SYNTHESIS AND CHARACTERIZATION OF SECONDARY AMINE FUNCTIONAL MICROPARTICLES

A THESIS SUBMITTED TO
DEPARTMENT OF CHEMISTRY
AND THE INSTITUTE OF ENGINEERING AND SCIENCE OF
BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE

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JULY 2003

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ABSTRACT

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MS in Chemistry

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July 2003

Secondary amine functional microparticles were prepared by the suspension polymerization of styrene (STY), divinylbenzene (DVB), and 2-(tert-butylamino)ethyl methacrylate (tBAEMA). Effects of polymerization parameters (such as polymerization time, stirring speed, temperature, STY, DVB, tBAEMA, initiator and stabilzer concentrations, etc.) on experimental amine content, average particle size, and particle size distribution were determined. The suspension polymerization experiments were carried out in three different systems. In the first one, conventional suspension polymerization system was used and the organic phase including monomers and initiator was dispersed in an aqueous medium by using sodium dodecylsulfate (SDS) as the stabilizer. In the second system, a similar experimental protocol was followed except a proper amount of $Al_2(SO_4)_3$ was used to replace SDS in the dispersion medium. The third method used to prepare the secondary amine functional microparticles was again similar to first polymerization protocol, except a proper amount of $Al_2(SO_4)_3$ was added to the aqueous dispersion medium as a co-stabilizer. When SDS was used alone as a stabilizer, polymerization product was agglomerated; individual and spherical microparticles were not obtained. Replacement of SDS with $Al_2(SO_4)_3$ resulted spherical microparticles within the size range of 50 - 200 μm. When SDS and $Al_2(SO_4)_3$ was used together, again individual and spherical microparticles were obtained within the size range of 130 - 250 μm.

Key Words: limited coalescence, amine functional microparticles, crosslinked microparticles, 2-(tert-butylamino)ethyl methacrylate, divinylbenzene

ÖZET

İKİNCİL AMİN FONKSİYONLU MİKROPARTİKÜLLERİN SENTEZ VE KARAKTERİZASYONU

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Temmuz 2003

İkincil amin fonksiyonlu mikropartiküller stiren (STY), divinilbenzen (DVB) ve 2-(ter-butilamino)etil metakrilatın (tBAEMA) süspansiyon polimerizasyonu ile hazırlandı. Polimerizasyon değişkenlerinin (polimerizasyon süresi, karıştırma hızı, sıcaklık, STY, DVB, tBAEMA, başlatıcı ve stabilizör derişimleri gibi) amin içeriğine, ortalama partikül büyüklüğüne ve partikül büyüklüğü dağılımına etkisi belirlendi. Süspansiyon polimerizasyonu deneyleri üç farklı sistemde yapıldı. Birincisinde klasik süspansiyon polimerizasyon sistemi kullanıldı, monomer ve başlatıcı içeren organik faz, sodyum dodesilsulfatın (SDS) stabilizör olarak kullanıldığı sulu faz içinde dağıtıldı (disperse edildi). İkinci sistemde, birinciye benzer bir yol izlenerek dağılma ortamındaki SDS'in yerine $Al_2(SO_4)_3$ kullanıldı. İkincil amin fonksiyonlu mikropartikül hazırlamak için kullanılan üçüncü yöntemde, dağılma ortamına uygun miktarda yardımcı stabilizör olarak $Al_2(SO_4)_3$ eklenerek birinci polimerizasyon işlemi izlendi. Sadece SDS stabilizör olarak kullanıldığında, polimerizasyon ürünü topaklaştı, ayrık ve küresel mikropartiküller elde edilemedi. SDS'in $Al_2(SO_4)_3$ ile yerdeğiştirmesi sonucunda 50 –200 μm büyüklüğünde ayrık ve küresel mikropartiküller elde edildi. SDS ve $Al_2(SO_4)_3$ birlikte kullanıldığında, 130 –250 μm büyüklüğünde yine ayrık ve küresel mikropartiküller elde edildi.

Anahtar Kelimeler: limited coalescence, amin fonksiyonlu mikropartiküller, çapraz bağlı mikropartiküller, divinilbenzen, 2-(tert-butilamino)etil metakrilat

ACKNOWLEDGEMENTS

I would like to thank to my supervisor Soner Kılıç for his endless helps, supports, and supervision throughout my studies.

I would like to express my deepest gratitude to my family, Arif, Aysel, Evren, Onur Altıntaş for their love and encouragement.

I also thank to my friends in Chemistry Department, and Aşkın Kocabaş for their friendship and helps.

Very special thanks to Gökhan Sağlam for his great moral support and endless love.

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CHAPTER 1

INTRODUCTION

It is known that the synthetic polymer microparticles as well as their combination with natural counterparts can be utilized as carrier matrices in a wide variety of medical, biological, and biochemical applications, such as affinity chromatography, immobilization techniques, drug delivery systems, and cell culturing.[1-3] The majority of these microparticles is based on polystyrene and its derivatives. Such polymer microparticles with different size range (50 nm - 2 mm) can be produced by various synthetic methods, such as suspension, emulsion, precipitation and dispersion polymerization.

Particle size, particle size distribution, porosity, pore structure, surface area and reactive sites affect the performance of the polymer microparticles. The major applications of polymer microparticles are depicted in Table 1.1.[3]

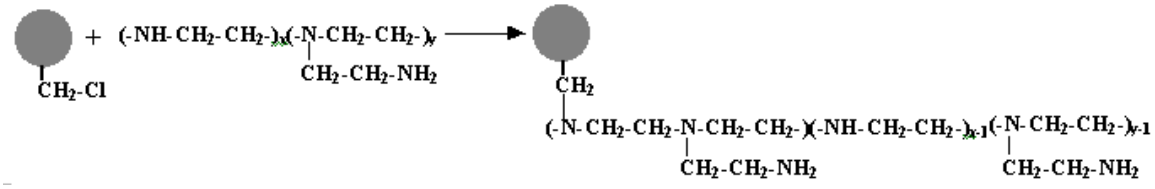
Table 1. 1: Major applications of polymer microparticles[3]

Application	**Particle functionality needed***
Chromatography:	
Gel permeation or size exclusion	Porosity
Ion-exchange	SO_3H (Na), CO_2H (Na), NR_3X
Affinity	OH, NH_2, CHO, COOH, COOAr
Biotransformations	OH, NH_2, COOH, porosity
Solid-phase peptide synthesis	OH, NH_2
General organic synthesis	Various
Chemical catalysis	PPh_3, NC, CN, others
Hydrometallurgy	Various
Diagnosis and immunoassay	OH, NH_2

*R= alkyl; X= Br, Cl, OH; Ar= activating/leaving group; Ph= phenyl.

Most of the microparticles used in the applications mentioned above have amine functional groups as reactive sites. Synthesis of some amine functional microparticles using various synthetic methods has been reported in the literature. In general, these synthetic methods can be divided into two groups. The most common one is to modify the pre-formed functional microparticles by amine containing reactants. The modification of chloromethyl styrene (CMST)[4] and glycidyl methacrylate (GMA)[5] containing microparticles using poly (ethylene imine) (PEI) and ammonia, respectively, are the examples of this type of synthesis (Figure 1.1.a and 1.1.b).

(a)



(b)

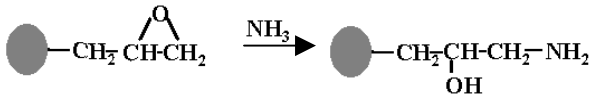


Figure 1.1: Preparation of amine functional microparticles (a) CMST microparticles with PEI;[4] (b) reaction of GMA microparticles with NH_3 [5]

The second approach is to use tertiary amine or blocked amine containing copolymerizable monomers. Recently, Tuncel *et. al.*[6] reported the synthesis of monodisperse polystyrene microparticles carrying functional groups on their surface. In their study, the synthesis of tertiary amine as well as acid and hydroxyl functional microparticles was carried out using polystyrene latex particles as seed and a mixture of styrene/acrylic comonomers comprising a functional monomer having the desired functional group. In another study,[7] butoxycarbonyl blocked p-amino styrene (Boc-p-amino styrene, Boc-p-AMST) was used during the synthesis. The aminated microparticles were obtained by the simple removal of the Boc- protective group under acidic conditions followed by neutralization, to produce p-amino styrene/styrene copolymers (Figure 1.2).

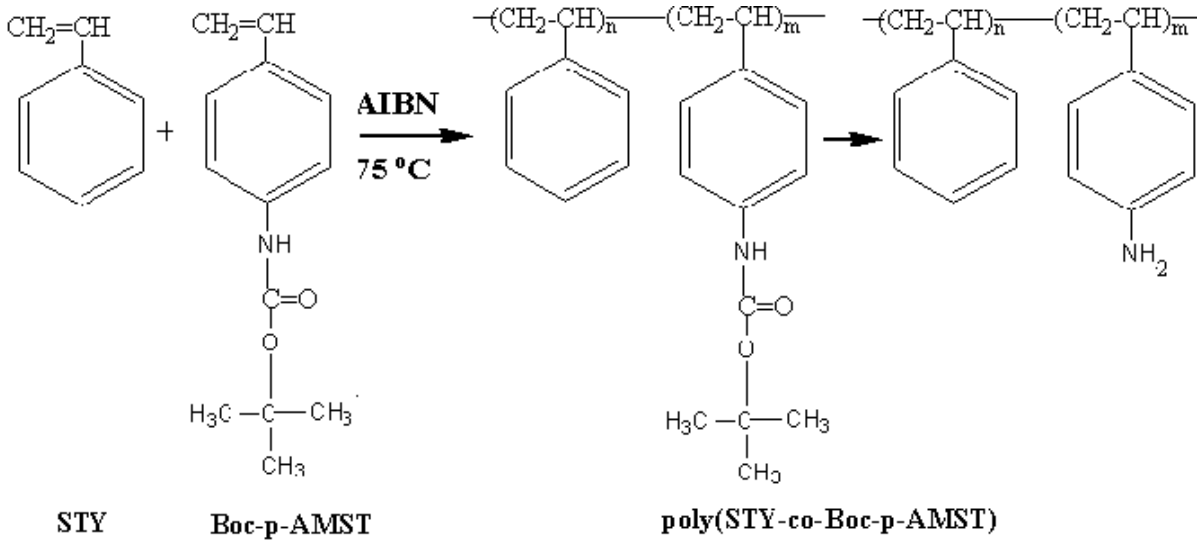


Figure 1.2: Preparation of amine functional microparticles by copolymerization of styrene and butoxycarbonyl protected p-amino styrene [7]

As mentioned above, in recent years, a number of articles have been published amino functional microparticles' preparation.[4-7] It has been known for some time that these microparticles can be used in a variety of applications.[2,3] However, any published report on the direct synthesis of active hydrogen containing amine functional microparticles could not be found in our literature survey.

Our main objective is to prepare secondary amine functional polymer microparticles (in size range of 50 – 250 μm) using unblocked amine functional copolymerizable monomer utilizing single-pot polymerization method. The microparticles will be prepared by suspension polymerization method via styrene and divinylbenzene as comonomers. In order to prepare individual and spherical particles, effects of several experimental parameters like polymerization time, agitation rate, initiator and stabilizer types and their concentrations, amine monomer and crosslinker concentrations will be studied. Also, the effects of these parameters on particle size and particle size distribution will be investigated.

This thesis represents a literature review in the next chapter, i.e., Chapter 2 which summarizes the properties of the microparticles and polymerization methods used in the

synthesis of microparticles. It also covers the synthesis of styrene based functional microparticles. A brief summary of the effects of polymerization parameters on the particle size and particle size distribution of microparticles is also included in this chapter.

The following chapter (Chapter 3) details the synthesis and characterization methods utilized in this project to prepare secondary amine functional microparticles.

Chapter 4 gives the results of this study and the discussion of the results on the bases of the published literature works. Effects of polymerization parameters on particle size, particle size distribution, and amine content of the prepared microparticles are discussed in this chapter.

The final chapter summarizes conclusions of this study.

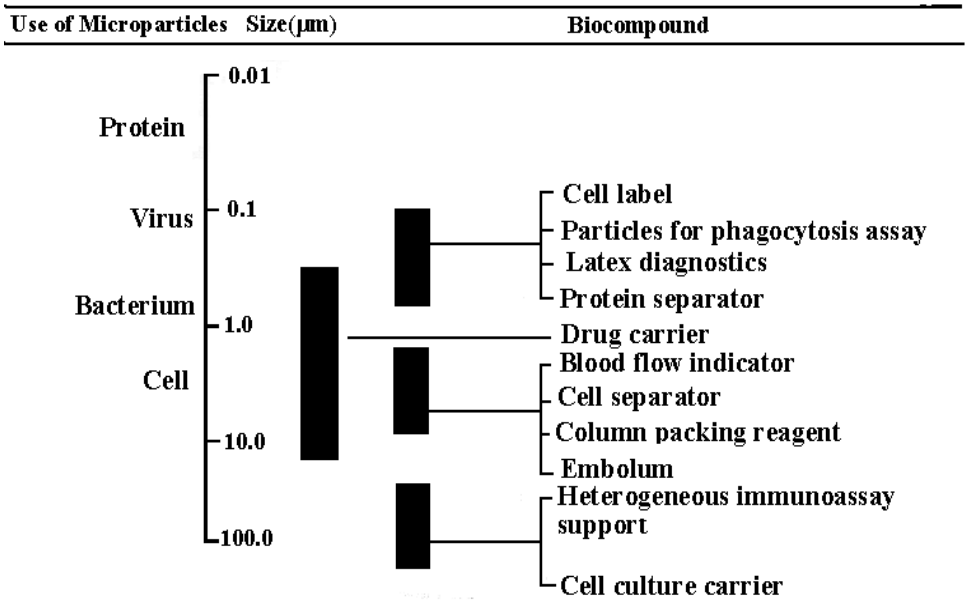
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Polymer microparticles have attracted considerable attention for many applications. Table 2.1 shows some medical and biological applications of microparticles which are being used as carrier matrices. The size of the microparticles varies depending on the type of application.[2]

Table 2.1: Biomedical applications of polymer microparticles [2]



There are several features of polymer microparticles that determine their performance. Recently, these properties were reported by Kawaguchi[2]. Properties of polymer microparticles given in this study are as follows:

Small size and volume. In general, a particle size cannot be less than 5 nm even in the case of it is composed of only a single polymer molecule since polymer molecules have a

molecular weight higher than 10,000 Da.[2] Fine particles can be considered as a microreactor with a high reaction rate due to their small volume.

Large Specific Surface Area. The total surface area of 1 g of microparticles having a diameter of 0.1 μm is about 60 m^2. The total surface area is inversely proportional to the diameter of the microparticle.[2] This large surface area is available for chemical reactions.

Uniformity. Monodisperse microparticles produce sharp, reliable and reproducible results in their applications. Uniformity of size, chemical composition, and morphology of the microparticles are important. Generally, the uniformity of the microparticles is reported by their polydispersity, which is the ratio of weight-average diameter to number-average diameter.

Variety. Polymer microparticles can be prepared by different physical and chemical polymerization methods. These preparative methods enable to produce a variety of microparticles with different size, surface chemistry, composition, surface texture and morphology. Polymer particles can be prepared by two routes as shown in Figure 2.1.

In route 1, existing polymers are fabricated to solid particles by various methods. These methods are solvent-in-emulsion evaporation, phase separation, spray drying, etc.

In route 2, particles having different features are formed depending on the method as shown in Figure 2.1. In general, this route is being used to prepare the polymer microparticles by heterogeneous polymerization methods starting from the desired monomer(s). The properties of microparticles are affected by the type and concentration of the monomers, stabilizers and initiators which are used during synthesis.

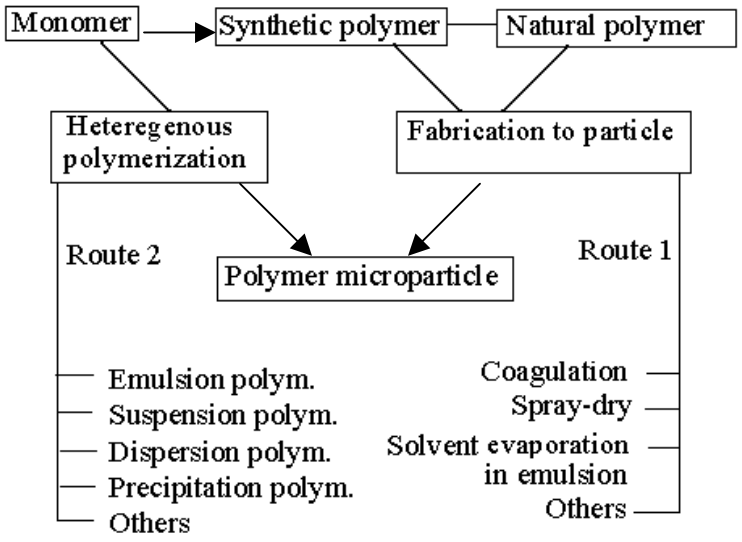


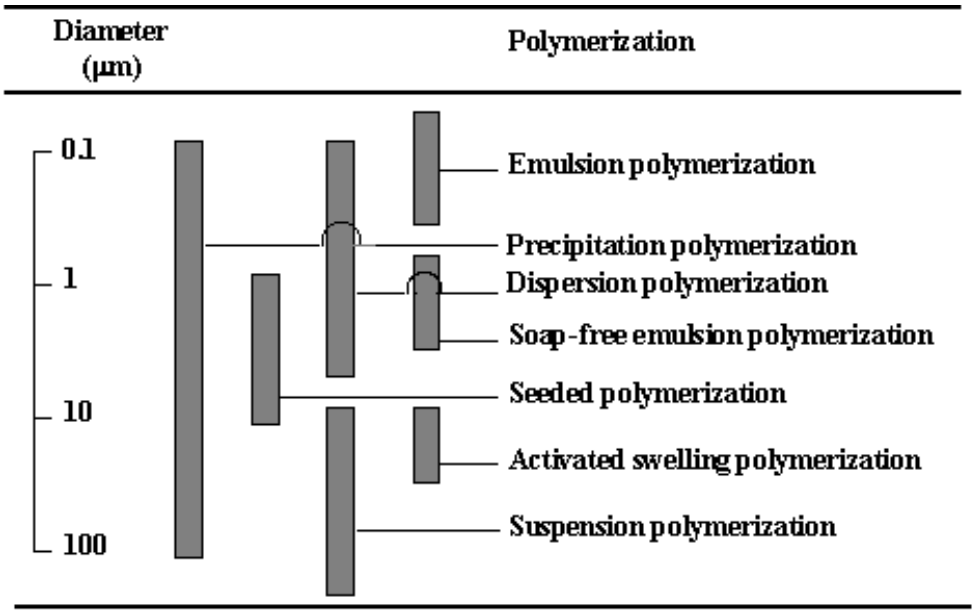
Figure 2.1: Preparative routes to polymer particles[2]

2.2 Polymerization Methods

In principle, a polymerization reaction may be carried out in different phases such as the solid phase, the liquid phase or the gas phase. In practice, the liquid phase is used in preparation of commercial scale polymerizations.[8]

Liquid phase polymerization can be subdivided into four types according to the nature of the physical system employed. These are bulk, solution, emulsion and suspension methods. Bulk and solution methods are single-phase, emulsion and suspension methods are two-phase systems. Particles within different size ranges can be obtained using various polymerization methods, as shown in Table 2.2.

Table 2.2: Particle-forming polymerizations and the size of the resulting particles[2]



2.2.1 Single-Phase Systems

2.2.1.1 Bulk Polymerization

In this polymerization method, the system is composed of only monomer(s) and polymer. This technique is commonly used for polymerizations, which are performed through functional groups in the presence of catalyst.[8] The method involves heating of directly monomer or monomer mixture. The system is maintained in the solution state by keeping the temperature sufficiently high.

