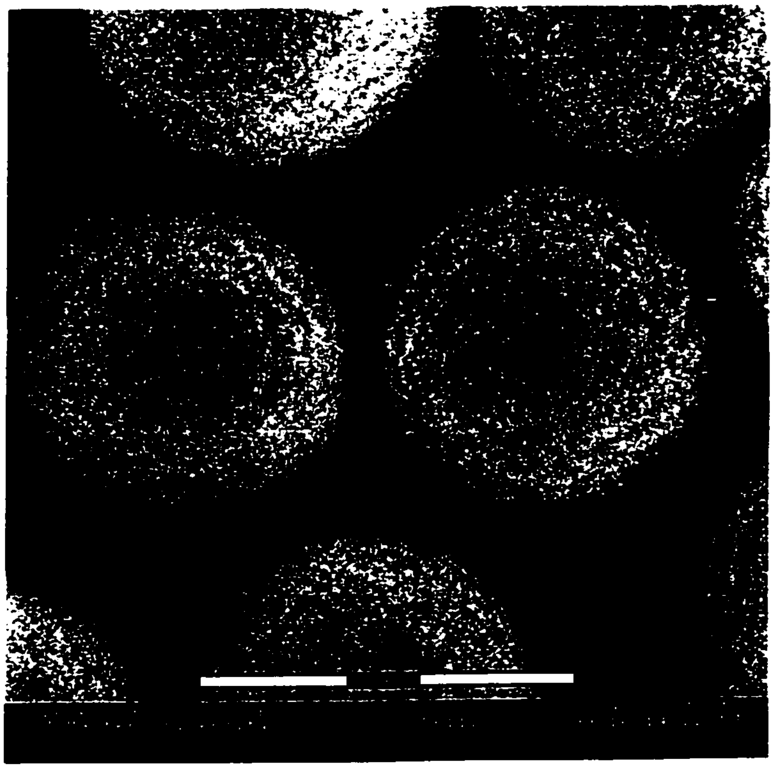

Figure 6. Electron micrograph of microspheres in the dry state prepared from 4 vol% DVB-55 in a mixture of 20:80 MEK:heptane. The scale bar is 5 μm in length.

MEK concentrations of 15 vol% or below led to the formation of coagulum. Apparently, the solvency of the continuous medium is now so poor that the forming polymer phase separates from solution to coat the inside of the reaction vessel. This coating does not dissolve or swell significantly in organic solvents such as THF, suggesting that the polymer is highly crosslinked in its collapsed state.

The transitions from space-filling macrogel to microspheres, and from microspheres to coagulum, take place over a narrow range of solvent composition. They are continuous transitions, where the structure of the polymer formed changes rapidly from one morphology to the other.

Such intermediate morphologies might bridge the gap between traditional microsphere resin beds and the more recent monolithic column blocks. For example in a parallel series of experiments DVB-55 at 4% monomer loading was polymerized in 87% THF and 13% water to give a space-filling macrogel comprised of interconnected microspheres. Heterogeneous macrogels having hybrid morphologies such as this could prove very useful in the synthesis of single step chromatographic column packings combining high flow rates with high surface area.

4.3.3 Effect of Crosslinker Concentration on Poly(DVB-*x*) Morphology

The effect of crosslinking monomer concentration will be discussed for a series of polymerizations carried out at a constant MEK solvent fraction of 25%. In the absence of the crosslinking monomer, linear poly(4-methylstyrene) with $\overline{M}_n$ of 3.0×10^3 g/mol and a polydispersity index, PI, of 1.6 was produced at a conversion of 18%, Table 1. This low molecular weight is due to the low monomer loading of 4 vol%, where the propagating chains terminate before they are able to add many monomer units.

Table 1. The effect of crosslinking monomer content on polymer morphology, total conversion, conversion to insoluble and to soluble polymer, and molecular weight of the soluble fraction. These samples consisted of 4 vol% monomer in 25:75 mixtures of MEK:heptane with 2 wt% AIBN.

Sample	Polymer Morphology	Yield Total (%)	Yield Insoluble (%)	Yield Soluble (%)	$\overline{M}_n$ (1x10^3 g/mol)	$\overline{M}_w$ (1x10^3 g/mol)	PI
DVB-0	Linear	18	0	18	3.0	4.7	1.6
DVB-10	Microgel	20	0	20	7.6	15.0	2.0
DVB-25	Mixture	32	24	8	4.4	21.5	4.9
DVB-40	Microspheres	47	43	4	2.5	33.6	13.4
DVB-55	Microspheres	64	61	3	2.5	8.6	3.4

In the presence of 10% crosslinker, DVB-10, a clear polymer solution with an apparent $\overline{M}_n$ of 7.6×10^3 g/mol and a PI of 2.0 was formed with a conversion of 20%. A turbid mixture was observed following the polymerization of DVB-15. This sample remained turbid even after the addition of excess THF, even though the sample could be precipitated into methanol. The size of these particles was determined to be 110±10 nm in THF as measured using a Coulter LS230. These particles are analogous to the microgels first prepared by Staudinger and Husemann,[25,26] and more recently by Antonietti,[21,27,28] Graham,[23] and expertly reviewed by Funke.[7] Macrogelation of the reaction mixture was observed at DVB-20 and its structure consisted of interconnected nodules with sizes of approximately 100 nm and this is shown in Figure 7.

