CROSSLINKING COPOLYMERIZATION OF DIVINYLBENZENE AND MALEIC ANHYDRIDE: MORPHOLOGIES, MECHANISMS AND KINETICS

By

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COPOLYMERIZATION OF DIVINYLBENZENE AND MALEIC ANHYDRIDE

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Abstract

Three distinct copolymer morphologies have been prepared by crosslinking copolymerization of divinylbenzene-55 and maleic anhydride at low monomer concentrations in methyl ethyl ketone / heptane mixtures; microspheres, microgels and macrogels. These morphologies depended primarily upon solvent composition and changed from microspheres and microgels to macrogels with increasing methyl ethyl ketone volume fractions. The effect of solvent composition, crosslinker concentration and monomer loading on the observed morphologies were investigated using electron microscopy, viscosity, and light scattering experiments. Microgels were found to be precursors to both macrogels and microspheres and mechanisms for the formation of each morphology are proposed.

Copolymerization of divinylbenzene-55 and maleic anhydride occurs at higher rates than homopolymerization of divinylbenzene-55. This affects several aspects of the precipitation polymerization leading to polydisperse nuclei and diffusion-controlled particle growth.

The divinyl components of divinylbenzene-55 were shown to exhibit increased reactivity over the ethylvinyl species. This different reactivity results in a crosslink gradient in DVB–55/MAn microspheres and variable crosslinking in microgels depending on what stage of the reaction they are formed in.

Acknowledgements

I wish to express my thanks to my research supervisor, Professor Harald Stöver, for his constant guidance and enthusiasm. Our contrasting styles have opened my eyes to whole different perspectives that have enhanced my experience greatly. Through both his support and criticisms, he has made me a better scientist and while doing so become a good friend.

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List of Abbreviations

MEK - Methyl Ethyl Ketone

Hp - Heptane

DVB-X - Mixture divinylbenzene isomers, ethylvinylbenzene isomers and optionally, 4-methylstyrene where X equals the mole % of divinyl components (eg. DVB-55)

MAn - Maleic Anhydride

AIBN - 2,2'-Azobisisobutyronitrile

CV% - Coefficient of Variance

SDS - Sodium Dodecyl Sulphate

PVP - Poly(N-vinylpyrrolidone)

SEM - Scanning Electron Microscope

PEG - Poly(ethylene glycol)

LCST - Lower Critical Solution Temperature

TEM - Transmission Electron Microscope

ESEM - Environmental Scanning Electron Microscope

PIDS - Polarization Intensity Differential Scattering

CTC - Charge Transfer Complex

Preface - Thesis Outline

This thesis has been prepared in a modified "sandwich" format. Each chapter is loosely based on a published journal article or manuscript but has an expanded introductory section. The overall objectives of the thesis research and a brief description of the work presented in each chapter are given below.

Chapter 1: Synthesis of Divinylbenzene-Maleic Anhydride Microspheres Using Precipitation Polymerization

Research Objective

The goal of this research was to adapt existing precipitation polymerization technologies to prepare functional microspheres from divinylbenzene-55 and maleic anhydride.

Synopsis

The first chapter of the thesis outlines the preliminary experiments in the precipitation polymerization of divinylbenzene-55 and maleic anhydride. An introduction to basic colloid science and the common techniques used to prepare polymer particles is included.

This chapter addresses the process of solvent selection for precipitation polymerization, which is critical to the preparation of narrow disperse microspheres. The effects of reaction solvency on morphology and particle diameter are discussed and the dependency of particle size on monomer loading is determined. In addition, the utility of the anhydride functionality in these particles was demonstrated by reaction of this group to prepare several new materials.

Associated Publication

"Synthesis of Divinylbenzene-Maleic Anhydride Microspheres Using Precipitation Polymerization" Randy S. Frank, Jeffrey S. Downey and H.D.H. Stöver, *J. Polym. Sci.: Part A: Polym. Chem.*, **36**, 2223 (1998).

Chapter 2: A Study of the Effects of Reaction Solvency and Crosslinking on the Precipitation Polymerization of Divinylbenzene and Maleic Anhydride

Research Objective

The objective of the work presented in this chapter was to determine the reasons for the solvent-dependent morphology transitions observed in the copolymerization of divinylbenzene-55 and maleic anhydride in methyl ethyl ketone / heptane mixtures.

Synopsis

This chapter presents a detailed study of the effects of solvency and crosslinking on the precipitation copolymerization of divinylbenzene and maleic anhydride. A discussion of polymer solution thermodynamics is presented in this chapter along with an introduction to polymer microgels.

The dependance of morphology and particle diameter on reaction solvency was studied using light scattering and electron microscopy techniques. Particle diameter and swelling were used to identify the solvency conditions under which the transition from microspheres to microgels took place. In addition, the transition from the formation of microgels to space-filling gel was observed using dilute solution viscometry. The effect of crosslinker concentration on particle size and morphology is discussed as well.

Manuscript in Preparation

"Poly(Divinylbenzene-alt-Maleic Anhydride) Microgels: Intermediates to Microspheres and Macrogels in Crosslinking Copolymerization" Randy S. Frank, Jeffrey S. Downey, Kui Yu and Harald D.H. Stöver.

Chapter 3: Copolymerization of Divinylbenzene-55 and Maleic Anhydride: Effect of Increased Reaction Rates on Precipitation Copolymerization

Research Objective

The aim of this segment of the thesis was to determine the effects of the enhanced reactivity of the copolymerization of divinylbenzene-55 and maleic anhydride on precipitation copolymerization

Synopsis

The rate of polymer production was expected to have an impact on precipitation polymerization. An introduction to free radical polymerization kinetics and charge transfer copolymerization is presented at the beginning of this chapter.

The rate of copolymerization for divinylbenzene-55 and maleic anhydride was measured and its effect on particle nucleation and growth is discussed. This enhanced reactivity allowed for the preparation of novel core-shell particles.

Manuscript in Preparation

"Copolymerization of Divinylbenzene-55 and Maleic Anhydride: Effect of Increased Reaction Rates on Precipitation Copolymerization" Randy S. Frank and Harald D. H. Stöver.

Chapter 4: Variable Consumption of DVB-55 Components in Copolymerization with Maleic Anhydride

Research Objective

The goal of the research in this chapter was to determine whether there is preferential consumption of any of the four components of DVB-55 when they are copolymerized with maleic anhydride.

Synopsis

The rates of consumption of the four components of DVB were measured using gas chromatography. First order analysis of the data provided apparent rate constants for each component and the repercussions of these relative rates of consumption on precipitation copolymerization are discussed.

Manuscript in Preparation

"Relative Rates of Consumption of the Components of Commercial Divinylbenzene in Copolymerization with Maleic Anhydride" Randy S. Frank and H. D. H. Stöver.

Chapter 1 - Preparation of Narrow Disperse Microspheres by Precipitation Polymerization of Divinylbenzene and Maleic Anhydride

1.0 Introduction

Colloidal dispersions of polymer particles have been used for a wide variety of applications including such commonplace items as paints and adhesives. A naturally-occurring example of a polymer-based colloidal dispersion is the sap, or latex, of *Hevea brasiliensis*, the rubber tree. Small particles of *cis*-1,4-polyisoprene are suspended in the sap which is harvested to produce many common rubber goods. Research into the synthesis of polymer particles was advanced significantly by the need to replace this natural latex when the supply was cutoff during World War II.[1] Since this time, a number of synthetic techniques have been developed that allow for the preparation of polymer particles in a wide range of sizes and compositions.

Monodisperse polymer particles, i.e., a group of particles that have a very narrow distribution of sizes, find specialized applications such as as chromatographic packing materials, solid-phase supports and microscopy standards. The preparation of monodisperse particles introduces a whole new set of challenges for the synthetic polymer chemist and hence much academic interest has been generated in this area.

This chapter will present a new class of narrow disperse microspheres prepared from divinylbenzene and maleic anhydride. These particles were prepared using a novel precipitation polymerization technique developed by our group. A general review of the relevant colloid science and the classical techniques for preparing polymer particles follows.

1.1 Basic Colloid Science

By definition, colloidal dispersions are finely-divided particles in the 1 nm to 1 mm size range suspended in a liquid medium.[2] The term colloids can refer to either the whole dispersion or just the particles themselves. The chemical nature of these particles can be very diverse, and includes inorganic and organic compounds, metals and polymers in the solid or liquid states. In addition, stable foams are considered to be colloidal and so we can also include gases amongst the potential states of matter for colloids.

One important property of colloids is their particle size distribution. As mentioned above, monodisperse particles are desirable for a number of specialty applications. A description of the requirements for monodispersity and its implications follows.

1.1.1 Monodisperse Colloids

Colloids are considered monodisperse when they have a coefficient of size variance (CV%), (Equation 1.1), of 5% or less.[3]

$$CV\% = \frac{\sigma}{\overline{D}_n} \qquad \textbf{(1.1)}$$

Here, σ is the standard deviation in the diameters of a sample of particles normalized to the average diameter, $\bar{D}_n$. Narrow disperse particles, on the other hand, can be considered to have a coefficient of variance larger than 5% but less than 15%. Uniform particles are useful because they pack in ordered arrays which provide well-defined interstitial volumes and flow paths. It is this feature that makes them useful in chromatography and solid phase synthesis/applications.

1.1.2 Particle Stabilization

An important requirement for colloidal dispersions is that they are stable; this means that the particles do not aggregate or coalesce, and that they do not settle at an appreciable rate. There are two methods by which the colloids can be stabilized: electrostatic stabilization and steric stabilization.

Electrostatic Stabilization

Electrostatic stabilization involves the introduction of a charged layer, either anionic or cationic, on the surface of the colloids (Figure 1.1) and is common for aqueous dispersions. The charged groups and their counterions form what is known as the electrical double layer which serves to stabilize the particles by electrostatic repulsion. However, the stabilization is considerably more complicated than simple repulsion.

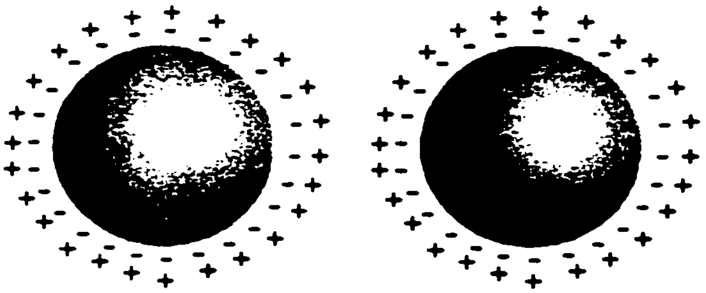


Figure 1.1 - Electrostatically Stabilized Particles

The forces between two charged particles are described by DLVO theory, which is named after the primary researchers in the area Derjaguin, Landau, Verwey and Overbeek.[4] This theory suggests that there are three forces between charged particles to consider: van der Waals attraction, electrostatic repulsion and Born repulsion. Van der Waals attractions result from permanent dipole and induced dipole interactions between the particles; these interactions increase as particles approach. The electrostatic repulsion exists due to the electrical double layer while Born repulsion occurs at very short distances as the molecular orbitals of the molecules approach overlap. The effect of these three forces is typically expressed in terms of the potential energy of the system, V_T, as in Equation 1.2,

$$V_T = V_V + V_E + V_B \qquad \textbf{(1.2)}$$

where V_V, V_E and V_B are the potential energies of van der Waals attraction, electrostatic repulsion and Born repulsion, respectively. Since each of these energies depend differently on the separation between the two particles, d, the significance of their contributions varies. At short distances, the magnitude of the Born repulsion is very large and hence determines the distance of closest approach of the two particles, d_0. Just beyond d_0, van der Waals attraction is strong resulting in a net attraction, as indicated by a primary minimum in a potential energy versus separation distance curve (Figure 1.2). At larger distances, the electrostatic repulsion decays exponentially while van der Waals attractions decrease as 1/d. This results in a secondary minimum in the potential energy

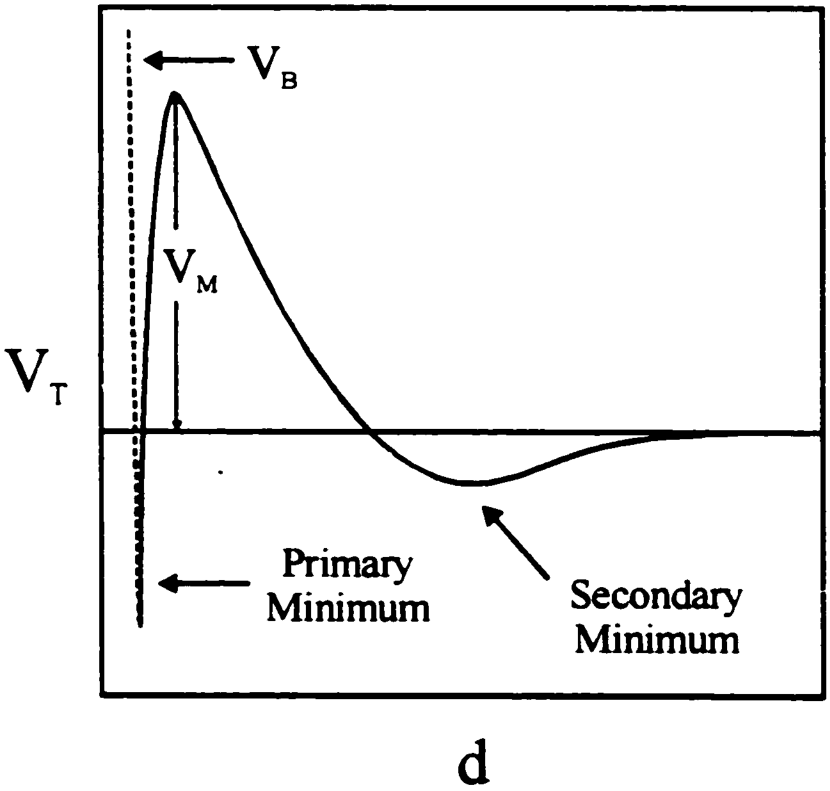
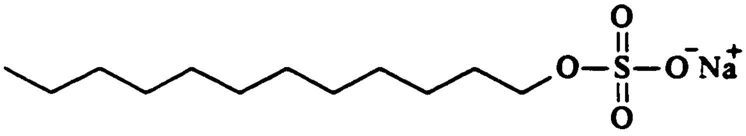


Figure 1.2 - Potential Energy Diagram for Two Charged Particles

curve, corresponding to a weak attraction. However, for electrostatically stabilized particles, at intermediate distances, electrostatic repulsion dominates as shown by the maximum in the potential energy curve. The magnitude of this maximum, V_M, represents the energy barrier that must be overcome for particle coagulation to occur.

The surface charge groups on the particles can be native, as in the case of some inorganic colloids and charged polymers, or they can be introduced by use of an ionic surfactant. A very common example of a surfactant is sodium dodecyl sulfate (SDS) (**1.1**).



(1.1)

In aqueous media, the non-polar hydrocarbon chain of SDS can associate with the surface of a non-polar particle and the polar head group is left exposed, resulting in the surface charge sufficient to stabilize the particles.

Steric Stabilization

Steric stabilization, the other method of stabilizing colloids, is achieved by addition of a diffuse polymer layer onto the surface of the particles (Figure 1.3).[2] The mechanism of stabilization

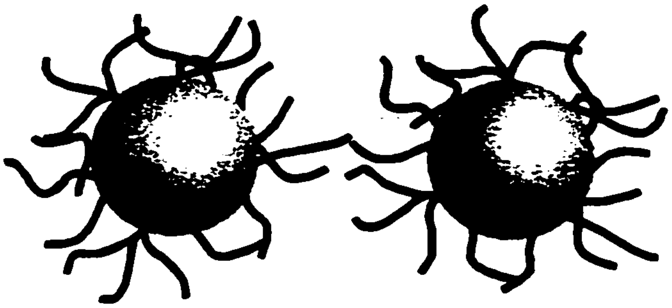
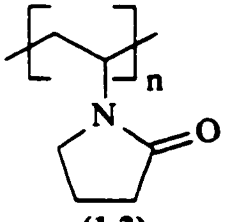


Figure 1.3 - Sterically Stabilized Particles

is a repulsive force between the particles that results from osmotic pressure. In this case, osmotic forces work to dilute the increasing concentration of polymer chain segments that occurs when two particles approach each other. This diffuse steric layer is normally introduced by adsorption or grafting of a polymer, that is more compatible with the continuous phase, onto the particles. For polar solvent systems, examples of common steric stabilizers are poly(N-vinyl pyrrolidone) (PVP) (**1.2**) and poly(vinyl alcohol) (**1.3**).



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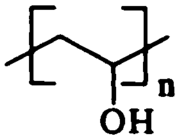


(1.3)

Either steric or electrostatic stabilization is commonly utilized in the current methods used to prepare polymer particles.

1.2 Preparation of Polymer Colloids

The first reports of a synthetic method to prepare dispersions of poly(isoprene) were published in 1927.[1] This discovery sparked a great deal of interest and at present, a variety of heterogeneous polymerization techniques are available to prepare related polymer colloids. As the name implies, heterogeneous polymerization is a free radical polymerization that involves two or more phases at some point during the reaction. In two of the methods, monomer is dispersed in a non-compatible solvent at the beginning of the reaction to create a two phase system. In all techniques, the resultant polymer precipitates during the course of the reaction to form the second or third phase. The four main classes of heterogeneous polymerization reactions are emulsion, suspension, dispersion and precipitation polymerizations.[5] The differences between these four types of reactions are based on whether or not they are biphasic at the beginning of the reaction and in which phase the polymerization takes place. Detailed descriptions of each system are presented in the following sections.

1.2.1 Emulsion Polymerization

Emulsion polymerization is the most widely used heterogeneous polymerization technique.[1] Polymer particles formed from emulsion polymerization are commonly referred to as latexes and fall in the 0.05 to 5 μm diameter range. The components of a typical emulsion system include: water (the continuous phase), monomer (only slightly soluble in water), an ionic surfactant (like SDS) and a thermally labile free radical initiator (water-soluble). The monomer is dispersed as droplets in the continuous phase and the reaction mixture is heated to induce polymerization.

The mechanism of particle formation in emulsion polymerization has been described by the Smith-Ewart model.[6] In this model, there are four important entities in the reaction mixture: monomer droplets, surfactant micelles, a small amount of dissolved monomer, **M**, and the initiator molecules, **I**, as shown in Figure 1.4. Upon heating, initiator molecules decompose to form radicals

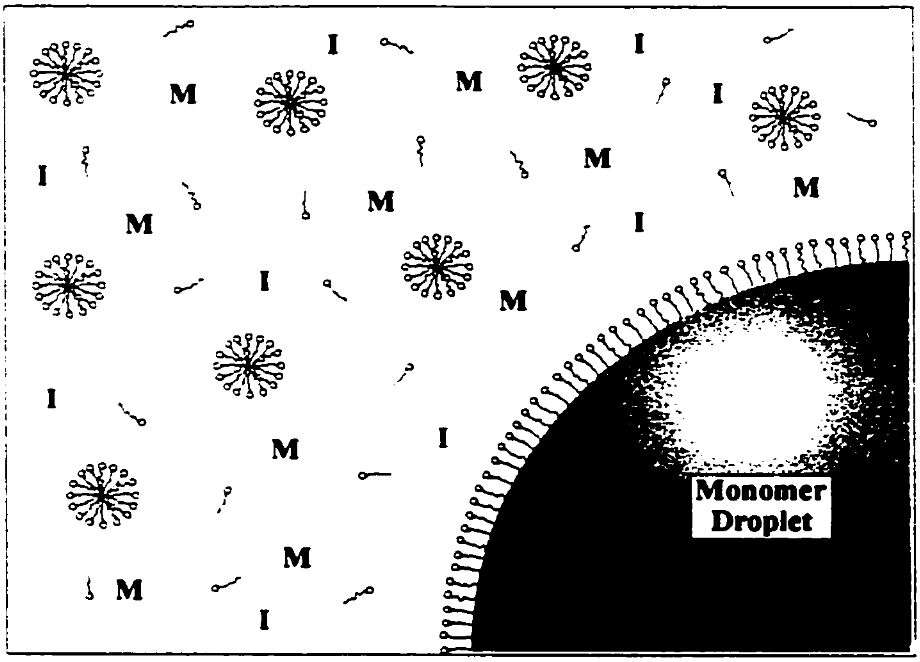


Figure 1.4 - Important Species in Emulsion Polymerization

which react with dissolved monomer in the continuous phase. Once formed, these oligoradicals, which are relatively insoluble in water, partition into the hydrophobic portion of the surfactant micelles. In addition, monomer molecules partition into the micelles causing them to swell. Polymerization then occurs within the micelles to produce particle nuclei. These nuclei grow further by reaction with oligoradicals and monomer which continues to partition into the micelles from the continuous phase. At this stage, no new particle nuclei are formed so that reaction occurs only within the nuclei already present. The role of the monomer droplets in this process is merely to act as a reservoir for the continuous phase and the micelles. The reaction continues until all the monomer droplets are depleted and the last of the dissolved monomer has been consumed. Particle size is controlled by the type and concentration of surfactant, the solubility of the monomer in water and the reaction temperature. A transmission electron micrograph of polystyrene latexes produced in our lab by emulsion polymerization using $K_2S_2O_8$ initiator is shown in Figure 1.5. The uniform size distribution of these latexes (CV% ~ 1%) is typical of emulsion polymerization and results from the fact that the total number of particle nuclei is fixed early in the reaction.

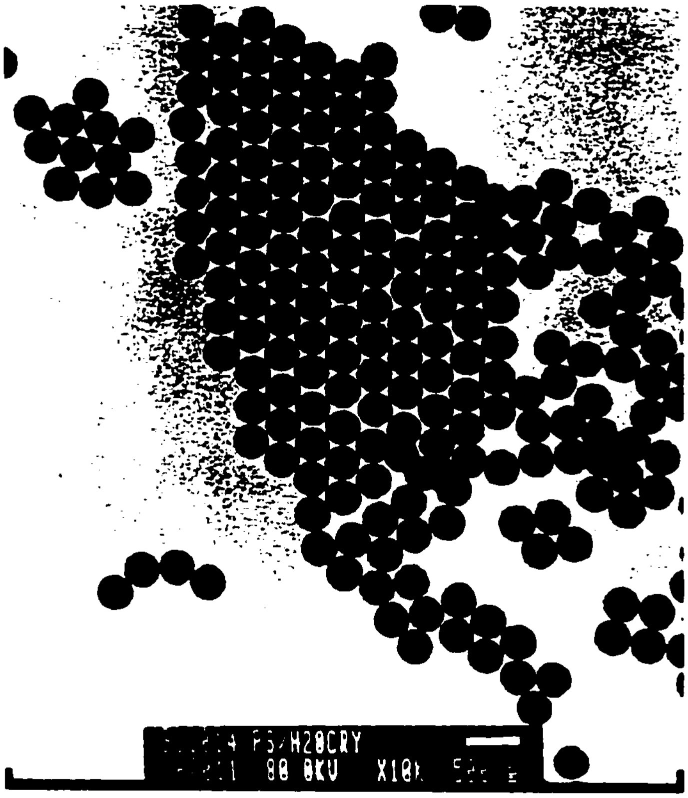


Figure 1.5 - Emulsion Polymerization Latexes

1.2.2 Suspension Polymerization

Particle formation in suspension polymerization is the simplest among all the heterogeneous polymerization techniques.[7] Monomer droplets are dispersed in an immiscible continuous phase, usually water, and stabilized by surfactant or steric stabilizers. A free radical initiator is dissolved in the monomer so that each droplet acts as a miniature bulk polymerization reactor. This process allows for the simplicity of bulk polymerization without the problems normally encountered in the bulk, such as poor heat transfer and high viscosities. Suspension polymerization is used to prepare the largest particles of all the heterogeneous polymerizations with particles falling in the 5 μm to 1 mm size range with broad particle size distributions. The particle size is a function of a number of experimental parameters including stirring speed, organic/aqueous ratio, droplet viscosity and the surfactant/stabilizer concentration. In addition to providing easy access to bulk polymers, suspension particles can be given a variety of internal pore morphologies and functionalities through the use of porogens and functional comonomers.[8-14] The resulting particles are key to Merrifield-type solid phase synthesis including present day combinatorial research.

1.2.3 Dispersion Polymerization

In contrast to emulsion and suspension polymerizations, dispersion polymerizations are usually carried out in organic solvents where the monomer is soluble and the polymer produced is not.[15] Consequently, the initial reaction mixture is a homogeneous solution of monomer, free radical initiator and a steric stabilizer such as PVP. Upon heating, the polymerization is initiated and as oligomers grow, they become insoluble and precipitate to form particle nuclei. The steric stabilizer adsorbs to the surface of the particle nuclei to introduce the diffuse steric layer discussed earlier. From this point on, the reaction proceeds to completion by diffusion of monomer and oligomers/oligoradicals into these nuclei. This process is used to prepare non-aqueous dispersions of monodisperse particles in the 0.5 to 5 μm diameter range where the particle size is controlled by a combination of solvency conditions, type and concentration of stabilizer and the reaction temperature.[16-18] Figure 1.6 illustrates polystyrene particles produced in our lab by dispersion polymerization in ethanol.