Bulk polymerization is widely used in the production of condensation (stepwise) polymers. These reactions are only mildly exothermic. Most of the reaction occurs when the viscosity of the mixture is still low enough to allow the mixing, heat transfer, and bubble elimination. Control of such polymerization is relatively easy.

This technique also appears to be the method for producing polymers by chain processes (free radical, addition polymerization), since the starting material consists of mainly pure monomer(s), with only traces of initiator and possible chain transfer agent.

This polymerization system has some problems. For example, viscosity of the reaction mixture increases as polymerization proceeds. High viscosity causes the handling difficulties of the product. Most of the chain reactions are generally exothermic, and high viscosity inhibits heat control. There can be local overheating which may cause charring and degradation of the product. Although advantages of bulk polymerization, it is not widely used in industry. Only three polymers are produced in this way, these are polyethylene (under high pressure), polystyrene, and poly (methyl methacrylate).[8]

2.2.1.2 Solution Polymerization

Monomers are dissolved in appropriate solvent to overcome some of the problems associated with bulk polymerization.[9] Temperature can be more easily controlled in solution state. By this way, heat and viscosity control difficulties may be overcome.

Solution polymerization is usually used for the ionic polymerization of gaseous vinyl monomers.[8] The solvent increases the contact of monomer(s) and initiator (which may/may not be soluble in the solvent) and helps the heat control of exothermic reaction.

However, there are some disadvantages with the solution polymerization. Firstly, reaction temperature is limited by the boiling point of the solvent which causes the restriction in reaction rate. Secondly, it is difficult to remove the traces of the solvent from the product. Finally, it is difficult to realize an inert solvent, which means that there is always chain transfer to the solvent. This restricts the molar mass of the product that can be achieved. Restriction of the molar mass is responsible for the rarity of solution polymerization in the manufacture of commercially important high molar mass polymers.[8]

2.2.2 Two-Phase Systems

Two phase polymerization systems are heterogeneous polymerization processes which the starting monomer(s) and/or the resulting polymer are in the form of a fine dispersion in reaction medium.

There are many published reports in literature about description and mechanisms of two-phase polymerization methods. One of the most useful one is written by Arshady[10] who explained the reaction mechanisms and properties of two-phase polymerization systems. Fine polymer particles are always produced by two-phase mixtures (heterophase systems). Auxiliary substances are used to stabilize the heterophase systems. Different forms of two-phase mixtures contains various types of auxiliary materials. They have completely different microscopic phase structures, and produce particles with different types, sizes and morphologies. Two-phase mixtures with predetermined microscopic phase structures and characteristic auxiliary substances are used to prepare well-defined microparticles.[10]

Arshady[10] defined the two-phase process according to the following criteria:

1. Initial state of the polymerization mixture.

2. Mechanism of particle formation.

3. Kinetics of polymerization.

4. Shape and size of the final particles.

There are some confusions in different heterophase polymerizations due to their similarity. The starting monomer mixture and/or the resulting particles are always in the form of a dispersion in polymerization medium. According to Arshady,[10] when above criteria is applied, this apparent similarity disappears.

One of the basic differences between different heteropahase polymerization systems is the nature of the auxiliary substance that is used to form or stabilize the reaction mixture. These materials can be divided into three main categories that are named as emulsifiers, stabilizers and solubilizers. All these substances are surface-active materials (surfactants).

Emulsifiers or soaps are usually small amphipatic molecules. They dissolve in the polymerization medium up to a critical concentration named as critical micelle concentration (CMC). Discrete nanometer size micelles form above critical micelle concentration.

Stabilizers and suspension agents are materials that increase the viscosity and change the density of the polymerization medium. Stabilizers do not lead to molecular solubilization or micellization of the monomer. They cover the surface of monomer droplets or polymer particles. Insoluble inorganic, or poorly soluble organic materials are used as stabilizer. They are immiscible with monomer droplets although they have strong affinity. Solubilizers are bipolar compounds that are highly soluble in both polar and non-polar media.[10]

Oil-in-water (o/w) systems are commonly employed type of emulsion and suspension polymerizations. Water-in-oil (w/o) systems are used in emulsion and suspension polymerizations of water-soluble monomers. Reaction mechanism is the same as o/w systems but w/o emulsifiers and stabilizers are used. There are some monomer mixtures that can be polymerized in oil-in-oil (o/o) systems. In all three systems o/w, w/o and o/o, reaction mechanism of emulsification and droplet formation are the same.

2.2.2.1. Emulsion Polymerization

Emulsion is a stable colloidal suspension that is dispersed and held in another liquid by an emulsifier. In emulsion polymerization, aqueous (continuous) phase and (nonaqueous) discontinuous phases present. The initiator is located in the aqueous phase and monomer/polymer are in the nonaqueous phase.[11]

A soap or emulsifier has two ends of different solubility. Tail is a long hydrocarbon that is soluble in nonpolar, organic compounds. Head is often anionic or cationic functional

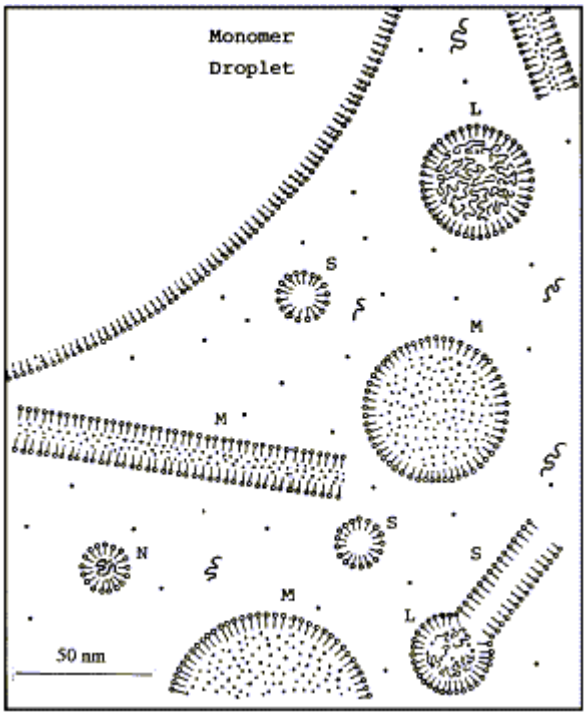
group (i.e. $–SO_3^-$, $-N(CH_3)_3^+$) which is water-soluble. At a certain concentration in water, surfactant molecules congregate and form micelles 1-10 nm in size depending on the length of hydrocarbon chain length. This size is much smaller than the droplets that can be formed by mechanical agitation.[9]

In an emulsion polymerization, the surfactant is dissolved in water until the critical micelle concentration (CMC) is reached. The interior of the micelle provides the site necessary for polymerization. A monomer and a water-soluble free radical initiator are added and the reaction system is shaken or stirred. Emulsion polymerizations are always performed free radically because the water would rapidly quench anionic and cationic chain ends. The product of an emulsion polymerization is called latex.

Once everything is put into the polymerization reactor, the monomer can be found in three different places. It can be in large monomer droplets floating around aimlessly in the water. It can be dissolved slightly in polymerization medium or monomer may be found in micelles. Hydrophobic monomer is the immiscible liquid, the polymerization medium is water.[10]

Initiator is decomposed into free radicals usually by heat. The propagation, chain growth begins. This occurs in the water as radicals react with monomer molecules to form dimers or trimers and the nucleation stage is reached. The polymeric radicals soon enter the micelles, where propagation of the chain is continued by attack on the solubilized monomer. The radicals enter to the micelles rather than the monomer droplets because the number of micelles is enormously greater. These radicals may also be viewed as surfactant-like bodies with ionic and nonionic portions, and since they are capable of participating in the dynamic equilibrium between micelle and dissolved surfactant, their movement into the micelles is favored. Once the molecularly dissolved monomer leaves the water, the equilibrium is disturbed and more monomer diffuses out of the droplets in order to restore equilibrium. As the micelles/particles expand, molecules of dissolved surfactant adsorbed on their surfaces. Those micelles which do not contain polymer then gradually break down and go into solution; they are adsorbed onto growing particles until, at about to 10 to 20 percent monomer conversion, all the micelles have disappeared, thus marking the end of the

nucleation stage. In the growth state, the number of monomer/polymer particles remains essentially constant. They continue to grow as more monomer diffuses from the droplets until all the droplets have disappeared. The number of the polymer particles is substantially less than the original number of micelles, because the latter have disintegrated after only a small proportion (about 1 in 700 to 1000) has furnished reaction sites. The usual concentration of polymer particles of 0.5-1 μm diameter is about 10^{13} to 10^{15} per milliliter of water compared with about 10^{18} micelles.[12]



M, Monomer containing micelle
S, Soap micelle
N, Polymer molecule
L, Latex particle

Figure 2.2: Schematic representation of early stages of emulsion polymerization [15]

Water-soluble initiators, such as peroxides and persulfates, are commonly used (this also prevents polymerization in the big monomer droplets). When polymerization reaction starts, the micelle is referred to as a particle. Polymer particles can grow to high molecular weights, especially if the initiator concentration is low. That makes the radical concentration and the rate of termination low as well. Sometimes a chain transfer agent is added to the mixture to prevent the molecular weight from getting too high.

Monomer migrates from the large monomer droplets to the micelles to sustain polymerization. On average, there is one radical per micelle. Because of this, there is not much competition for monomer between the growing chains in the particles, so they grow to nearly identical molecular weights and the polydispersity is very close to one. Practically all the monomer is consumed in emulsion polymerizations. This means that the latex can be used without purification. This is important for paints and coatings.

Also, each micelle can be considered as a mini bulk polymerization reactor. Unlike bulk polymerizations there is no unreacted monomer left, and no thermal hot spots form. In bulk polymerizations (no solvent, just monomer and initiator), thermal hot spots cause degradation and charring of polymerization product. Also chain transfer broadens the molecular weight distribution. An increase in temperature sometimes causes the rate of polymerization to increase explosively. The water acts as a heat bath for all those mini reactors and keeps the polymerization reactor from blowing up.

The rate of polymerization is the same as the rate of disappearance of monomer. Monomer disappears faster when there are more particles. In order to have more particles there must be more micelles. If the surfactant concentration is increased, number micelles increase (when the concentration of initiator is the same). This will give more particles and less radicals, the rate of termination will be low since there are less radicals. Result is this: decreasing the initiator concentration increases molecular weight and rate of polymerization. This is completely opposite from bulk and solution polymerization. To increase the rate of polymerization for those, reaction should be heated or initiator concentration should be increased. Both of these parameters increase the rate of termination and results products with lower molecular weight.

In industry, poly(vinyl acetate), poly(vinyl chloride), polyacrylamide, and copolymers of styrene, butadiene, and acrylonitrile are prepared usually be emulsion polymerizations.

2.2.2.2 Suspension Polymerization

The term suspension polymerization refers to polymerization in aqueous system with monomer as a dispersed phase, and the polymer as a dispersed phase. The process is

distinguished from emulsion polymerization by the location of initiator and the reaction kinetics. In a typical suspension polymerization, initiator is dissolved in the monomer phase, and the reaction kinetics is the same as bulk polymerization.[11]

The technique is very similar to solution polymerization, but monomer is not dissolved in an inert solvent, it is usually suspended in solvent. Heat transfer and reduction in viscosity are comparable with solution polymerization. Mechanical stirring and suspending agents are needed to maintain the stability of monomer droplets in suspension medium. The technique effectively works since there is a large number of micro droplets that undergo bulk polymerization.[9]

Dispersion is maintained by mechanical stirring and stabilizers. Various types of stabilizer are used to prevent agglomeration of the monomer droplets. These stabilizers are water-soluble organic polymers such as gelatin, poly (vinyl alcohol), electrolytes and water-insoluble inorganic compounds such as kaolin, magnesium silicates, and aluminum hydroxide.[13]

Arshady describes the basic aspects of suspension polymerization in one of his studies.[3] The suspension polymerization of water insoluble monomers involves the formation of a droplet, suspension of the monomer in water and direct conversion of the individual monomer droplets into polymer microparticles. Suspension system is similar for the water-soluble monomers, difference is that an aqueous solution of the monomer is dispersed in an oil to form a water-in-oil droplet suspension. This process is often named as inverse suspension polymerization.[3]

2.2.2.2.1 Droplet Formation

The most important feature of o/w suspension polymerization is the formation of a droplet suspension of the monomer in suspension medium, and the maintenance of the individual droplets throughout the polymerization process. Droplet formation in an oil-water mixture is performed by mechanical stirring. For most practical purposes, the volume ratio of the monomer phase to water is usually kept between 1:10 - 1:12.

In a non-polymerizing suspension system, the suspended droplets collide with each other, coalescence into larger ones and re-divide into smaller ones again. Under these conditions the system is in dynamic equilibrium and remains stable during continued mixing.

In a polymerizing suspension system the same principles are valid initially. As a result of polymerization and increasing viscosity of reaction mixture, re-division of the coalesced monomer droplets becomes more difficult. At the beginning of sticky stage, re-division of the partially polymerized droplets becomes almost impossible. Droplet coalescence may cause to coagulation of the polymerization product. Also, polymerization reaction leads to hardening of the droplets. At the end of sticky period, the hardened droplets will not coalescence anymore in any collision between the polymer particles. The period that partially polymerized droplets can combine but not re-divide is termed as sticky stage. It is usually observed between 25 and 75 % conversion depending on the nature and composition of the monomer mixture.[3]

2.2.2.2.2 Droplet Stabilization

Reducing the surface tension of the droplets and minimizing the force with which they collide can prevent mass coagulation during the sticky stage. Surface tension can be reduced by using a small amount of suitable droplet stabilizer.[3]

In o/w suspension polymerization, the addition of a small amount of water insoluble inorganic salts causes the formation of a very thin film around the monomer droplets. This thin film reduces the coagulation danger of droplets. Organic polymers, which are insoluble in the monomer droplets and have relatively low solubility in the suspension medium, are also highly effective as droplet stabilizer. Organic polymers are preferred to insoluble inorganic salts since they are more easily removed from the surface of the particles by aqueous stripping.[3]

Low concentration of stabilizer is needed to maintain a stable suspension system under constant stirring conditions. Minimum stabilizer concentration is required for full monolayer coverage of particle surface. The high concentration of stabilizer may increase in monomer solubilization. This may produce poorer quality of polymer particles with lower

yields. The type and concentrations of stabilizer are determined experimentally. Also, design of the polymerization reactor is important in the stabilization of the suspension system.[3]

The agglomeration may become critical when the polymer particles become sticky. At the end of the polymerization reaction, stabilizer is removed from polymer product by aqueous washing. The polymer is relatively free from contaminants and there is no need to solvent recovery.[8]

However, there are some disadvantages with suspension polymerization. If the polymers are very soluble in their monomer, extremely high stirring speed has to be applied during synthesis or the partially reacted droplets may agglomerate. Since some polymers have high tendency for agglomeration, suspension polymerization can not be used for the synthesis of these polymers.[3]

2.2.2.2.3 Droplet/Particle Size Control

Polymer particles with in the size range of 100 nm – 2 mm can be prepared by using suspension polymerization. For addition polymerization reactions of vinyl monomers, polymer particles within the size range of 20 μm - 2 mm can be produced by suspension polymerization. Preparation of particles smaller than 20 μm becomes complicated as a result of emulsion polymerization and formation of very small particles.[15]

It was reported by many authors that the average size of particles can be controlled by varying the stirring speed, volume ratio of the monomer to suspension medium, concentration of the stabilizer, and the viscosities of both phases. The following equation represents the most of the empirical relationships, which was reported by many authors. Arshady[15] made a combination of these relationships and reported as an equation

$$d = k\frac{D_V.R.v_d.\varepsilon}{D_S.N.v_m.C_S} \qquad \textbf{(2.1)}$$

where;

d: average particle size;

k: parameters such as apparatus design, type of stirrer, etc.;

D_v: diameter of the vessel;

D_s: diameter of stirrer;

R: volume ratio of the droplet phase to suspension medium;

N: stirring speed;

ν_d: viscosity of the droplet phase;

ν_m: viscosity of the suspension medium;

ε: interfacial tension between two immiscible phases; and

C_s: stabilizer concentration.

Quantitative expressions reported by different authors for various parameters in Eq. 2.1 may differ from each other depending on the details of the studied suspension system. However, Eq. 2.1 provides a useful guide for planning a new suspension polymerization process, and a semi-quantitative basis for understanding particle size data of the produced product.

2.2.2.2.4 Particle Morphology

An important aspect of polymer particles prepared by suspension polymerization is the surface and bulk morphology of the individual particles.[15] This morphology is related to the polymer solubility in its monomer phase.

Basic aspects of suspension polymerization have been reported in early papers.[15] On the basis of these studies, it is assumed that polymerization kinetics in suspension polymerization are similar to bulk/solution polymerization, depending on the absence/presence of monomer diluents in the monomer phase. Suspension polymerization may be described as “micro bulk” or “micro solution” polymerization. Individual monomer droplets represent bulk or solution reactors. The suspension medium acts as an efficient heat transfer agent. High polymerization rates can be achieved to complete the conversion.

There are some industrially important polymers that are produced by oil-in-water suspension polymerization such as polystyrene, poly (vinyl chloride), polyacrylates, and poly

(vinyl acetate). Styrene-based resins are also used for the preparation of ion exchange resins and polymer supports[14] are also obtained by oil-in-water suspension copolymerization of styrene and divinylbenzene (and a functional monomer). For all these polymers usually an azo compound (e.g., AIBN), or an organic peroxide (e.g., benzoyl peroxide) are used as initiator, and the polymerization reaction is carried out 50-100 ^{o}C.

Major examples of polymers produced by water-in-oil suspension polymerization include polyacrylamide and water soluble acrylates. An aqueous solution that contains the monomer(s) and the initiator is suspended in liquid paraffin or chlorocarbon (polymerization medium). Polymerization reaction is conducted at 20-50 ^{o}C. A water-soluble catalyst may also be used for these preparations.[15]

2.2.2.2.5 Effect of Polymerization Parameters

2.2.2.2.5.1 Effect of Stirring Speed

According to Nunes, *et.al.,*[16] a suspension polymerization can be divided into three stages, reported these stages as follows. First stage is the existence of liquid-liquid dispersion. The liquid monomers containing soluble initiator is dispersed as small droplets, and stabilized by stirring and stabilizers. The second stage is sticky stage, equilibrium of monomer-polymer droplets determines the final particle size. The droplets collide with each other and coalescence into larger ones and re-divide again. In the third stage, there is no coalescence between polymer particles, they are solid and they do not stick.[16]

Stirring speed is one of the most important factors, which influences the control of particle sizes. Geometric factors (such as type and size of the reactor and type and diameter of the stirrer impellers relative to the reactor dimensions) and operating parameters (such as stirring speed, time and temperature of polymerization, water /organic phase ratio, stabilizer and electrolyte, see Eq. 2.1) influence the organic droplet size and the particle size distribution of copolymer beads.[14]

Various parameters influence particle size. Stirring speed enables to control particle size easily. Also, there are limits to control particle size by the adjustment of the stirring speed. These limits depend on the size and the configuration of the polymerization reactor, lower stirring speed may not be sufficient to establish droplet stabilization, whereas too high stirring speed may destroy the polymerization set-up.[14]

Another important consideration about the dependence of particle size on stirring speed is that smaller droplets/particles produced by faster mixing require high stabilizer concentrations. In the absence of sufficient stabilizer, the smaller droplets coalescence easily during the hardening stage. This produces larger and irregular shaped particles. This may also lead to partial or full coagulation of the microparticles.[14]

Higher stirring speed is provides to improve the homogenization of aqueous and organic phases before starting the suspension polymerization. It improves the contact of the two phases, produces uniform particles which contributes to the narrowing of the particle size distribution.[16]

2.2.2.2.5.2 Effect of Initiator Type and Its Concentration

Polymerization reactions take place under different conditions. Various types of initiators can be used for each specific case. Generally, organic peroxides and azo compounds are used as initiators for bulk, suspension, or solution polymerization. In industries, benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) are the most widely used initiators.[16] Initiator half-life determines the rate of initiator decomposition. The following table shows some of the decomposition times (half-life) of BPO and AIBN at different temperatures.