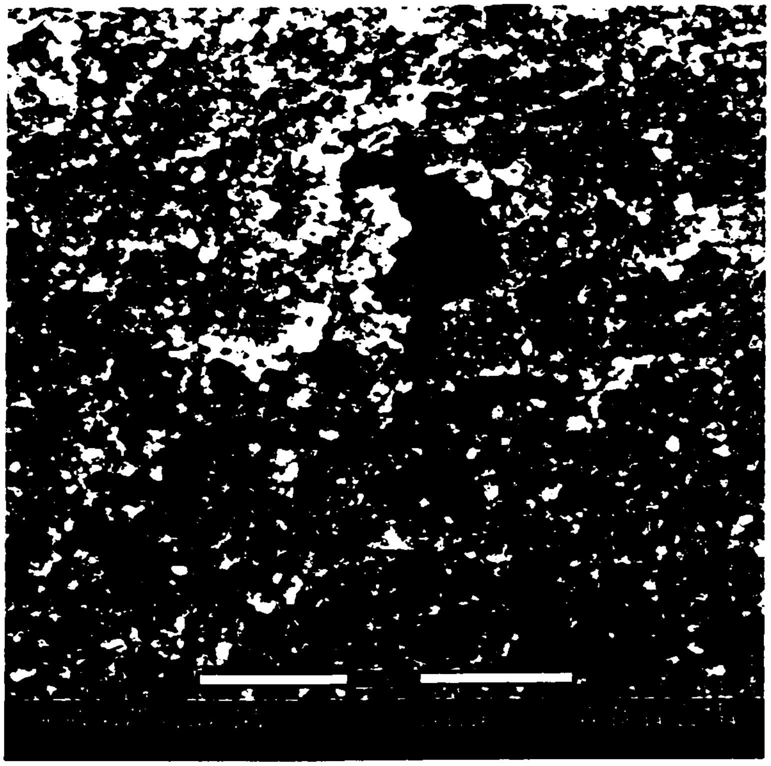

Figure 7. Electron micrograph of the space-filling macrogel in the dry state prepared from 4 vol% DVB-20 in a mixture of 25:75 MEK:heptane. The scale bar is 5 μm in length.

Further increasing the divinylbenzene content to DVB-25 resulted in a 32% combined yield which was comprised of both 8% soluble and 24% insoluble material. The soluble fraction had an apparent $\overline{M}_n$ of $4.4\text{x}10^3$ g/mol and a PI of 4.9. The insoluble fraction consisted of irregular shaped particles individually dispersed throughout the reaction mixture and this is shown in Figure 8.

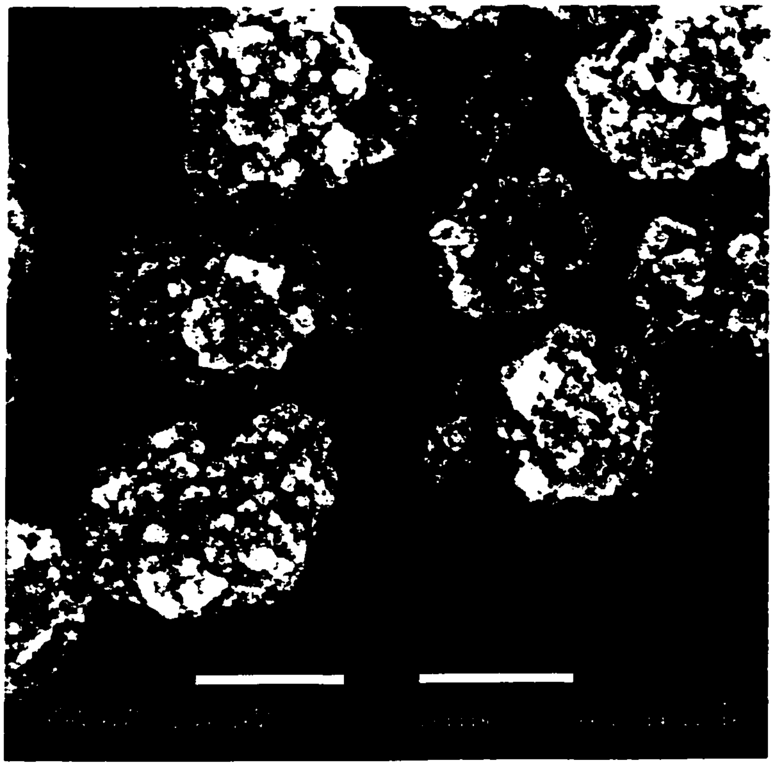

Figure 8. Electron micrograph of irregular shaped particles in the dry state prepared from 4 vol% DVB-25 in a mixture of 25:75 MEK:heptane. The scale bar is 5 μm in length.