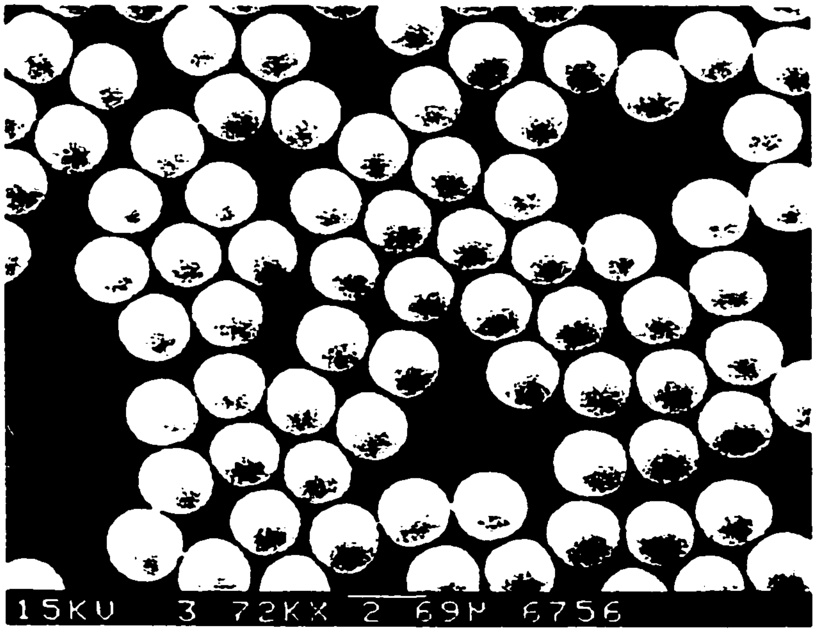


Figure 1.6 - Dispersion Polymerization Particles

1.2.4 Precipitation Polymerization

Precipitation polymerizations resemble dispersion polymerization systems except that no stabilizer is present. In conventional precipitation polymerizations, the particles formed are colloidally unstable and rapidly coagulate to form polydisperse, misshapen particles. Precipitation polymerization is used to prepare such industrial polymers as poly(vinyl chloride) and poly(acrylonitrile).[19]

It has recently been discovered that not all precipitation polymerization processes result in such irregularly-shaped particles. Our group and others have reported the synthesis of narrow dispersity spherical particles from precipitation polymerization of crosslinking monomers.[20-29]

1.2.5 Precipitation Polymerization of Crosslinking Monomers

In 1993, our group was the first to report the preparation of monodisperse microspheres from precipitation polymerization of technical grade divinylbenzene (DVB-55) as shown in Figure 1.7.

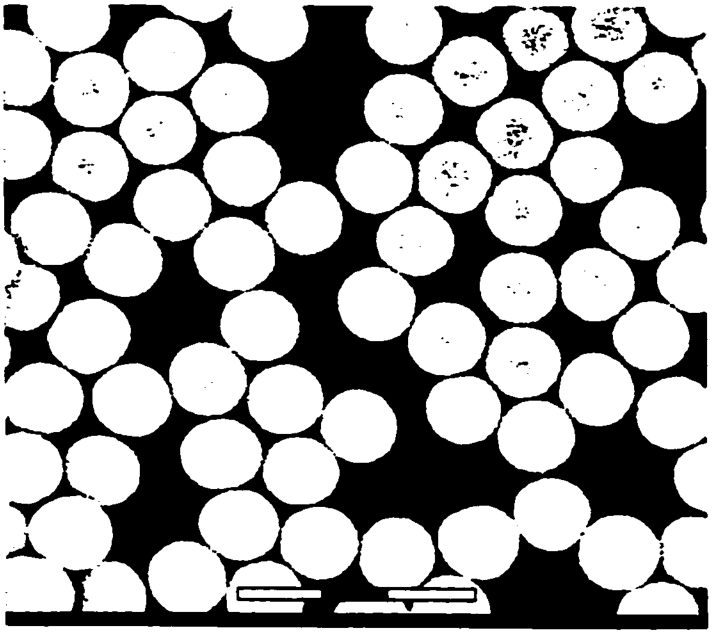
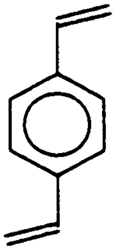


Figure 1.7 - DVB-55 Precipitation Microspheres

Technical grade DVB-55 is a mixture of the *para* and *meta* isomers of divinylbenzene, (**1.7**) and (**1.8**), and the *para* and *meta* isomers of ethylvinylbenzene, (**1.9**) and (**1.10**). These reactions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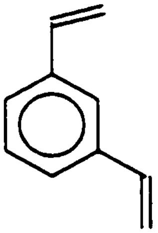
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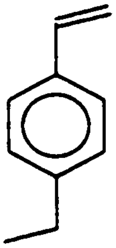
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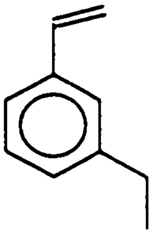
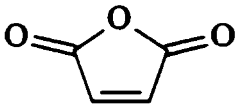

(1.10)

differed from classical precipitation polymerizations as they utilized low monomer loadings (≤4 wt%), a crosslinking monomer, gentle agitation and marginal or near *theta* solvency conditions. The DVB particles produced in these reactions were in the 3-5 μm diameter range and lacked charged groups or added steric stabilizer on their surfaces which made them very interesting for potential chromatographic and other applications.

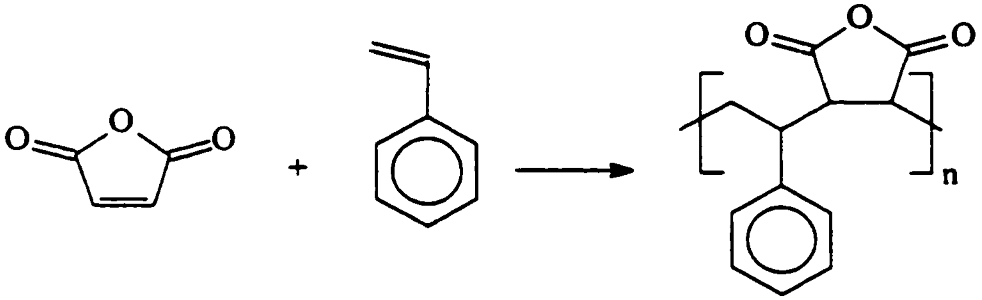
1.3 Objective and Scope of Research

It was the objective of this research to adapt this existing technology to the preparation of



(1.11)

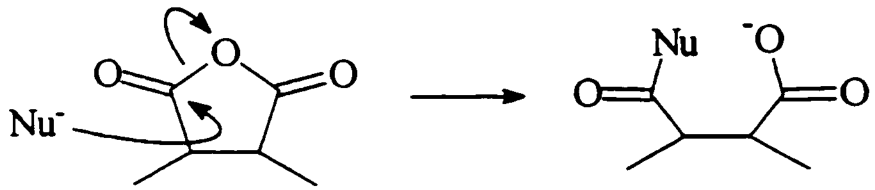
functional microspheres. Maleic anhydride (**1.11**) was chosen as a functional comonomer for DVB-55 because it readily polymerizes with styrenic monomers to form alternating copolymers as shown in Scheme 1.1.



Scheme 1.1 - Styrene-Maleic Anhydride Copolymerization

These copolymers have been intensively studied as model systems for alternating copolymers.[30-36] The functionality of these copolymers exists due to the residual anhydride group, shown on the right in Scheme 1.1, that can be utilized for further chemistry after polymerization. This anhydride group can be hydrolyzed to carboxylate groups or reacted with a variety of other nucleophiles, like alcohols and amines, as shown in Scheme 1.2.

Copolymer particles of styrene-maleic anhydride have been prepared in the past using suspension polymerization techniques.[37-39] These reactions resulted in spherical, polydisperse



Scheme 1.2 - Nucleophilic Attack at Anhydride Functionality

particles with high degrees of porosity. Following hydrolysis of the maleic anhydride units, these particles were intended for use as ion-exchange resins.

This chapter outlines preliminary experiments of the precipitation polymerization of divinylbenzene-55 and maleic anhydride to prepare microspheres. This work presented a challenge because for this new comonomer system, one monomer was polar and the other was non-polar. This led to number of problems particularly in the area of solvent selection. The difficulties lie in trying to find a solvent that would dissolve both monomers but also be a poor enough solvent to allow for the phase separation required to form microspheres. Solvent selection was the main focus of these experiments. The other system parameter that will be described in this chapter is the monomer loading. The results of these experiments are discussed at the end of the chapter.

The functionality of the maleic anhydride unit was demonstrated by two methods: hydrolysis and reaction with a polymeric alcohol; these results are given at the end of the chapter.

1.4 Experimental

Reagents and Solvents

Divinylbenzene (DVB-55, tech., 55% mixture of isomers) and maleic anhydride (MAn, 99%) were used as received from Aldrich. The solvents, *n*-heptane (Hp, 99%), methyl ethyl ketone (MEK, 99%) and acetonitrile (99+%) were acquired from Caledon Laboratories. All other solvents were reagent grade obtained from Aldrich. 2,2'-Azobisisobutyronitrile (AIBN, >99%) was obtained from American Polymer Standards Laboratories and used without further purification.

Reaction Mixture (Typical Procedure)

Maleic anhydride (0.80 g, 8.2 mmol) was dissolved in 8 mL of methyl ethyl ketone in a 25 mL glass vial (2.6 cm diameter x 4.8 cm height), and 12 mL of heptane was added resulting in a solvent mixture of 60 vol% heptane to 40 vol% MEK. DVB-55 (0.73 g, 8.6 mmol of vinyl bonds) and 0.016 g of AIBN (0.097 mmol) were added.

Polymerization Reactor

The polymerization reactions were carried out in a modified commercial hotdog roller (Figure 1.8). The main modifications involved enclosing the heated area and addition of a flexible heater for more accurate control of the internal temperature of the reactor.

The reaction vials were placed in the polymerization reactor, which was thermostatted at

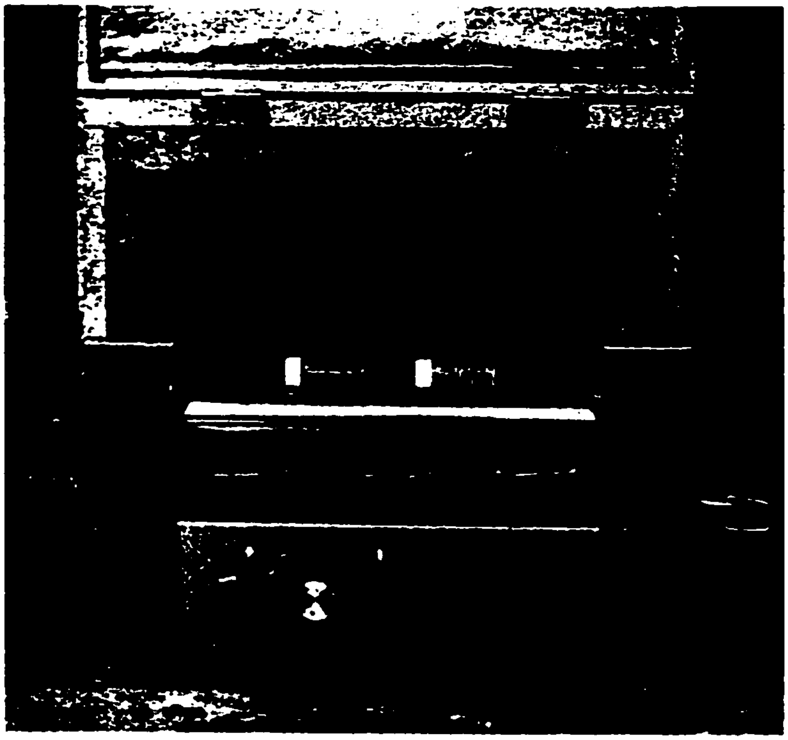


Figure 1.8 - Polymerization Reactor

70°C, and rolled at a rate of approximately 5 vial revolutions per minute. After 24 hours, the reaction mixture was centrifuged and the supernatant removed. The particles were resuspended in acetone and centrifuged three times to remove residual reaction solvents and monomers.

Characterization

The particles were imaged using an ISI DS130 scanning electron microscope (SEM). Particle sizes were obtained from the electron micrographs by measuring 100 particles and calculating the average particle diameter and coefficient of variance (CV%). Particle yield was measured gravimetrically after drying the particles in vacuo.

1.5 Results and Discussion

1.5.1 Solvent Selection

The first step in these experiments was to choose an appropriate solvent or solvent mixture that resulted in the precipitation of the forming polymer into narrow disperse particles. In the synthesis of divinylbenzene particles in our lab, acetonitrile was the only single solvent that had been shown to result in monodisperse particles.[24] Apparently, acetonitrile meets the basic solvency conditions required for monodisperse particle formation, that is, it dissolves the monomer but precipitates the forming polymer. Acetonitrile is a non-solvent for poly(divinylbenzene) as indicated by comparison of their δ-parameters; 24.3 MPa$^{1/2}$ for CH_3CN versus 18.6 MPa$^{1/2}$ for polyDVB.[40] However, we have observed that acetonitrile still dissolves oligomeric polyDVB making it what we refer to as a "marginal" solvent. The preparation of new copolymer microspheres of DVB and maleic anhydride presented an opportunity to both pursue the discovery of new materials and further investigate the solubility conditions required for particle formation. To test the hypothesis that a "marginal" solvent was required for particle formation, reactions were performed in various solvents. Similar solubility conditions to the PDVB/acetonitrile case were desired, however, δ-parameter values for DVB-*alt*-MAn copolymer were unavailable. Consequently, a variety of solvents were chosen such that a wide range of solvent polarities (based on their δ-parameters) were used while maintaining monomer solubility.

Table 1.1 shows the solvents chosen for the initial experiments, their δ-parameters and the resulting products of the reaction. It is apparent that none of the single solvents investigated met the marginal solubility conditions necessary for particle formation.

Table 1.1 - Morphology Produced from Various Solvents

Reaction Solvent	**δ*** **(MPa$^{1/2}$)**	**Observations**
Ethanol	26.0	Coagulum
Acetonitrile	24.3	Coagulum
n-Butanol	23.3	Microgels
MEK	19.0	Microgels
1,2-Dimethoxyethane	17.6	Microgels
Heptane	15.1	MAn Insoluble

* ref. 40

The reactions carried out in acetonitrile and ethanol resulted in coagulum indicating that these solvents did not allow for sufficient stabilization of the forming particles, resulting in rapid and uncontrolled aggregation. The other solvents resulted in swollen gels suggesting that the polymer had too high an affinity for these solvents and never collapsed to form particle nuclei. The existence of the gels was discovered when the reaction mixture was precipitated using heptane. The final reaction mixture in these cases appeared slightly turbid yet still translucent. Upon addition to an excess of heptane, the gels coagulated to form large aggregates of approximately 1 mm.

1.5.2 Solvent Mixtures

In order to study the solvency region below δ = 17.6 MPa$^{1/2}$, solvent mixtures were investigated for use as the reaction medium. In this case, a good solvent for the copolymer, methyl

ethyl ketone, and a poor solvent, heptane, were used in different proportions to provide a range of polarities. The advantage of using solvent mixtures was that the maleic anhydride could be dissolved in the methyl ethyl ketone prior to mixing which reduces the problem of monomer solubility in the less-polar mixtures. The solvent mixtures used for the reaction are listed in Table 1.2.

Table 1.2 - Morphology Produced from Binary Solvent Mixture

% MEK	**δ_m* ($MPa^{1/2}$)**	**Observations**
100	19.0	Space-filling Gel
90	18.6	Microgels
80	18.2	Microgels
60	17.4	Microgels
50	17.2	Microgels
40	16.8	Particles
30	16.4	Particles
20	16.0	Particles
10	15.5	Coagulum

* δ_m approximated using $\delta_m = \Phi_1\delta_1 + \Phi_2\delta_2$ where Φ is the volume fraction.

Particle formation was observed in the solvent mixtures containing between 20 and 40 vol% MEK. Similar to the single solvent reactions, gels were obtained for the reactions where the polymer solubility is high (50 vol% MEK or greater). Figure 1.9 shows an SEM micrograph of the particles produced with 40% MEK.

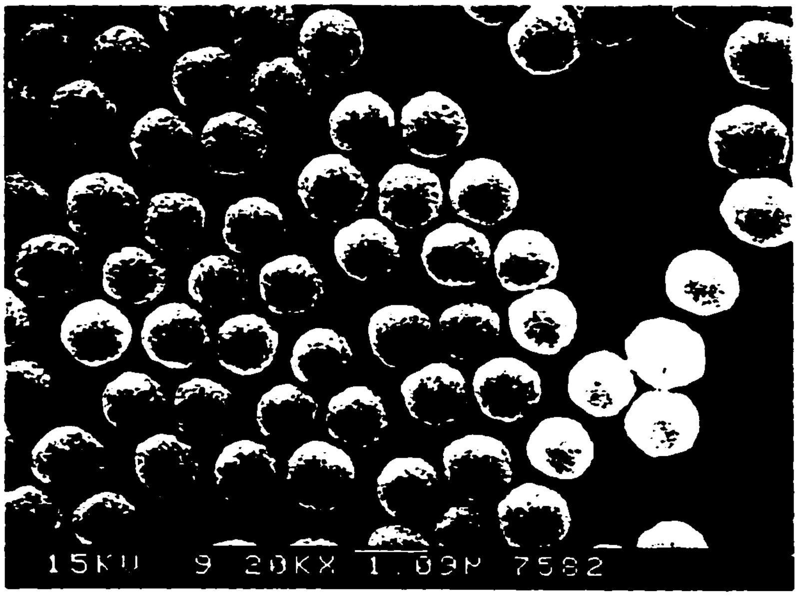


Figure 1.9 - DVB/MAn Particles Prepared in 40:60 MEK:Hp

The micrograph shows that these particles are spherical with narrow dispersity and a fairly smooth surface. Figures 1.10 and 1.11 show the particles produced in 30% and 20% MEK, respectively, on the same scale as Fig 1.9. It is apparent that with decreasing proportions of MEK, and hence decreasing polymer solubility, the surface becomes rougher. Under the poorest solubility conditions, the particles assume a cauliflower-like shape (Figure 1.11). This change in morphology is attributed to the increase in both the rate of precipitation onto the growing centres and the size of the precipitating entities.

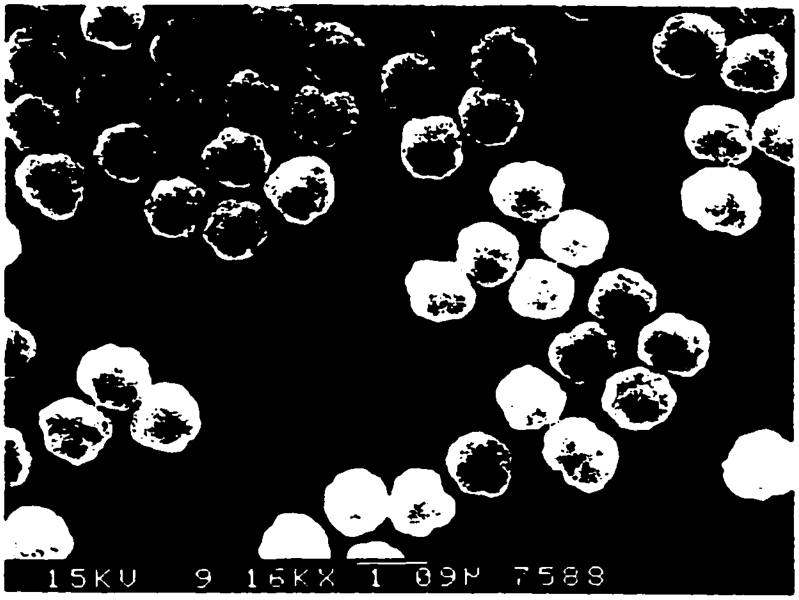


Figure 1.10 - DVB/MAn Particles Prepared in 30:70 MEK:Hp

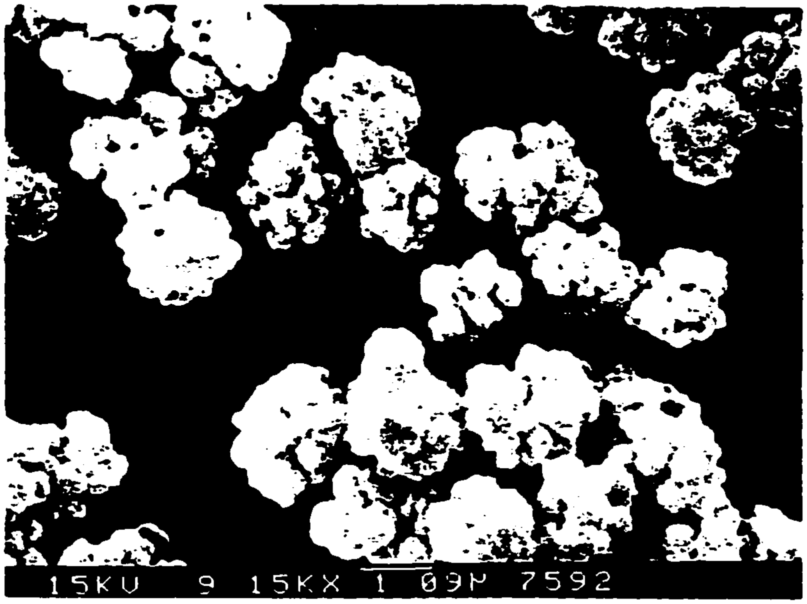


Figure 1.11 - DVB/MAn Particles Prepared in 20:80 MEK:Hp

The region between 40% and 50% MEK was investigated further in another series of experiments where the amount of MEK was varied in 2% increments. The particle size of each sample was measured and the data combined with those from the previous experiments to construct the graph shown in Figure 1.12. This graph indicates that there is a finite solvency window (MEK/Hp ratio) in which it is possible to prepare DVB-MAn particles.

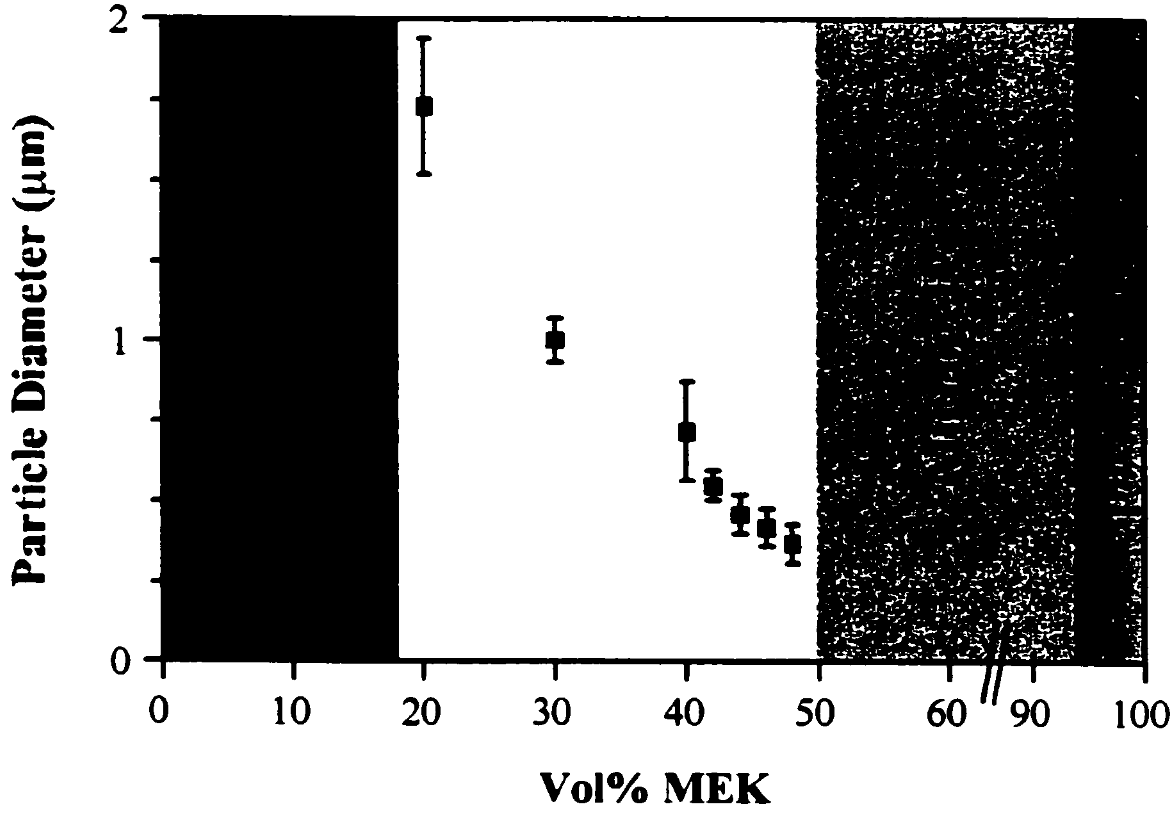


Figure 1.12 - Effect of Solvency on Particle Diameter

At 10% MEK, coagulation occurs presumably because the solvent mixture cannot solvate the surface polymer chains on the particles and hence cannot provide enough steric stabilization to form colloidally stable particles. The required stabilization is present in the window between 20 and 50% MEK which results in stable particles. As the proportion of good solvent increases, the particle size decreases. This results from the fact that the particle nuclei become colloidally stable at a smaller size in better solvents. For solvent mixtures with greater than 50% MEK, the initially formed microgels never collapse into dense particles.