Table 2.3: Half-life of the initiators for various temperatures[16]

	70 °C	90 °C	100 °C
BPO	14 h	1.2 h	-
AIBN	7 h	-	0.12 h

Monomer droplets undergo constant collisions, which results in some degree of coalescence. Dynamic equilibrium is established and leads to stationary particle size. Individual drops do not maintain their identity but they undergo continuous coalescence and re-division. In more advanced polymerization stage, a low viscosity liquid monomer is converted gradually into viscous polymer. As conversion increases, the dispersed phase takes the characteristics of a solid particle.[16]

In the sticky stage, individual polymer particles tend to form incompletely fused particles. At this stage of conversion, agglomeration is slightly inhibited by stabilizer. Rapid polymerization during the sticky stage minimizes the number of effective collisions between polymer particles. This reduces agglomeration. These two values of critical viscosity are reached earlier for AIBN than BPO since AIBN has a shorter half-life time. Therefore, AIBN will produce a higher free radical concentration that will initiate a high number of propagating polymer chain. As a result, the period of the sticky stage will decrease, and smaller particles will be produced.

2.2.2.2.5.3 Effect of Crosslinking Agent and Its Concentration

Kiatkamjornwong, *et. al.*[17] reported that at very low crosslinking agent (such as DVB) concentration, the polymeric particles are clustered and fused. Particle formation cannot be observed, because the crosslinking agent concentration is too low to produce enough crosslinking sites to maintain the dimensions of the particles. Thus, low conversion or yield is observed.

An increase in the amount of crosslinking agent concentration produces an increasing crosslinking density of the polymer chains. The polymer beads become harder. Also, shrinkage of the copolymer bead surface decrease. Particle surfaces become smoother when the crosslinking agent is copolymerized.[17]

2.2.2.2.5.4 Effect of Diluent

Diluent composition does not affect the overall conversion of polymerization reactions. Also, changes in diluent composition do not affect the average particle size of the copolymers. The function of a diluent between a good and poor solvent is to develop surface morphology of the polymer particles.[17]

However, the type and amount of the diluent are important factors to control the heterogeneity of porous network of polymers. Solvating diluents produce small pores while non-solvating ones produce larger pores. Therefore, the polymer-solvent interaction is the main factor controlling the pore structure.[17]

2.2.2.2.5.5 Effect of Stabilizer Type and Its Concentration

Stabilizer type and concentration is one of the most important parameters in suspension polymerization. There are many publications in literature.[3,16,19-23] In the absence of sufficient stabilizer, the smaller droplets coalescence easily during the hardening stage. This produces larger, irregular particles and lead to partial or full coagulation of the particles. The average size of microparticles decreases with increasing stabilizer concentration.

2.2.2.3 Dispersion Polymerization

Dispersion polymerization is widely used to prepare polymer particles.[15,18,19] In dispersion polymerization the monomer and the initiator are both soluble in the polymerization medium, but the medium is poor solvent for the resulting polymer. The reaction mixture is homogeneous at the beginning of the polymerization, and the polymerization reaction is initiated in homogeneous solution. Phase separation occurs at an early stage of polymerization. This depends on the medium solvency for the resulting polymers. This leads to nucleation and the formation of the primary particles. Primary

particles formed in dispersion medium are swollen by the polymerization medium and/or the monomer. As a result, polymerization occurs within individual particles. Spherical particles are obtained within the size range of 0.1-10 μm.

Particles produced by dispersion polymerization in the absence of stabilizer are not sufficiently stable. Particles may coagulate during their formation. Small percentage of stabilizer is added to the polymerization mixture to obtain stable particle dispersions. Particle stabilization in dispersion polymerization is usually referred as steric stabilization compared with emulsion polymerization. Polymers and oligomers with low solubility in the polymerization medium and have moderate affinity for the polymer particles are used as stabilizers for dispersion polymerization. For dispersion polymerizations in alcohols and other polar solvents, a variety of polar organic polymers can be used such as polyvinylpyrrolidone, poly (vinyl alcohol), and cellulose derivatives.[18,19]

The polymerization temperature, concentrations of monomer and initiator, and the type and concentrations of the stabilizer affect the particle size in dispersion polymerization. In addition, the solvency of the polymerization medium strongly influences the particle size.[15]

There are some typical examples of dispersion polymerization are as follows. Styrene and methyl methacrylate in hydrocarbons or in C_1-C_5 alcohols. Various aspects of dispersion polymerization in petroleum hydrocarbons were discussed by Ober *et. al*.[18] who reported dispersion polymerization of styrene and methyl methacrylate in alcohols and various alcohol-water mixtures. More recently, Tseng *et. al.,*[19] have studied the effects of medium solvency, and concentrations of monomer, stabilizer, and initiator on polymer particle size produced by dispersion polymerization. They also discussed the preparation of reactive and crosslinked particles.

2.2.2.4 Precipitation Polymerization

In precipitation polymerization, the initial state of the reaction mixture is a homogeneous solution, same as dispersion polymerization. However, primary particles do not swell in the reaction medium. Under these conditions, initiation and polymerization take place in the homogeneous medium. Continuous nucleation and the coagulation of the nuclei to form larger and larger particles. Thus, precipitation polymerization produces irregularly shaped and polydisperse particles.[15]

Medium solvency for the polymer is a used to distinguish between dispersion and precipitation polymerization, but a sharp distinction may not exist. In the precipitation polymerization, the use of particle stabilizers may produce more uniform particles, but the particles remain irregularly shaped due to their growth mechanism.[15]

2.3 Polystyrene Microparticles

Crosslinked polymethacrylate was used as a polymer support for synthesis reactions in 1960s. Following this use, crosslinked polystyrene (pSTY) has been used in large number of chemical transformations. These polymers are referred as polymeric supports or polymeric reagents. They are produced by suspension polymerization in spherical form that is suitable for chemical modification. Synthetic organic polymers, which are used as polymer supports, are mainly based on polystyrene and polyacrylamides. Polymethacrylates and poly (vinyl alcohol) are also used.[20]

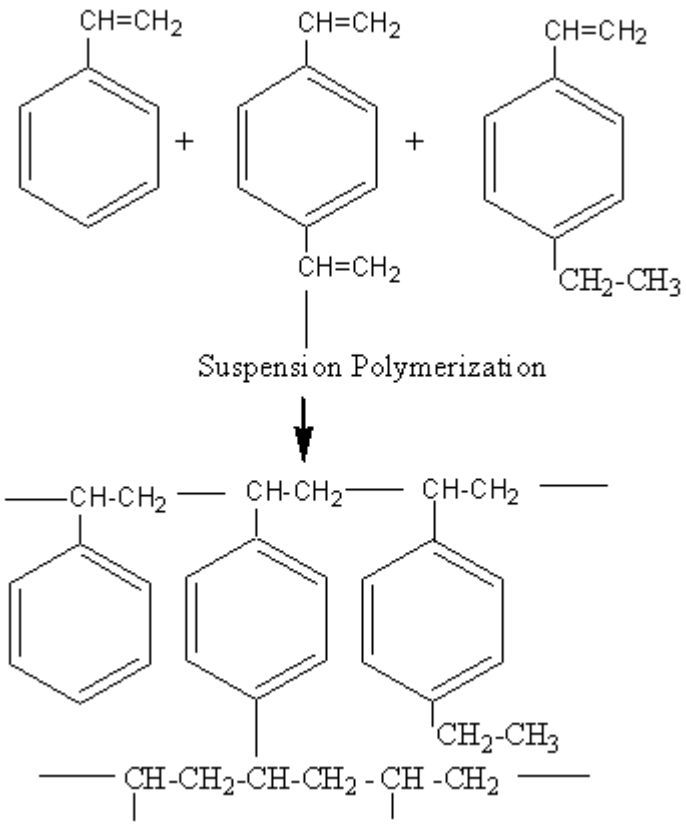


Figure 2.3: Synthesis of styrene-based polymer supports by copolymerization of styrene, divinylbenzene, and ethylvinylbenzene[19]

Styrene based polymer supports are produced by copolymerization of styrene and divinylbenzene (DVB), in oil-in-water suspension systems as depicted in Figure 2.2. The DVB monomer commonly used is a mixture composed of divinylbenzene isomers, ethylvinylbenzenes and small percentages of aromatic compounds. A monomer soluble initiator such as benzoyl peroxide (BPO) or 2,2′-azobisisobutyronitrile (AIBN) is used to initiate suspension polymerization. initiator concentration is kept between 1-2 % (w/w) based on monomer. Temperature is usually kept between 60-80 ^{o}C. Polymerization time depends on initiator concentration, temperature, and the exact composition of the monomer mixture. It is determined experimentally, but it is usually between 5 and 15 hours.[19]

Monodisperse polystyrene beads are produced by a special mode of seeded polymerization developed by Elingsen *et. al*.,[21] According to this method, aqueous polystyrene latex is equilibrated with a suitable oligomer and then with styrene and DVB.

Under controlled experimental conditions, the monomers are absorbed uniformly by the seed latex particles. Subsequent polymerization of the swollen particles produces the corresponding polymer beads. The size and crosslinking of the resulting particles are determined by the amount of the monomers used for swelling. This method is generally useful for producing particles in the range of 2-20 μm.

Due to its chemical structure, polystyrene is more inert than other commonly available polymer supports. It is compatible with organic solvents. Styrene based polymer supports have been used in many biological applications. They are also used for a wide range of other analytical, catalytic and synthetic applications.[14] Chloromethylated and brominated polystyrene is an intermediate for the synthesis of styrene based polymer supports. However, chloromethylation and bromination reactions give a variety of side reactions depending on the experimental conditions and functionalization.[14]

2.4 Functional Microparticles

Reactive or functional microparticles are produced by two methods. These are copolymerization of suitably functionalized monomers, and functionalization of preformed microparticles.[1]

Desired functionality of the polymer microparticles can be achieved either during, or after the polymerization as illustrated in Figure 2.4. By direct polymerization method, mixture of styrene, divinylbenzene, and a functional monomer is copolymerized to produce the microparticle with functional groups. The alternative method involves the copolymerization of styrene with divinylbenzene, and obtained crosslinked particles are functionalized.[2]

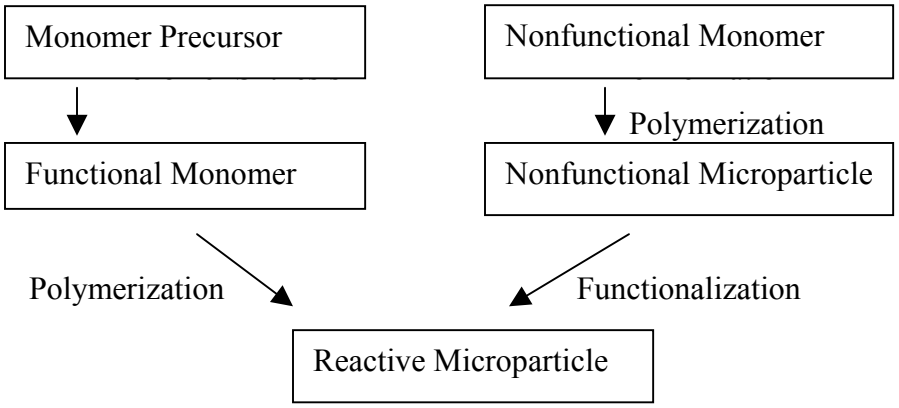


Figure 2.4: Conventional routes for the synthesis of reactive microparticles by copolymerization of functional monomers and functionalization of preformed microparticles[2]

Generally, direct polymerization is a preferred, but it is difficult to synthesize the functional monomer. Functionalization of pre-formed particles is not available for the crosslinked polystyrene microparticles. During the functionalization reactions, organic chemical procedures are applied.[1]

Side reactions that are taking place on the polymer are a major problem with the preparation of polymer supports by polymer derivatization. In fact, very few aromatic substitution reactions occur without any side reactions. On a polymer support, the side products of the reaction cannot be removed from the derivatized polymer. They always remain as contaminants on the polymer. For some applications, these impurities may not be a problem. Effects of these impurities cannot be predicted since the nature of the contaminants is not known.[1]

When a suitably reactive styrene monomer and suitable suspension setup are available, direct suspension polymerization of styrene, divinylbenzene, and functional monomer provides a more suitable way to styrene based functional polymer supports. Direct suspension copolymerization can be used to produce microparticles with low or high degrees of functionality. Adjustment of the concentration of divinylbenzene in the monomer mixture provides to control crosslinking density of the polymerization product.[1]

For many applications, low concentration of functional groups on the particles is needed. For this reason, functional monomers and various crosslinking monomers are often copolymerized with suitable structural monomers obtain crosslinked (insoluble) and functional microparticles.[1]

An important feature of microparticle formation by copolymerization is that the resulting microparticles may/may not, have the same composition with the starting monomer mixture. This may be due to copolymerization reactivity ratios.[1] Polymer fractions formed at different intervals during polymerization reaction may have different compositions which means that functional groups may not be equally distributed throughout the particles.

Many hydrophobic polymer microparticles are produced by oil-in-water polymerization medium that contains small quantities charged comonomers. In these systems, the charged comonomer is incorporated into a small fraction of the polymer initially formed. This charged and hydrophilic polymer fraction remains at particle-water interface during and after particle growth. A portion of the charged functional comonomer units is available at the particle surface, as seen Figure 2.5. This type of copolymerization is used for ionic and polar comonomers. This provides an ideal way to prepare crosslinked and functional particles.

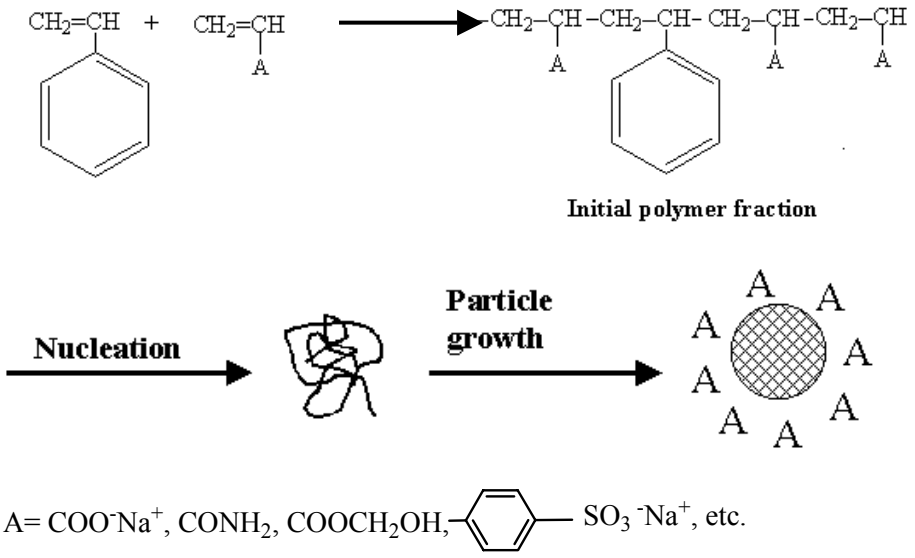


Figure 2.5: Schematic orientation of charged/polar groups on the particle surface in emulsion copolymerization of styrene with small quantities of ionic/polar groups[2]

Chemical activation of surface functional groups (hydroxyl, carboxyl, etc.) with suitable reagents (tosyl chloride) is used to produce amine functional particles. These particles are reacted with diamine carrying ligand to obtain amine functionality.[22] Also, amine functional uniform latex particles can be produced by copolymerization of styrene with the tertiary amine functional comonomers.[6]

Surface modification is an efficient tool for improving the properties of polymeric materials that are used in various biomedical applications.[23] Chemical modification methods are used in many biotechnological applications, such as the interaction of polymeric particles with cells, proteins, enzymes and nucleic acids. Stable DNA immobilization can be obtained by complexation between the amino groups of the polymer and the phosphorus carrying DNA segments.[23,24] For this reason, amine functional supports are commonly used in DNA immobilization. Polymer microparticles may have various functional groups such as NH_2, COOH, SH and/or OH. They also may be labile to biodegradation and hydrolytic degradation. Each of these properties may represent a desirable feature, or a drawback, depending on the intended application of the microparticles.[1]

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Styrene (STY; Sigma-Aldrich, Steinheim, Germany) and divinyl benzene (DVB; containing 65 % mixture of m- and p-isomers of DVB and 33 % ethylvinylbenzene isomers, EVB; Merck, Hohenbrunn, Germany) were purified by passing through a column packed with activated aluminum oxide and kept in a refrigerator until use. 2-(tert-butylamino)ethyl methacrylate (tBAEMA; 97 %) was obtained from Aldrich, Milwaukee, WI, USA). 2,2´-Azobis(2-methylpropionitrile) (2,2´-azobisisobutyronitrile; AIBN; Merck, Hohenbrunn, Germany) was recrystallized from methanol and kept refrigerated until used as the initiator. Sodium dodecylsulfate (SDS; 98 %, Sigma-Aldrich, Steinheim, Germany), poly(vinyl alcohol) (PVA; 87-89 % hydrolyzed, average M_w = 85,000-146,000 Aldrich, Milwaukee, WI, USA), Triton X-100 (X-100, polyoxyethylene(10) isooctyl phenyl ether; Sigma-Aldrich, Steinheim, Germany), and sodium dioctyl sulfosuccinate (SDSS; 98 %, Sigma-Aldrich, Steinheim, Germany) were used without further purification. Aluminum sulfate ($Al_2(SO_4)_3.10H_2O$; Aldrich, Milwaukee, WI, USA) and activated aluminum oxide (Al_2O_3; acidic, Brockmann I; Sigma-Aldrich, Steinheim, Germany) were used as received without further purification. Absolute ethanol was purchased from Riedel-deHaën (Sigma-Aldrich, Seeize, Germany) and used without further purification. HCl and NaOH were purchased from Aldrich, Milwaukee, WI, USA and used without further purification. All polymerizations were performed using deionized water as continuous medium. In all experiments, the monomer to water ratio was 6:50.

3.2 Preparation of Microparticles

The secondary amine functional microparticles were synthesized in the glass polymerization vessels (120-mL) having screw caps by applying three different methods. In a typical suspension polymerization procedure, the aqueous dispersion medium was prepared by dissolving desired amount of surfactant such as SDS, within 50 mL of distilled water. The proper amount of water insoluble initiator was dissolved within the monomer mixture. The prepared aqueous and organic solutions were charged to the polymerization vessel and the reaction mixture was flushed by bubbling nitrogen for 5 minutes to remove the oxygen and then was capped. The reaction vessel then put into a water bath shaker (Gyrotory Model 676, Scientific Co., Inc., New Brunswick, NJ, USA) at room temperature and shaked for 45 min. at selected shaker rate, cpm. Then, the water bath was heated to polymerization temperature and the reaction mixture was held at this temperature for a period of time for the polymerization. The polymerization conditions are tabulated in Table 3.1.