The physical appearance of these particles is very similar to that of the DVB-20 macrogel, however, in this case the particles are not covalently linked together into a single cohesive mass. At DVB concentrations above 35% and at this solvent composition, microspheres are the predominant morphology. Figure 9 shows an electron micrograph of the 3.1±0.8 μm microspheres prepared at DVB-40, in a yield of 43%. The soluble portion isolated from this reaction mixture had a $\bar{M}_n$ of 2.5×10^3 g/mol with a PI of 13.4 and was formed at a yield of 4% for a total yield of 47%.

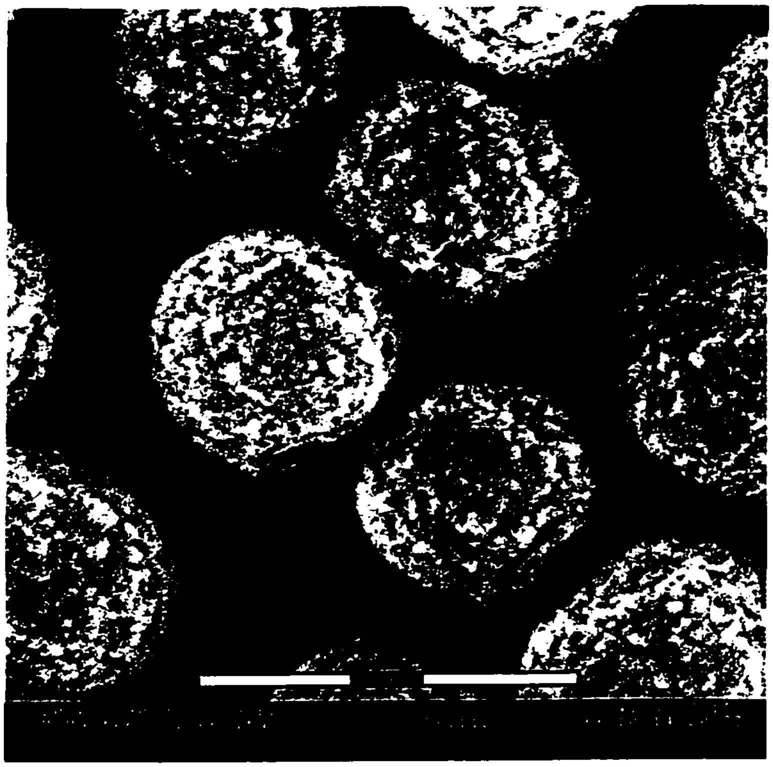

Figure 9. Electron micrograph of microspheres in the dry state prepared from 4 vol% DVB-40 in a mixture of 25:75 MEK:heptane. The scale bar is 5 μm in length.

The surface of the microspheres continues to become smoother as the concentration of DVB in the monomer mixture is increased. Polymerization of DVB-55 resulted in the production of an insoluble fraction at a conversion of 61% and a soluble fraction comprising 3% of total monomer. The insoluble material consisted of microspheres with a particle size of 3.8 ± 0.3 μm (Figure 5) and their surfaces were considerably smoother than microspheres prepared at lower DVB concentrations. The isolated soluble fraction was found to have an apparent $\bar{M}_n$ of 2.5×10^3 g/mol with a PI of 3.4.

4.3.4 Conversion and Molecular Weight

Table 1 shows the conversion of monomer to soluble polymer and to insoluble polymer, as well as the molecular weight averages of the soluble fraction, for samples containing differing DVB levels. The solvent mixture for all of these samples consisted of 25% MEK and 75% heptane.

The conversion of monomer to total polymer increases with increasing DVB level. Only soluble polymer and microgels are obtained at DVB levels up to 15% and the conversions for the DVB-0 and DVB-10 samples are shown in Table 1. At DVB levels greater than 20%, the samples consisted of both, insoluble and soluble fractions and the conversions for the DVB-25, DVB-40 and DVB-55 samples are shown in Table 1. The yield of the insoluble polymer fraction increases continuously above DVB-25 whereas the yield of soluble polymer shows a maximum at DVB-10, and then decreases for higher DVB levels.