One of the very attractive features of this reaction, as opposed to the divinylbenzene particles synthesized previously, is that DVB-MAn particles are produced and isolated in near quantitative yield, typically >95%. Only small quantities (<1%) of soluble materials (oligomers and residual maleic anhydride) were recovered from these reactions.

1.5.3 Monomer Loading Effects

All the reactions described above were conducted at 8% total monomer loading. To investigate the effects of monomer loading on particle size, subsequent reactions were performed at monomer loadings of 4 and 6% while maintaining the 1:1 molar ratio of maleic anhydride to styrenic vinyl bond ratio. These particles were prepared in the 40% MEK/60% Hp solvent mixture as this appeared to produce particles with the smoothest surface morphologies. Table 1.3 illustrates the effect on particle diameter as determined by SEM.

Table 1.3 - Effect of Monomer Loading on Particle Diameter

Monomer Loading (wt%)	**Particle Diameter (μm)**	**CV%**
4	0.4	12
6	0.8	11
8	1.1	9

In these cases, doubling the monomer loading more than doubles the particle diameter and hence shows an approximately eight-fold in particle volume. This non-proportional result would only be obtained through the formation of fewer, larger particles at higher monomer loadings. This condition is likely due to extended homocoagulation early in the reaction. It is evident that this homocoagulation must have occurred early in the reaction because the smooth morphology of the particle surfaces did not change as a function of monomer loading.

1.5.4 Functionalization Reactions

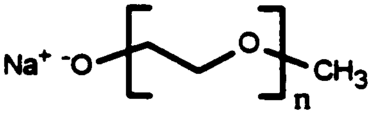
As mentioned earlier, the utility of the anhydride group was demonstrated in some preliminary experiments. These reactions included hydrolysis to diacid and esterification of the anhydride functionality to afford an acid ester.

Hydrolysis

When a small quantity of DVB/MAn microspheres was placed in 1 M aqueous NaOH, the particles quickly aggregated and floated on the surface of the liquid. However, after 12 hours at ambient temperature, the particles readily dispersed in the aqueous solution. This indicates that hydrolysis of the surface anhydride functionalities had occurred to produce sodium carboxylate groups on the particles which accounts for the hydrophilicity. This theory was tested by acidification of the aqueous solution using 1 M HCl which caused rapid coagulation of the particles following protonation of the carboxylate groups.

Esterification

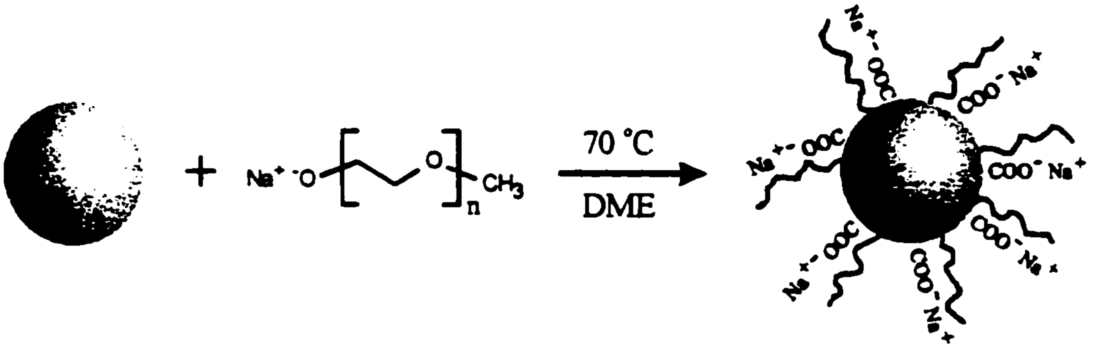
A sample of particles was also reacted with the sodium salt of poly(ethylene glycol) monomethyl ether, (PEG) (**1.12**), a water soluble oligomer with some interesting properties. The



(1.12)

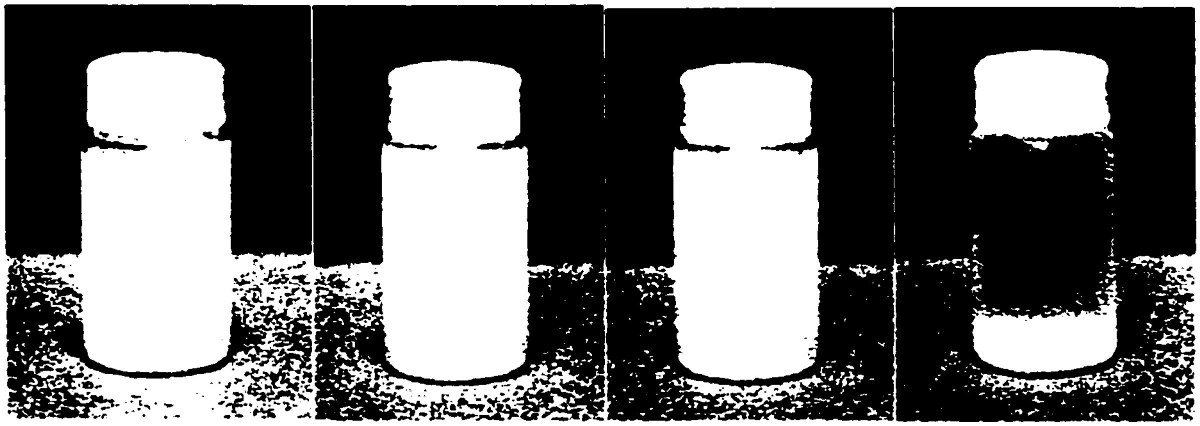
PEG sample chosen had an average molecular weight of 300 g/mol, suggesting that is was primarily a mixture of PEG chains containing 5 and 6 repeat units. Poly(ethylene glycol) is soluble in water due to hydrogen-bonding of water molecules to the oxygen atoms in the polymer backbone. At elevated temperatures, this hydrogen-bonding is disturbed due to increased motion of the polymer chains and they consequently precipitate from solution.[6] The temperature at which this precipitation takes place is known as the lower critical solution temperature (LCST). The LCST for PEG is known to be around 100°C, depending on its molecular weight, and can be even lower in the presence of carboxylic acid groups.[41,42]

When the PEG was reacted with DVB/MAn microspheres, the alcoholate groups of the PEG attacked the anhydride functionality on the particles surface, resulting in microspheres with both PEG chains and carboxylate groups on their surfaces (Scheme 1.3). These reactions were carried out at 70 °C in 1,2-dimethoxyethane as the solvent. These particles are now both sterically-stabilized by the PEG chains and electrostatically-stabilized by the carboxylate groups. This gives them some interesting pH and temperature sensitivity.



Scheme 1.3 - Grafting Reaction of PEG onto DVB/MAn Microspheres

When the pH was reduced, the carboxylate groups became protonated and the particles lost their electrostatic stabilization. However, the steric stabilization remained. Conversely, when the temperature is increased to 90 °C, the PEG chains desolvate but the carboxylate groups are still ionized. Therefore, there is a loss of steric stabilization but the electrostatic component still exists. For these two cases, the particles should remain dispersed in the aqueous medium since in both, one of the two means of stabilization persists. Photographs of samples of grafted particles at low pH and high temperature, that had been let stand undisturbed for 10 minutes, show that this is indeed the case (Figure 1.13). When both the pH is lowered and the temperature is increased, rapid coagulation of the particles is evident as they settle quickly to the bottom of the vial. This occurs due to desolvation of the PEG chains and protonation of the acid groups and hence, loss of both means of stabilization.



25 °C - pH 7　25 °C - pH 2　90 °C - pH 7　90 °C - pH 2

Figure 1.13 - Temperature/pH Sensitivity of Grafted DVB/MAn Microspheres

1.6 Conclusions

The precipitation polymerization method developed in this work is an effective means for preparing spherical narrow disperse divinylbenzene-maleic anhydride particles in the micron and submicron size ranges. Mixtures of heptane and MEK proved to be suitable reaction media. Discrete particles were formed in a relatively narrow solvency window ranging from 20 to 48% MEK with narrow disperse particles obtained at 40% MEK. These results support the hypothesis that a marginal solvent is required to prepare narrow disperse particles. The mechanism of particle formation will be discussed further in the forthcoming chapter. The functionality of the residual anhydride groups in these particle can be used to produce novel materials.

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Chapter 2 - Effects of Reaction Solvency and Crosslinking on the Precipitation Polymerization of Divinylbenzene and Maleic Anhydride

2.0 Introduction

As demonstrated in the previous chapter, during the preparation of polymer microspheres from divinylbenzene-55 and maleic anhydride, several other interesting morphologies were observed. Of particular interest, are the polymer microgels that were formed under slightly better solvency conditions than those used to produce microspheres.

2.1 Polymer Microgels

Since the 1970's, interest in polymer microgels has grown dramatically in both the scientific and industrial communities due to their interesting properties. Microgels are a unique type of polymer molecule that is considered intermediate to branched polymers and macroscopic polymer networks.[1] Specifically, Funke et al. defined microgels as intramolecularly crosslinked polymer molecules with a globular structure in the colloidal size range (10-1000 nm).[2]

Historically, the earliest reports of polymer microgels described them as precursors to macroscopic polymer networks. However, the best known example of these crosslinked polymer molecules was reported by Staudinger in 1934 where they were observed as a by-product of the solution polymerization of styrene which contained small amounts of divinylbenzene as an impurity.[3] Subsequently, Staudinger showed that it was possible to prepare divinylbenzene microgels by dilute solution polymerization of divinylbenzene in good solvents such as benzene.[4]

Initially considered a problem in solution copolymerization, microgels were later recognized to have useful properties, which include lower solution viscosities than their linear counterparts, and excellent film forming properties. The surface coatings industry soon incorporated microgels into their formulations to increase solids loading while reducing solvent emissions and maintaining viscosity. With regards to film formation, microgels have been shown to produce less brittle films than crosslinked linear polymers without affecting desirable film properties like gloss and durability.[5]

From an academic standpoint, polymer microgels offer a convenient route to the study of polymer networks. The internal structure of microgels is similar to that of macroscopic networks and so reflects their properties, especially their swelling behaviour which can be determined using classical methods such as light scattering. In addition, microgels are much easier to purify than macroscopic gels, using conventional precipitation techniques.

Microgels are typically prepared by one of two routes: dilute solution polymerization, as pioneered by Staudinger, and emulsion (or microemulsion) polymerization. Dilute solution polymerization can produce microgels because the probability of intramolecular crosslinking and cyclization are increased at high dilution, as described by the Ziegler dilution law, while intermolecular reactions are inhibited.[6] Emulsion polymerization, on the other hand, can lead to microgels because the polymerization takes place in the restricted volume of the surfactant micelles thereby preventing macrogelation. Antonietti categorized these classes of microgels as Type A (dilute solution) and Type B (emulsion) microgels.[6] In addition to these classical examples, newer techniques to prepare microgels have been reported that involve anionic polymerization,[7-9] endlinking of polymer chains[10] and step-growth crosslinking reactions.[11,12]

The microgels discussed in the Chapter 1 are Type A and prove very interesting from a mechanistic standpoint. These kind of solvent-dependent morphology transitions deserve further study. However, in order to clarify the expected effects of solvency and crosslinking on polymer solubility, a brief introduction to polymers in solution follows.

2.2 Polymer-Solvent Interactions and Polymer Solution Thermodynamics

The age-old phrase "like dissolves like" generally applies not only to solutions of small molecules but also to polymer solutions. Dissolution of a polymer in a solvent is dependent on the strength of the intermolecular forces present between the polymer chains and solvent molecules. Dissolution occurs when the polymer segment-solvent molecule interactions are comparable to the attractive forces between two polymer chain segments. Solvents with a structure similar to the polymer backbone typically dissolve the polymer because the strength of the intermolecular forces are also similar. These intermolecular forces, or van der Waals forces, result from five possible interactions: dipole-dipole forces, dipole-induced dipole forces, instantaneous dipole-induced dipole forces, hydrogen bonding and charge transfer interactions. The degree to which each of these forces contributes to the overall intermolecular force between molecules is typically dependent on the polarity of polymer segments and solvent molecules.

The solution behaviour of polymers is usually described using a thermodynamic treatment. The solution thermodynamics of polymers are decidedly different from those of a solution of small molecules. There are many deviations from ideality that need to be addressed when considering polymer-solvent interactions. However, before discussing polymer solutions, it is necessary to review basic solution thermodynamics.

2.2.1 Ideal Solutions

The ability of a solvent to dissolve a solute, whether it be a small molecule or an amorphous polymer, is described by the Gibb's free energy of mixing, ΔG_m, as shown in Equation 2.1,

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad \textbf{(2.1)}$$

where ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively, and T is temperature in Kelvin. The solute will dissolve in the solvent as long as ΔG_m is negative to which there are two contributing terms, an enthalpic term and an entropic term. Ideal solutions are ones in which the solute and solvent are similar in dimensions, and the solute-solvent and solvent-solvent interactions are equal such that $\Delta H_m = 0$. Consequently, the only contribution to mixing or dissolution in these solutions is entropy. The entropy of these systems can be estimated using the Boltzmann law (Equation 2.2),

$$S = k \ln W \qquad \textbf{(2.2)}$$

where k is the Boltzmann constant and W is the number of ways that the solute molecules can arrange themselves within the matrix of solvent molecules. To simplify this situation, consider a two dimensional lattice with n_0 cells in which are placed n_1 solvent molecules and n_2 molecules of solute such that $n_0 = n_1 + n_2$. The magnitude of W for this lattice can be expressed as in (Equation 2.3).

$$W = \frac{(n_1 + n_2)!}{n_1!n_2!} = \frac{n_0!}{n_1!n_2!} \qquad \textbf{(2.3)}$$

Substituting this equation into (Equation 2.2) and expressing n_i/n_0 as the mole fraction of each component, x_i, yields the Van't Hoff equation, (Equation 2.4).

$$S = -k \ln\left[n_1 \ln x_1 + n_2 \ln x_2\right] = \Delta S_m \qquad \textbf{(2.4)}$$

For the pure solute and pure solvent, S = 0 and consequently, the difference in entropy between the pure states and the solution state, i.e. the entropy of mixing, ΔS_m, is equal to Equation 2.4 alone.

As mentioned, for an ideal solution, dissolution of the solute in the solvent is an entropically driven process. However, there are very few cases where solutions exhibit this ideal behaviour. There are three other type of solutions that are more commonly observed: athermal, regular and irregular solutions. An athermal solution exists when $\Delta H_m = 0$ but ΔS_m does not conform to Equation 2.4. Regular solutions are formed when ΔS_m is ideal but ΔH_m does not equal 0 and finally, a solution is irregular when both ΔH_m and ΔS_m deviate from ideal behaviour.

2.2.2 Flory-Huggins Theory

Polymer solutions typically exhibit irregular solution characteristics because polymer-solvent interactions are rarely equal to solvent-solvent interactions, leading to a non-zero ΔH_m. In addition, deviations from ideal behaviour for the entropy of mixing exist because for ideal behaviour, the solute and solvent molecules must be comparable in dimensions. Obviously for polymers and solvent molecules this is not true. Flory and Huggins attempted to account for these non-ideal entropy values in their theory for the thermodynamics of polymer solutions.[13] The first assumption of this theory was that a polymer chain could be considered as a group of segments strung together where the volume of each segment was equal to that of a solvent molecule. Now each segment of the polymer could occupy one lattice cell and thus compensate for the massive difference in size of the polymer and the solvent. This approach however, complicates Equation 2.3 because each repeat unit must still be attached to the other units in the chain, thereby reducing the number of possible conformations of the molecules. Equation 2.5 was developed for the number of ways in which polymer molecules can be placed in the lattice.

$$W = \frac{1}{n_2!}\frac{n_0!}{(n_0 - n_2y)!}\left(\frac{z-1}{n_0}\right)^{n_2(y-1)} \qquad \textbf{(2.5)}$$

Here, y represents the number of segments in one polymer chain, n_2 is the number of polymer chains, z is the coordination number of each cell in the lattice and n_0 is once again the total number of lattice cells. Substituting this equation into Equation 2.2 results in Equation 2.6. Now there are two contributions to the entropy of the system that are expressed in Equation 2.6. The first two

$$S = -kn_1 \ln\left(\frac{n_1}{n_1 + yn_2}\right) + kn_2 \ln\left(\frac{yn_2}{n_1 + yn_2}\right) + kn_2 \ln y - kn_2(y-1)\ln\left(\frac{z-1}{e}\right) - kn_2 \ln y \qquad \textbf{(2.6)}$$

terms represent the entropy of mixing, ΔS_m, while the last three terms account for disorientation of the polymer molecules themselves, ΔS_{dis}. ΔS_{dis} exists because the polymer molecules have gone from a more ordered state in the solid to a more disordered state in solution. Since we are only concerned with the entropy of mixing, this equation simplifies to Equation 2.7.

$$\Delta S_m = -k\left(n_1 \ln \Phi_1 + n_2 \ln \Phi_2\right) \qquad \textbf{(2.7)}$$

Note the use of volume fractions in this equation instead of mole fractions like in the Van't Hoff equation. Flory used volume fractions because they better reflect the intramolecular interactions of the polymer chains. These interactions affect how closely the chains pack and hence can distort the volume of the chain in solution; and mole fractions fail to show the differences in these interactions.

As mentioned previously, the enthalpy of mixing of a polymer solution is rarely equal to 0. Flory also attempted to explain this behaviour in terms of contact energy. Contact energy is the change in energy resulting from the breaking of solvent-solvent (1-1) and polymer-polymer (2-2) contacts and the formation of solvent-polymer (1-2) contacts. The change in energy for the formation of one 1-2 contact can be expressed as in Equation 2.8.

$$\Delta E_{1-2} = E_{1-2} - \tfrac{1}{2}\left(E_{1-1} + E_{2-2}\right) \qquad \textbf{(2.8)}$$

The total number of 1-2 contacts formed in a solution can be approximated using Equation 2.9.

$$\#\, of\ 1-2\ contacts = zyn_1\Phi_2 \qquad \textbf{(2.9)}$$

The product of Equations 2.8 and 2.9 provides us with the total change in energy for formation of the new contacts, i.e., the enthalpy of mixing, ΔH_m, as shown in Equation 2.10.

$$\Delta H_m = zyn_1\Phi_2\Delta E_{1-2} \qquad \textbf{(2.10)}$$

Flory combined some of the terms in this equation to give a new form of the expression in Equation 2.11.

$$\Delta H_m = kT\chi\, n_1\Phi_2 \qquad \textbf{(2.11)}$$

The symbol χ, is known as the Flory interaction parameter and is a very important measure in polymer science as it relates the effect the polymer chains have on the energetic state of the solvent molecules. This term reflects the solubility of a polymer in a solvent, typically requiring χ values of less than 0.5 for solubility. This parameter is unique because it is specific to a particular polymer-solvent combination. For example, polystyrene dissolved in toluene, a good solvent, has a χ-parameter of approximately 0.4 while χ for polystyrene in methanol, a poor solvent, can be as high as 2.2.[14] Now the Gibb's free energy of mixing can be calculated by combining Equations 2.7 and

2.10 to give Equation 2.12.

$$\Delta G_m = kT\left[\left(n_1 \ln\Phi_1 + n_2 \ln\Phi_2\right) + \chi n_1 \Phi_2\right] \qquad \textbf{(2.12)}$$

2.2.3 Hildebrand Solubility Parameter, δ

Hildebrand used a different approach to calculate the enthalpy of mixing for a solution where he modified an equation developed for calculating the heat produced from the vapour pressure of a binary mixture of liquids. This modified equation is of the form of,

$$\Delta E = (n_1 V_1 + n_2 V_2)\left[\left(\frac{\Delta E_1^v}{V_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_2^v}{V_2}\right)^{\frac{1}{2}}\right]^2 \Phi_1 \Phi_2 \qquad \textbf{(2.13)}$$

where ΔE^v is the heat of vaporization of the solvent and solute. The term $\Delta E^v/V$ is known as the cohesive energy density as it reflects the intermolecular forces per unit volume in a solution. More important to the polymer scientist is the entire term, as shown in Equation 2.14, which Hildebrand designated with the symbol δ, and hence known as the Hildebrand solubility parameter.

$$\left(\frac{\Delta E^V}{V}\right)^{\frac{1}{2}} = \delta \qquad \textbf{(2.14)}$$

Substituting δ into Equation 2.13, the heat of mixing of a solute and solvent becomes,

$$\Delta H_m = V_m(\delta_1 - \delta_2)^2 \Phi_1 \Phi_2 \qquad \textbf{(2.15)}$$

where V_m is the volume of the mixture. The Hildebrand solubility parameter, δ, and the Flory interaction parameter, χ, are related by Equation 2.16.[14]

$$\chi = 0.34 + \frac{V_1}{RT}\left(\delta_1 - \delta_2\right)^2 \qquad \textbf{(2.16)}$$

Both these terms are of interest to the polymer scientist for application in estimating polymer-solvent interactions. Each is a measurable quantity, and can be determined using a variety of techniques such as refractive index and vapour pressure measurements.

2.3 Thermodynamics of Precipitation Copolymerization of Crosslinking Monomers

In the preceding sections, it has been shown that the solubility of a polymer in a solvent is dependent on both the enthalpy and entropy of mixing. The ability of Flory-Huggins theory to predict accurately the solubility of a polymer in a solvent is limited for a number of reasons.[13] For example, when considering the two-dimensional lattice, Flory-Huggins theory assumes that placement of the chain segments in the lattice is statistical thus neglecting inherent properties of the polymer chain like flexibility. In addition, this theory was derived for linear polymers only and consequently ignores the effect of crosslinking on polymer solubility. However, Flory-Huggins theory is easily extended to crosslinked systems for the qualitative determination of the factors that effect polymer solubility and swellability.

2.3.1 Reaction Solvency Effects

As shown in Chapter 1, the choice of reaction solvent in crosslinking precipitation polymerization is critical in determining the resulting morphology. The most obvious effect solvency has on polymer solubility is illustrated by Equation 2.1, the Gibb's free energy of mixing. The better the solvent for the polymer, the smaller the value of ΔH_m and consequently the lower the value of ΔG_m. To cause precipitation of polymer in polymerizations of this type, appropriate solvents should be chosen such that ΔH_m is maximized. Precipitation that is primarily driven by reaction solvency can be referred to as enthalpic desolvation. Referring to Equation 2.15, the magnitude of this effect can be predicted using the Hildebrand solubility parameters. The δ-parameter is commonly used in polymer science to estimate the solubility characteristics of a polymer in a particular solvent. The value of this parameter typically ranges from approximately 11 $MPa^{1/2}$ for very non-polar solvents to as high as 48 $MPa^{1/2}$ for water.[14] As Equation 2.15 indicates, if the δ-parameter of a polymer is equal to that of the solvent, the heat of mixing for the system will be zero and hence approach ideality. In practice, the solubility parameters do not actually have to be equal for solubility but typically fall within about 4 $MPa^{1/2}$.[15] The predictive reliability of the δ-parameter is only adequate for linear, non-polar polymers and deviations have been encountered with more polar polymers and solvents. Polar systems cause problems because the Hildebrand parameter neglects to account for hydrogen-bonding and dipole-dipole interactions. Consequently, Hansen developed Hildebrand's concept further, by breaking the δ-parameter down into Van der Waals, hydrogen bonding and dipolar contributions.[14] Nevertheless, the basic δ-parameter still provides a good starting point in estimating polymer-solvent interactions.

2.3.2 Crosslinking Effects

Crosslinking polymerizations also deviate from the expected behaviour described by these theories because crosslinking affects the entropy of a polymer solution which along with the enthalpic contributions to the free energy of mixing, plays a significant role in determining polymer solubility. As mentioned previously, the entropy of a polymer solution is related to the number of ways, W, in which the polymer chains can arrange themselves in the matrix of solvent molecules. Crosslinking drastically reduces the value of W as it inhibits rearrangement of the polymer chains and thus causes a large decrease in the entropy of mixing. This causes the free energy of mixing to become more positive and can ultimately lead to precipitation of the polymer chains. This process can be referred to as entropic desolvation and is of primary importance when considering crosslinking precipitation polymerization.

2.4 Objective and Scope of Research

The previous chapter covered the preliminary experiments in the precipitation polymerization of divinylbenzene-55 and maleic anhydride. Not only did it result in an interesting new morphology, microgels, but also raised a number of questions about the mechanism of particle formation in these systems.