Table 3.1: Experimental Conditions for Suspension Polymerization in the Presence of Surfactant (AIBN = 0.33 wt% on monomers)

Exp. No.	Time (h)	Temp. (^{o}C)	Stirring (cpm)	tBAEMA (%)	DVB (%)	EVB (%)	STY (%)	SDS (%)	PVA (%)	X-100 (%)	SDSS (%)
Effect of Polymerization Time											
1	3	78	240	25	25	13.5	36.5	3.3	-	-	-
2	4.5	78	240	25	25	13.5	36.5	3.3	-	-	-
3	6	78	240	25	25	13.5	36.5	3.3	-	-	-
4	10	78	240	25	25	13.5	36.5	3.3	-	-	-
5	16	78	240	25	25	13.5	36.5	3.3	-	-	-
Effect of Stirring Speed											
6	10	78	180	25	25	13.5	36.5	3.3	-	-	-
7	10	78	300	25	25	13.5	36.5	3.3	-	-	-
Effect of Temperature											
8	10	67	300	25	25	13.5	36.5	3.3	-	-	-
9	10	74	300	25	25	13.5	36.5	3.3	-	-	-
Effect of DVB Concentration											
10	10	78	300	25	5	2.7	67.3	3.3	-	-	-
11	10	78	300	25	12.5	6.7	55.8	3.3	-	-	-
Effect of tBAEMA Concentration											
12	10	78	300	0	25	13.5	61.5	3.3	-	-	-
13	10	78	300	5	25	13.5	56.5	3.3	-	-	-
14	10	78	300	10	25	13.5	51.5	3.3	-	-	-
15	10	78	300	15	25	13.5	46.5	3.3	-	-	-
16	10	78	300	50	25	13.5	12.5	3.3	-	-	-
Effect of Stabilizer Type											
17	10	78	300	25	25	13.5	36.5	-	-	-	3.3
18	10	78	300	25	25	13.5	36.5	-	-	3.3	-
19	10	78	300	25	25	13.5	36.5	-	3.3	-	-
20	10	78	300	25	25	13.5	36.5	2.6	0.7	-	-

The procedure of preparing the amine functional microparticles using the second method was a similar procedure given above, except a proper amount of $Al_2(SO_4)_3$ was used to replace SDS in the dispersion medium. The polymerization conditions are summarized in Table 3.2.

Table 3.2: Experimental Conditions for Suspension Polymerization in the Presence of $Al_2(SO_4)_3$

Exp. No.	Time (h)	Temp. (^oC)	Stirring Speed (cpm)	tBAEMA (%)	DVB (%)	EVB (%)	STY (%)	$Al_2(SO_4)_3$ (%)	AIBN (%)
Effect of Stirring Speed									
21	10	78	180	25	25	13.5	36.5	0.83	0.33
22	10	78	240	25	25	13.5	36.5	0.83	0.33
23	10	78	300	25	25	13.5	36.5	0.83	0.33
Effect of DVB Concentration									
24	10	78	300	25	5	2.7	67.3	0.83	0.33
25	10	78	300	25	17.5	9.1	48.4	0.83	0.33
Effect of tBAEMA Concentration									
26	10	78	300	5	25	13.5	56.5	0.83	0.33
27	10	78	300	50	25	13.5	11.5	0.83	0.33
Effect of AIBN Concentration									
28	10	78	300	25	25	13.5	36.5	0.83	0.17
29	10	78	300	25	25	13.5	36.5	0.83	0.66
Effect of $Al_2(SO_4)_3$ Concentration									
30	10	78	300	25	25	13.5	36.5	1.67	0.33
31	10	78	300	25	25	13.5	36.5	2.49	0.33

The third method used to prepare the secondary amine functional microparticles was again similar to first polymerization procedure, except a proper amount of $Al_2(SO_4)_3$ was added to the aqueous dispersion medium. The polymerization experiments in the presence of a surfactant and $Al_2(SO_4)_3$were carried out according the conditions reported in Table 3.3.

Table 3.3: Experimental Conditions for Suspension Polymerization in the Presence of SDS and $Al_2(SO_4)_3$

Exp. No.	Time (h)	Temp. (^oC)	Stirring Speed (cpm)	tBAEMA (%)	DVB (%)	EVB (%)	STY (%)	SDS (%)	$Al_2(SO_4)_3$ (%)	AIBN (%)
Effect of tBAEMA Concentration										
32	6	78	180	0	25	13.5	61.5	0.17	0.46	0.33
33	6	78	180	5	25	13.5	56.5	0.17	0.46	0.33
34	6	78	180	10	25	13.5	51.5	0.17	0.46	0.33
35	6	78	180	15	25	13.5	46.5	0.17	0.46	0.33
Effect of SDS Concentration										
36	6	78	180	5	25	13.5	56.5	0.83	0.46	0.33
37	6	78	180	5	25	13.5	56.5	1.67	0.46	0.33
Effect of AIBN Concentration										
38	6	78	180	5	25	13.5	56.5	0.17	0.46	0.58
39	6	78	180	5	25	13.5	56.5	0.17	0.46	0.83
Effect of DVB Concentration										
40	6	78	180	5	5	4.3	78.2	0.17	0.46	0.33
41	6	78	180	5	12.5	2.7	87.3	0.17	0.46	0.33

In order to remove the stabilizer(s) and unreacted monomers, an extensive cleaning procedure was applied. First, the microparticles were separated from the aqueous phase by decantation of the supernatant after centrifugated the dispersion at 6000 rpm for 5 min. using Hettich Universal 32 bench-top centrifuge. Then, the microparticles were redispersed in ethanol (50 mL), centrifugated and the liquid phase decanted. After repeating the washing 5 times with ethanol, the same washing procedure was repeated with water (50 mL, 5 times). The microparticles were washed, centrifugated, and separated once again using ethanol. Finally, the microparticles were dried at 50^oC under vacuum to a constant weight.

3.3 Yield of Microparticles

The microparticles yield was determined gravimetrically and the percent yield was calculated by the following equation:

Microparticle yield, % = (W_p/W_m) x 100 **(3.1)**

where, W_p and W_m are the weight of dry microparticles and the total weight of the monomers initially charged to the reactor, respectively.

3.4 Microparticles Characterization

Optical microscopy photomicrographs were taken on OLYMPUS-BH2 microscope. A drop of dilute microparticle dispersion in water was spread onto a glass surface and dried in a dust-free environment at room temperature. Particle size and distribution were determined by measuring at least 200 microparticles for each sample from the photographs. The average size of produced microparticles can be calculated using various equations

$$D_n = \frac{\sum D_i . N_i}{\sum N_i} \quad \textbf{(3.2)}$$

$$D_w = \frac{\sum D_i^2 . N_i}{\sum D_i . N_i} \quad \textbf{(3.3)}$$

$$D_z = \frac{\sum D_i^3 . N_i}{\sum D_i^2 N_i} \quad \textbf{(3.4)}$$

$$D_{z+1} = \frac{\sum D_i^4 . N_i}{\sum D_i^3 . N_i} \quad \textbf{(3.5)}$$

where, N_i is the number of particles with diameter D_i (μm). Particle size distribution was characterized by polydispersity index (PDI) calculated as ratio of D_{z+1}/D_n. Average size values were calculated as number average particle size (D_n).

3.5 Determination of Amine Content

The amine content of the prepared polymer microparticles was determined by acid-base titration. For this purpose, 10 mL of a 0.3 N HCl solution were added to 0.2 g of dried microparticles and the mixture was held at room temperature for 24 h in a tightly sealed glass container. The mixture was filtered and 5 mL of the filtrate was titrated with a 0.1 N NaOH solution. The tBAEMA contents of the microparticles in terms of weight percent were calculated based on the following expression:

$$\text{tBAEMA}, \% = \frac{\left[V_{HCl} N_{HCl} - 2\,(N_{NaOH} V_{NaOH})\right] \text{x}\, 10^{-3} \text{x}\, 185.3}{\text{w}} \text{ x}\, 100 \qquad (\mathbf{3.6})$$

where, w is the dried microparticles weight, V_{HCl} , V_{NaOH} , N_{HCl} and N_{NaOH} are the volumes and normalities of HCl and NaOH used, respectively.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 SDS Stabilized Suspension Polymerizations

At the first part of this study, microparticles were produced by a conventional suspension method using 2,2'-azobisisobutyronitrile (AIBN) as an initiator and sodium dodecylsulfate, SDS, as a stabilizer. A set of experiments was carried out to investigate the effects of some polymerization parameters (polymerization time, temperature, stirring speed, amine concentration, crosslinking agent concentration, etc.) on percent yield, particle size, particle size distribution, and amine content of the particles. The weight percent of 2-(tert-butylamino) ethyl methacrylate (tBAEMA) content of the polymers were reported as experimental or available amine.

4.1.1 Effect of Polymerization Time

The effect of polymerization time on the percent yield and available amine content was studied by keeping the monomers, initiator, and stabilizer concentrations constant at 78 ^{o}C at 240 cpm stirring speed (Experiment nos.1-5, tables 3.1and 4.1).

Table 4.1: Effect of polymerization time on percent yield and available amine content in SDS stabilized suspension polymerization

Exp. No.	Time (h)	Available Amine (wt. %)	Yield (wt. %)
1	3.0	8.1	67
2	4.5	9.4	72
3	6.0	13.5	71
4	10.0	18.8	83
5	16.0	18.9	78

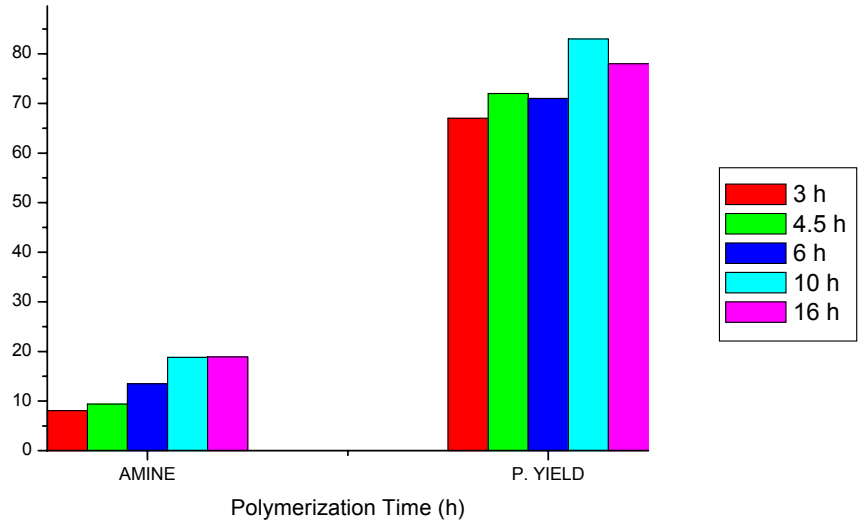


Figure 4.1: Changes in available amine content and percent yield for different polymerization times (Experiment nos.1-5, tables 3.1 and 4.1).

As seen in Figure 4.1, percent yield did not change significantly when the polymerization time was increased from 10 to 16 hours. However, as the polymerization time was increased from 3 to 16 hours, the experimental amine content increased from 8.1 to 18.9 percent. It was also observed that when the polymerization time was less than 10 hours the resulting products had monomer odor which indicated the incompletion of polymerization. Two experiments which were carried out for 10 and 16 hours yielded odor-free products. This time dependency of the polymerization may be explained as follows.

In concentrated solutions, the viscosity of the reaction mixture becomes high as polymer chains form especially in crosslinked systems. This high viscosity hinders the diffusion of chains because of entanglements and crosslinkings. In uncrosslinked and dilute solutions, the viscosity never builds up to the point where the diffusion of chains is slowed. For neat monomer(s) (i.e., monomer(s) droplets in suspension polymerization), often in cases where the polymer formed has a high glass transition temperature, there can come a point at which even the diffusion of monomer(s) is slow. The mixture has become a hard glass, and unreacted radicals become trapped inside. Therefore, a longer time is needed for the diffusion of monomer(s) to be polymerized.

In this set of experiments, the polymerization products were agglomerated and irregular in shape. A representative micrograph of a sample is given in Figure 4.1. Agglomeration of polymerization product may be due to insufficient stirring speed or stabilization.

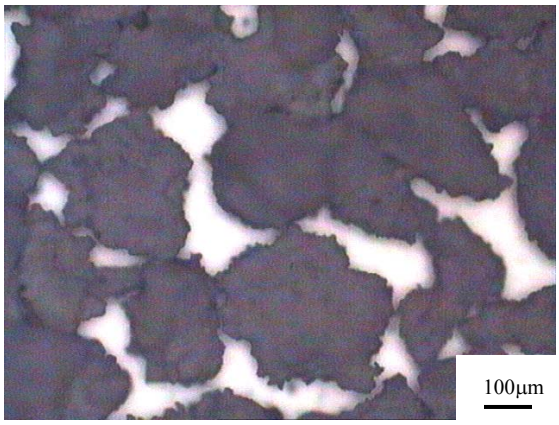


Figure 4.2: Optical micrograph of particles with 10 hours polymerization time (Experiment no. 4, tables 3.1 and 4.1) (Magnification 100x).

4.1.2 Effect of Stirring Speed

In suspension polymerization, stirring speed is one of the most important parameters to control the particle size. Lower stirring speed may not be enough for droplet stabilization. To explore the effect of stirring speed, a set of experiments was carried out by varying the stirring speed between 180 and 300 cpm (Experiment nos. 4, 6, and 7 in tables 3.1 and 4.2). In these experiments, polymerization time, monomers, initiator, and stabilizer concentrations were kept constant and the polymerizations were conducted at 78 ^{o}C for 10 hours.

Table 4.2: Effect of stirring speed on percent yield and available amine content in SDS stabilized suspension polymerization

Exp. No.	Stirring Speed (cpm)	Available Amine (wt. %)	Yield (wt. %)
6	180	21.5	89
4	240	18.8	83
7	300	18.8	87

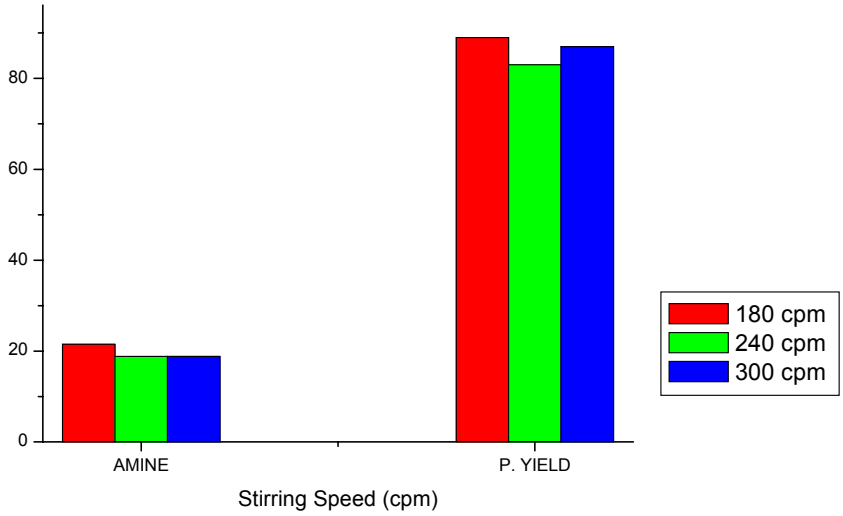


Figure 4.3: Changes in available amine content and percent yield for different stirring speed cpm (Experiment nos. 4, 6, and 7 in tables 3.1 and 4.2).

As stirring speed increases from 180 to 300 cpm, available amine content decreased from 21.5 to 18.8 percent, while the change in percent yield was not significant. Changes in available amine content and percent yield for different polymerization systems are shown in Figure 4.3. Varying the stirring speed did not change the morphology of the polymerization product. Again in this set of experiments, agglomerated polymerization product was obtained which may be due to insufficient stbilizing conditions for droplet stabilization.

4.1.3 Effect of Temperature

Polymerization temperature is also an important parameter that affects the features of the polymerization product. In order to examine the effect of polymerization temperature on percent yield and available amine content, the polymerization temperature was varied between 67 and 78 ^{o}C. In these experiments, the concentrations of monomers, initiator, and stabilizer were kept constant and the polymerizations were carried out for 10 hours at 300 cpm stirring speed (Experiment nos, 7-9 in tables 3.1 and 4.3).

Table 4.3: Effect of temperature on percent yield and available amine content in SDS stabilized suspension polymerization

Exp. No.	Polymerization Temperature (^{o}C)	Available Amine (wt. %)	Yield (wt. %)
8	67	10.8	70
9	74	16.2	82
7	78	18.8	87

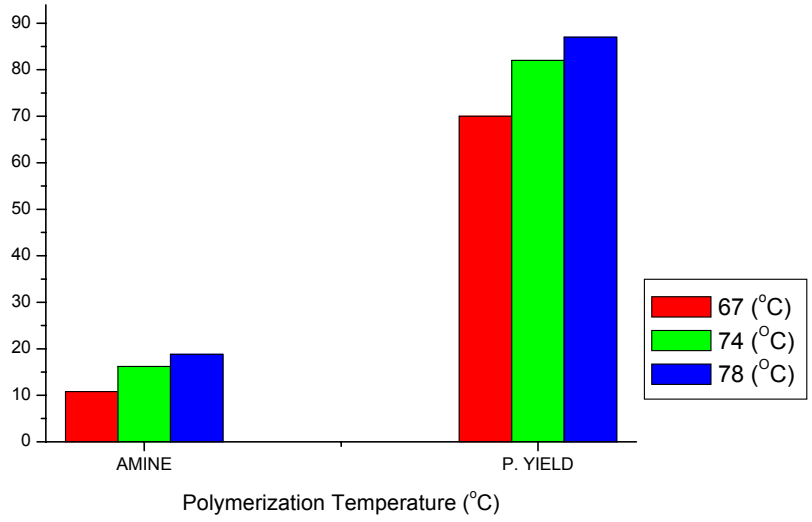


Figure 4.4: Changes in available amine content and percent yield for different polymerization temperatures (Experiment nos, 7-9 in tables 3.1 and 4.3).

Half-life of AIBN is 10, 2.45, and 1.64 hours at 67, 74, and 78 ^{o}C, respectively. As expected, the lowest percent yield was obtained when the polymerization temperature was 67 ^{o}C. The percent yield increased from 70 to 87 percent with increasing polymerization temperature from 67 to 78 ^{o}C. Also, for the same increasement in temperature, the available amine content increases from 10.8 to 18.8 percent, as demonstrated in Figure 4.4. The increase in percent yield can be attributed to an increase in the number of generated free radicals and, thus, the concentration of growing polymer chains, as a function of polymerization temperature. The increase in available amine content with increasing conversion may be explained by the copolymerization reactivity of tBAEMA. At high conversions about 75 percent of tBAEMA are on the surface which may be speculated that tBAEMA copolymerized after the majority of styrene and divinylbenzene were consumed. In this set of experiments, agglomerated polymerization product was obtained.

4.1.4 Effect of Crosslinking Agent Concentration

In this part of work, effect of crosslinking agent concentration on percent yield and available amine content was investigated by varying the divinylbenzene, DVB concentration. The percentages of DVB in tables 3.1 and 4.4 are based on meta and para isomers of DVB. The crosslinker concentrations in the monomer phase were varied between 5 and 25 percent based on total monomers weight. In these experiments, polymerization time, initiator, tBAEMA, and stabilizer concentrations were kept constant at 78 ^{o}C polymerization temperature and 300 cpm stirring speed (Experiment nos. 7,10 and 11 in tables 3.1 and 4.4).