The molecular weight of the soluble polymer fraction formed in the reaction increases with DVB concentration. That is, at DVB concentrations below 15% only soluble polymers or microgels are formed whereas at DVB concentration above 20% insoluble, crosslinked polymers are observed. The molecular weight of the insoluble fraction can be considered infinite in comparison to that of the soluble fraction. The reason for this increasing molecular weight trend is that polymer chains having more and more pendent vinyl bonds are produced when the concentration of DVB in the monomer mixture is raised. Normally, termination of the propagating radicals leads to the formation of dead chains, however, the pendent vinyl bonds permit re-initiation and the formation of high molecular weight polymer. Therefore, the chains containing pendent vinyl bonds and without an active radical can be considered as dormant species. Since, dormant chains could undergo several reactive periods during the course of the reaction there would be a greater chance that they would be captured by the insoluble fraction and as a result the yield of the soluble polymer would decrease with increasing amounts of DVB.

4.3.5 Polymer Network Contraction

The volumes occupied by poly(DVB-55) at differing solvent compositions are shown in Figure 10. The conversions of monomer to insoluble polymer for all samples in Figure 10 were 63% ± 3%, and thus, can be considered identical within experimental error. Macrogel prepared in 100% MEK had a swollen volume of 15 mL in THF, and a dry volume of 0.6 mL which corresponds to a swelling ratio of 25. The sample prepared at 75 vol% MEK had a swollen volume of 15 mL and a dry volume of 0.9 mL for a swelling ratio of 17.

A swollen volume of 14 mL and a dry volume of 1.6 mL was measured for the sample prepared in 50 vol% MEK, and thus, its calculated swelling ratio was 8.8. The swelling ratio for the macrogel prepared in 40 vol% MEK was recorded as 4.1 corresponding to a swollen volume of 12 mL and a dry volume of 2.9 mL. At 35 vol% MEK and below, irregular shaped particles or microspheres were formed and in order to determine the volume they occupied, the reaction solvent was replaced with THF and the particles were allowed to settle. This takes place within hours but to ensure complete settling the samples were left to stand for one week after which time the volume of the layer of settled particles was measured. Hence, the volumes recorded for these samples includes interstial volume between particles as well as the volume occupied by the polymer. The polymer from the 35 vol% MEK sample occupied 4.2 mL in THF, whereas the polymer from the 34 vol% MEK sample occupied 3.2 mL. The volume decreases further to 2.7 mL when the reaction mixture consisted of 33 vol% MEK and reached a plateau of approximately 1.8 mL between 25 and 20 vol% MEK. In Figure 10, a swelling ratio of 1 has been assumed for the microsphere samples, although they may have swelling ratios as high as 1.2. At lower fractions of MEK coagulum was formed, and thus, it was impossible to measure its volume since much of it had precipitated onto the vessel walls.

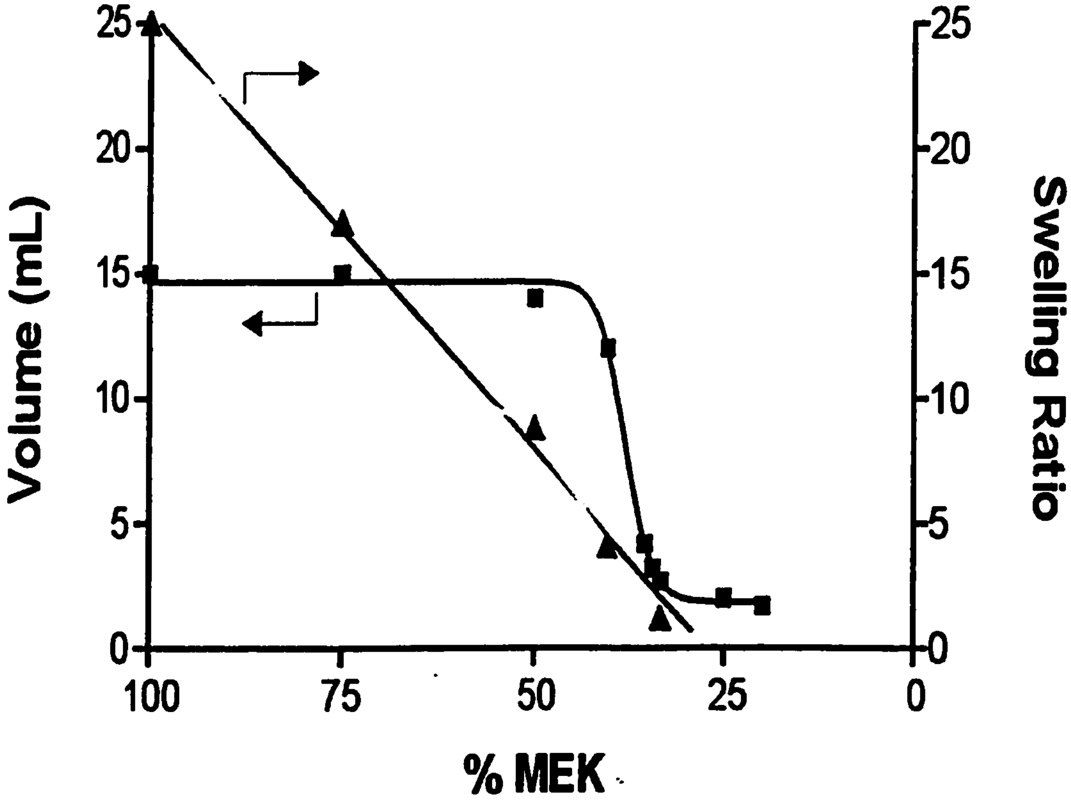

Figure 10. The volume occupied by polymer (■) and their swelling ratios (▲) as a function of the reaction solvent composition at 4 vol% DVB-55. In the range of 36-100% MEK space-filling macrogels are obtained. In the range of 34-35% MEK irregular shaped individually dispersed particles are obtained. Microspheres are observed in the range of 20-33% MEK.