In particular, the reasons for the change in morphology from microspheres to microgels was unclear. In order to better understand exactly where and why these morphology transitions took place, we embarked on a more detailed study of the effects of reaction solvency on the size and morphology of the particles produced. The study described in this chapter, entails analysis of the products of a series of reactions carried out in various mixtures of MEK and heptane. In contrast to the previous chapter, emphasis was placed on the area of transition between microspheres and the microgel products. In addition, the level of DVB was adjusted for a series of experiments to determine the role of the crosslinker in these reactions. These experiments were carried out in an attempt to better understand the thermodynamics effects of solvent and crosslinking on precipitation polymerizations, as well as to gather information about the mechanism of particle formation in these systems. To this end, the effect of total monomer concentration on the microsphere and microgel products was also investigated in more detail.

2.5 Experimental

Materials and Synthesis

The materials and procedures for the preparation of DVB/MAn microspheres/microgels were described in Chapter 1.

Purification

Sol/gel separation, in the case of microspheres and microgels, was carried out by repeated washing/centrifugation steps using MEK as the wash solvent. Particle and polymer yields were determined gravimetrically.

Electron Microscopy

Transmission electron microscopy (TEM) samples were prepared by diluting the reaction mixtures with a twenty-fold excess of MEK and placing a drop of the resulting dispersion onto a carbon film-coated 200 mesh copper grid. The grids were allowed to air dry and images were obtained on a Philips CM12 transmission electron microscope.

Sample solutions for environmental scanning electron microscopy (ESEM) were prepared in the same manner as for TEM. Aluminum ESEM stubs were modified by adhering a small piece of a glass microscope cover slip to the stub using double-sided adhesive tape. A drop of the diluted sample solution was placed on the glass surface and allowed to air dry. The stubs were sputter-coated with an 8 nm gold film to ensure conductivity and the samples were then imaged on a Philips Electroscan 2020 environmental scanning electron microscope.

Particle Sizing

Particle sizing was carried out in MEK using a Coulter LS230 particle sizer which operates on the principles of Fraunhofer diffraction for large particles (>0.8 µm) and polarization intensity differential scattering (PIDS) for small particles (< 0.04-0.8 µm).

Viscosity

Dilute solution viscosity measurements were carried out using an Ubbelodhe-type viscometer in a temperature-controlled water bath held at 25°C. A series of solutions was prepared for each sample ranging in concentration from approximately 0.1 g/dL to 0.001 g/dL.

2.6 Results and Discussion

2.6.1 Reaction Solvent Effect on Product Morphology

In our earlier work on the precipitation copolymerization of divinylbenzene-55 and maleic anhydride to prepare copolymer microspheres, mixtures of a good solvent, methyl ethyl ketone ($\delta = 19.0$ MPa^{½}) and a poor solvent, heptane ($\delta = 15.1$ MPa^{½}), were employed, allowing the reaction solvency to be adjusted by varying the ratio of both solvents. In that study, four distinct copolymer morphologies were observed as a function of solvent composition; coagulum, microspheres, macrogels and microgels. Coagulum was formed under the poorest solvency conditions, at less than 20 vol% MEK in the solvent mixture. Macrogels (space-filling gels) were formed under the best solvency conditions, at MEK levels of greater than 95 vol%. Microspheres and microgels were formed at intermediate MEK concentrations of approximately 40 vol% MEK and 80 vol% MEK, respectively.

We observed earlier, that the size of the DVB-55/MAn microspheres decreased with increasing proportions of MEK until it appeared that microgels were formed at greater than 50 vol% MEK. However, it was not clear whether this was a smooth transition from microspheres to microgels or whether a critical solvency condition was exceeded that resulted in the change in morphology. One of the goals of the present study was to accurately identify the conditions under which the transitions from microspheres to microgels and from microgels to macrogels took place.

The Microsphere to Microgel Transition

Figure 2.1 shows a series of transmission electron microscopy (TEM) images of DVB-55/MAn copolymer particles prepared at MEK concentrations ranging from 40 to 80 vol%. Due to the wide size range of the products, it was impossible to show images at the same magnification and so the size bar on each micrograph should be taken into consideration. The transition from hard, spherical particles to soft, irregular microgels is clearly visible in these images. All the copolymerizations were carried out at a constant total monomer loading of 4 wt/vol% and typically gave polymer yields of greater than 95%. Figures 2.1 a-c shows microspheres in the 0.1-0.5 μm diameter range, formed in 40, 50 and 60 vol% MEK, respectively. The smaller microgel particles in Figure 2.1 d and e, formed in 70 and 80 vol% MEK, are connected by thin copolymer strands, reflecting the significant swellability of these microgel products.

Figure 2.2 compares the particle diameter measured by TEM, with the diameters of the same particles dispersed in neat MEK measured by light scattering on a Coulter LS230. While the samples prepared in 70 vol% MEK still retain a semi-spherical shape in the TEM images, the microgels formed in 80 vol% MEK were clearly non-spherical when dried and consequently, diameters from TEM were only estimated.

Both the diameters for dry and swollen particles showed a dramatic decrease with increasing solvency of the polymerization medium, corresponding to the transition from the microsphere to microgel morphology between 40 and 60 vol% MEK.

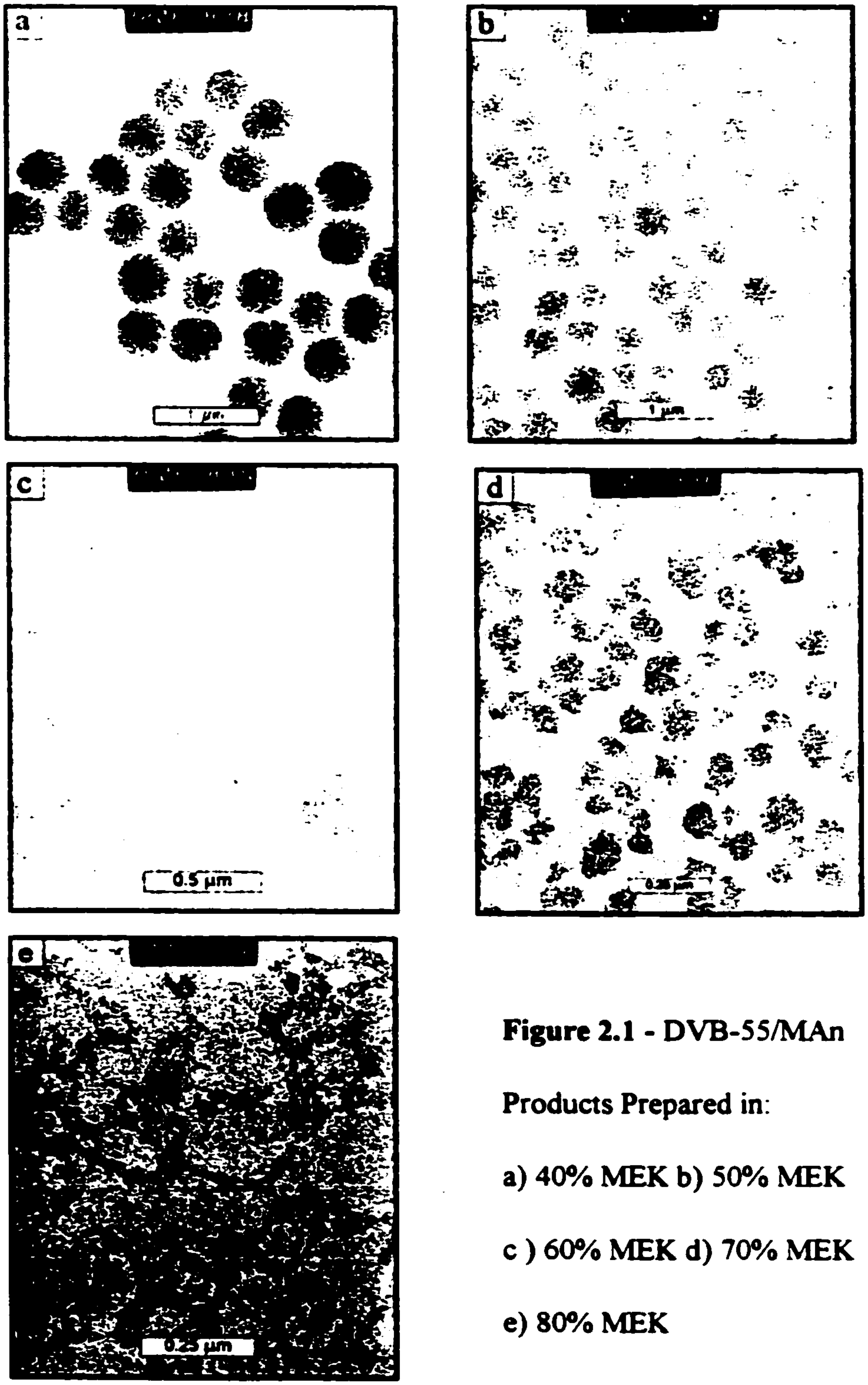

Figure 2.1 - DVB-55/MAn

Products Prepared in:

a) 40% MEK b) 50% MEK

c) 60% MEK d) 70% MEK

e) 80% MEK

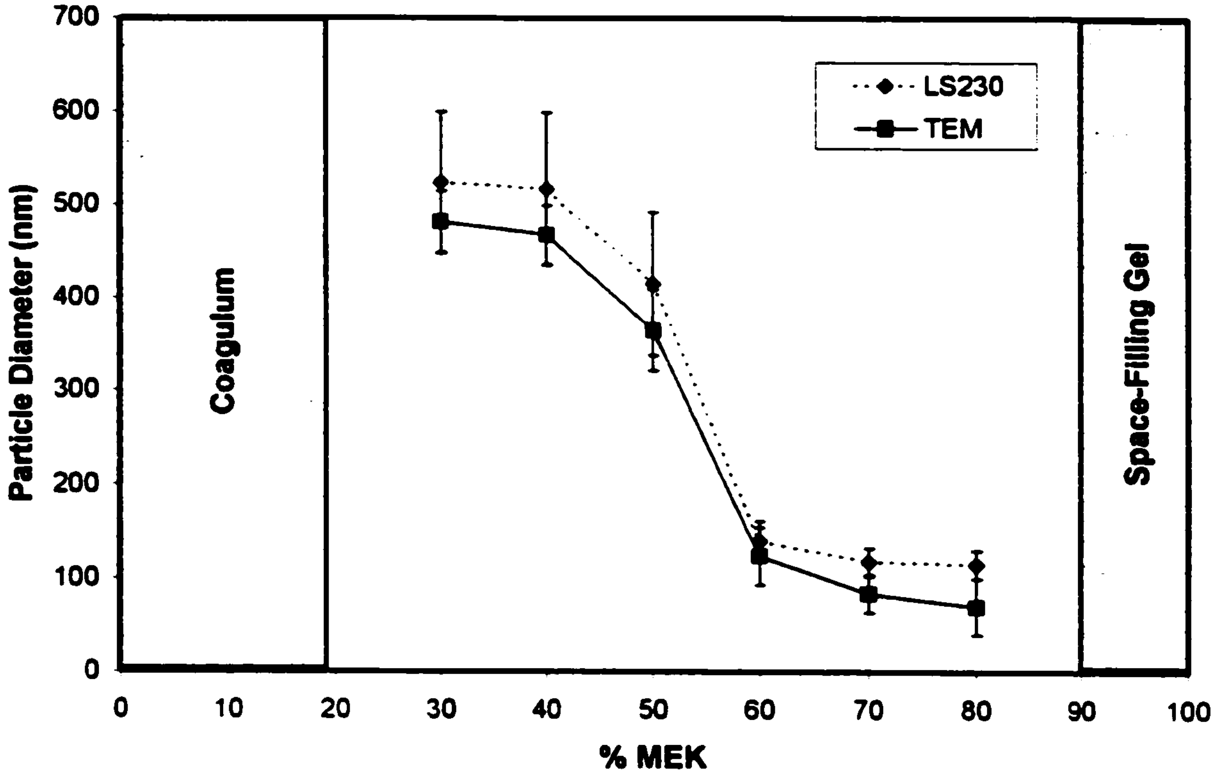

Figure 2.2 - Effect of Solvency on Particle Diameter

The transition from microspheres to microgels is indicated by both the decrease in the average diameters of the particles and the increase in swellability shown in the TEM images. While the crosslinker concentration remains constant in each of these reactions, the onset of swelling for the microgel products suggests that with increasing solvency there is an associated decrease in the efficiency of the crosslinking reaction. This is likely caused by increased solvation of the growing oligomeric species inhibiting crosslinking and also preventing entropy-driven phase separation, which results from this reaction.

The Microgel to Macrogel Transition

At approximately 95 vol% MEK, we observed the transition from microgels to macroscopic gels. However, this transition could not be easily studied using the techniques we have discussed previously. In particular, electron microscopy became more difficult since the resulting macroscopic gels and their immediate precursors tend to be homogeneous and hence without contrast.

Consequently, dilute solution viscosity was used to study this transition. The viscosity measurements themselves were carried out in neat MEK and the data are displayed as Huggins

$$\eta_{red} = \frac{1}{c}\left(\frac{\eta}{\eta_0} - 1\right) = \frac{1}{c}\left(\frac{t}{t_0} - 1\right) = [\eta] + k_H[\eta]^2 c \qquad \textbf{(2.17)}$$

plots.[16] The Huggins equation, Equation 2.17, relates the reduced viscosity of a polymer solution, η_{red}, to both the intrinsic viscosity, $[\eta]$, of the polymer and its concentration, c. Figure 2.3 shows the viscometric results obtained for a series of DVB-55/MAn microgels which were prepared at different levels of MEK.

For dilute solutions, the ratio of the viscosity of the polymer solution and the pure solvent, η and η_0, respectively, is approximated by the ratio of the flow time of each liquid in the viscometer, t and t_0. The constant k_H, termed the Huggins coefficient, is typically around 0.3 for linear polymers in good solvents. This term can be affected by a variety of conditions including solvency, branching and the breadth of the molecular weight distribution.[16]

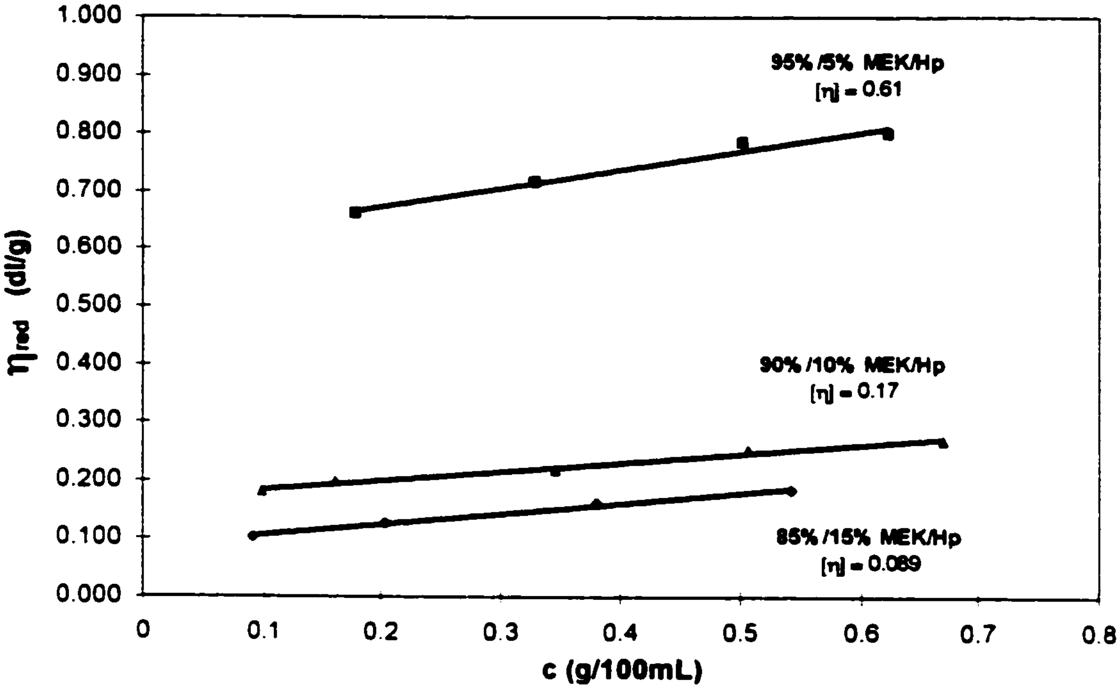

Figure 2.3 - Huggins Plots for DVB/MAn Microgels

When viscometric methods are applied to the present system, they clearly demonstrate the onset of macrogelation, which is observed as a large increase in the intrinsic viscosity for microgels prepared in 95 vol% MEK, the immediate precursors to macrogels. This increase in viscosity is caused by intermolecular crosslink formation between microgels resulting in a dramatic increase in the molecular weight of these species.

Good solvency conditions, i.e., more than 85 vol% MEK, have a two-fold effect on the growing microgels. Firstly, the swelling of the microgels is increased which reduces the interstitial distance between the dispersed microgels, enhancing intermolecular reactions. Secondly, better solvency further reduces the crosslinking efficiency which also leads to a higher degree of swelling. These effects cause the microgels to exceed the critical overlap conditions described by DeGennes,[17] resulting in intermolecular reactions with other microgels that lead to macrogelation.

Of note here is the absence of the so-called "excluded volume effect" which has been used to describe the repression of macrogelation under near ideal solvency conditions.[18] In these cases, microgels are formed under the best solvency conditions while macrogelation resulted from slightly poorer solvents. This phenomenon was explained by the fact that intermolecular crosslinking reactions require the displacement of neighboring solvent molecules from the vicinity of the microgels which is more difficult when polymer-solvent interactions are strong. The absence of this effect in the DVB-55/MAn system suggests that neat MEK, although a good solvent, is not an ideal solvent for the copolymer.

To determine the validity of this statement, the δ-parameter, or Hildebrand parameter, can be used to estimate the polymer/solvent interactions. As mentioned previously, a good solvent for a particular polymer typically has a comparable δ-parameter, within about 4 MPa$^{1/2}$ for solubility. Using group contribution theory, the δ-parameter for styrene-maleic anhydride copolymer was calculated to be approximately 26 MPa$^{1/2}$.[14] Compared to the δ-parameter for MEK of 19.0 MPa$^{1/2}$, the difference of 6 MPa$^{1/2}$ suggests that MEK is, as expected, not an ideal solvent for the copolymer.

2.6.2 Crosslinking Effects on Polymer Morphology

As mentioned previously, we expected that increasing the MEK content of the reaction mixture would decrease the efficiency of the crosslinking reaction. In an attempt to separate the effects of solvency and crosslinking, we carried out copolymerizations at constant solvent compositions, but with varying DVB crosslinker concentrations. The crosslinker concentration was adjusted by using 4-methylstyrene as a monovinyl diluent for DVB-55 such that mixtures containing from 5 to 36 mol% DVB, referred as DVB-5, DVB-11, DVB-24 and DVB-36 hereafter, were prepared and copolymerized with maleic anhydride. Two solvent mixtures were chosen for this study, 40 vol% MEK / 60 vol% Hp (microsphere domain) and 80 vol% MEK / 20 vol% Hp (microgel domain). It was expected that varying the crosslinker concentration in each of these systems would cause morphology changes equivalent to those observed upon changing the reaction solvent quality. Figure 2.4 shows scanning electron micrographs for a series of samples, all prepared in 40 vol% MEK but with various amounts of divinylbenzene. For DVB-55/MAn, typical, hard microspheres are observed while at lower crosslinker concentrations down to DVB-5/MAn, soft particles are produced. Table 2.1 shows the particle diameters and coefficients of variance for these samples. A slight increase in particle diameter observed with decreasing DVB concentration, along with the increase in the deformability of the particles, reflects their reduced crosslink density.

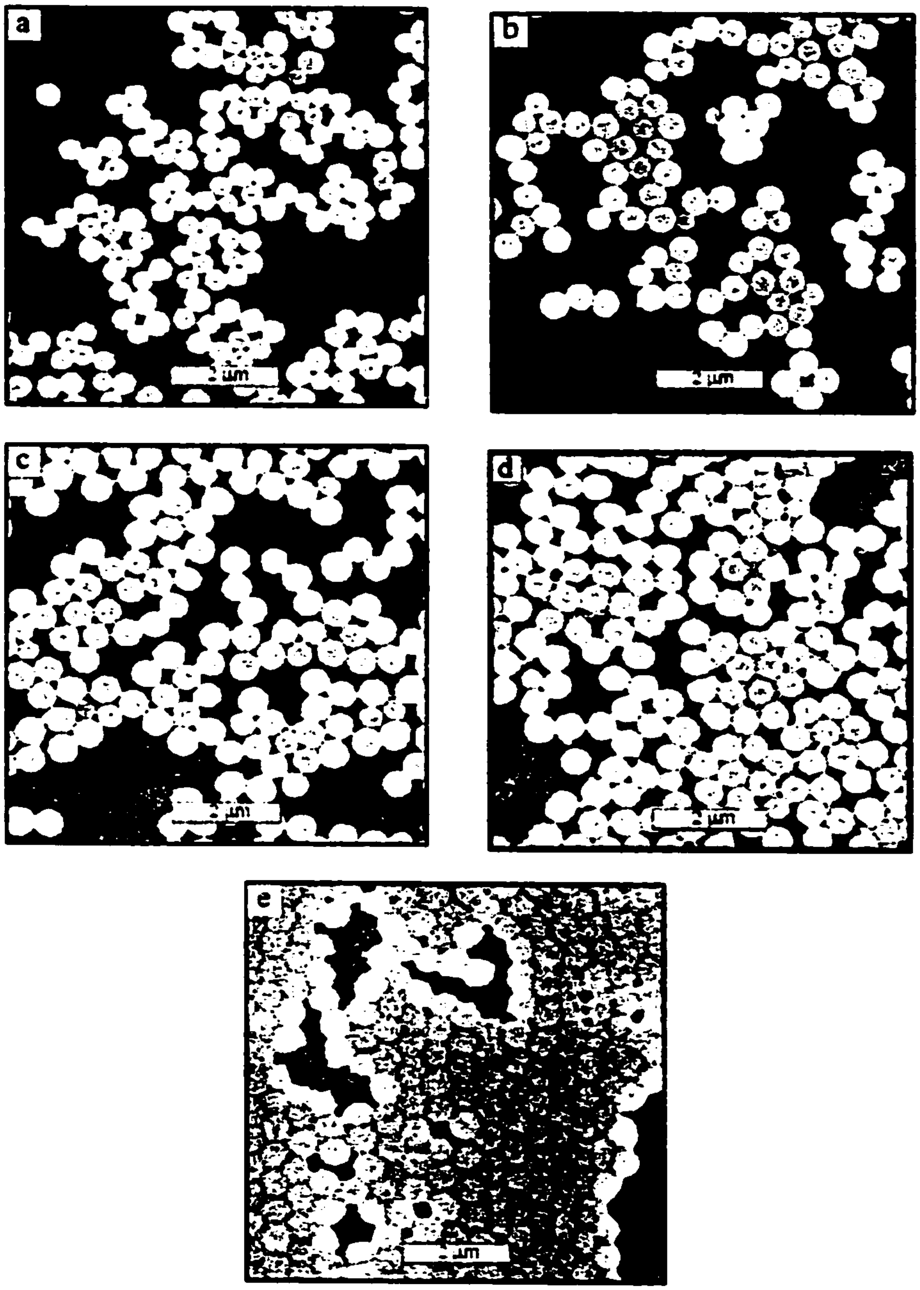

Figure 2.4 - Effect of DVB Level on DVB/MAn Microspheres: a) DVB-55 b) DVB-36 c) DVB-24 d) DVB-11 e) DVB-5

Table 2.1 - Particle Diameters for 40% MEK Reactions

DVB%	Diameter (nm)	CV%
55	481	15.1
38	498	15.2
24	518	15.4
11	532	15.8
5	571	16.6

In an analogous series carried out at 80 vol% MEK, the diameter of the polymer particles formed increases with decreasing crosslinker concentration. Examples of these samples are shown in Figure 2.5.

The increase in particle size in going from DVB-55 to DVB-11 (Figures 2.5a-d) can be attributed to more effective intermolecular reactions in the mixtures containing less DVB since the polymer chains will be much more highly swollen in these cases. Only soluble products are formed in the DVB-5/MAn reaction and hence no image is shown for this sample. However, when the MEK proportion is decreased to 70 vol%, very soft, semi-spherical structures are formed as shown in Figure 2.6.