Table 4.4: Effect of crosslinker concentration on percent yield and available amine content in SDS stabilized suspension polymerization

Exp. No.	DVB (wt. %)	A. Amine (wt. %)	Yield (wt. %)
10	5.0	-	-
11	12.5	18.8	65
7	25.0	18.8	87

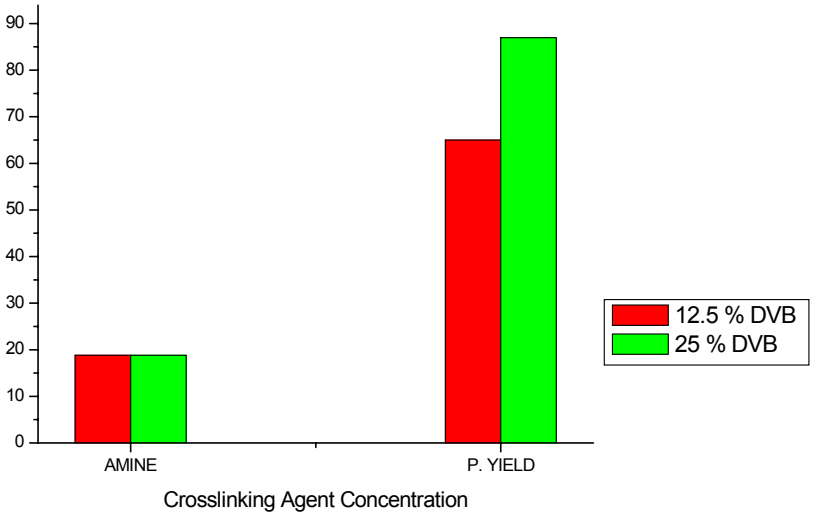


Figure 4.5: Changes in available amine content and percent yield for different DVB concentrations (Experiment nos. 7,10 and 11 in tables 3.1 and 4.4).

In this set of experiments, at very low DVB concentration (5 weight percent), polymerization product was coalesced, no individual particles formation was observed. This may be due to low crosslinking sites, which may not be enough to maintain the dimensions of the microparticles during the synthesis. When the DVB concentration was increased to 12.5 percent, the individual particle formation was observed. However, the majority of the product was agglomerated or fused form (Figure 4.2). Increasing the DVB content to 25 % only agglomerated particles were obtained. As DVB concentration increased from 12.5 to 25 percent, the percent yield increased while the available amine content did not change (Figure 4.5).

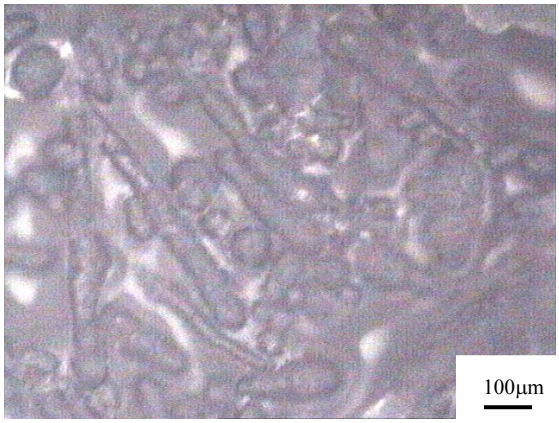


Figure 4.6: Optical micrograph of particles prepared in presence of 12.5 wt. % DVB (Experiment no. 11 in tables 3.1 and 4.1). (Magnification 100x).

4.1.5 Effect of Amine Concentration

2-(tert-Butylamino)ethyl methacrylate, tBAEMA, concentration was varied between 0 and 50 percent on total weight of monomers to examine its effect on percent yield and available amine content. Polymerizations were carried out at 78 ^{o}C, with a stirring speed of 300 cpm, while initiator, DVB, and stabilizer concentrations were kept constant during 10 hours polymerization time. The percent yield and the available amine content values with different tBAEMA feed concentrations are given in Table 4.5.

Table 4.5: Effect of 2-(tert-butylamino)ethyl methacrylate concentration on percent yield and available amine content in SDS stabilized suspension polymerization

Exp. No.	tBAEMA (wt. %)	Available Amine (wt. %)	Yield (wt. %)
12	0.0	-	92
13	5.0	3.7	81
14	10.0	8.2	82
15	15.0	12.3	72
7	25.0	18.8	87
16	50.0	37.5	53

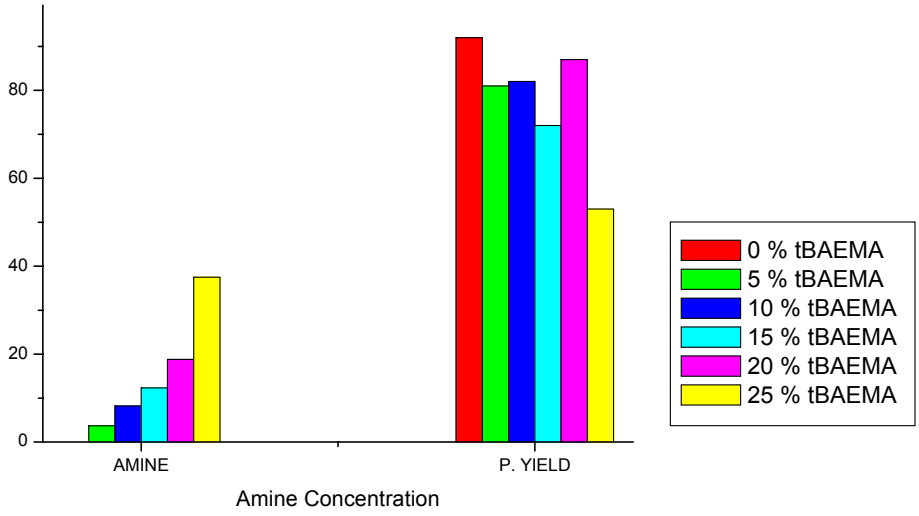


Figure 4.7: Changes in available amine content and percent yield for different tBAEMA concentrations (Experiment nos. 7,12-16 in tables 4.5 and 3.1).

As seen in Figure 4.7, the percent yield decreased with increasing tBAEMA feed concentration which may be attributed to formation of smaller particles and, thus, lowering recoverable polymer amount at higher tBAEMA concentrations. The available amine contents of the polymers were found to be about 75 % of the charged tBAEMA amount. For Exp. no. 16, polymerization pruduct could not be separated completely from the liquid phase by centrifugation due to very small particle size.

In Exp. no. 12, feed was free from tBAEMA obtained polymerization product was like a blackberry berry with a few mm in size, although highest yield was obtained. In remaining experiments, obtained products were agglomerated.

4.1.6 Effect of Stabilizer Type

The effect of stabilizer type was studied by conducting the polymerization reactions at 78 ^{o}C with a stirring speed of 300 cpm for 10 hours. For these polymerizations the type of stabilizer was changed while the concentrations of monomers, initiator, and stabilizer were kept constant (Experiment nos. 7, 17-20 in tables 3.1 and 4.6).

Table 4.6: Effect of stabilizer type on percent yield and available amine content in SDS stabilized suspension polymerization

Exp. No.	Stabilizer Type	Stabilizer (wt. %)	Available Amine (wt. %)	Yield (wt. %)
7	SDS	3.3	18.8	87
17	SDSS	3.3	3.5	75
18	X-100	3.3	2.7	94
19	PVA	3.3	5.7	70
20	SDS+PVA	2.6+0.7	13.5	67

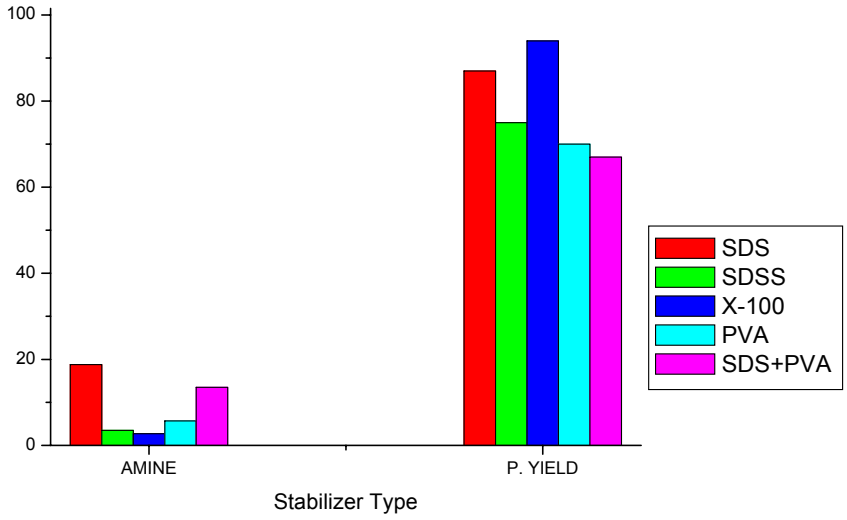


Figure 4.8: Changes in available amine content and percent yield for different stabilizer types (Experiment nos. 7, 17-20 in tables 3.1 and 4.6).

During this study the effects of anionic and non-ionic stabilizers were investigated using various types of stabilizers. For this purpose, sodium dodecylsulfate (SDS), poly(vinyl alcohol) (PVA), poly(oxyethylene(10) isooctyl phenyl ether) (X-100), and sodium dioctyl sulfosuccinate (SDSS) were used as single or mixed stabilizer(s). It was found that SDS was the most effective stabilizer in terms of percent yield and available amine content, as seen in Figure 4.8. It was also found that SDS and PVA produced agglomerated microparticles

whereas X-100 and SDSS produced irregular shaped large particles, which may be due to insufficient stabilization of these stabilizers.

When a mixture of SDS and PVA stabilizers was used, the available amine content value determined to be between the values obtained in SDS and PVA alone.

Also, variation in the SDS concentration up to three fold did not affect the particle morphology. Again, polymerization product was agglomerated.

4.2 $Al_2(SO_4)_3$ Stabilized Suspension Polymerizations

It has been known that various types of stabilizers are being used to prevent agglomeration of the monomer droplets in suspension polymerizations. These include water-soluble organic polymers, electrolytes, and water-insoluble inorganic compounds. In this set of experiments, $Al_2(SO_4)_3$ was used to obtain water-insoluble $Al(OH)_3$ at pH greater than 7 to stabilize the monomer droplets and polymer particles by limited coalescence. The effects of some polymerization parameters on particle formation, percent yield, and available amine content are presented and discussed in the following sections.

4.2.1 Effect of Stirring Speed

Stirring speed in suspension polymerization determines the particle size and particle size distribution. Stirring speed affects the stability of monomer droplets in the aqueous phase. In this part of the study, three different stirring speeds (i.e., 180, 240, and 300 cpm) were applied during the synthesis of microparticles. The concentrations of monomers, initiator, and $Al_2(SO_4)_3$ were kept constant and the polymerizations were conducted at 78 ^oC for 10 hours (Experiment nos. 21-23 in tables 3.2 and 4.7).

Table 4.7: Effect of stirring speed on percent yield, available amine content, and average size in $Al_2(SO_4)_3$ stabilized suspension polymerization

Exp. No.	Stirring Speed (cpm)	Available Amine (wt. %)	Yield (wt. %)	Average Size (μm)	PDI (D_{z+1}/D_n)
21	180	-	-	-	-
22	240	20.2	69	189	1.04
23	300	21.0	65	106	1.15

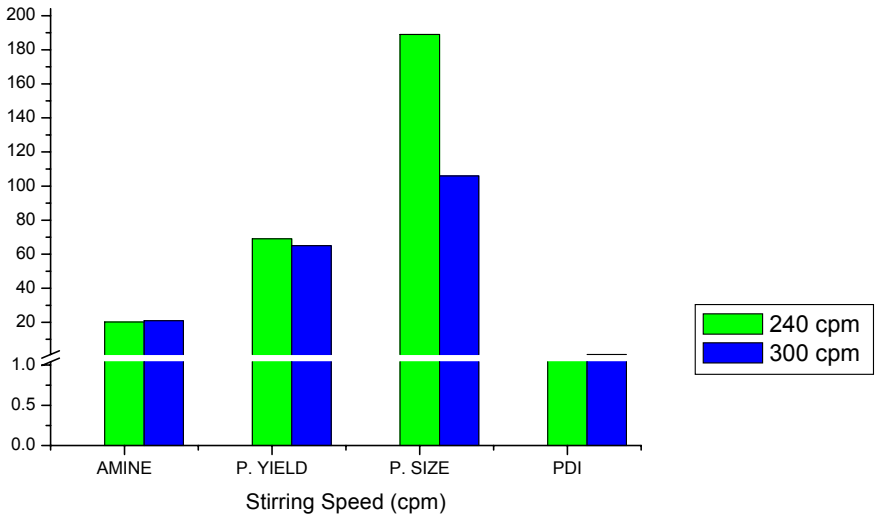


Figure 4.9: Changes in available amine content, percent yield, particle size, and particle size distribution for different stirring speeds (Experiment nos. 21-23 in tables 3.2 and 4.7).

The properties of the microparticles with different stirring speeds are given in Table 4.7, and changes in polymer properties are given in Figure 4.9. As seen here, the percent yield and average size of the microparticles decreased with increasing speed from 240 to 300 cpm. At 180 cpm stirring speed, the resulting polymer particles were fused and could not be characterized. The fusing of microparticles at low stirring speed indicates that the stirring speed may not be sufficient to establish a droplet stabilization.

A decrease in average particle size with increasing stirring speed is described in the literature for different suspension polymerization systems.[22, 25-27] Tuncel,[22] studied the effects of polymerization parameters in suspension polymerization systems. The properties of beads did not change significantly with the stirring rate however the average particle size decreased with increasing stirring speed. The PDI values showed that size distribution was slightly narrower with lower stirring speeds, and wider PDI value for higher stirring speeds. Generally, high stirring speed homogenizes the organic phase droplets and produces particles of smaller size.

The lower yields comparing to SDS stabilized systems may be attributed to unrecoverable very small particles. The optical micrographs of microparticles produced with 240 and 300 cpm are shown in Figure 4.10. As seen in the figure, individual and spherical microparticles were obtained with different sizes. The histograms indicating the size distribution of the microparticles produced with 240 and 300 cpm stirring speeds are shown in Figure 4.11.

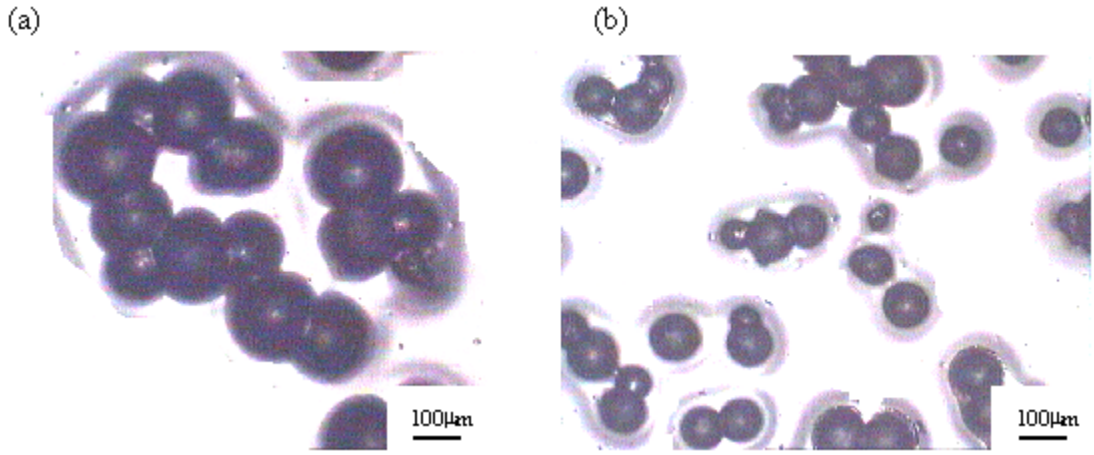


Figure 4.10: Optical micrographs of particles prepared with (a) 240 and (b) 300 cpm stirring speed, respectively (Experiment nos. 22 and 23 tables 3.2 and 4.7). (Magnification 100x).

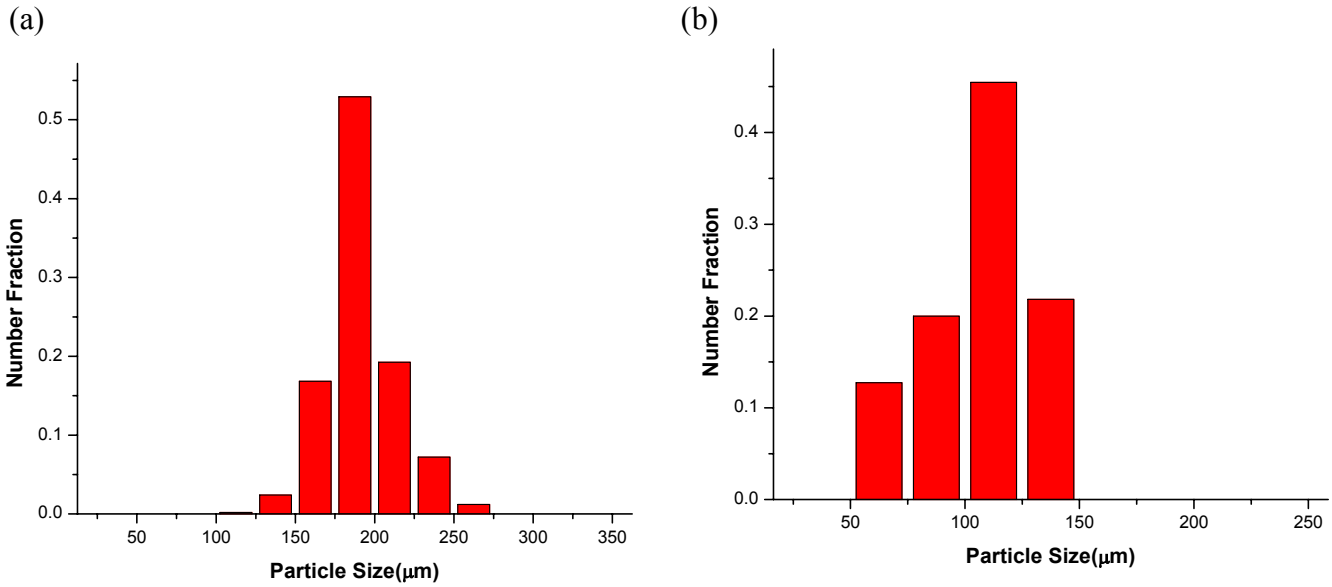


Figure 4.11: Particle size distributions of particles prepared with (a) 240 and (b) 300 cpm stirring speed, respectively (Experiment nos. 23 and 24 in tables 3.2 and 4.7).

The histograms and polydispersity index values indicate that there is a small increase in the size distribution with the stirring speed. As also seen in Table 4.7, and Figure 4.9, a slight effect of the stirring speed was observed on available amine content.

4.2.2 Effect of Crosslinking Agent Concentration

The effect of the crosslinking agent concentration was investigated for $Al_2(SO_4)_3$ stabilized system by changing the crosslinking agent concentration and keeping the other conditions constant (Experiment nos. 23, 24 and 25 in tables 3.2 and 4.8).

The percent yield, available amine content, and average size values of the microparticles obtained with different crosslinker concentrations are given in Table 4.8, and demonstrated in Figure 4.12.

Table 4.8: Effect of crosslinking agent concentration on percent yield, available amine content and average size in $Al_2(SO_4)_3$ stabilized suspension polymerization

Exp. No.	DVB (wt. %)	Available Amine (wt. %)	Yield (wt. %)	Average Size (µm)	PDI (D_{z+1}/D_n)
24	5.0	-	-	-	-
25	17.5	19.6	48	75	1.29
23	25.0	21.0	65	106	1.15

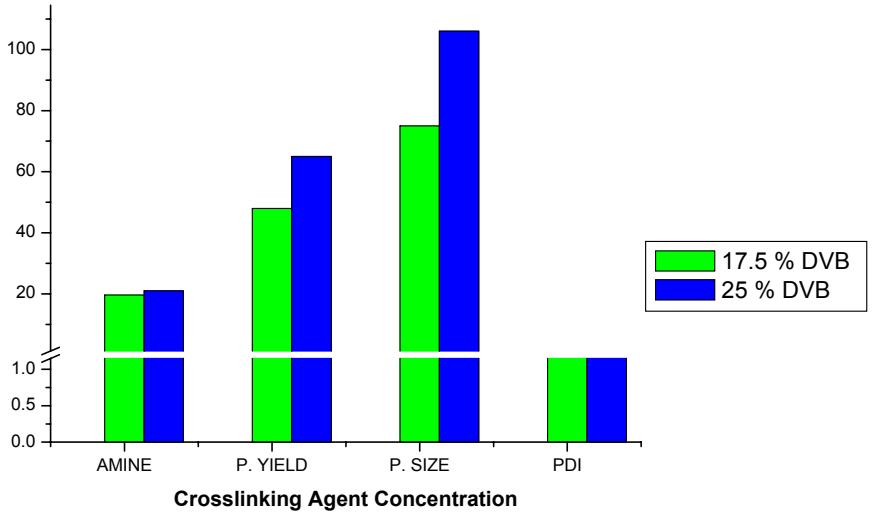


Figure 4.12: Changes in available amine content, percent yield, particle size, and particle size distribution for different stirring speeds (Experiment nos. 23, 24 and 25 in tables 3.2 and 4.8).