Macrogels are formed in good solvents, 100 to 36 vol% MEK, where the polymer network exists in an extended state. Decreasing the quality of the solvent for the forming network causes a corresponding decrease in the volume occupied by the network. Thus at 35 vol% MEK the polymer network has contracted slightly and the chains attached to opposing surfaces were unable to overlap and crosslink. The end result is the formation of individual particles instead of a macrogel. Between 33 and 20 vol% MEK the polymer network partially collapses to form microspheres that are stabilized against coagulation by their surface gel layer which performs the function of a steric stabilizer. At MEK concentrations below 20 vol% the reaction mixture becomes too poor to swell this surface layer, causing the polymer to precipitate as a crosslinked, coagulated mass. Examination of this material by optical microscopy show it to consist of coagulated microspheres of varying sizes. This suggests an initial collapse of the forming polymer into microspheres which then lose colloidal stability as the reaction continues. It is possible that the conversion of monomer to polymer further reduces the quality of the solvent and thus causes a complete collapse of the polymer such that the surface has the characteristics of bulk polymer and not a gel. This would result in a loss of colloidal stability only in the later stages of the reaction and account for the microsphere shapes formed in the coagulum.

The effect of DVB level on the volumes occupied by the polymer formed at a constant MEK fraction of 25 vol% are shown in Figure 11. At crosslinker concentrations below DVB-20, microgel and soluble polymer were formed. Macrogel which had a swollen volume of 13 mL and a dry volume of 0.8 mL was formed at DVB-20 and this corresponds to a swelling ratio of 16. The conversion of monomer to insoluble polymer was quite low at 28% for this sample. Further increasing the crosslinker concentration to DVB-25 resulted in the formation of individual particles at a yield of 24% and they collectively occupied 4.6 mL. The volume decreased further as the DVB content increased, to a plateau of approximately 1.8 mL above DVB-45. The conversion of monomer to insoluble polymer for the DVB-30, -35, -40, -45, -50 and -55 samples were 32, 36, 43, 49, 51 and 61%, respectively.

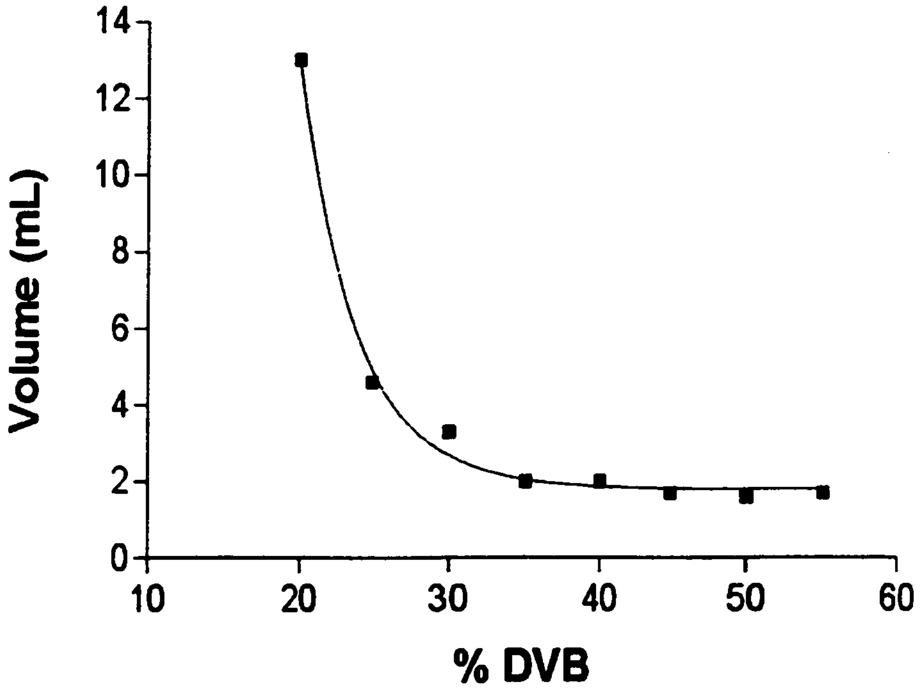

Figure 11. The volume occupied by polymer as a function of the DVB level in the 4 vol% monomer feed. The reaction solvent consisted of 25:75 MEK:heptane. Below DVB-20 soluble polymers were observed whereas a space-filling macrogel was obtained at DVB-20. Irregular shaped particles were observed in the range of 25-35% DVB while microspheres were prepared in the range of 40-55% DVB.