The conversion to particles for all reactions incorporating 55 mol% DVB are nearly quantitative at >90%. This value falls to approximately 60% for the DVB-5 reactions while the total polymer yield remains at greater than 90% showing an increase in soluble material. This result is expected since the divinyl monomer has been shown to play a significant role in particle growth as it is necessary to capture oligomers from solution.[19]

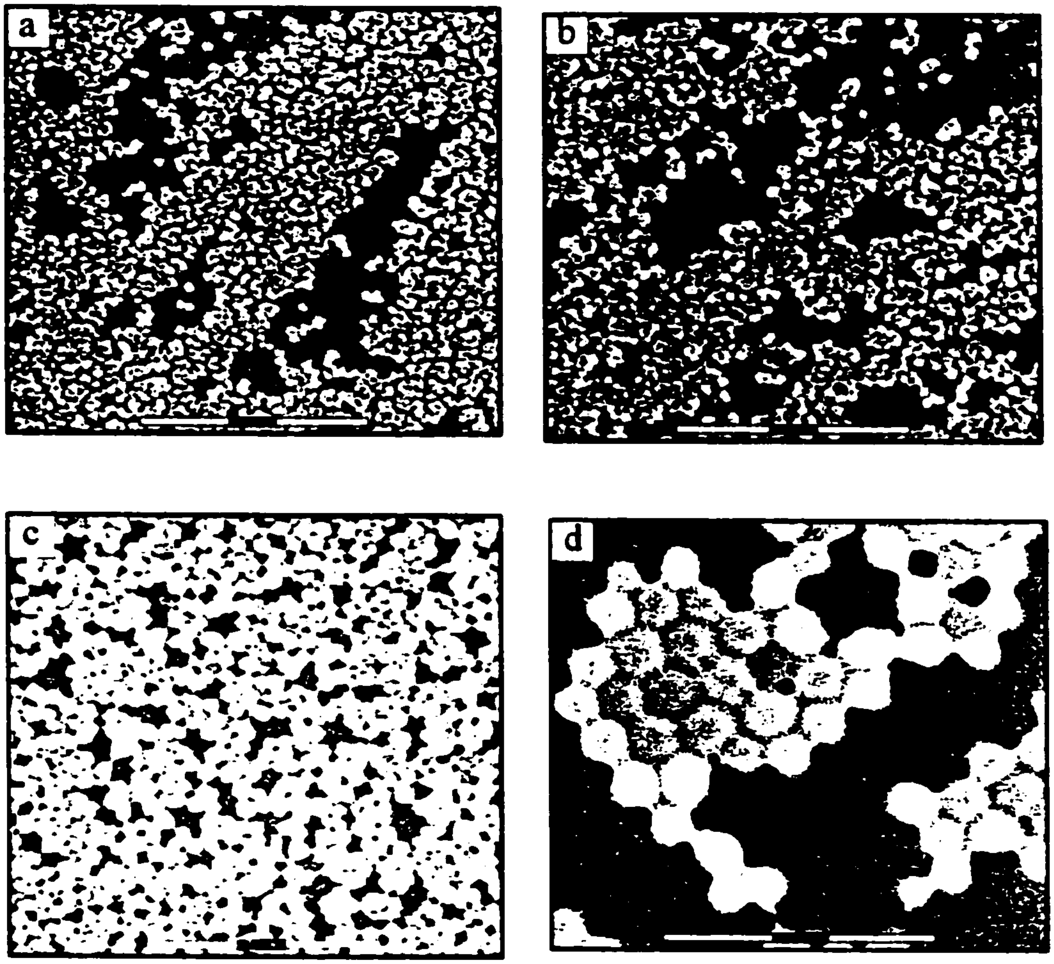

Figure 2.5 - Effect of DVB Level on DVB/MAn Microgels Prepared in 80% MEK:

a) DVB-55 b) DVB-36 c) DVB-24 d) DVB-11

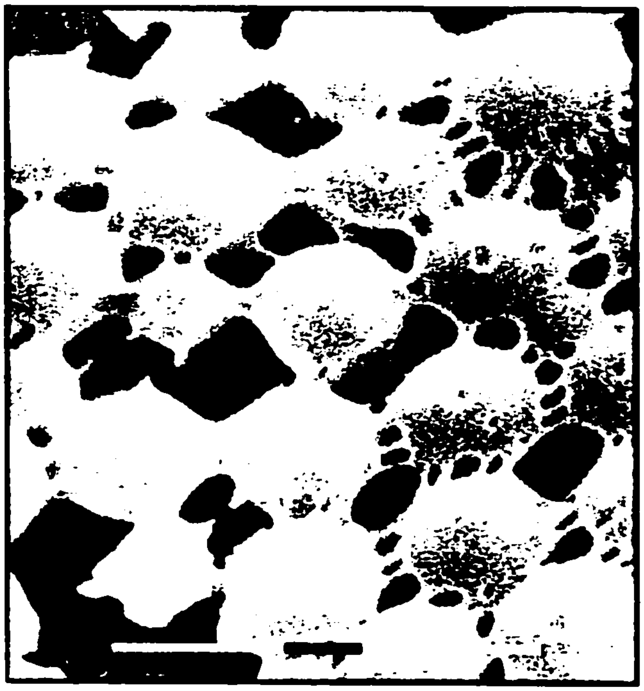

Figure 2.6 - DVB-5/MAn Microgel Prepared in 70% MEK

2.6.3 Effect of Monomer Concentration on Particle Size

Total monomer concentration represents the third dimension of the reaction parameter system reported here. Figure 2.7 illustrates the effect of changing the total monomer concentration, on the volume of the individual particles for two series of DVB-55/MAn reactions at 40 and 80 vol% MEK as measured using the Coulter LS230.

At 40 vol% MEK, the particle volume increases quickly with increasing monomer concentration in a non-linear fashion. This suggests that the number of particle nuclei produced in these reactions is not proportional to the monomer concentration. In contrast, at 80 vol% MEK, there seems to be little effect of monomer concentration on particle volume. These results suggest that there are two different nucleation mechanisms for these species which are explained in the following section.

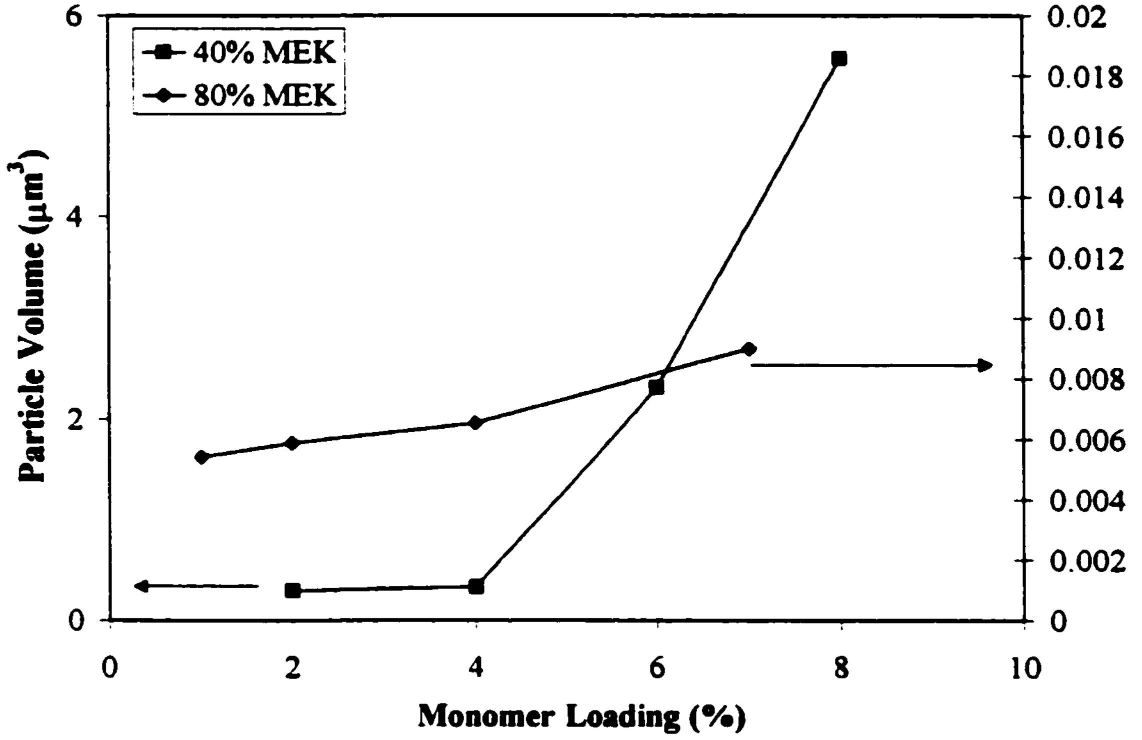

Figure 2.7 - Effect of Monomer Loading on Particle Diameter

2.6.4 Mechanistic Aspects of Microgel and Microsphere Formation

As mentioned previously, the preparation of microgels by polymerization of crosslinking monomers in dilute solution has been demonstrated many times in the past.[6,20-22] This work illustrates an example of microgel preparation with relatively high crosslinker concentrations where subtle changes in solvency can lead to different morphologies. The key question here concerns the cause for the morphology transition from microspheres to microgels. This question can be answered based on differences in the mechanisms of nucleation for these two morphologies.

Microsphere Formation Mechanism

A proposed mechanism for the formation of microspheres (40 vol% MEK) is shown in Figure 2.8. The reaction proceeds in three stages; oligomer formation, nucleation and particle growth. The oligomer formation stage is the conversion of monomer to oligomer as in a classical solution polymerization. These oligomers can then undergo three processes; continued growth by intermolecular reactions, intramolecular crosslinking and cyclization. All three of these processes cause a decrease in the entropy of mixing and hence, contribute to the entropic desolvation of the oligomers. The insoluble oligomers then homocoagulate to form particle nuclei (particle nucleation step in Figure 2.8). As discussed earlier, the ultimate particle volume for DVB-55/MAn microspheres does not scale linearly with monomer concentration (see Figure 2.7). This supports the existence of this homocoagulation step which would be expected to be concentration-dependent. At higher monomer concentrations, the homocoagulation step would be more efficient and produce a proportionally smaller number of particle nuclei. These nuclei would then ultimately result in the larger final particles observed at higher monomer concentrations. Particle nucleation continues only until there are enough particles to capture all newly formed oligomers from solution.

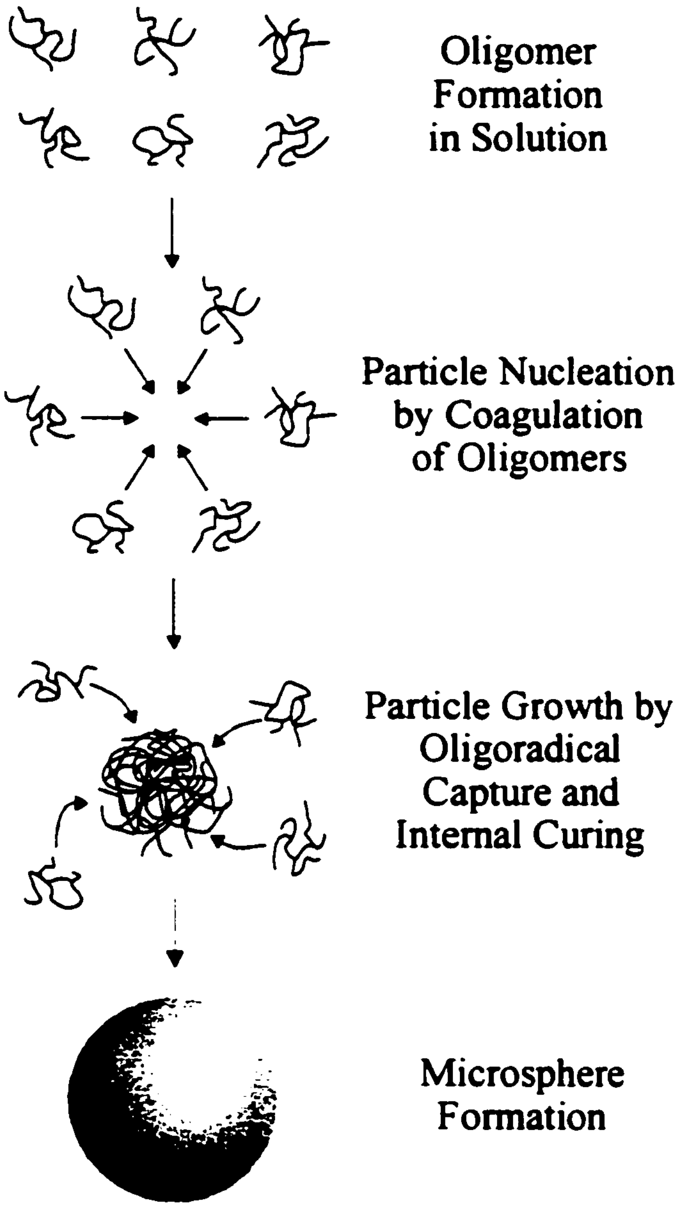

Figure 2.8 - Microsphere Formation Mechanism

Capture of oligomers from solution serves two purposes: continued growth of the particle and steric stabilization. The newly captured oligomers, create a steric layer on the surface of the growing particles that prevents them from coagulating. This gel-like steric layer then continues to crosslink, or "cure", thereby causing growth of the particle core. Simultaneously, more oligomers are captured from solution to regenerate the steric layer. In the case of the DVB-55/MAn system, these processes continues until effectively all the monomer is consumed. A marginal solvent, like 40% MEK / 60% Hp, is necessary in these systems to provide a good enough solvent to swell the steric layer but poor enough to allow the crosslinking reactions that cause nucleation and curing.

Microgel Formation Mechanism

There are a number of key observations for the microgel systems that differ from the reactions that produce microspheres. When the effect of monomer concentration was studied for a reaction solvent composition of 80 vol% MEK, the final microgel volumes were unaffected by varying the monomer concentration, contrary to the results at 40 vol% MEK. Since the volume of the microgels is unaffected by monomer concentration, there cannot be a concentration-dependent homocoagulation step at the particle nucleation stage. In the absence of homocoagulation, a linear relationship between microgel volume and monomer concentration is expected. However, the microgel volume remained constant in this case which indicates that another effect is acting on this system that prevents the microgels from growing beyond their final diameter of ~100 nm. The proposed mechanism of microgel formation in these systems is outlined in Figure 2.9.

In this case, the reactions occur in only two stages; oligomer formation and microgel

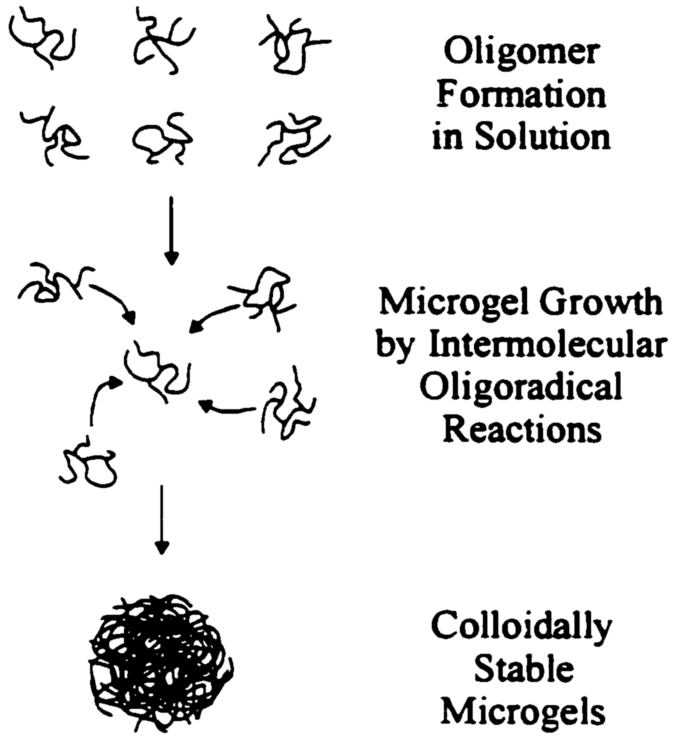

Figure 2.9 - Microgel Formation Mechanism

growth. Oligomer formation is similar to that in the microsphere formation mechanism with the exception that the oligomers are more swollen in 80 vol% MEK. The microgel growth stage occurs by intermolecular reactions between oligomers. In addition to these bimolecular reactions, intramolecular crosslinking and cyclization also occur. Under conditions of increased solvency such as in 80 vol% MEK, it is expected that cyclization will predominate since internal crosslinking will be inhibited by the highly swollen nature of the forming polymer network. This dominance of cyclization contributes to the fact that the growing microgels do not desolvate as in the case of microsphere formation. Instead, these species continue to react with oligomers and monomer until they reach this limiting diameter of ~100 nm at which point growth ceases. This cessation of growth may be caused by one of two effects: (1) a predominance of cyclization may result in a reduced number of vinyl bonds at the microgel's surface being accessible to incoming oligomers, or (2) the increased solvency in this case may cause enhanced steric stabilization when the number of polymer chains at the microgel surface reaches a sufficient density. This increased stabilization would inhibit reactions with incoming oligomers and thereby limit further growth.

Another key difference between the microgel and microsphere mechanisms is that this limiting diameter would suggest that for the reactions to go to completion, new microgels must be formed throughout the course of the reaction. This is in clear contradiction to the distinct nucleation period of the microsphere-forming reactions.

2.7 Conclusions

The crosslinking copolymerization of divinylbenzene and maleic anhydride can be used to prepare different polymer morphologies by varying the reaction solvency and crosslinker concentration. Coagulum results under the poorest solvency conditions while space-filling macrogel is formed in the best solvents. The two most interesting morphologies, microspheres and microgels are formed at intermediate solvencies and by significantly different mechanisms. Microsphere nucleation appears to occur through a concentration-dependent coagulative process that stops early in the polymerization. Microgel nucleation on the other hand continues throughout the polymerization, leading to a constant final microgel diameter that is independent of monomer loading. Varying the crosslinker concentration has little effect under conditions of poor solvency, such as 40 vol% MEK, where the polymer enthalpically desolvates to form microspheres. Conversely, varying the crosslinker concentration under conditions of good solvency, i.e. 80 vol% MEK, dramatically affects the resulting morphology through control of the swelling of the forming microgels which suggests that under these conditions, the formation of microgels is, primarily, an entropically driven process.

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Chapter 3 - An Investigation of the Effects of Increased Reaction Rates on Precipitation Copolymerization

3.0 Introduction

In the previous chapters, it has been shown that precipitation polymerization of divinylbenzene and maleic anhydride results in a number of interesting polymer morphologies. These morphologies result from changes in the solvency of the reaction medium and was explained in terms of a synergistic effect of solvency and crosslinking.

A factor that has yet to be considered in these processes is the rate of polymerization. The rate of divinylbenzene-maleic anhydride copolymerization is expected to be considerably higher than that of divinylbenzene alone because electron-donating monomers, like styrene, copolymerize with electron deficient monomers such as maleic anhydride by what has become known as a charge transfer mechanism, to form alternating copolymers. The rates of charge transfer reactions are considerably greater than those of classical free radical polymerizations. The reasons for this increased rate are discussed in Section 3.2.

This chapter therefore begins with a discussion of the basics of free radical polymerization kinetics, followed by a description of charge transfer polymerizations.

3.1 Free Radical Polymerization Kinetics

A free radical polymerization reaction can be broken down into three stages: initiation, propagation and termination (Scheme 3.1).[1]

Initiation

$$\mathrm{I} \xrightarrow{k_d} 2\ \mathrm{R}\bullet$$

$$\mathrm{R}\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{R\text{-}M}\bullet$$

Propagation

$$\mathrm{R\text{-}M}\bullet + n\mathrm{M} \xrightarrow{k_p} \mathrm{R\text{-}M_nM}\bullet$$

Termination

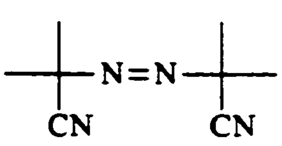
$$\mathrm{R\text{-}M_nM}\bullet + \mathrm{R\text{-}M_mM}\bullet \xrightarrow{k_{tc}} \mathrm{R\text{-}M_{(m+n+2)}\text{-}R}$$

$$\mathrm{R\text{-}M_nM}\bullet + \mathrm{R\text{-}M_mM}\bullet \xrightarrow{k_{td}} \mathrm{R\text{-}M_{n+1}} + \mathrm{R\text{-}M_{m+1}}$$

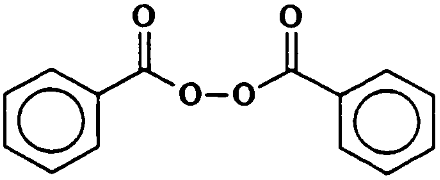
Scheme 3.1 - Stages of Free Radical Polymerization

3.1.1 Initiation

The first step in free radical polymerization is the initiation reaction which occurs by decomposition of a free radical initiator, **I**, to produce two radical species (**R•**). Common examples of free radical initiators are 2,2'-azobisisobutyronitrile (AIBN), (**3.1**), and benzoyl peroxide (BPO), (**3.2**). These molecules are thermally labile and decompose homolytically into



(3.1)



(3.2)

two initiating radicals upon heating. The rate at which these radicals are produced is described by Equation 3.1.

$$\frac{d[R\bullet]}{dt} = 2k_d[I] \qquad (3.1)$$

These radicals may then dimerize, decompose further, or, desirably react with a molecule of monomer to produce the radical species, **R-M•**. Although a rate constant, k_i, is given for this reaction, it is more common in polymer chemistry to describe it in terms of the initiator efficiency, f. This efficiency is given as the fraction of initiator radicals that are captured by monomer. Consequently, the overall rate of initiation can be expressed as in Equation 3.2.

$$R_i = 2f\,k_d[I] \qquad (3.2)$$

3.1.2 Propagation

Propagation reactions involve reactions of the initiating radical with many monomer molecules to produce the polymer chain. The rate of this reaction, R_p, is dependent on both the monomer concentration, **[M]** and the radical concentration, **[M•]**, as shown in Equation 3.3.

$$R_p = k_p[M][M\bullet] \qquad (3.3)$$

3.1.3 Termination

Termination occurs when the radical chain ends of the polymer molecules react to become inactive. Two different mechanisms for termination are shown in Scheme 3.1. The first mechanism is known as termination by combination and occurs when two radicals react to form a single bond and hence result in one inactive chain. The molecular weight of this chain is equal to the sum of the weights of the two reacting polymer chains. The second mechanism, termination by disproportionation, involves hydrogen abstraction from the penultimate carbon of one active polymer chain by another active chain. This results in two inactive polymer chains, one with a residual double bond, resulting from the hydrogen abstraction. For styrenic monomers, termination occurs almost exclusively by combination while disproportionation is more common in acrylic monomers. The rate constant for termination incorporates both mechanisms as shown in Equation 3.4.

$$k_t = k_{tc} + k_{td} \qquad \textbf{(3.4)}$$

The overall rate of termination is second order with respect to the radical concentration as shown in Equation 3.5.

$$R_t = 2k_t[M\bullet]^2 \qquad \textbf{(3.5)}$$

3.1.4 Overall Rate of Polymerization

To derive an overall rate of polymerization from the equations above, the concentration of radicals in a polymerization system must be known. This poses a problem as this is a difficult quantity to measure. Consequently, the steady state assumption was proposed to simplify the situation. This assumption suggests that, after a very short period of time, the concentration of radicals in a free radical polymerization is actually constant because the rate of initiation and the rate of termination are approximately equal, as expressed in Equation 3.6.

$$R_i = R_t \qquad \textbf{(3.6)}$$

Substituting Equations 3.2 and 3.5 into Equation 3.6, an expression for [M•] can be derived as

$$[M\bullet] = \left[\frac{f\,k_d[I]}{k_t}\right]^{1/2} \qquad \textbf{(3.7)}$$

shown in Equation 3.7. Now we have the radical concentration in terms of variables that are much easier to determine and which allows us to proceed towards an expression for the overall rate of polymerization, the rate at which monomer is consumed. This rate can be expressed in terms of the rates of the two processes that consume monomer, initiation and propagation (Equation 3.8).

$$-\frac{d[M]}{dt} = R_i + R_p \qquad \textbf{(3.8)}$$

Assuming high molecular weight polymer is being produced, propagation consumes a great deal more monomer than initiation and hence $R_p >> R_i$. Consequently, the overall rate of monomer consumption can be expressed in terms of the rate of propagation alone. In addition to this assumption, Equation 3.7 can be substituted into Equation 3.8 resulting in Equation 3.9.

$$-\frac{d[M]}{dt} = k_{app}[M] \qquad \textbf{(3.10)}$$

$$-\frac{d[M]}{dt} = R_p = k_p[M][M\cdot] = \left(\frac{k_p}{k_t^{1/2}}\right)[M](f\,k_d[I])^{1/2} \qquad \textbf{(3.9)}$$

When the initiator is available in large excess, the initiator concentration can also be taken as a constant, and hence all the terms on the right side of Equation 3.9 except the monomer concentration can be grouped into a single rate constant as in Equation 3.10, where k_{app} is the apparent first order rate constant.

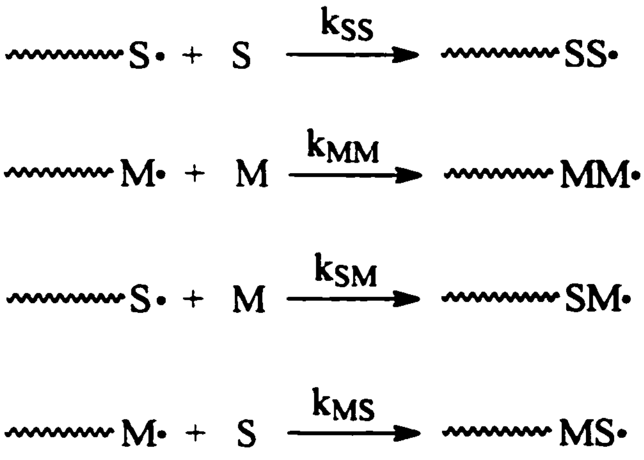
This simple first order differential can be solved by separation of variables resulting in Equation 3.11.

$$\ln\frac{[M_0]}{[M]} = k_{app}t \qquad \textbf{(3.11)}$$

Now the apparent rate constant for polymerization can be determined from the slope of a plot of $\ln([M_0]/[M])$ versus time, t.