The produced polymerization product with 5 weight percent DVB was obtained as flake probably due to insufficient amount of crosslinker to maintain the stability of the particles. This result is in correlation with previous studies. Kiatkamjornwong, *et. al.*[17] studied with styrene/DVB monomers (95:5 wt. %)in toluene polymerization medium. They obtained fused polymerization product, and reported that a small amount of the crosslinking agent is not sufficient to copolymerize with styrene and lead to particle formation. When DVB concentration was increased from 5 to 17.5 percent individual spherical microparticles

were obtained (Figure 4.13). As said before, individual and spherical microparticles was observed at 25 percent DVB also.

The average size as well as the percent yield of microparticles increased with increasing crosslinker concentration. These changes can be seen in Figure 4.12. Increase in particle size with increasing DVB concentration is related to previous results presented by Tuncel.[28]

The increase in yield of the resulting microparticles with crosslinking agent concentration may be again attributed to larger particle size of the microparticles obtained. The amine content of the resulting polymers slightly increased as the crosslinker concentration increased. The PDI value increased from 1.15 to 1.29 as DVB concentration decreased from 25 to 17.5 percent based on total monomer weight.

The optical micrograph and particle size histogram of 17.5 weight percent DVB containing particles are shown in Figure 4.13 and 4.14. Examining Figure 4.13 indicates that lower DVB content causes some shape defects.

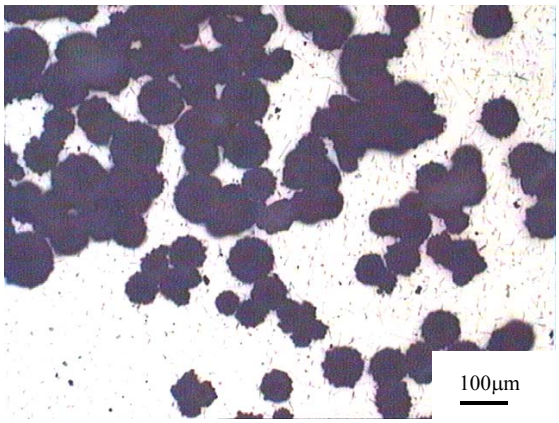


Figure 4.13: Optical micrograph of microparticles prepared in presence of 17.5 wt. % DVB (Experiment no. 25 in Table 3.2 and 4.8). (Magnification 100x).

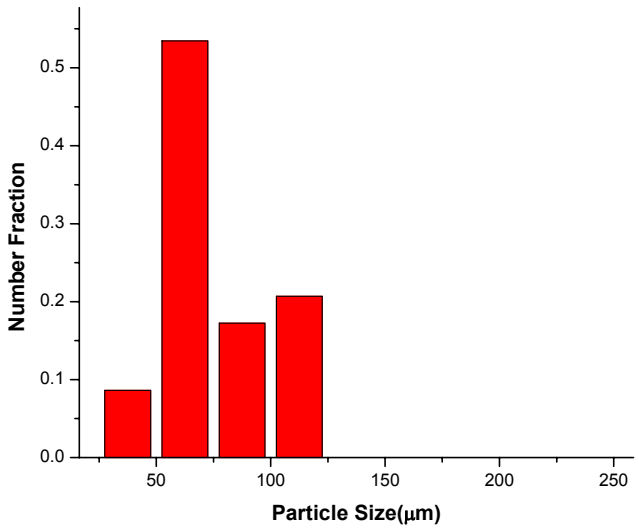


Figure 4.14: Particle size distribution of microparticles prepared in presence of 17.5 wt. % DVB (Experiment no. 25 in Table 3.2 and 4.8).

4.2.3 Effect of Amine Concentration

In this set of experiments, tBAEMA concentration was varied between 5 and 50 weight percent (based on total monomers), while other polymerization conditions were kept constant at 300 cpm stirring speed (Experiment nos. 23, 26 and 27 in tables 3.2 and 4.9).The percent yield, available amine content, and average size values of the microparticles obtained with various tBAEMA concentrations are given in Table 4.9.

Table 4.9: Effect of tBAEMA concentration on available amine content, percent yield and average particle size in $Al_2(SO_4)_3$ stabilized suspension polymerization

Exp. No.	tBAEMA (wt.%)	Available Amine (wt. %)	Yield (wt. %)	Average Size (μm)	PDI (D_{z+1}/D_n)
26	5.0	4.3	70	140	1.30
23	25.0	21.0	65	106	1.15
27	50.0	41.2	55	73	1.22

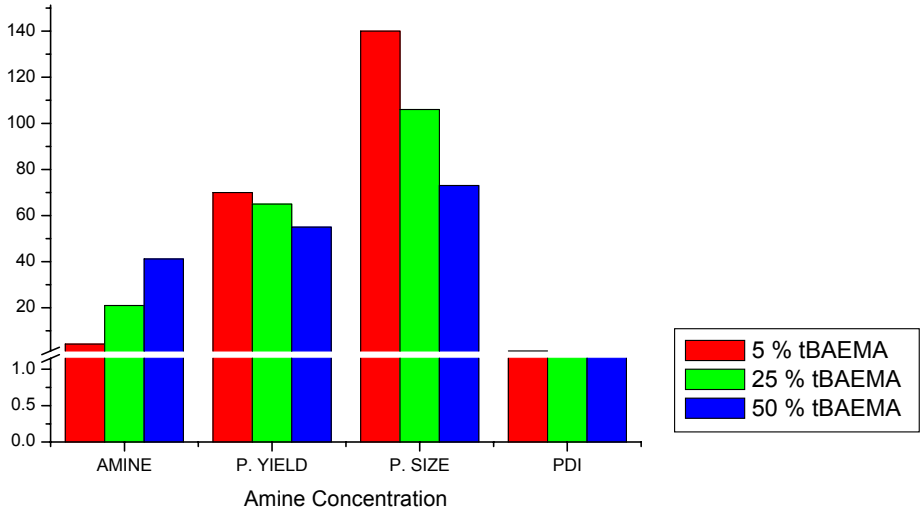


Figure 4.15: Changes in available amine content, percent yield, particle size, and particle size distribution for different tBAEMA concentrations (Experiment nos. 23, 26 and 27 in tables 3.2 and 4.9).

Figure 4.15 displays the changes in amine content, percent yield, particle size and particle size distributions of samples with different tBAEMA feed concentrations. An increase in the average size of microparticles was observed with decreasing tBAEMA concentration. The yield of microparticles also increased from 55 to 70 weight percent with decreasing tBAEMA concentration from 50 to 5 weight percent, which may be attributed to larger particle size of the microparticles obtained.The available amine content of the produced microparticles were found to be about 80 % of the charged tBAEMA amount.

In this set of experiments, the particles were obtained in spherical form wih diffent sizes. The optical micrographs and particle size histograms of 5 and 50 weight percent tBAEMA containing particles are shown in Figure 4.16 and 4.17. When tBAEMA feed concentration was varied, PDI values showed some fluctuations. PDI value had the smallest value at 25 percent tBAEMA concentration.

(a) (b)

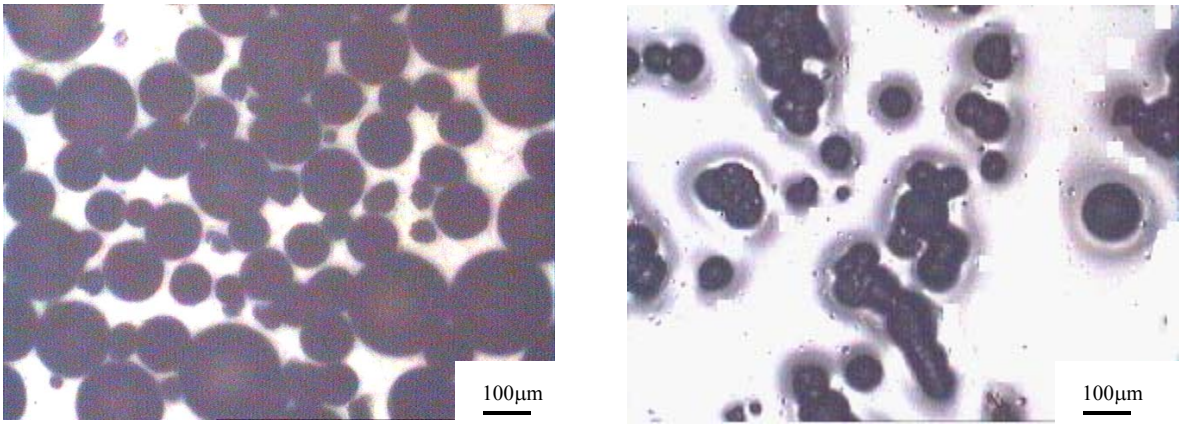


Figure 4.16: Optical micrographs of microparticles prepared in presence of (a) 5 and (b) 50 wt. % tBAEMA, respectively (Experiment nos.26 and 27 in tables 3.2 and 4.9). (Magnification 100x).

(a) (b)

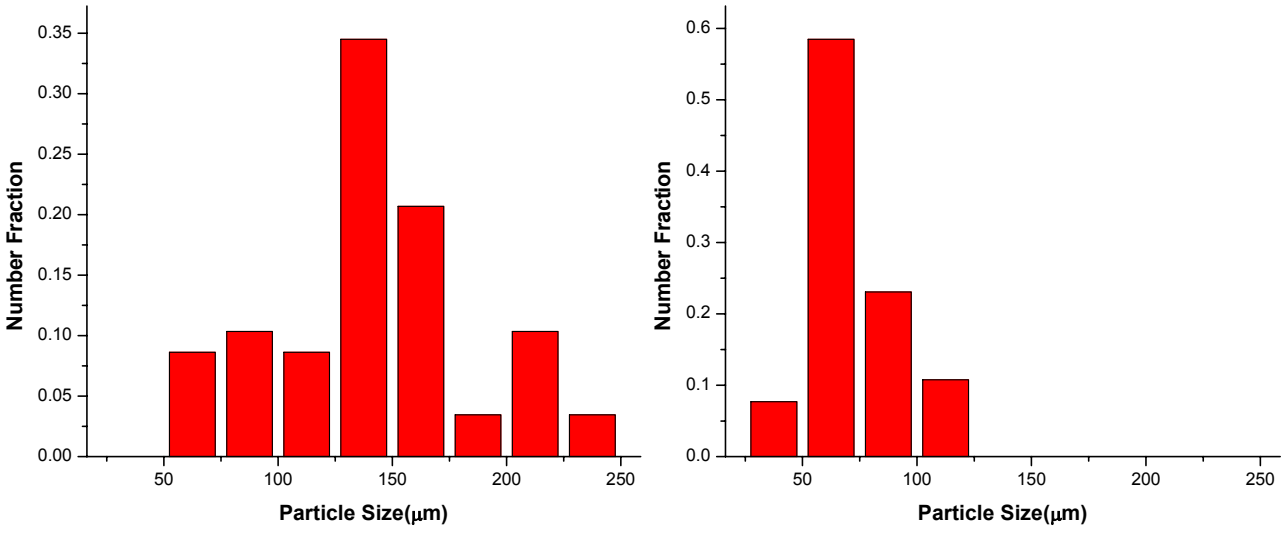


Figure 4.17: Particle size distribution of microparticles prepared in presence of (a) 5 and (b) 50 wt. % tBAEMA, respectively (Experiment nos. 26 and 27 in tables 3.2 and 4.9).

4.2.4 Effect of Initiator Concentration

The effect of initiator concentration on the properties of produced microparticles was investigated by varying the AIBN concentration while maintaining the other polymerization parameters fixed (Experiment nos. 23, 28, 29 in tables 3.2 and 4.10).

Table 4.10: Effect of AIBN concentration on available amine content, percent yield, and average particle size in $Al_2(SO_4)_3$ stabilized suspension polymerization

Exp. No.	AIBN (wt. %)	Available Amine (wt. %)	Yield (wt. %)	Average Size (µm)	PDI (D_{z+1}/D_n)
28	0.17	22.7	71	132	1.27
23	0.33	21.0	65	106	1.15
29	0.66	22.1	70	100	1.32

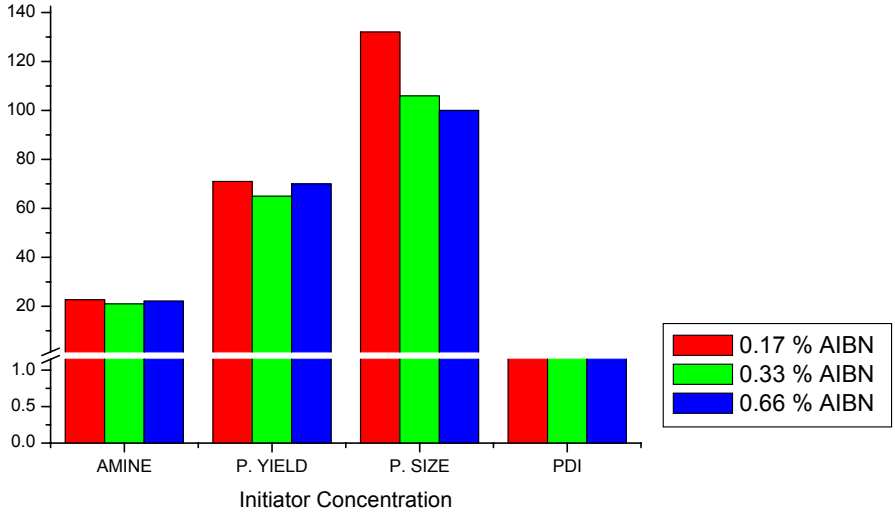


Figure 4.18: Changes in available amine content, percent yield, particle size, and particle size distribution for different AIBN concentrations (Experiment nos. 23, 28, and 29 in tables 3.2 and 4.10).

As seen in Figure 4.18, it was found that the available amine content and percent yield showed some fluctuations but did not change significantly with the variation of initiator concentration between 0.17 and 0.66 weight percent based on the monomers. However, average particle size increased from 100 to 132 μm with decreasing initiator concentration 0.66 to 0.17 weight percent. As AIBN concentration increases, higher number of free radicals is produced. High concentration of free radicals initiates higher number of polymer chains. Particles with smaller size are produced.

This trend is similar to previous studies by Choi *et. al*.,[27] and Tseng *et. al.,*[19], Piskin, *et. al.*[29] who reported an increase in the average size with decreasing initiator concentration. Spherical particles with narrow particle size distribution were obtained by varying initiator composition.[27] Initiators that have moderate half-lives produced uniform particles with narrow size distributions.[19]

The optical micrograph and particle size histogram of 0.17 and 0.66 weight percent AIBN containing particles are shown in Figure 4.19 and 4.20. Individual and spherical microparticles were produced. PDI values of indicated a relatively wider particle size distribution for the studied initiator concentration range.

(a) (b)

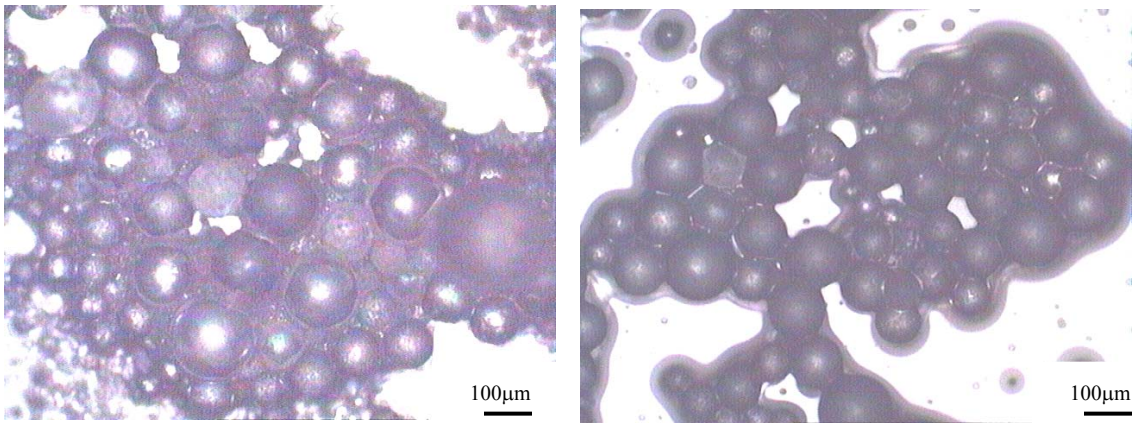


Figure 4.19: Optical micrographs of microparticles prepared in presence of (a) 0.17 and (b) 0.66 wt. % AIBN (Experiment nos. 28 and 29 in tables 3.2 and 4.10). (Magnification 100x).

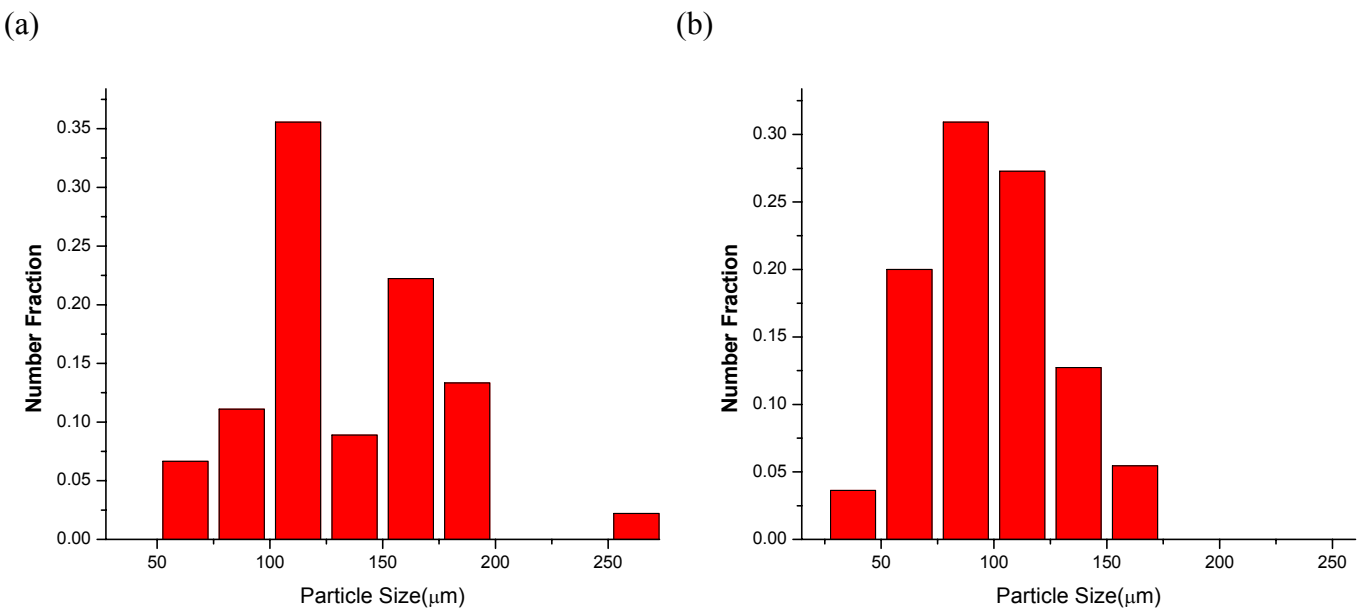


Figure 4.20: Particle size distribution of microparticles prepared in presence of (a) 0.17 and (b) 0.66 wt. % AIBN (Experiment nos. 28 and 29 in tables 3.2 and 4.10).