The transition from microgel particles to macrogel with increasing DVB content is due to the greater opportunity to form intermolecular crosslinks. It is well known that microgels are precursors to macrogel[7,20] and thus at DVB-20, microgels are formed initially, which then crosslink to become the macrogel observed at the end of the reaction. The solvent composition for the preparation of the DVB-20 macrogel was identical to that used for the production of the DVB-55 microspheres and yet the polymer microspheres occupied less volume. This phenomenon can not be explained based on conversion since the insoluble polymer yield at DVB-55 was 61% and at DVB-20 was only 28%. Therefore, in addition to the solvent induced network contraction, there must be a driving force for the collapse of the network into the more dense polymer particles. Crosslinking is the chemical process which drives this de-solvation. A similar phenomenon has been cited by Naka and coworkers in the formation of microspheres by γ-ray initiated polymerization of dimethylene glycol dimethacrylate in ethylacetate. In this case, the polymer chains attached near the surface were suggested to have considerable mobility and thus as adjacent chains came within close proximity to each other they could react between their pendent vinyl groups and this process would prevent them from moving away from each other. This would, effectively, increase the concentration of pendent vinyl groups within this region and further facilitate crosslinking reactions.

Very few publications have appeared on the preparation of mono- or narrow-disperse microspheres by precipitation polymerization, however, the morphology of suspension polymer particles has been much more rigorously investigated.[29] In a typical crosslinking suspension system, monomer, initiator, and porogen are dispersed in aqueous media. Small droplets containing the organic fraction are formed by stirring or other means and each droplet is converted into a particle by polymerization. Each organic phase droplet can be considered as a "microreactor" comparable to the reaction vials used in this study, except that the higher total monomer loading in suspension polymerization ensures that each droplet is converted into a space-filling macrogel during the polymerization. The internal morphology of individual particles can be controlled by the choice of porogen.[15,30] In the suspension copolymerization of 2-hydroxyethyl methacrylate (HEMA), and ethylene dimethacrylate (EDMA), dissolved in cyclohexanol and porogen, and then dispersed in water, Horák and co-workers found that glassy particles were obtained if benzyl alcohol, 1-butanol, or cyclohexanone where choosen as the porogens. Under these conditions the forming polymer is solvated by the organic mixture and does not phase separate during polymerization. In contrast, if 1-octanol was used as the porogen the interior of an individual suspension bead consisted of interconnected microspheres and their average diameters increased from 0.5μm at 20% to 3μm at 40% 1-octanol. In this case, 1-octanol is a poor solvent for the forming network and as a result the polymer phase separates early in the reaction to produce individual microspheres which become linked together at a later stage.[31] This is analogous to the precipitation polymerization system, although in this case, the microspheres remain individually dispersed because polymer chains on opposing surfaces are unable to overlap and crosslink as a result of the low monomer loading.

4.3.6 Proposed Particle Formation Mechanism

Previous experimental results have indicated that the growth mechanism for monodisperse polyDVB microspheres occurs by an entropic precipitation mechanism where soluble oligomeric species are captured from solution by reaction with pendent vinyl groups on the surface of existing particles. Once the oligomers are captured they undergo a de-solvation or phase separation which can be driven by either decreasing solvency of the continuous phase or by increasing crosslinking of the polymer network. In the DVB-*x* case, both of these driving forces contribute to the collapse of the network. This is evident if one considers that reactions carried out at solvent fractions of 25 vol% MEK lead to space-filling macrogels for DVB-20, and to microspheres for DVB-55. The higher concentration of crosslinking monomer induces a collapse in the forming network and prevents macrogelation. Although crosslinking is required to induce the collapse of the network, in the DVB-*x* case this is not sufficient for the preparation of microspheres. Rather, the solvency of the continuous phase must be such that crosslinking the network drives the polymer below the *theta*-condition and causes phase separation. Microspheres were observed in the γ-ray initiated polymerization of DEGMA in good solvents such as ethyl acetate, by Naka.[17,18] Presumably the crosslinking efficiency in this system is much higher than that of the thermally initiated systems and this is supported by the very weak absorption of the residual vinyl groups observed in the FTIR spectra for the poly-DEGMA microspheres. Therefore, collapse of the forming network in Naka's system would be driven almost exclusively by crosslinking.