3.2 Charge Transfer Copolymerization

As mentioned above, electron-donating monomers copolymerize with strong electron-acceptor comonomers, like maleic anhydride, to form highly alternating copolymers. In addition, these reactions proceed at elevated rates compared to classical free radical polymerization. Copolymers of styrene and maleic anhydride have been used as the standard for these alternating systems and consequently have been studied extensively. The mechanism of these reactions has



Scheme 3.2 - Propagation Reactions in the Copolymerization of Styrene and Maleic Anhydride

been disputed for many years and several schools of thought have emerged. Two of the more predominant mechanisms are the polar transition states theory[2] and the complex participation models.[3-5] Clarification of the copolymerization itself will facilitate explanation of these models. Scheme 3.2 outlines the four propagation reactions that can occur in a styrene-maleic anhydride copolymerization. The first two reactions exhibit self-propagation while the second are the cross-propagation reactions. The rate constants for each reaction are also given in Scheme 3.2. The reactivity ratios for this copolymerization are defined as shown in Equation 3.12.

$$r_S = \frac{k_{SS}}{k_{SM}} \qquad r_M = \frac{k_{MM}}{k_{MS}} \qquad (3.12)$$

For copolymerization of styrene and maleic anhydride, the values of these reactivity ratios approach zero, which suggests a strong tendency towards cross-propagation. This propensity to crosspropagate leads to the alternating microstructure in the products as well as the increased reaction rates. The models that attempt to explain this trend are outlined below.

3.2.1 Polar Transition States Theory

The tendency towards alternation in these systems has been explained in terms of the transition state of the polymer chain end as a monomer unit is added. The two potential transition states for a styrene-maleic anhydride copolymerization are shown in Figure 3.1. The uppermost set of "resonance" structures in Figure 3.1 shows the addition of a styrene monomer to a maleic anhydride terminus. The structure on the left is the radical transition state which "resonates" with the polarized structure on the right. This essentially involves shifting of electron density toward the

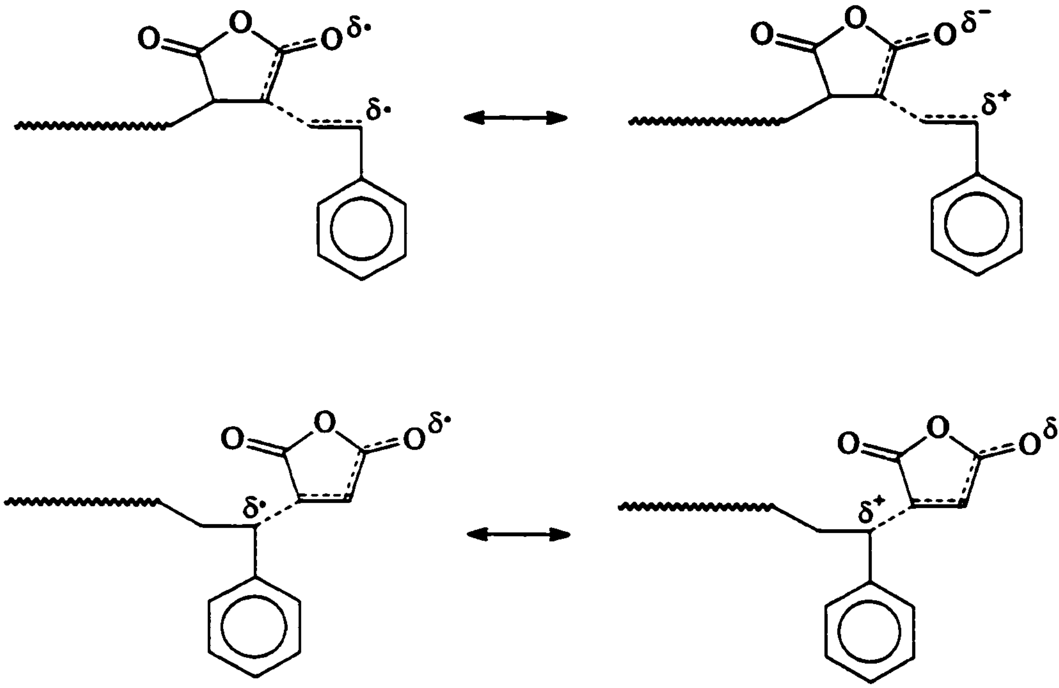


Figure 3.1 - Transition States of Styrene-Maleic Anhydride Copolymerization

electronegative oxygen atom in the anhydride group. A similar set of "resonance" structures are shown for the addition of a maleic anhydride monomer to a styrene terminus in the lower half of Figure 3.1. The high degree of charge separation in these structures stabilizes the transition states, resulting in a lower activation energy for the cross-propagation reactions. This reduction in the activation energy explains both the elevated rates of reaction and the alternating microstructure of the products, since these polarized transition states are only possible when the added monomer is different from the terminal unit.

3.2.2 Complex Participation Models

The complex participation models propose that a charge transfer complex between maleic anhydride and styrene, shown in Figure 3.2, is involved in the copolymerization reaction. Again, this complex is formed due to strong electron donor/acceptor interactions of the two monomers.

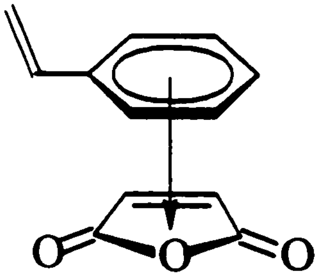


Figure 3.2 - CT Complex of Styrene and Maleic Anhydride

The existence of these complexes has been proven using both UV absorption and ^{1}H-NMR studies.[4] Addition of this complex to the radical chain end would result in the alternating microstructure. There are a number of experimental observations that support this theory. Firstly, copolymerizations carried out at elevated temperatures (>120 °C) produce random copolymers.[5] At this temperature, no UV absorbance was observed for the complex indicating that it was completely dissociated. The second reason that it is likely to have a role in the copolymerization is that the rate of reaction appears to be dependent on the concentration of the charge transfer complex where the highest reaction rates are observed when the complex concentration is the highest.

There are two possible mechanisms by which the complex can participate in copolymerization. The first is the complex addition model where both monomer units add to the chain end at the same time. The other mechanism, and probably the more likely one, is the complex dissociation model. In this case, one monomer unit in the complex reacts with the chain end and the other monomer is dissociated to become free monomer. This model was forwarded to replace the complex addition model because of an argument based on the exothermicity of polymerization. When a monomer unit is added to a polymer chain end, between 40 and 60 kcal/mol of energy is released. Meanwhile, the binding energy of the complex itself is only about 20 kcal/mol and consequently the complex does not remain intact during polymerization. If both monomers in the complex do not add simultaneously, the alternating microstructure of the products must still be related to the structural differences in the comonomers.

A molecular orbital approach has also been utilized to explain both the selectivity and the high reactivity of this type of system. The reactive orbital of a radical chain end is the SOMO

(Singly Occupied Molecular Orbital) as shown in Figure 3.3.

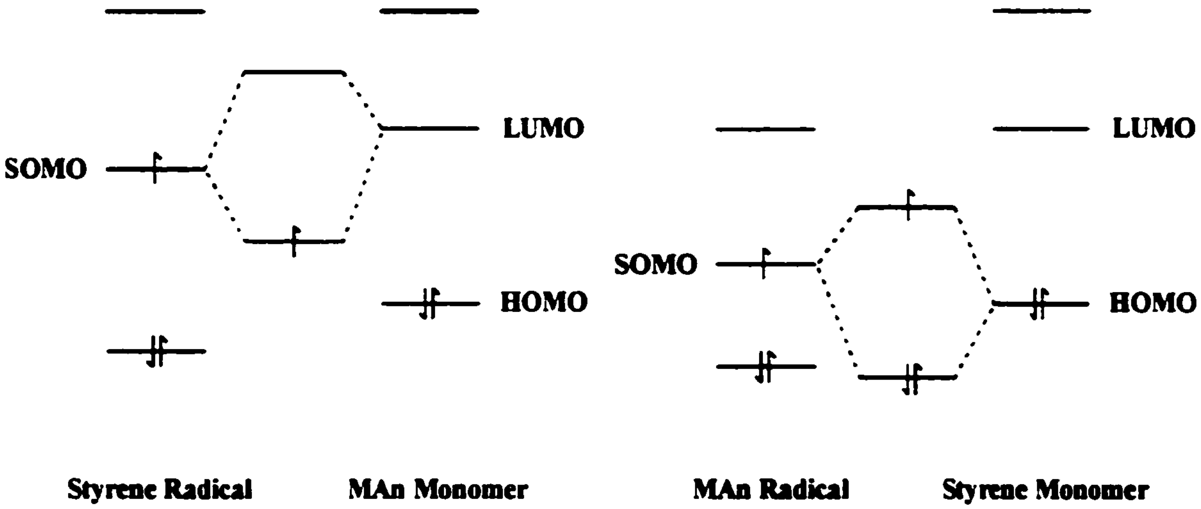


Figure 3.3 - MO Approach to Alternating Copolymerization

A polymer chain end with a nucleophilic radical like styrene, on the left in Figure 3.3, has a high energy SOMO, and hence reacts with the LUMO (Lowest Unoccupied Molecular Orbital) of an incoming monomer. Conversely, an electrophilic radical like maleic anhydride has a lower energy SOMO, which reacts with the HOMO (Highest Occupied Molecular Orbital) of the incoming monomer. The difference in energy between the SOMO of the chain end and the reactive orbital of the incoming monomer will determine the rate of the reaction. Styrene has a higher energy HOMO than maleic anhydride and hence will preferentially react with a maleic anhydride chain end. Similarly, maleic anhydride has a lower energy LUMO and will react preferentially with a styrene radical. When the monomers are present in the complexed form, this MO interaction is even more favourable because complexation increases the energy of the styrene HOMO and decreases the energy of the maleic anhydride LUMO. This approach explains the enhanced reactivity of this type of reaction, the role of the complex and the resulting alternating microstructure.

3.3 Objective and Scope of Research

It was the objective of this work to study the effect of an increased reaction rate on precipitation copolymerization. When extending this type of reaction to the copolymerization of divinylbenzene-55 and maleic anhydride, we observed a number of unusual results including extremely high conversions (>95%), small particle diameters (0.4-1.0 μm) and unexpected monomer loading effects. The key difference between this reaction and those which we had previously studied was that the rate of reaction was significantly higher and it was thought that this feature was at least partly responsible for this interesting behaviour.

Precipitation polymerizations of this type are thought to occur in three stages: oligomer formation, particle nucleation and particle growth. The oligomer formation stage is a typical solution polymerization of monomer that continues until the oligomers reach a point of insolubility, caused by crosslinking. At this stage, particle nucleation takes place by coagulation of these oligomers to form particle nuclei. These particle nuclei then grow by capture of oligomers from solution via oligoradical reactions with unreacted vinyl groups on the surface of the nuclei.[6] In the past, it was thought that a key to the formation of monodisperse polymer particles, is that the particle nucleation stage is short such that all the nuclei have similar opportunities for subsequent growth, resulting in similar ultimate particle diameters. In this type of system, nucleation will only continue until there is a sufficient amount of particle nuclei surface area to capture all the newly formed oligomers before they have the opportunity to nucleate. After this stage, only particle growth occurs and hence the total number of particles is fixed. Obviously, all these steps in the polymerization are sensitive to the experimental conditions including the rate of propagation of the forming oligomers.

An analysis of the effects of the high reaction rates of the DVB/MAn system on precipitation copolymerization is the focus of this chapter. The overall rates of polymerizations for DVB-55/MAn copolymerization were measured and compared to rate values for DVB-55 homopolymerization. The effects on particle nucleation and growth were investigated by acquisition and characterization of samples taken throughout the course of reactions. In addition, the difference in the reactivity between the two reactions was utilized to prepare some interesting, new core-shell type particles.

3.4 Experimental

Materials

Maleic anhydride (MAn, 99%, Aldrich) was recrystallized from chloroform prior to use. The inhibitor was removed from the divinylbenzene (DVB-55, 55% mixture of isomers, technical grade, Aldrich) by running the neat monomer through a 20 cm silica gel column. The cosolvents, methyl ethyl ketone (MEK) and heptane (Hp), were both reagent grade and were used as received from Caledon Laboratories. 2,2'-Azobisisobutyronitrile (AIBN, Eastman Kodak) was recrystallized from methanol prior to use.

Kinetic Experiments

The conversion experiments were carried out on a larger scale in order to be able to obtain multiple samples from a single reaction. A typical reaction procedure was as follows:

In a 1L three-neck flask, 500 mL of the solvent mixture was preheated to 70 °C and degassed with N_2 for 15 minutes prior to addition of the monomers and initiator. After this period, maleic anhydride (10.0 g, 0.10 mol) was dissolved in the solvent followed by addition of 10 mL (0.10 mol of vinyl groups) of DVB-55. The reaction was then initiated by the addition of AIBN (0.383 g, 2.3 mmol). Samples (20 mL) were removed at various time intervals throughout the reaction, and the samples were quenched in an ice bath and inhibited with the addition of 100 mg (0.91 mmol) of hydroquinone.

Gravimetric Conversion

Conversion measurements were carried out gravimetrically by placing 4 mL aliquots of the reaction mixtures in preweighed aluminum pans. The samples were allowed to dry at ambient temperature for four days then dried to a constant weight in vacuo at 70 °C.

Electron Microscopy and Light Scattering

As described in Chapter 2.

3.5 Results and Discussion

3.5.1 Rate Measurements

The rate of copolymerization of DVB-55 and maleic anhydride is significantly higher than that of DVB-55 alone. Figure 3.4 shows the dependence of polymer conversion on reaction time for two solvent mixtures, 40 vol% MEK / 60 vol% Hp and 80 vol% MEK / 20 vol% Hp. Curves for DVB-55 homopolymerization in the same solvent mixtures are also shown for comparison.

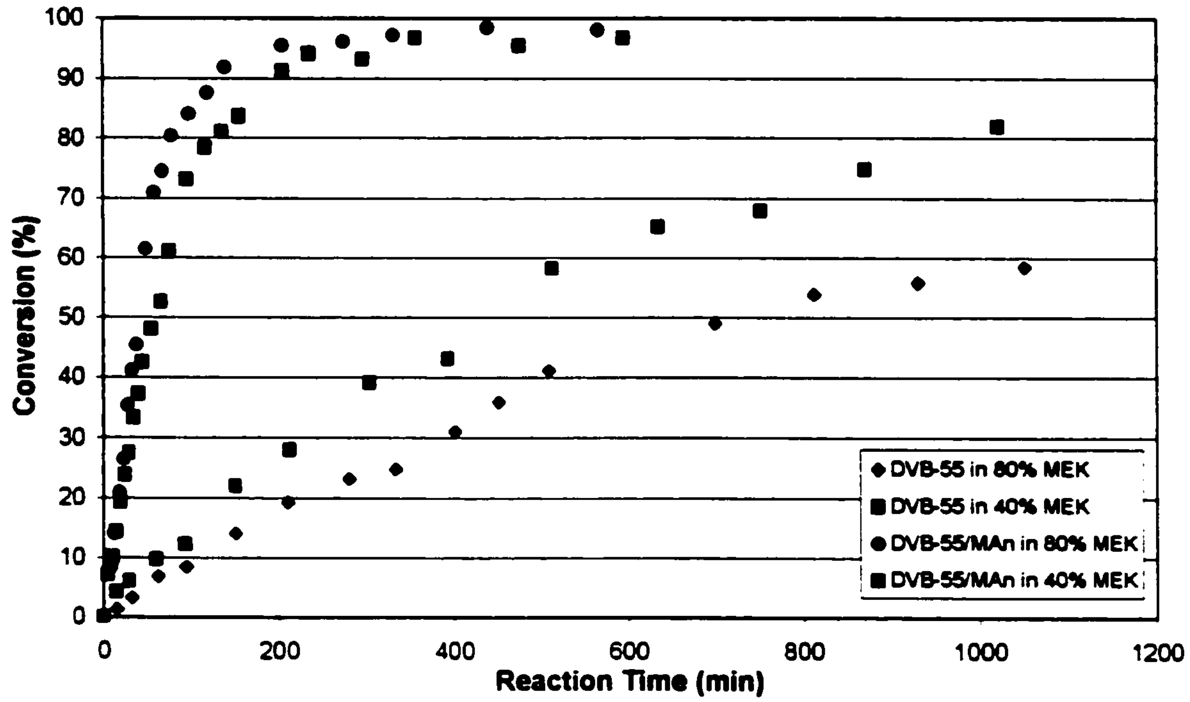


Figure 3.4 - Conversion of DVB-55 Copolymerizations with and without MAn

From these data, the residual monomer concentration in the feed can be calculated. Linear regression of the initial portions of monomer concentration versus reaction time plots yields the overall rate of polymerization, R_p. For the DVB-55 reactions this meant regressions up to approximately 200 minutes while for the DVB-55/MAn reactions, the time range was 0-50 minutes. Table 3.1 shows the values of these rates for the four reactions considered above. These data indicate that the rates of copolymerization for the DVB-55/MAn system are approximately one order of magnitude higher than the DVB-55 homopolymerizations.

Table 3.1 - Overall Rates of Polymerization for DVB-55 Copolymerization

Comonomers	Solvent Mixture	R_p (mol L^{-1} s^{-1})	r^2	Morphology
DVB-55	80% MEK / 20% Hp	4.0×10^{-9}	0.993	Macrogel
DVB-55	40% MEK / 60% Hp	5.6×10^{-9}	0.989	Microspheres
DVB-55/MAn	80% MEK / 20% Hp	7.4×10^{-8}	0.997	Microgels
DVB-55/MAn	40% MEK / 60% Hp	5.1×10^{-8}	0.995	Microspheres

There are two important considerations when comparing these rates of reaction: solvent effects and the effect of the morphology of the copolymers produced.

Solvent Effects on DVB Copolymerization

The choice of reaction solvent can have significant effects on the rate of free radical polymerizations. These effects are related to the polarity and the viscosity of the solvent which can influence the initiation step of the polymerization. The rate of decomposition of azo initiators, like

AIBN, increases up to three-fold with increasing dielectric constant of the reaction solvent.[1] The solvent viscosity influences the initiator efficiency due to the so-called "cage reaction". In this case, the two radicals that result from decomposition of the initiator molecule can recombine resulting in a reduction in the initiator efficiency. The degree to which this process occurs is related to the rate of diffusion of the initiator fragments away from each other following decomposition. Consequently, the rate of diffusion is lower in more viscous solvents and the cage reaction is more predominant.

Unlike the initiation reaction, the choice of solvent has been shown to have little effect on the rate of the propagation reaction for styrene homopolymerization.[7] This observation can be extended to DVB copolymerization since the propagating radicals are similar in structure.

Based on these observations, classical free radical polymerizations would be expected to have higher rates in pure MEK than in pure Hp. This should occur because MEK is more polar, and lower in viscosity, thereby increasing the rate of decomposition of the initiator and the initiator efficiency. However, when comparing the rates of DVB copolymerization in 80% and 40% MEK, it is apparent that the behaviour is in fact reversed. Here, the rate of copolymerization in 40% MEK is approximately 25% higher than the copolymerization in 80% MEK.

Solvent Effects on DVB/MAn Copolymerization

The rate of copolymerization of styrenic monomers with maleic anhydride is sensitive to the concentration of the charge transfer complex in the reaction medium. Accordingly, the reaction solvent plays a key role in the equilibrium between free and complexed monomer. Polar solvents such as MEK competitively complex the maleic anhydride monomer and thereby reduce the concentration of charge transfer complex in the reaction medium. The rate of reaction can decrease up to two-fold in polar solvents compared to non-polar solvents like heptane.[5] In the case of DVB-55/MAn copolymerization, one would expect the rate to decrease with increasing proportions of MEK. However, both reactions still have a large excess of MEK to DVB and so the competitive complexation of the MAn may not be very different. In addition, the equilibrium constant for the complexation of MEK with MAn is approximately twice that of styrene with MAn.[3] This fact may even further diminish the effect of the solvent since the MEK will preferentially complex with MAn. When considering the data in Table 3.1, this appears to be the case since the rate in 80% MEK is higher than in 40% MEK. This suggests that the morphology produced plays a more significant role in determining the reaction rate than the choice of reaction solvent.

Morphology Effects

The results of the copolymerization rate of DVB-55 alone suggest that the rate is strongly affected by the morphology of the products. One such effect is the occlusion of radicals which would be expected to be most predominant in the densest morphology, microspheres. Conversely, the rate of reaction for the microgel morphology should be higher since they are highly swollen. This swollen morphology will be more accessible to incoming radicals and monomer and hence should not inhibit reactions of trapped radicals near the centre of the polymer molecules.

When considering the results for the DVB-55 homopolymerization shown in Table 3.1, the rate of reaction for the microsphere reaction is actually faster than that of the macrogel reaction. So in this case, the relative rates of the reaction appear to be the opposite of what we would expect in terms of both solvent effects and morphology effects.

For the DVB-55/MAn reaction system, the rate of reaction for the microsphere reaction is significantly lower than for the microgel-forming reaction. This result was expected since the rate of consumption of monomer would be reduced if some of the residual vinyl groups become inaccessible to oligoradicals. This result also shows that the morphology of the copolymers produced is more significant than the effect of solvent on the rate of copolymerization for this system since the rates behave oppositely from what would be expected in terms of the reaction solvent but conform to the expected morphology effects.

3.5.2 Effect of Reaction Rate on Precipitation Polymerization

A. Particle Nucleation

The focus of this study was to show the effects of high reaction rates on precipitation polymerization. Particle nucleation is strongly affected by the rate at which polymer is produced. In order to understand this effect, we must break down the observables of this kind of reaction.

The first characteristic of the reaction is the cloud point which can be considered the onset of particle nucleation. For the DVB-55 reaction in 40% MEK, the cloud point occurs at approximately 1 hour and 45 minutes. In contrast, the DVB-55/MAn reaction in 40% MEK clouds at around 35 minutes, clearly demonstrating the increased reactivity of this latter system.

The second property of these systems that we will discuss is the size and dispersity of the particle nuclei immediately following the cloud point (~5% conversion). Figure 3.5 shows a TEM image of the nuclei from a DVB-55/MAn reaction in 40% MEK, a microsphere reaction. The nuclei for this reaction are polydisperse, with a coefficient of variance of 27%, which is counter to what we have observed in the past for DVB-55 alone where the nuclei were narrow disperse and significantly larger. This difference occurs because the rate of polymerization in these systems will determine the length of the nucleation period. In the case of fast reactions, like DVB-55/MAn

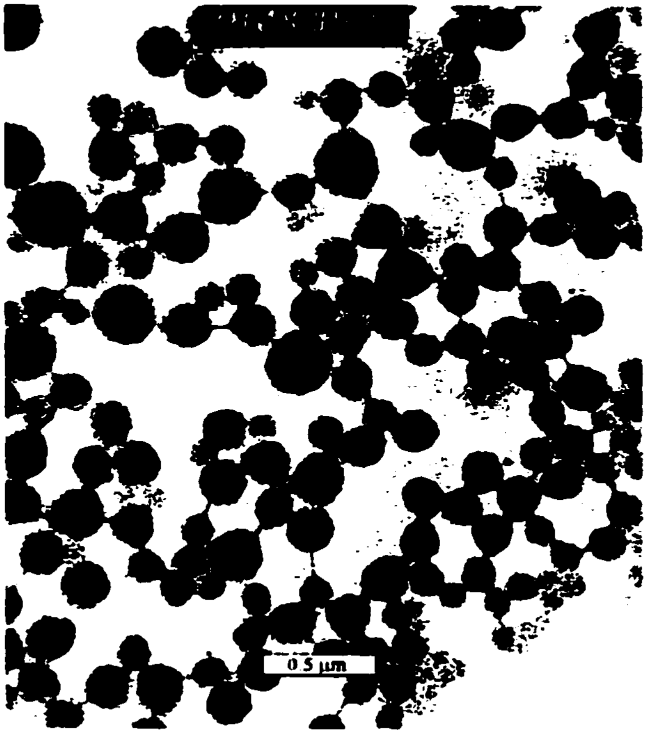


Figure 3.5 - Nuclei of DVB-55/MAn Microspheres, 5% conversion, d = 173 nm, CV% = 27

copolymerization, the first particles are nucleated quickly. Nucleation then continues until enough particle nuclei are generated to capture all the newly formed oligomers. Critical to this oligomer capture is the rate of diffusion of the oligomers compared to the rate at which they grow and crosslink since these oligomers have to diffuse to a particle's surface before they nucleate themselves. Oligomers ofDVB-55 and DVB-55/MAn will diffuse at approximately the same rate but the DVB/MAn oligomers grow much faster. This means that these oligomers travel much shorter distances before nucleating themselves. Consequently, a larger number of nuclei are required to capture the oligomers to prevent further nucleation. This results in an extended nucleation period and smaller nuclei. The fact that the nuclei are polydisperse results because the first particles are nucleated early in the reaction and have the opportunity to grow for a longer period than the later formed nuclei. In the case of the DVB-55 reaction, the nuclei are narrow disperse because the nucleation period is shorter.