4.2.5 Effect of $Al_2(SO_4)_3$ Concentration

In patent literature, water insoluble inorganic compounds such as $BaSO_4$, $Ca_3(PO_4)_2$, and $Al(OH)_3$ are being used commercially to produce small size particles with narrow size sistributions in toner applications.[30,31] In one of the patent application, water-soluble $Al_2(SO_4)_3$ was used at pH greater than 7 to produce in situ water insoluble $Al(OH)_3$ to stabilize particles. In this part of our study $Al_2(SO_4)_3$ was used at pH greater than 7 to produce insoluble colloidal $Al(OH)_3$ because pH of dispersion medium is greater than 7 due to presence of tBAEMA.

Polymerization products with smaller particle size and narrow particle size distributions are correlated with the patent results that are used production microparticles in industry. A solid colloidal stabilizer limits the coalescence of the droplets and produces polymer particles with narrow particle size distribution. The surface of polymer particles has a core covered by a layer of the smaller stabilizer particles. This layer provides a hydrophilic

surface, which covers the hydrophobic surface of the polymer core. Reaction mixture is stirred to reduce the size of the droplets. During this time an equilibrium is reached and the size of the droplets is stabilized by the action of the colloidal stabilizer that is coating the surface of the droplets.[30,31]

To examine the effect of $Al_2(SO_4)_3$, its concentration was varied between 0.83 and 2.49 weight percent based on monomers while the other polymerization parameters were kept constant (Experiment nos. 23, 30, and 31 in table 3.2 and 4.11).The effect of $Al_2(SO_4)_3$ concentration on the features of produced microparticles are summarized in Table 4.11 and demonstrated in Figure 4.18.

Table 4.11: Effect of $Al_2(SO_4)_3$ concentration on available amine content, percent yield, and average particle size in $Al_2(SO_4)_3$ stabilized suspension polymerization

Exp. No.	**$Al_2(SO_4)_3$ (wt. %)**	**Available Amine (wt. %)**	**Yield (wt. %)**	**Average Size (μm)**	**PDI (D_{z+1}/D_n)**
23	0.83	21.0	65	106	1.15
30	1.67	21.0	61	59	1.10
31	2.49	22.1	68	52	1.07

Although, the percent yield and available amine content did not change significantly, the average size decreased dramatically. These changes can be seen in Figure 4.21. This sharp decrease in the average particle size may be explained by better stabilization of microparticles and prevention of them from agglomeration. The polydispersity of microparticles was also affected very little by variation of $Al_2(SO_4)_3$ concentration. As shown in Table 4.11, the PDI values slightly decreased from 1.15 to 1.07 when the $Al_2(SO_4)_3$ concentration was increased three times.

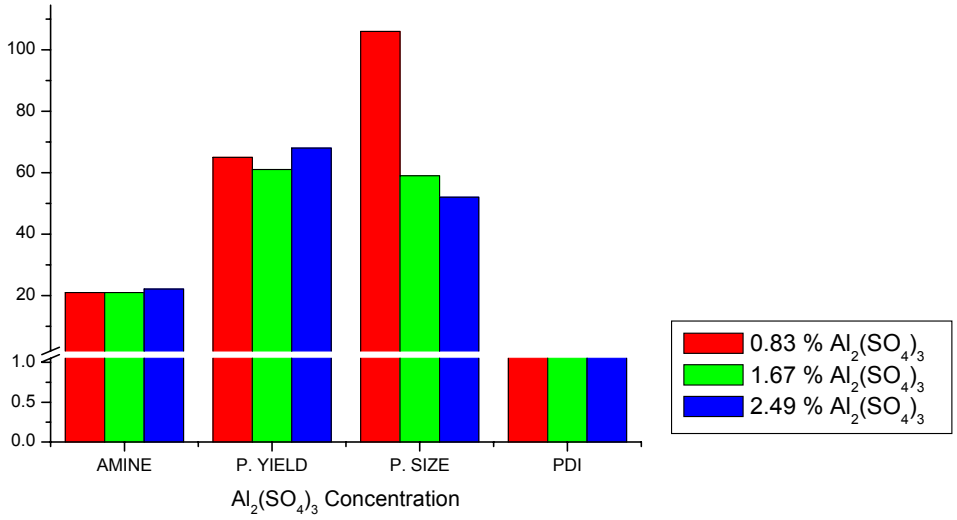


Figure 4.21: Changes in available amine content, percent yield, particle size, and particle size distribution for different $Al_2(SO_4)_3$ concentrations (Experiment nos. 23, 30, and 31 in table 3.2 and 4.11).

The optical micrographs and particle size distribution histograms were given in Figure 4.22 and 23, respectively.

(a) (b)

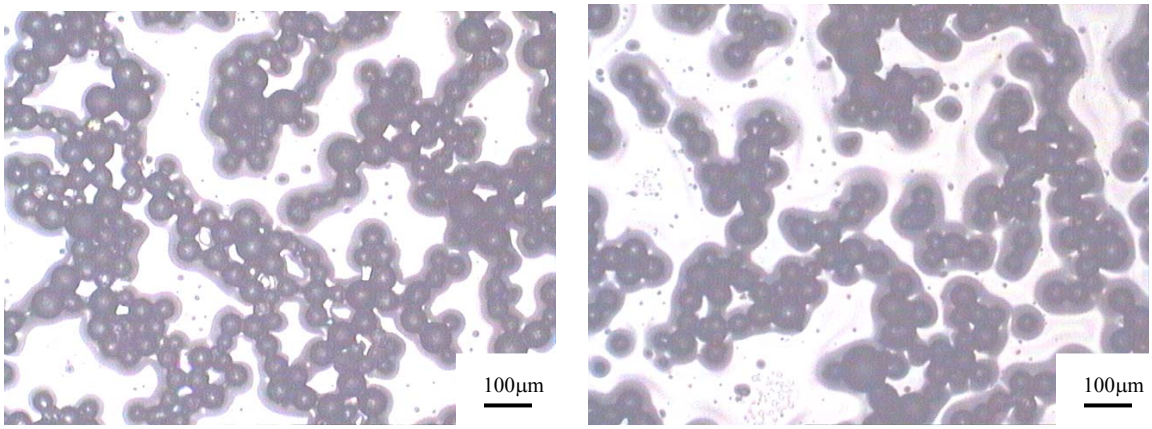


Figure 4.22: Optical micrographs of microparticles prepared in presence of (a) 1.67 and (b) 2.49 wt. % $Al_2(SO_4)_3$ (Experiment nos. 30 and 31 in tables 3.2 and 4.11). (Magnification 100x)

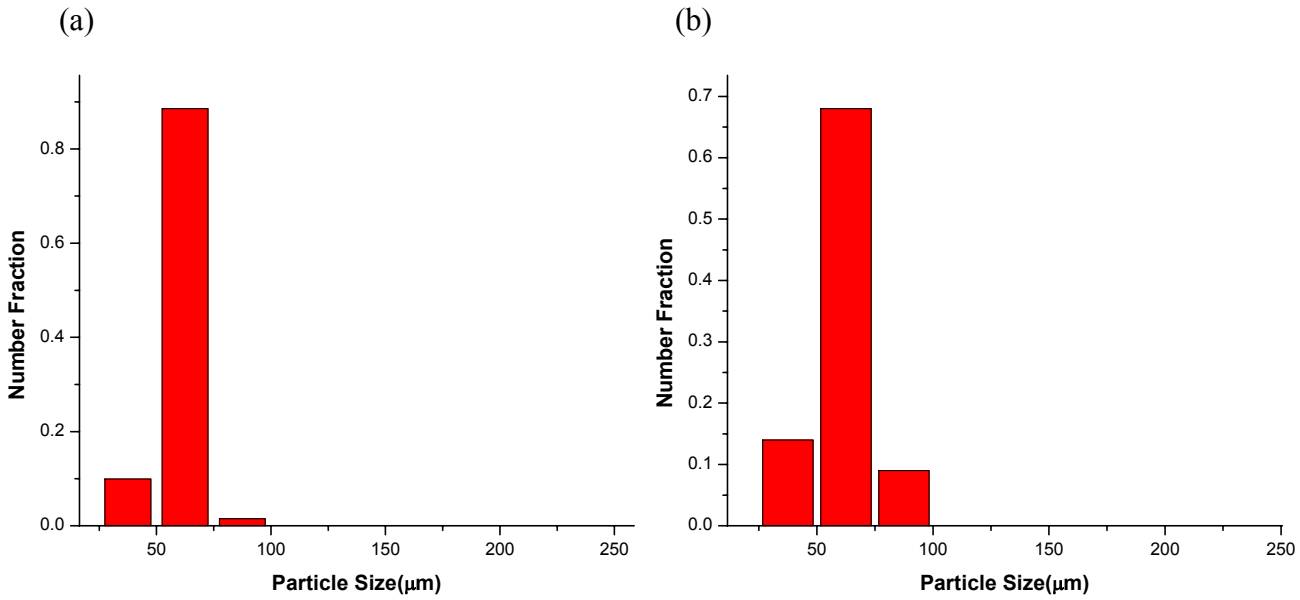


Figure 4.23: Particle size distribution of microparticles prepared in presence of (a) 1.67 and (b) 2.49 wt. % $Al_2(SO_4)_3$ (Experiment nos. 30 and 31 in tables 3.2 and 4.11).

4.3 SDS and $Al_2(SO_4)_3$ Co-Stabilized Suspension Polymerizations

The attempts to produce spherical and individual microparticles using SDS as a sole stabilizer failed as the results are presented and discussed in Section 4.1. To examine the effect of an $Al_2(SO_4)_3$ on the particle formation in these systems, 0.46 weight percent $Al_2(SO_4)_3$ on basis of monomers was used as a co-stabilizer. Also, the effect of some polymerization parameters on these co-stabilized systems were investigated (Table 3.3).

4.3.1 Effect of Amine Concentration

The effect of 2-(tert-butylamino)ethyl methacrylate, tBAEMA, concentration on percent yield, available amine content, and average particle size was explored by varying the tBAEMA concentration between 0 and 15 weight percent on total weight of monomers while the other polymerization parameters were kept constant (Experiment nos. 32 - 35 in Table 3.3). The effects of tBAEMA concentration on particle formation in co-stabilized suspension polymerization are given in Table 4.12.

Table 4.12: Effect of tBAEMA concentration on available amine content, percent yield, and average particle size in SDS and $Al_2(SO_4)_3$ co-stabilized suspension polymerization

Exp. No.	tBAEMA (wt. %)	Available Amine (wt. %)	Yield (wt. %)	Average Size (µm)	PDI (D_{z+1}/D_n)
32	0.0	-	-	-	-
33	5.0	4.3	74	254	1.07
34	10.0	8.1	81	161	1.18
35	15.0	13.1	72	159	1.13

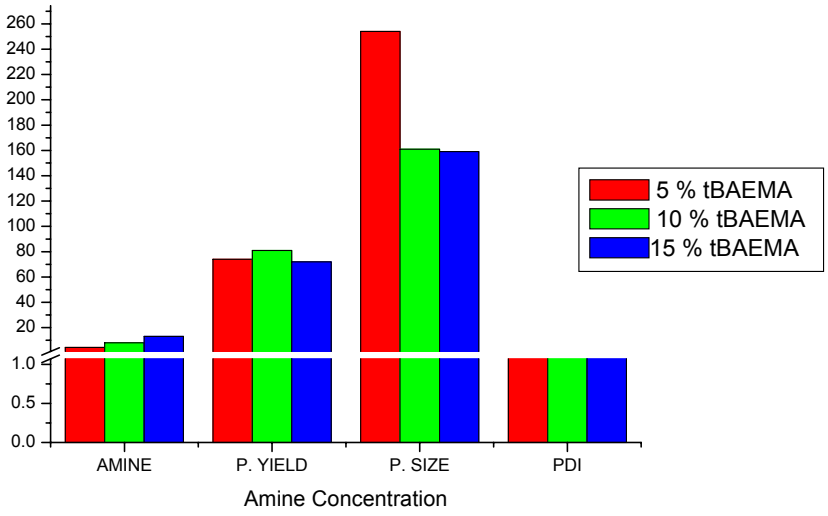
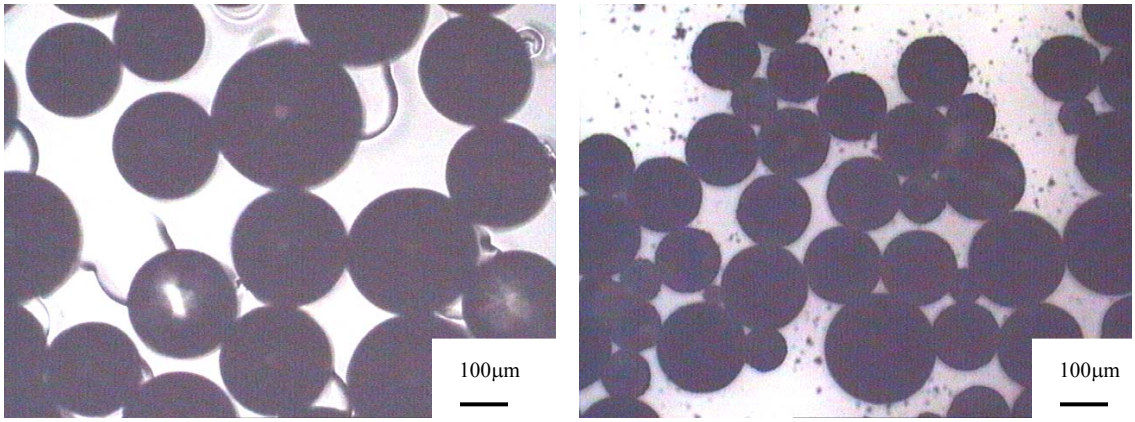


Figure 4.24: Changes in available amine content, percent yield, particle size, and particle size distribution for different tBAEMA concentrations (Experiment nos. 32 - 35 in 3.3).

The attempt to prepare amine-free microparticles using SDS and $Al_2(SO_4)_3$ co-stabilized suspension polymerization resulted individual beads in size of 1 – 2 mm. In this experiments, white color appearence of the suspension mixture at the room temperatue was disappeared at polymerization temperature and turned into colorless appearence (water-clear). In Exp. no. 12, polymerization product was not obtained in the form of microparticles. However, with the addition of amine containing monomer into the mixture, suspension

mixture was white color at polymerization temperature, and small individual particles were obtained. The average size of produced microparticles decreased to less than half value as the amine concentration was increased from 5 to 15 weight percent in the monomers mixture, as demonstrated in Figure 4.24. The optical micrographs and particle size distribution histograms are given in Figure 4.25 and 26, respectively.

(a) (b)



(c)

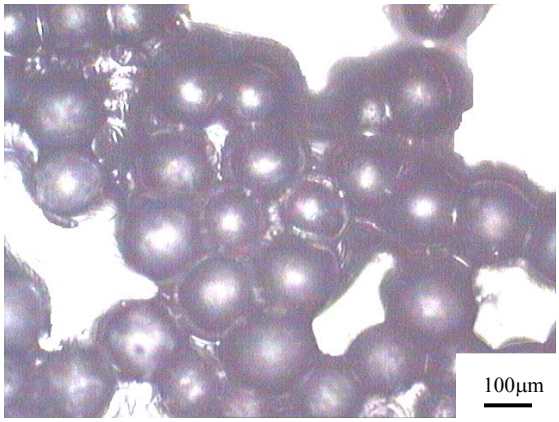


Figure 4.25: Optical micrograph of microparticles in presence of (a) 5, (b) 10 and (c) 15 wt. % tBAEMA (Experiment nos.33-35 in tables 3.3 and 4.12). (Magnification 100x).

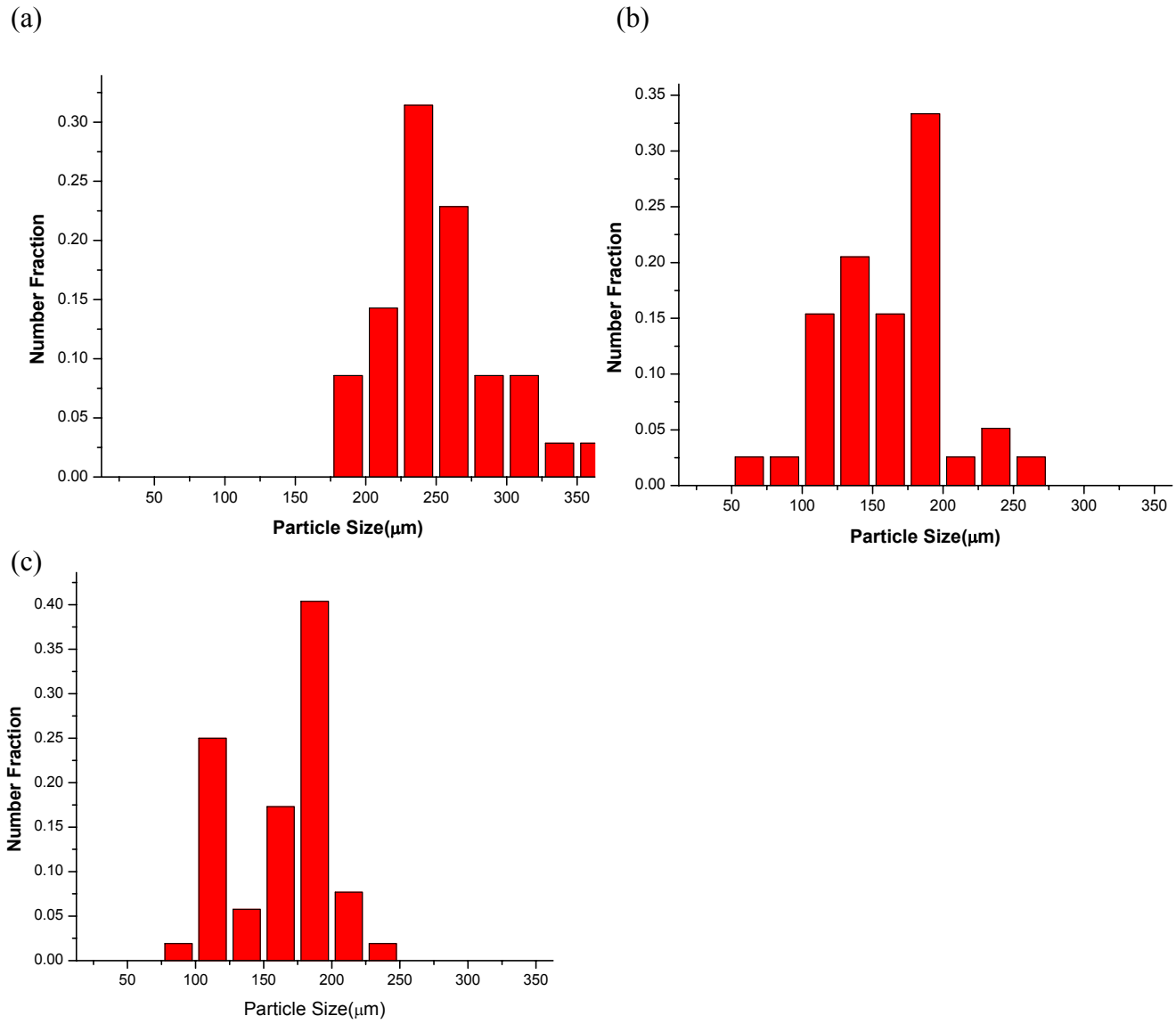


Figure 4.26: Particle size distribution of microparticles in presence of (a) 5, (b) 10 and (c) 15 wt. % tBAEMA (Experiment nos.33-35 in tables 3.3 and 4.12).