4.4 Conclusions

A morphology map based on a two dimensional matrix of DVB level and continuous phase solvency was developed. This map indicated that poly(DVB-*x*) microspheres were formed as an intermediate morphology between microgels, macrogels and coagulum. The solvent composition strongly affects the polymerization of DVB-*x* by controlling the dimensions of the polymer coil as it is formed. Neat MEK, a good solvent for styrenic polymers, leads to a typical solution type polymerization with or without crosslinking. Neat heptane on the other hand, leads to classical precipitation polymerization. In mixtures of MEK and heptane there is a transition from solution polymerization to precipitation polymerization. In the intermediate or "marginal" solvency range, and at higher DVB concentrations, a solvent composition range where the polymer contracts to form discrete microspheres is observed. However, the solvency of the organic diluent must be sufficient to swell the particle surface slightly. It is the role of the crosslinking monomer, DVB, to force the polymer below its *theta*-condition and to cause it to collapse to form microspheres. The surface of the microspheres remains partially swollen since it would be only lightly crosslinked, and that this gel layer provides steric stabilization between microspheres.

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CHAPTER 5

Conclusions and Future Work

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5.0 Thesis Conclusions

Previous work showed that monodisperse microspheres can be prepared by precipitation copolymerization using crosslinking monomers. The mechanism of particle formation in reactions of this type were unknown. This thesis described the nucleation, stabilization and growth processes in the precipitation copolymerization of divinylbenzene. The effects of the crosslinking monomer concentration and the polymerization solvent composition on particle formation and network morphology were investigated.

Precipitation polymerization begins in solution where the monomer and initiator are dissolved in the reaction solvent. Initially, low molecular weight soluble oligomers are formed and eventually their concentration increases to a point where intermolecular reactions between them become significant. This reaction leads to the formation of transient microgels that in turn serve as nuclei of the final particles. These microgels grow into particles by two concurrent processes: i) They capture soluble oligomers by a reactive mechanism. This can occur by an oligoradical attacking a pendent vinyl bond on a microsphere or by a radical on a microsphere attacking a pendent vinyl bond on an oligomer and also by radical coupling reactions between oligomers and particles. ii) Curing reactions inside the microspheres occur continuously during polymerization and changes their structure from soft and deformable, similar to gel particles, to the more rigid structures observed at the end of the reaction.

The solvent swollen microgels formed during nucleation are inherently colloidally stable. The reason for the observed colloidal stability of the microspheres following nucleation was investigated. The reaction medium is a good solvent for the particle surface, and hence, the oligomers that are captured from solution remain swollen in the reaction solvent to form a swollen surface gel. This in turn sterically stabilizes the particles. Exposing these same particles to a poor solvent following polymerization, collapses this gel and causes the particles to aggregate.

Investigations of the polymer morphology formed both as a function of solvency of the continuous media, and as a function of the crosslinking monomer concentration indicated that collapse of the polymer network could be induced by either of these two variables. Microspheres were observed to form at high crosslinking monomer concentrations in solvents that were otherwise good solvents for the polymer. This is confirmed by the observation that at lower crosslinking monomer concentrations, space-filling macrogels were formed and also by the *theta*-point determinations conducted using poly(4-methyl styrene). Crosslinking causes the polymer network to contract in near *theta* solvents. Therefore, crosslinking monomers are necessary for the preparation of monodisperse microspheres by precipitation polymerization since they are central to the processes of contraction/de-solvation.

An understanding of these mechanisms has already lead to the preparation of both new copolymer microspheres and narrow-disperse microgels by precipitation polymerization.[1-4] It is hypothesized that the mechanisms presented in this thesis should apply to a wide variety of precipitation polymerizations carried out in either organic or aqueous media. They may also provide a greater understanding of the structure of suspension polymerization beads and monolithic materials.

5.1 Future Work

The objectives of this thesis were to determine the particle formation mechanisms in the precipitation polymerization of divinylbenzene to monodisperse microspheres. An understanding of these mechanisms should prove useful for the preparation of new materials and the following section gives some insight into the concepts that could make use of the mechanisms presented here.

5.1.1 Preparation of New Materials

The morphology map presented in Chapter 4 described the morphologies that are observed as a function of both changing solvency and changing crosslinking monomer concentration. A third axis consisting of monomer concentration should be added to the morphology map since this would provide great insight into the evolution of the internal structure of suspension polymerization beads. Such information could be useful in tailoring the structure of such resins to applications such as chromatography.

The mechanisms reported here should also apply to precipitation polymerization of crosslinking monomers in aqueous solution. Constructing a morphology map for these types of materials would give insight into new materials that are responsive to external stimuli such as temperature and pH.

Chromatographic applications are an important area of research for microspheres and new polymer architectures. The morphology map presented in Chapter 4 indicated that microspheres are formed in solvents slightly less "good" than those required for the preparation of macrogels. The single step synthesis of chromatography columns would be an interesting area of research where polymer microspheres would be synthesized directly within chromatography columns. Also, the space filling macrogels prepared in Chapter 4, using 40 vol% MEK and DVB-55 could be useful for size exclusion chromatography due to their macroporous structure. Similarly, composite columns could be designed where the macrogel consists of porous microspheres. These single step syntheses would significantly reduce the time required for the preparation of such products since column packing would be completed at the end of the reaction. Also, the resin purification step normally conducted prior to packing could be conducted by simply flushing it with solvent to remove residual monomer and soluble polymer.