B. Particle Growth

Once sufficient surface area of particle nuclei is produced to capture all the newly formed oligomers, only particle growth occurs. Particle growth is also affected by the rate of copolymerization where there are two models to consider; reaction-controlled and diffusion-controlled growth. The former involves systems with lower reactivity such that the rate of oligomer capture is dependent on the rate at which oligomers are produced and the rate of their reaction with the particle surfaces. Diffusion-controlled growth on the other hand, occurs for reactions with high rates where the rate of particle growth is dependent on the rate of diffusion of the oligomers and particle nuclei in the reaction medium.

The nuclei from DVB-55 reactions are narrow disperse. It follows then that these particles should grow into narrow or monodisperse particles. More interesting behaviour is observed for the DVB-55/MAn copolymerization, as shown in Figure 3.6.

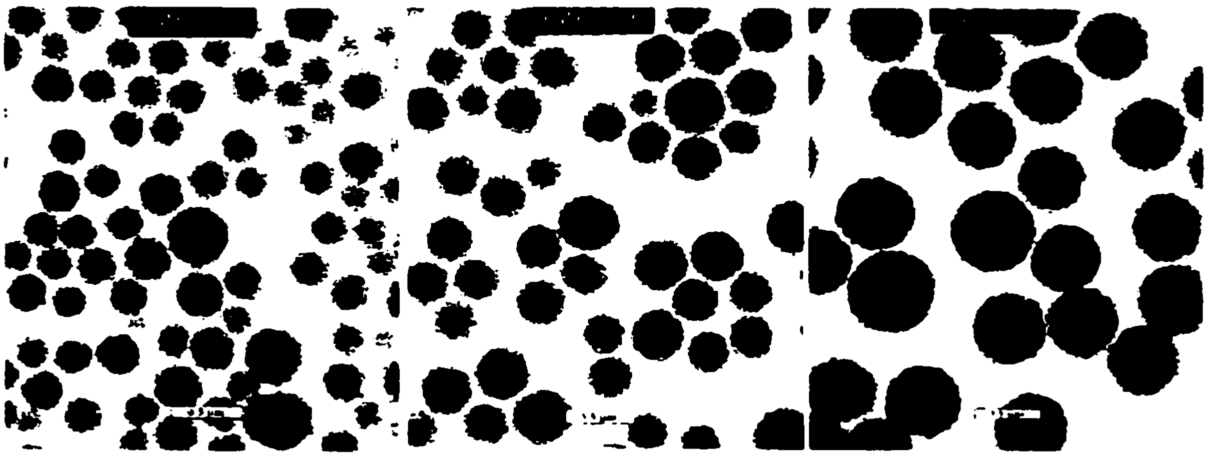


Figure 3.6 - Particle Size Distribution Develpoment for DVB/MAn Microspheres: From left to right; a) 12% conv., d = 277 nm, CV% = 17 b) 19% conv, d = 350 nm, CV% = 13 c) 96% conversion, d = 636 nm, CV% = 8

These TEM images show as series of samples taken during the course of a reaction at various degrees of conversion. The particle nuclei for the DVB-55/MAn reaction are clearly polydisperse yet still result in narrow disperse particles. There are two possible explanations for this behaviour; coalescence of the nuclei to produce fewer but less disperse nuclei or diffusion-controlled growth of the nuclei.

A simple way to test the first case is to plot the average volume of the individual particles against the conversion of the reaction. A linear relationship here would indicate the absence of coalescence. Figure 3.7 shows this relationship for the DVB-55/MAn reaction in 40% MEK which demonstrates the absence of both further nucleation and significant coalescence. This indicates that we are observing a diffusion-controlled particle growth mechanism.

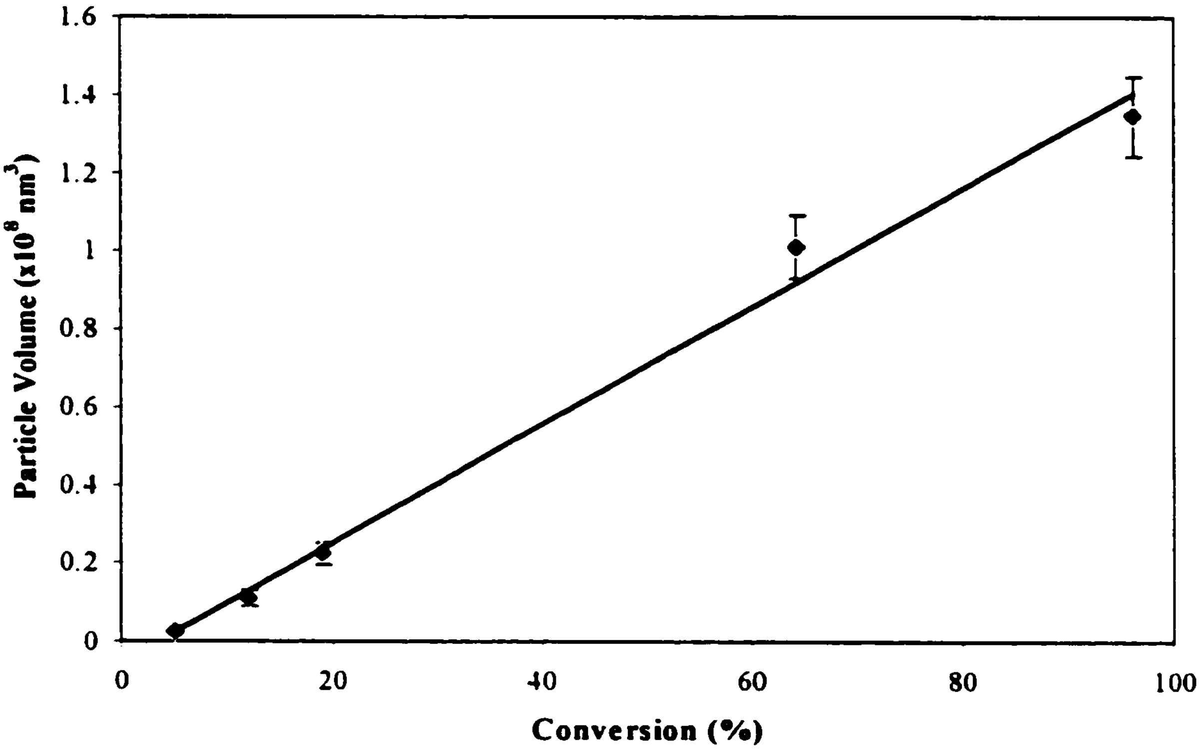


Figure 3.7 - Dependance of Individual Microsphere Volume on Conversion

Diffusion-controlled particle growth in inorganic colloids has been studied for many years. A unique characteristic of such a system is a narrowing of the particle size distribution throughout the course of the reaction. In our system, similar results are observed since the smaller particle nuclei diffuse faster than the larger ones and require less oligomers to cover their surface. Consequently, these nuclei grow at a higher rate than the larger ones resulting in the narrowing of the particle size distribution. These observations along with the high reaction rates of the DVB-55/MAn system support a diffusion-controlled mechanism for the microsphere-forming reaction.

We also were interested in investigating the development of the microgels produced in the DVB-55/MAn reaction in 80% MEK. Figure 3.8 shows the relationship between the average volume of the individual microgels and the polymer conversion. This seeming independence of the microgel volume on conversion demonstrates a fundamental difference in the mechanism of these reactions which was proposed in Chapter 2. Here, the microgels seem to reach a limiting diameter at which point they become colloidally stable and cease to grow. This indicates that for the microgel reaction to proceed to high conversion, new microgels must be generated throughout the course of the reaction in contrast to the microsphere-forming reaction which has a discrete nucleation period as demonstrated by Figure 3.7.

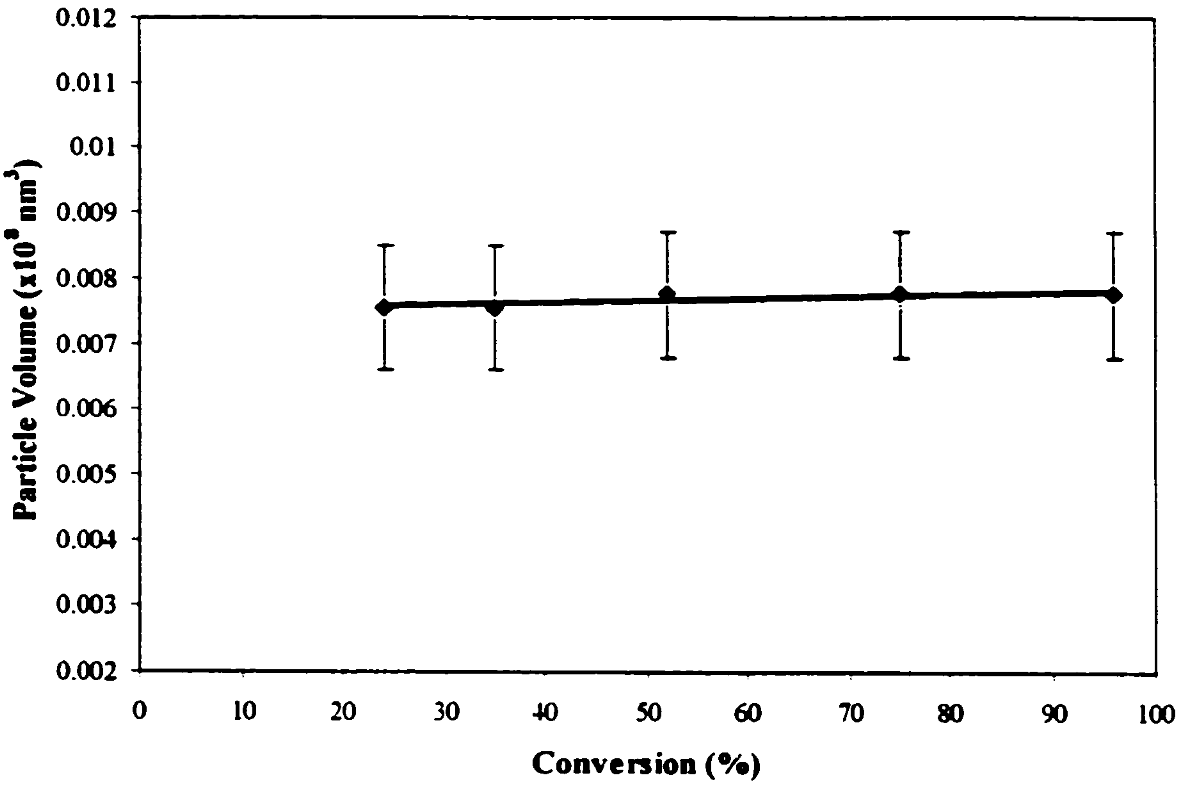


Figure 3.8 - Dependance of Individual Microgel Volume on Conversion

3.5.3 In-Situ Core-Shell Particles

We have utilized the increased reactivity of the DVB-55/MAn system to prepare some interesting new core-shell particles. A DVB-55/MAn copolymerization was carried out where there was a two-fold excess of DVB-55. For these reactions, a solvent composition of 40% MEK / 60% Hp was chosen, where microspheres are formed for DVB-55/MAn and space-filling gel is observed for DVB-55 alone. A TEM image of these particles, which consist of a DVB-55/MAn core and a DVB-55 homopolymer shell, is shown in Figure 3.9. The enhanced reactivity of the

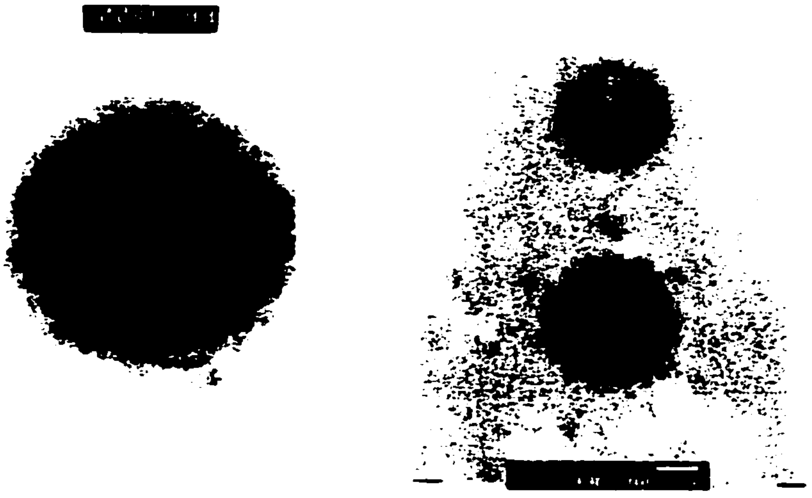


Figure 3.9 - In Situ Core-Shell Particles

DVB-55/MAn system caused preferential copolymerization of these comonomers to form the particle nuclei. These nuclei continued to grow until all the maleic anhydride was consumed at which point a shell of just DVB-55 was formed over the DVB-55/MAn cores. This shell is apparent in the TEM images as the soft, gel-like material on the particle surface. To verify the core-shell structure of these particles, a microtomed sample was imaged and is also shown in Figure 3.9. It appears that the centre of the particles is more dense than the periphery which is very soft and gel-like. The nature of the shell material was confirmed by comparison of the solubility characteristics of these new particles with those of standard DVB-55 and DVB-55/MAn particles. These particles displayed identical solvent behaviour to the DVB-55 particles. The fact that preparation of this type of core-shell particle is possible supports our earlier reports that particle growth in precipitation polymerizations of this type occurs by a radial growth mechanism.

3.6 Conclusions

The increased reactivity of the crosslinking copolymerization of divinylbenzene-55 and maleic anhydride was demonstrated by measurement of the gravimetric conversion versus time. The DVB-55/MAn copolymerization proceeds at a rate one order of magnitude faster than DVB-55 homopolymerization. This elevated reaction rate has pronounced effects on both particle nucleation and growth. The nucleation period in microsphere-forming reactions is extended resulting in smaller, polydisperse nuclei. Particle growth occurs by a diffusion-controlled mechanism which is represented by a narrowing of the particle size distribution over the course of the reaction. Microgels, on the other hand, seem to reach a limiting diameter and then cease to grow. Preparation of in situ core-shell particles with a DVB-55/MAn core and a DVB-55 shell demonstrates that the particles grow by a radial growth mechanism.

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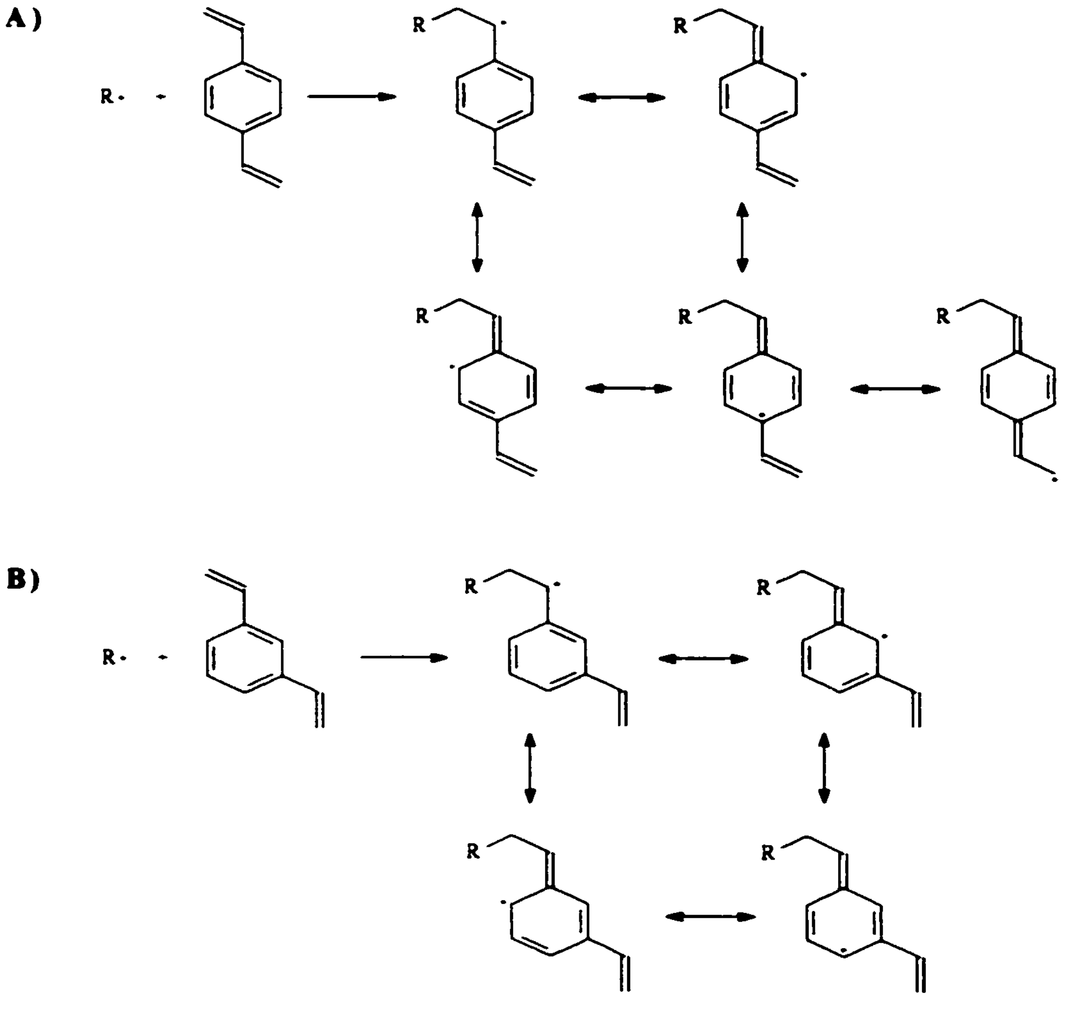
Chapter 4 - The Rate of Consumption of the Various Components of DVB-55 and its Effect on Precipitation Polymerization

4.0 Introduction

As discussed in the first three chapters, the preparation of polymer microspheres and microgels from divinylbenzene-55 and maleic anhydride using precipitation polymerization has posed a number of new challenges that were not encountered with divinylbenzene-55 alone. Some of this unique behaviour originates from the high reactivity of this copolymerization, as shown in Chapter 3. In addition to the high overall rates of copolymerization of styrenic monomers with maleic anhydride, the selectivity of these reactions towards the various components of technical grade divinylbenzene must be considered.

4.1 Reactivity of Isomers of Divinylbenzene and Ethylvinylbenzene

As mentioned previously, technical grade divinylbenzene is composed of four components; *p*-divinylbenzene (~15%), *m*-divinylbenzene (~36%), *p*-ethylvinylbenzene (~12%) and *m*-ethylvinylbenzene (~37%). In the free radical polymerization of these isomers, these components have shown pronounced differences in reactivity.[1-7] In one study, *p*-divinylbenzene was shown to be approximately 7 times more reactive than the ethylvinylbenzene isomers while *m*-divinylbenzene was 4 times more reactive.[8] The enhanced reactivity of the divinyl monomers over the ethylvinylbenzenes stems from the extra vinyl group which statistically increases their chance for reaction. The further increase in reactivity of the *para* isomer of divinylbenzene results from the increased resonance stabilization of its radical species (5 resonance structures) over that of *m*-DVB



Scheme 4.1 - Resonance Structures of *p*-DVB (A) and *m*-DVB (B) Radicals

(4 resonance structures). Scheme 4.1 shows these resonance structures for *p*- and *m*-divinylbenzene.

In the precipitation polymerization of DVB-55, this could lead to interesting morphological properties. However, precipitation polymerization of DVB-55 alone typically only proceeds to about 60% monomer conversion and consequently, this effect is less significant.[9-11] However, the precipitation copolymerization of divinylbenzene-55 and maleic anhydride regularly results in monomer conversions of greater than 95% and so these differing reactivities become much more important.

The reactivity of the individual components of divinylbenzene-55 in reactions incorporating charge transfer comonomers, like maleic anhydride are unknown. Several studies have been carried out involving ternary copolymerization of DVB-55, styrene and maleic anhydride to prepare suspension polymerization particles.[12-14] In all these cases, the DVB-55 was a only a small component and no reactivity information is included. In addition, the crosslinking copolymerization of maleic anhydride and pure *p*-DVB has been investigated and the reactivity ratios for the copolymerization were determined.[15] These ratios indicated that MAn and *p*-DVB form alternating copolymers but unfortunately, this type of study with pure components does not provide information with regards to the selectivity.

4.2 Objective and Scope of Research

It was the objective of the work described in this chapter to measure the relative rates of consumption of the components of DVB-55 in copolymerization with maleic anhydride in order to determine its effect on precipitation polymerization.

This study involved performing a series of large scale reactions with acquisition of samples throughout the course of each reaction. The concentration of each component of DVB-55 in these samples was subsequently measurement by gas chromatography. The data was analyzed using a first order rate equation, similar to Equation 3.11, in order to extract apparent rate constants for the consumption of each component of DVB-55.

4.3 Experimental

Samples used for this study were obtained simultaneously to those in Chapter 3 and hence the materials and reaction conditions are described there.

Conversion by Gas Chromatography

Sample Preparation

Samples were prepared for gas chromatography by addition of 0.15 mL of reaction mixture to 1.35 mL of HPLC grade heptane in a 2 mL vial, which caused precipitation of the polymer and maleic anhydride. The vials were then centrifuged and the supernatant was removed for GC analysis.

GCMS Analysis

Gas chromatography was carried out on a Varian Saturn GCMS system which consists of a Varian 3800 gas chromatograph and a Varian Saturn 2000 ion trap mass spectrometer. The column was a 30 m Varian CP-Sil 8CB-MS silica capillary column with an inner diameter of 0.25 mm. Ultra high purity helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. Injections were 2 μL in volume and the injector was set to 350 °C and to a split ratio of 30:1. Two temperature programs were used; one for the DVB-55/MAn reactions and the other for the DVB-55 reactions. These programs are listed in Tables 4.1 and 4.2. The data was collected at a rate of 1 scan/s with each scan consisting of 8 microscans.

Table 4.1 - DVB/MAn GC Temperature Program

Temperature (°C)	Rate (°C/min)	Hold (min)	Total Time (min)
50	0	0	0
140	15	0	6
290	50	1	10

Table 4.2 - DVB GC Temperature Program

Temperature (°C)	Rate (°C/min)	Hold (min)	Total Time (min)
80	0	0	0
120	7	0	5.71
290	75	0.02	8

The peak area for each analyte were normalized to the area of the internal standard, *p*-xylene, and the areas were quantified using the count of the most abundant ion in the mass spectrum of each analyte and these are listed in Table 4.3.

Table 4.3 - Quantitation Ions for Area Analysis

Analyte	Quantitation Ion
p-Xylene	91
MAn	82
m-EVB	117
p-EVB	117
m-DVB	130
p-DVB	130

4.4 Results and Discussion

Two solvent mixtures were chosen for this study: 40% MEK / 60% Hp and 80% MEK / 20% Hp. These two solvency regimes correspond to the microsphere and microgel regions for DVB-55/MAn copolymerization, respectively. Both a DVB-55/MAn copolymerization and a DVB-55 homopolymerization, for comparison, were carried out for each solvent mixture.

4.4.1 GCMS Analysis of Reaction Components

Figure 4.1 shows a typical chromatogram for the initial reaction mixture of a DVB-55/MAn copolymerization. The peaks were assigned based on the mass of the parent ion and the expected amount of each component. Baseline separation of the peaks for these chromatograms is significantly better than that published for DVB-55 in the past.[1,16]

Figure 4.2 illustrates a series of chromatograms for samples taken from a DVB-55/MAn anhydride copolymerization throughout the reaction. In this example, the percentage figures correspond to the amount of each component that is unreacted at the time of sampling. The difference in reactivity of the comonomers is apparent, as the p-DVB component is consumed at a much higher rate than the other three.