The oligomer capture mechanism reported in Chapter 3 depends on the reactivity of the surface and is irrespective of its colloidal properties. Thus, this mechanism could be applied to the preparation of polymer microcapsules. Amphiphilic macromonomers could be designed that orient themselves at an oil-water interface and would provide a reactive surface to the polymer forming in solution. This process could be applied to both *water-in-oil* and *oil-in-water* dispersions and this concept is shown in Figure 1. This procedure would have an advantage over the more common interfacial polymerization technique in that the reaction could be isolated in the phase opposite to the material being encapsulated and this would minimize the opportunity for side reactions.

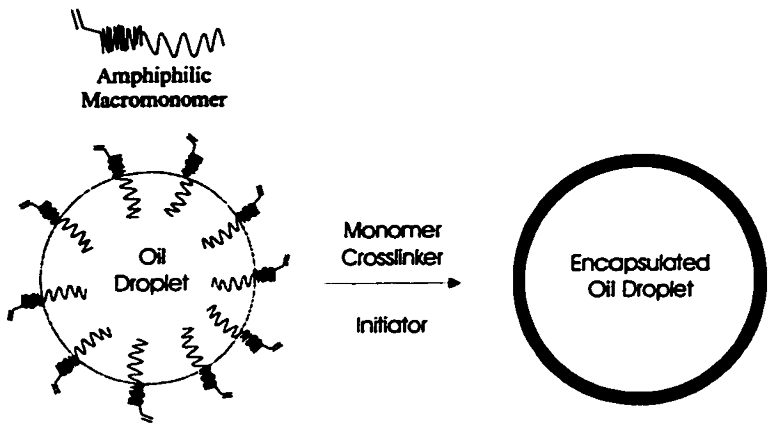

Figure 1. The reactive growth mechanism as applied to the preparation of polymer microcapsules.

5.1.3 Analysis of Pore Structure

The precipitation polymerization of DVB-55 in acetonitrile containing from 5 to 40 vol% toluene results in the formation of porous microspheres that could be useful for chromatography applications.[3] Over the solvent compositions mentioned above, the total pore volume ranges from 0.013 cm^3/g to 0.516 cm^3/g and surface area ranges from $9m^2/g$ to $810m^2/g$, respectively. The average pore diameter is between 15 Å and 21 Å for all samples. Preliminary investigations of the pore structure by Small Angle X-ray Scattering, SAXS, where the scattering profiles of the dry state were compared to those obtained in good solvents have suggested that the porosity may not be permanent. It is possible that the pores have a gel structure that swells in good solvents and this is shown in Figure 2. It is unclear what effect this type of pore structure would have on the use of these materials for chromatography applications.

In order to confirm these preliminary results a comprehensive investigation of the pore structure needs to be conducted. Currently, the SAXS results suggest that the pores "disappear" in good solvents, however, it is unknown if this result is real or if this is simply a result of low contrast between the polymer particle and a solvent filled pore. The contrast between the polymer and solvent could be increased by copolymerizing a monomer containing an electron dense atom such as bromomethyl styrene. Also, solvents containing electron dense atoms may enhance the contrast between the solvent and polymer. It would be useful if the method could be calibrated to structures with known responses to the solvent environment. Porous suspension polymerization beads of varying crosslink densities should be suited to such a study. At a high crosslink density their pores are rigid and permanent whereas at lower crosslink densities the polymer would swell in good solvents fill the pore volume.

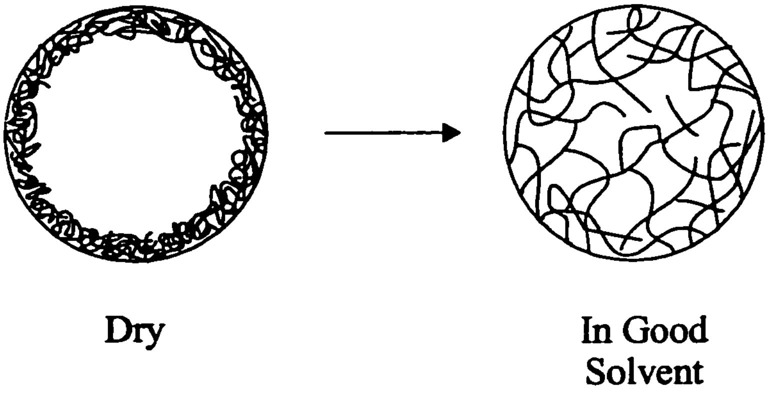

Figure 2. Schematic of the pore structure in the dry state and in good solvents. The polymer collapses to become part of the pore wall in the dry state whereas in good solvents the polymer swells to fill the pore volume.

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