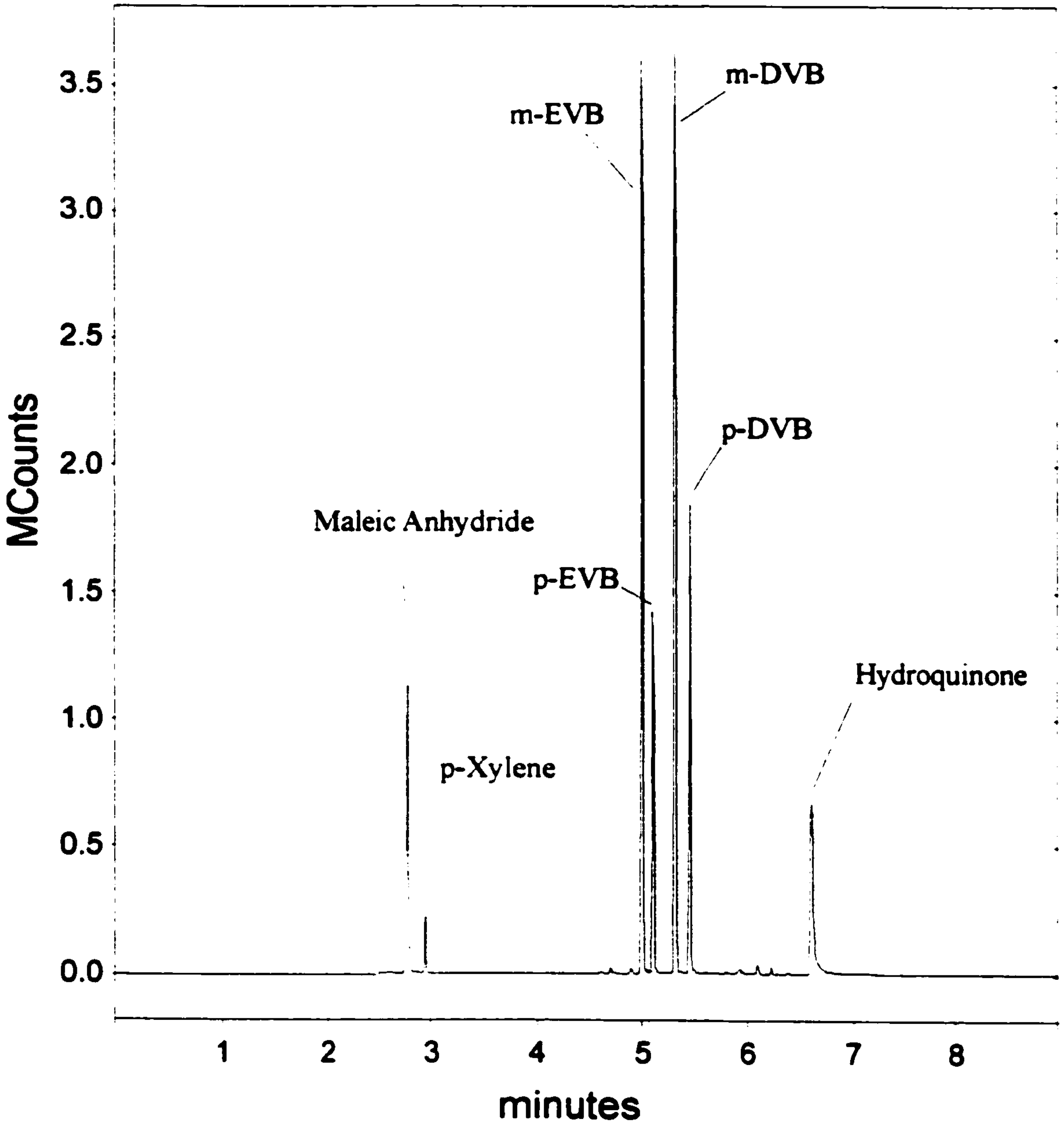


Figure 4.1 - Gas Chromatogram of DVB-55/MAn Reaction Mixture

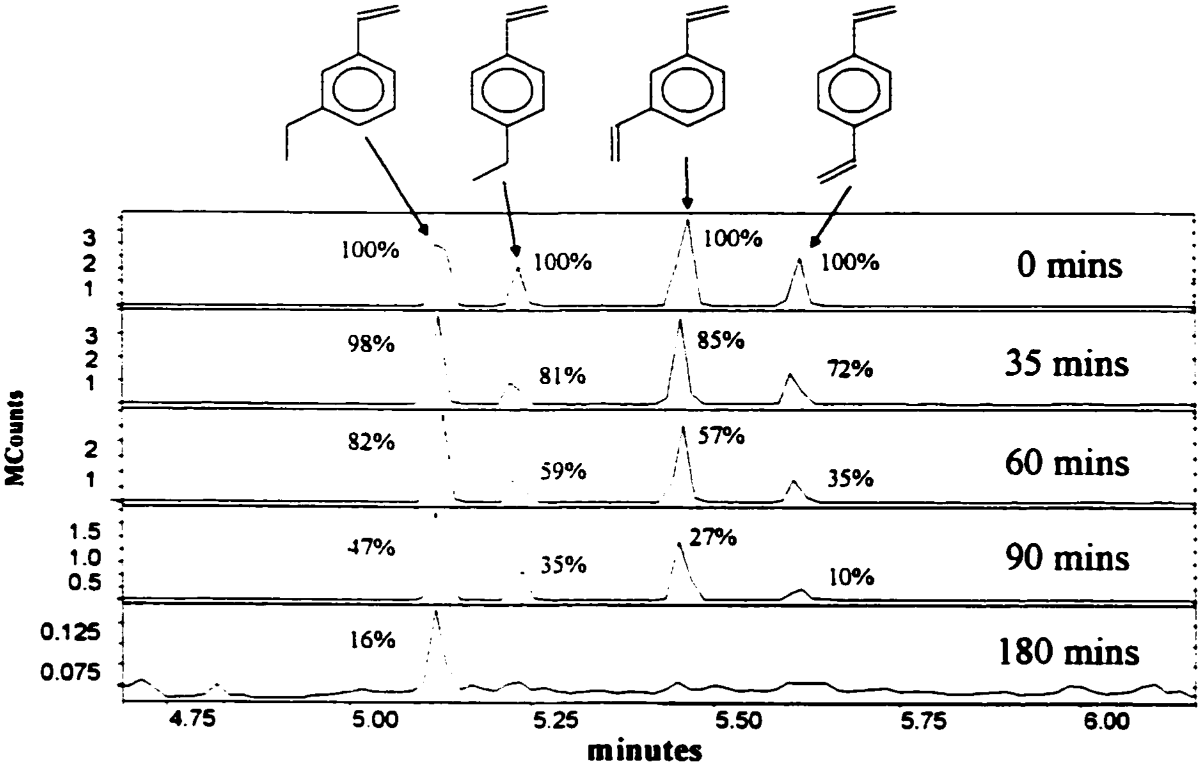


Figure 4.2 - Gas Chromatograms of DVB-55 Components

The area of the DVB and EVB peaks were compared to the zero time peak for each component to determine the monomer concentration and percentage conversion for that sample. The data was then fit using a first order rate expression as discussed in Chapter 3. A typical first order plot for a DVB-55 homopolymerization is shown in Figure 4.3. The linearity of these curves shows that the first order expression holds up to a reaction time of about 18 hours. On the other hand, Figure 4.4 shows a similar plot for the DVB-55/MAn copolymerization which does not conform to the first order rate equation. The deviation from linearity that occurs early in the reaction is common to all the copolymerizations with MAn that were performed. A likely

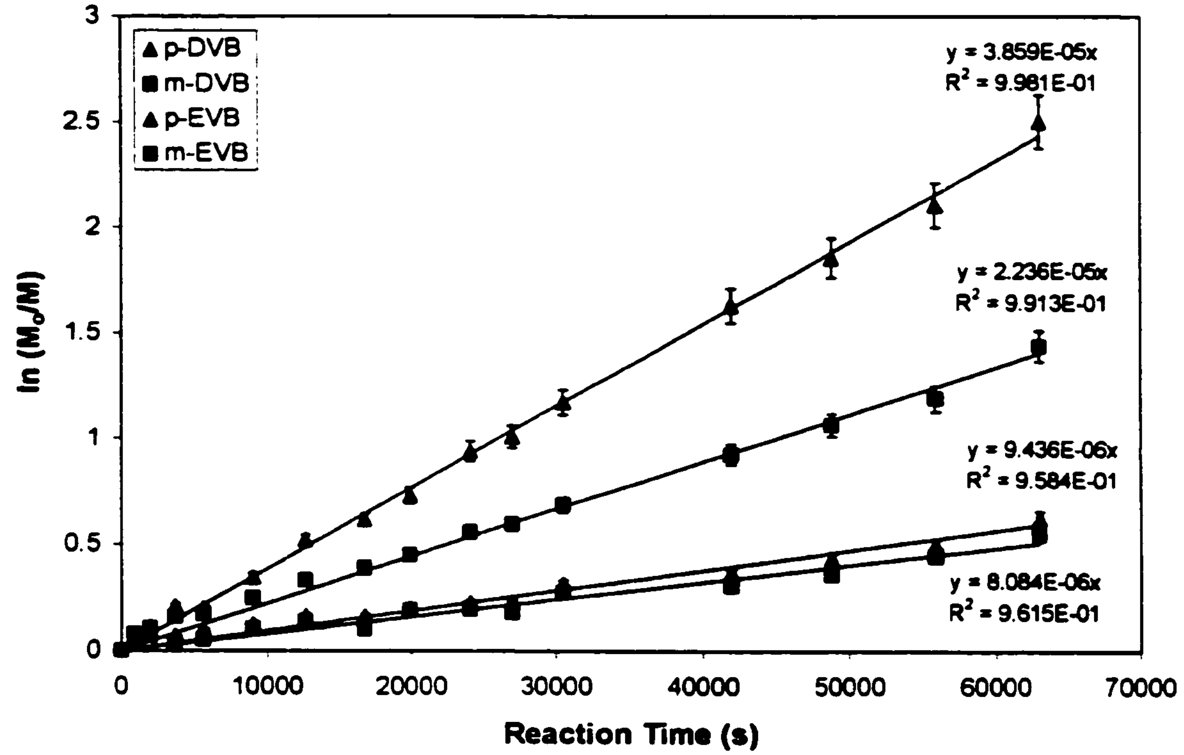


Figure 4.3 - First Order Plot for DVB-55 Homopolymerization

explanation of this result is that the system has not yet reached steady state conditions, resulting in lower than expected conversion of monomer. Recall that for steady state conditions, the radical concentration must relatively constant. Since these copolymerization reactions are fast, the time scale of the reaction is much shorter than for the DVB-55 reactions and hence the radical concentration may not have reached a constant level at this stage of the reaction. Consequently, regression of the linear portion of the curve after the early stages of the reaction (>1000 s) may more accurately reflects the rate of consumption of the monomers (as shown in Figure 4.5). This type of analysis, although not rigorous, is still useful for comparison of the reactivity of the four

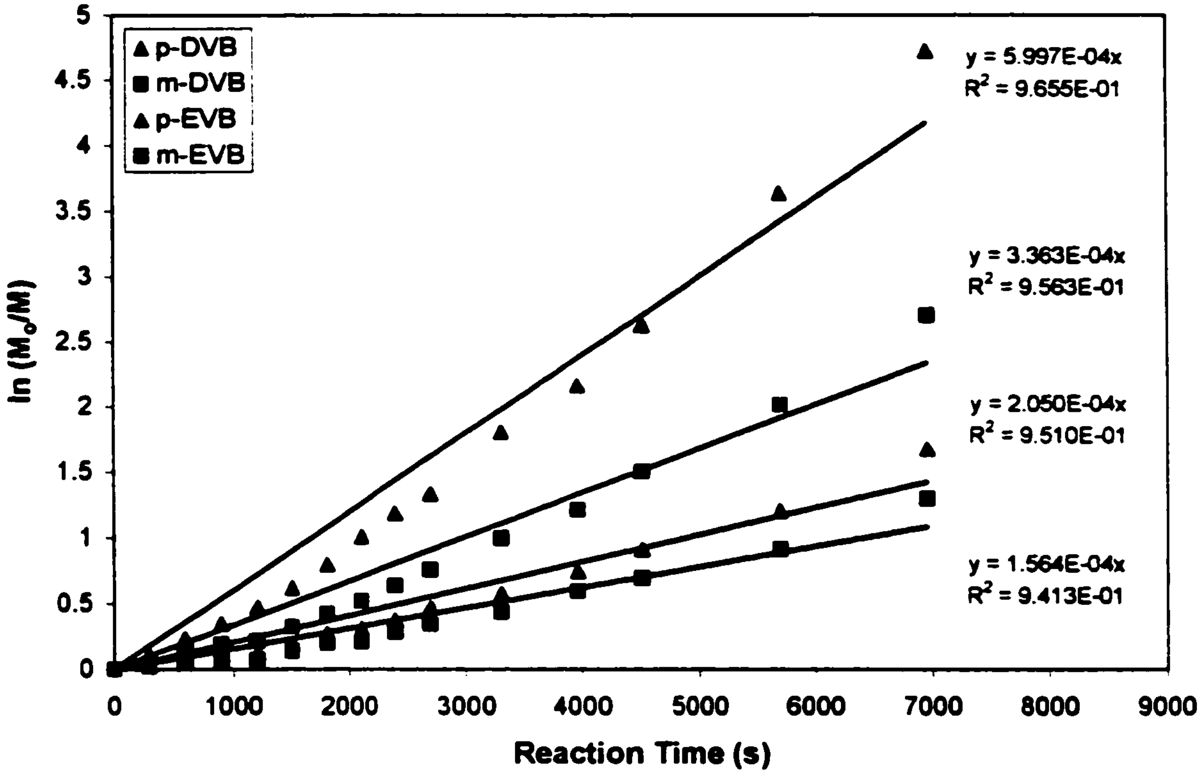


Figure 4.4 - Deviations from Linearity in DVB-55/MAn Copolymerization

components of DVB-55.

Table 4.4 shows the measured rate constants for the five reactions mentioned above. Similar to the overall rates of polymerization given in Chapter 3, these data indicate that individual components of DVB-55 are consumed approximately 15 times faster when copolymerized with maleic anhydride than when polymerized on their own.

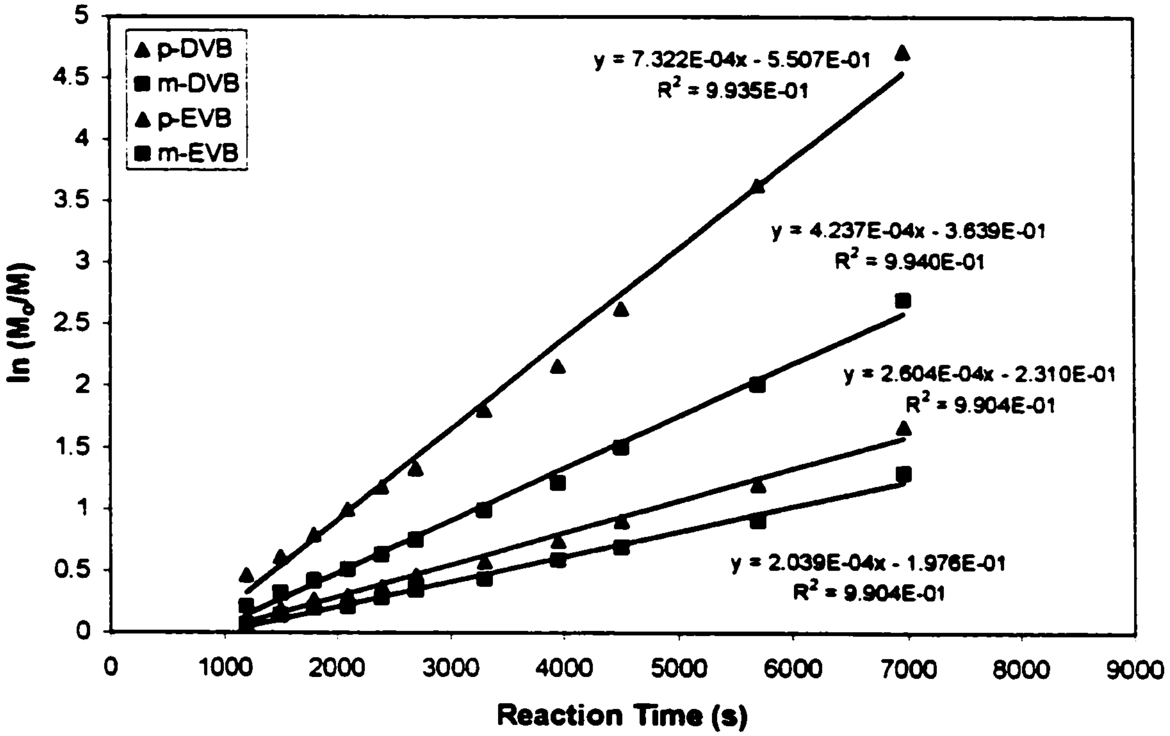


Figure 4.5 - Corrected First Order Plot for DVB/MAn Copolymerization

For the DVB-55 homopolymerizations, the relative rates of consumption of the divinyl components are lower than those given in the literature but the trend is still the same with *p*-DVB being approximately 5 times more reactive than the ethylvinylbenzenes.

In copolymerization with maleic anhydride, the relative rates for the divinyl isomers decrease which is in accordance with the reactivity-selectivity principle which states that selectivity decreases with increasing reaction rates. However, the trend in these rates remains the same, in that *p*-DVB and *m*-DVB are more reactive than the ethylvinyl components.

Table 4.4 - Apparent Rate Constants for DVB-55 Components

		k_{app} (s^{-1})			
Comonomers	**Reaction Solvent**	***m*-EVB**	***p*-EVB**	***m*-DVB**	***p*-DVB**
DVB-55	40% MEK / 60% Hp	1.3×10^{-5}	1.4×10^{-5}	3.2×10^{-5}	5.5×10^{-5}
DVB-55	80% MEK / 20% Hp	8.1×10^{-6}	9.4×10^{-6}	2.2×10^{-5}	3.9×10^{-5}
DVB-55/MAn	40% MEK / 60% Hp	2.0×10^{-4}	2.6×10^{-4}	4.2×10^{-4}	7.3×10^{-4}
DVB-55/MAn	80% MEK / 20% Hp	2.5×10^{-4}	2.8×10^{-4}	3.8×10^{-4}	7.5×10^{-4}
		Relative k_{app}			
DVB-55	40% MEK / 60% Hp	1.0	1.1	2.6	4.4
DVB-55	80% MEK / 20% Hp	1.0	1.2	2.8	4.8
DVB-55/MAn	40% MEK / 60% Hp	1.0	1.3	2.1	3.6
DVB-55/MAn	80% MEK / 20% Hp	1.0	1.2	1.5	3.0

4.4.2 Implications of DVB-55 Reactivity on Copolymerization Products

Based on the models proposed in Chapter 2, the difference in reactivity of the components of DVB-55 should have a significant effect on the microspheres and microgels produced in these systems. For clarity, each of these morphologies will be discussed separately.

DVB-55/MAn Microspheres

As mentioned earlier, the formation of microspheres in these systems is thought to take place in three steps: oligomer formation, nucleation and particle growth.

The initial oligomers formed in these systems should be rich in the divinylbenzene components of DVB-55. This will facilitate entropic desolvation of the oligomers as there will be more double bonds available for crosslinking.

As desolvation takes place, these oligomers coagulate to form particle nuclei. Although the nucleation period for the DVB-55/MAn microspheres is relatively long compared to DVB-55 homopolymerization, the fact that it is complete at fairly low conversions, suggests that the nucleation stage of the reaction will be unaffected by the reactivity of the DVB-55 components.

However, this is not the case for particle growth since the majority of the reaction takes place during this stage and hence it should be most strongly affected. Based on the radial growth model discussed in the previous chapters, the centre of microspheres prepared using this technique should be divinylbenzene-rich resulting in a crosslink gradient from the core of the particle to the periphery. In the case of DVB-55/MAn microspheres, this explains a phenomenon that has been observed that was previously unexplained. Although these microspheres are not deformable, a layer of soft gel-like material has always been observed on the particle's surface, as shown in the TEM image in Figure 4.5. This gel layer forms bridges between particles, that was originally thought to be soluble polymer that was a by-product of the reaction. However, even after multiple washings with good solvents, these bridges remained. Now, it is clear that these bridges result because the periphery of the particles are poorly crosslinked because of depletion of the divinyl monomers. However, since the reactions still go to high particle conversions, a small amount of divinyl species must still be present near the end of the reactions.

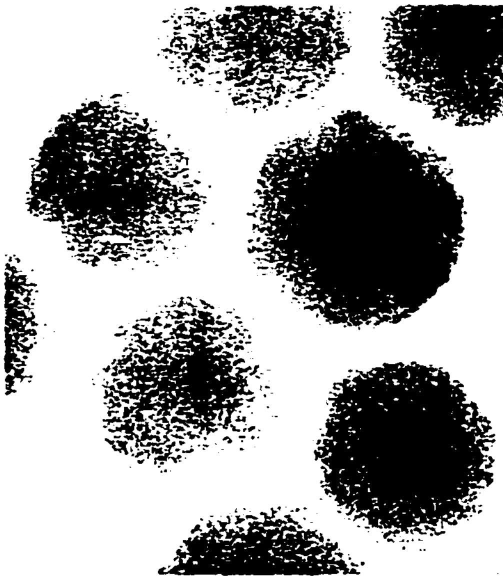


Figure 4.5 - Bridging Between DVB-55/MAn Microspheres

DVB-55/MAn Microgels

Unlike microspheres, microgels form in these systems throughout the course of the reaction. Consequently, those microgels formed early in the reaction would be expected to have higher proportions of the divinyl monomers than those formed later. Rather than a gradient of crosslinking within each particle, these microgels exhibit variable crosslinking levels from microgel to microgel.

This explains another curious result that we had encountered in earlier studies. The size distribution of microgels when measured by light scattering in good solvents was significantly narrower than it appeared in TEM images of the same samples. This now makes sense because although the microgels are in fact polydisperse, when swollen in good solvents, the smaller microgels, i.e., those formed later in the reaction, swell more than the larger ones because they have less crosslinker. This results in an apparent narrowing of the particle size distribution for the light scattering measurements.

4.5 Conclusions

The rates of consumption of the components of DVB-55 in copolymerization with maleic anhydride are similar to those of the copolymerization of DVB-55 alone. The selectivity of the reaction decreases presumably due to the increased rates of reaction.

Microspheres prepared by precipitation copolymerization of DVB-55 and maleic anhydride have a crosslink gradient from the interior to the exterior with the centre being more highly crosslinked.

Microgels, on the other hand, will have variable crosslinking from gel to gel in a sample as those that are formed early in the reaction will have more DVB than those formed later.

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Epilogue - Thesis Summary

The preface to this thesis described the objectives of this work. This section summarizes the outcome of the efforts to achieve those goals and the resulting contributions to this area of polymer science. The objectives are reprinted for clarity.

Chapter 1: Synthesis of Divinylbenzene-Maleic Anhydride Microspheres Using Precipitation Polymerization

Research Objective:

The goal of this research was to adapt existing precipitation polymerization technologies to prepare functional microspheres from divinylbenzene-55 and maleic anhydride.

Outcome of Research:

Functional microspheres were successfully prepared from DVB-55 and maleic anhydride. The best reaction solvent among those investigated was a mixture of methyl ethyl ketone and heptane. Microspheres were formed in 40 vol% MEK / 60 vol% Hp.

In addition to microspheres, a microgel morphology was observed at 80 vol% MEK / 20 vol% Hp that proved interesting.

The functionality of the DVB-55/MAn microspheres was demonstrated by hydrolysis and esterification reactions.

Chapter 2: A Study of the Effects of Reaction Solvency and Crosslinking on the Precipitation Polymerization of Divinylbenzene and Maleic Anhydride

Research Objective:

The objective of the work presented in this chapter was to determine the reasons for the solvent-dependent morphology transitions observed in the copolymerization of divinylbenzene-55 and maleic anhydride in methyl ethyl ketone / heptane mixtures.

Outcome of Research:

The transition from microspheres to microgels occurs at a solvent composition of between 50 and 60% MEK while macrogelation occurs at >95% MEK. These transitions take place due to decreased crosslinking under better solvency conditions caused by increased swelling of the forming oligomers.

These studies suggest a synergistic relationship between solvency and crosslinking that results in the absence of entropic desolvation in the microgel reactions. This results in the absence of a coagulation step in these reactions which is different from microsphere-forming reactions.

Chapter 3: Copolymerization of Divinylbenzene-55 and Maleic Anhydride: Effect of Increased Reaction Rates on Precipitation Copolymerization

Research Objective:

The aim of this segment of the thesis was to determine the effects of the enhanced reactivity of the copolymerization of divinylbenzene-55 and maleic anhydride on precipitation copolymerization

Outcome of Research:

The overall rate of polymerization in DVB-55 / MAn copolymerization is approximately 15 times faster than for DVB-55 alone.

The increased reactions rates of DVB-55 / MAn copolymerization were shown to affect both the nucleation and particle growth stages of precipitation polymerization. Nucleation is extended in these systems resulting in polydisperse particle nuclei. Particle growth occurs by a diffusion-controlled mechanism that causes narrowing of the particle size distribution as the reaction proceeds.

Chapter 4: Variable Consumption of DVB-55 Components in Copolymerization with Maleic Anhydride

Research Objective:

The goal of the research in this chapter was to determine if there is preferential consumption of any of the four components of DVB-55 when they are copolymerized with maleic anhydride.

Outcome of Research:

The *para* isomer of divinylbenzene is approximately 3.5 times more than the ethylvinylbenzenes in DVB-55. The *meta* isomer of DVB is slightly less reactive with a rate constant that is about 2 times bigger than the EVB isomers.

This difference in reactivity of the components of DVB-55 results in a crosslink gradient from the interior to the exterior of DVB-55/MAn microspheres. DVB-55/MAn microgels have a distribution of crosslinking throughout each sample.