The percent yield and PDI values showed some variation with tBAEMA concentration (see Figure 4.24). However, the particle size reduced as the tBAEMA concentration increased from 5 to 10 and 15 percent based on the monomers. The available amine content of these particles were in the range of 80 percent on basis of theoretical amine content. This may arise as a result of unfavorable copolymerization parameters reactivity ratios. Polymer fractions formed at different intervals of polymerization may have different compositions. Functional groups may not be distributed equally throughout the particles.

4.3.2 Effect of SDS Concentration

As it is known that stabilizer concentration is one of the most important parameters in suspension polymerization to control the particle size. In the absence of sufficient stabilizer, the smaller droplets coalescence easily during the hardening stage. This causes the formation of larger and irregular particles. To explore the effect of stabilizer concentration on available amine content, particle size and particle size distribution, concentration of SDS was varied keeping other parameters constant (Experiment nos. 33, 36 and 37 in tables 3.3 and 4.13).

Table 4.13: Effect of SDS concentration on available amine content, percent yield, and average particle size in SDS and $Al_2(SO_4)_3$ co-stabilized suspension polymerization

Exp. No.	SDS (wt. %)	Available Amine (wt. %)	Yield (wt. %)	Average Size (µm)	PDI (D_{z+1}/D_n)
33	0.17	4.3	74	254	1.07
36	0.83	4.2	71	190	1.09
37	1.67	-	-	-	-

Except decrease in particle size, almost no effect on produced particle features was observed by varying the SDS concentration from 0.17 to 1.67 weight percent on basis of monomers and keeping the other polymerization parameters constant. Spherical and individual microparticles were produced in this set of experiments. The experimental results are given in Table 4.13 and Figure 4.27.

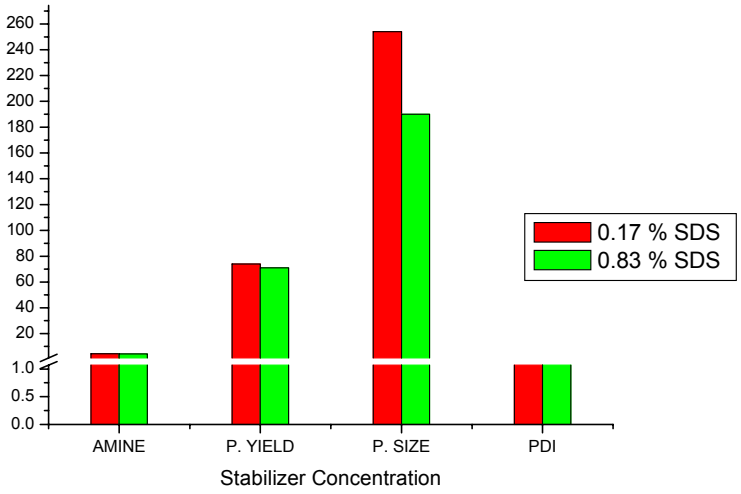


Figure 4.27: Changes in available amine content, percent yield, particle size, and particle size distribution for different SDS concentrations (Experiment nos. 33, 36 and 37 in tables 3.3 and 4.13).

The available amine content and percent yield and PDI value of produced microparticles were not affected by variation in SDS concentration, as seen in Figure 4.27. In Exp. no. 37, coagulated polymerization product was obtained at 1.67 percent SDS concentration. Average particle size decreased with increasing SDS concentration as stated in related literature.[3,15,16,29] Piskin, *et. al.*[29] showed that stabilizer concentration almost did not affect the percent yield although particle size decreased significantly. Also, Choi, *et. al.*[27], demonstrated the particle size decrease depending on increasing initiator concentration and suggested that specific reaction conditions are needed to produce monodisperse particles.

The optical micrographs and particle size distribution histograms of produced microparticles are given in Figure 4.28 and 29, respectively.

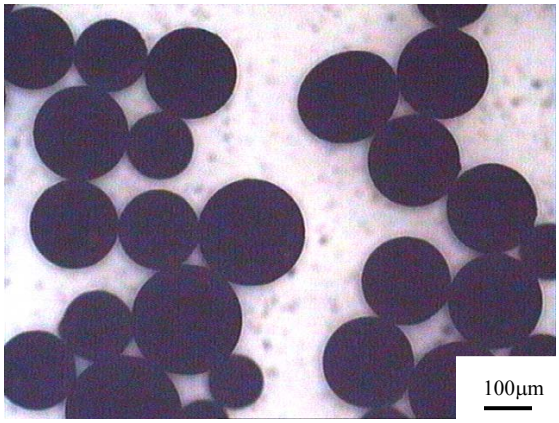


Figure 4.28: Optical micrograph of microparticles prepared in presence of 0.83 wt. % SDS (Experiment no. 36 in tables 3.3 and 4.13). (Magnification 100x).

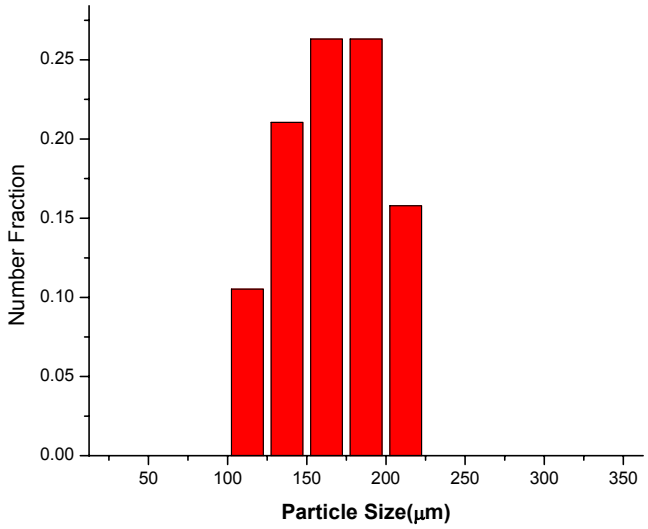


Figure 4. 29: Particle size distribution of microparticles prepared in presence of 0.83 wt. % SDS (Experiment no. 36 in tables 3.3 and 4.13).

4.3.3 Effect of Initiator Concentration

The effect of initiator concentration on the properties of produced microparticles was investigated by varying the AIBN concentration while maintaining the other polymerization

parameters fixed (Experiment nos. 33, 38, 39 in tables 3.3 and 4.14). The experimental results are given in Table 4.14 and Figure 4.30.

Table 4.14: Effect of AIBN concentration on available amine content, percent yield, and average particle size in SDS and $Al_2(SO_4)_3$ co-stabilized suspension polymerization

Exp. No.	AIBN (wt. %)	Available Amine (wt. %)	Yield (wt. %)	Average Size (µm)	PDI (D_{z+1}/D_n)
33	0.33	4.3	74	254	1.07
38	0.58	4.3	80	161	1.11
39	0.83	4.4	79	131	1.28

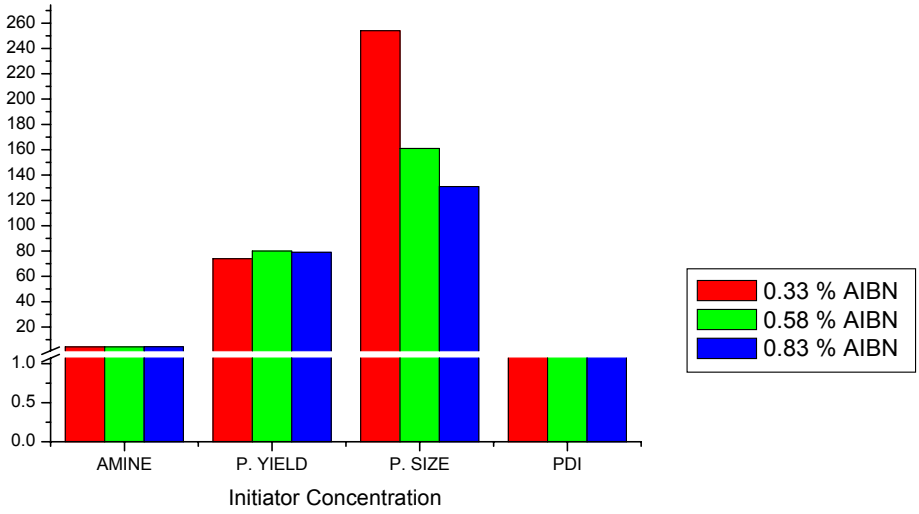


Figure 4.30: Changes in available amine content, percent yield, particle size, and particle size distribution for different AIBN concentrations (Experiment nos. 33, 38, 39 in tables 3.3 and 4.14)

Effects of initiator concentration on properties of produced microparticles were given in Figure 4.30. There was no appreciable change in available amine content of produced microparticles by variation in initiator concentration. However, the percent yield, polydispersity and average particle size were affected. The average particle size decreased

about to one half by increasing the initiator concentration from 0.33 to 0.83 weight percent. The decrease in average particle size may is related to previous studies.[27,29] As AIBN concentration increases, number of produced radicals increases. Higher free radical concentration initiates a high number of propagating polymer chain. Period of sticky stage decreases and smaller particles are produced.

The percent yield increased about 5 percent for the same variation in initiator concentration. The PDI value became wider, as the initiator concentration increased.

Optical micrographs and particle size distribution of microparticles are given in Figure 4.31 and 4.32, respectively.

(a) (b)

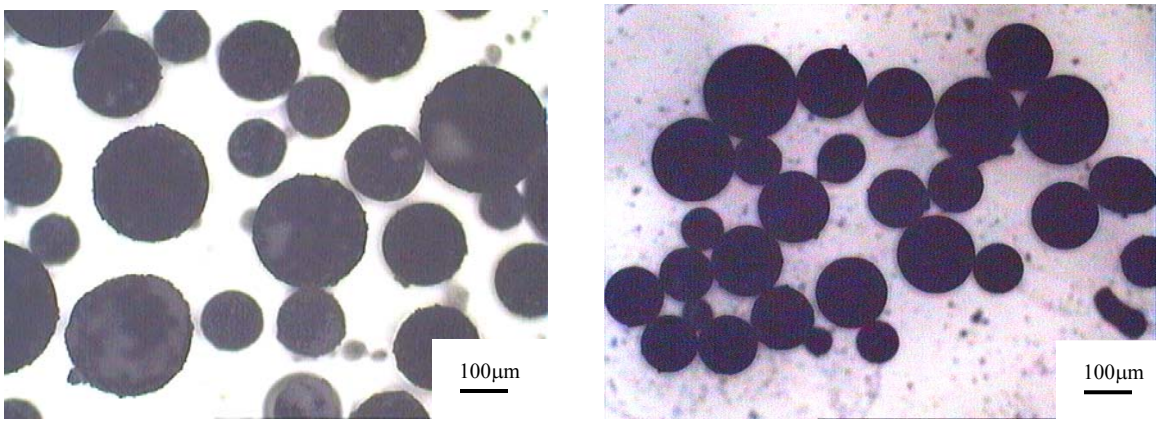


Figure 4.31 : Optical micrographs of microparticles prepared in presence of (a) 0.58 and (b) 0.83 wt. % AIBN (Experiment Nos. 38 and 39 in tables 3.3 and 4.14). (Magnification 100x).

(a) (b)

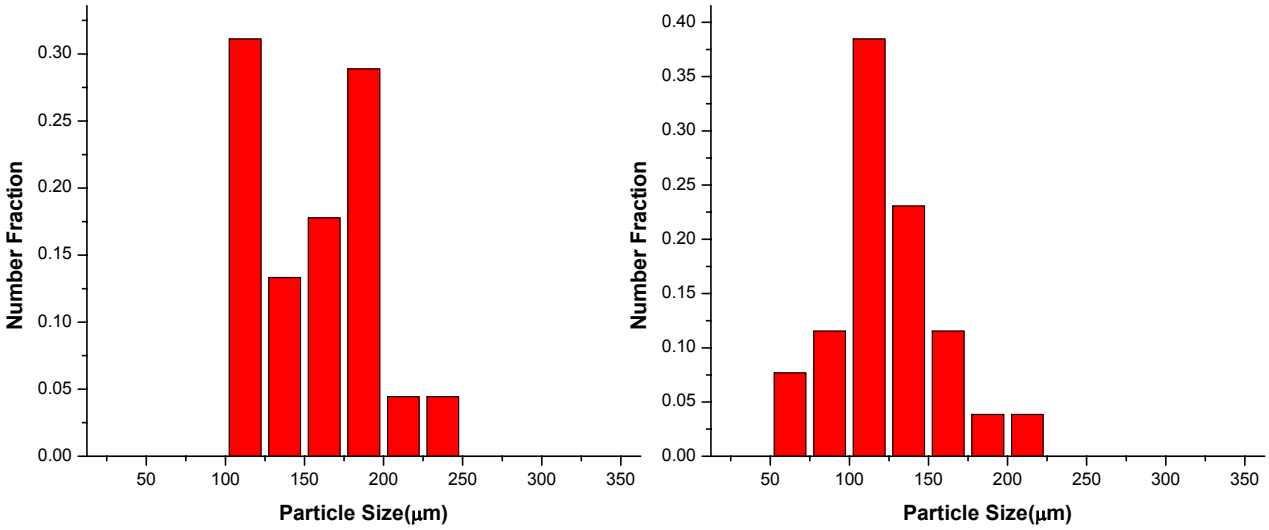


Figure 4. 32: Particle size distribution of microparticles prepared in presence of (a) 0.58 and (b) 0.83 wt. % AIBN (Experiment Nos. 38,39 in tables 3.3 and 4.14).

4.3.4 Effect of Crosslinking Agent Concentration

DVB concentration was increased from 5 to 25 weight percent (based on monomer) while keeping other polymerization parameters constant. (Experiment nos. 33, 40, 41 in tables 3.3 and 4.15). The experimental results are given in Table 4.15 and Figure 4.33.

Table 4.15: Effect of DVB concentration on available amine content, percent yield, and average particle size in SDS and $Al_2(SO_4)_3$ co-stabilized suspension polymerization

Exp. No.	DVB (wt. %)	Available Amine (wt. %)	Yield (wt. %)	Average Size (μm)	PDI (D_{z+1}/D_n)
40	5.0	-	-	-	-
41	12.5	4.2	58	159	1.29
33	25.0	4.3	74	254	1.07

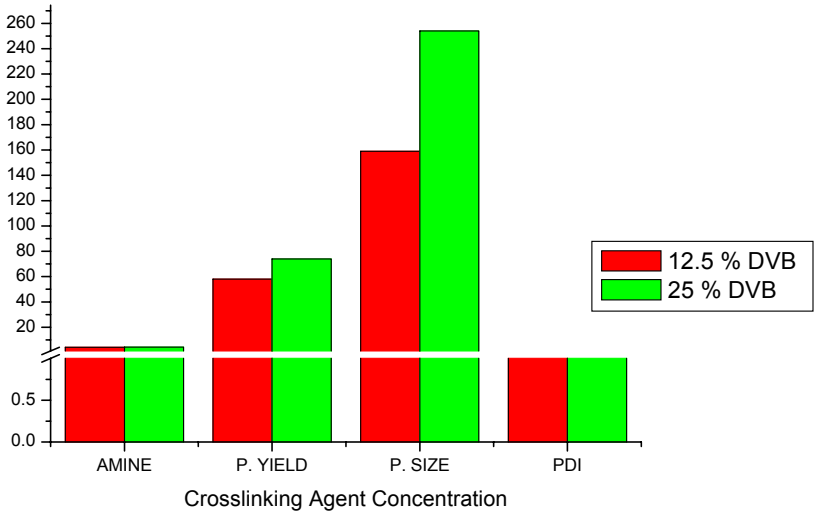


Figure 4.33: Changes in available amine content, percent yield, particle size, and particle size distribution for different DVB concentrations (Experiment nos. 33, 40, 41 in tables 3.3 and 4.15).

At very low DVB concentration (5 wt. %), microparticles were fused. This may be explained that low crosslinking sites could not maintain the dimensions of the particles. When DVB concentration was increased from 12.5 to 25 wt. %, particle size increased from 159 to 254 μm. Percent yield increased from 58 to 74 this may be a result of increase in the particle size. Experimental amine content remained nearly the same. The PDI value became wider as DVB concentration decreased. An increase in the amount of crosslinking agent produces an increasing crosslinking density of the polymer chains, thus the polymer beads are harder. The bead surfaces become smoother when the crosslinking agent was copolymerized with structural monomer.

The optical micrographs and particle size distribution histograms of produced microparticles are given in Figure 4.34 and 35, respectively.

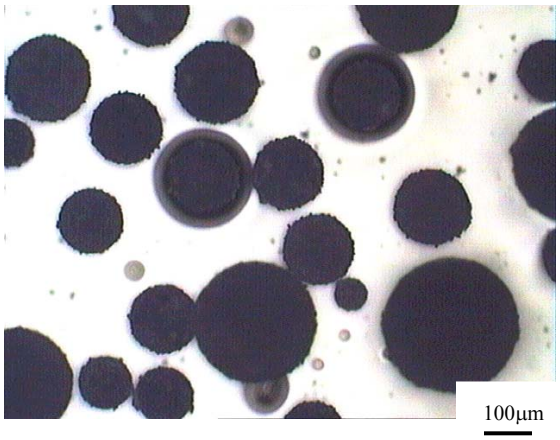


Figure 4. 34: Optical micrograph of microparticles prepared in presence of 12.5 wt. % DVB (Experiment nos. 41 in tables 3.3 and 4.15). (Magnification 100x).

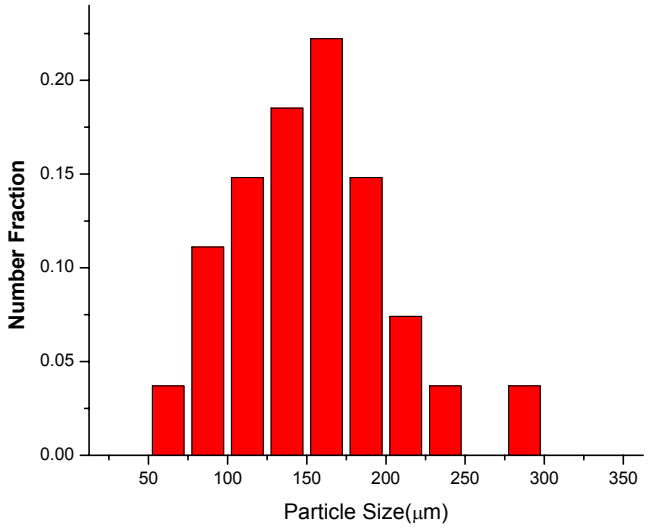


Figure 4. 35: Particle size distribution of microparticles prepared in presence of 12.5 wt. % DVB (Experiment nos. 41 in tables 3.3 and 4.15).

CHAPTER 5

CONCLUSION

In this thesis, synthesis of secondary amine functional microparticles in the average size of 50 – 250 μm with various amine contents and degree of crosslinking by single-pot suspension polymerization was studied. Also, the effects of some polymerization parameters on the morphology, particle size, and its distribution have been investigated. These polymerizations were carried out for three differently stabilized systems.

The attempts to synthesize secondary amine functional, individual and spherical particles in SDS stabilized system failed probably due to insufficient stabilization efficiency of SDS. The products were either in irregular shape or agglomerated spherical particles.

In the second system, aluminum sulfate was used to stabilize and prevent the agglomeration of the particles. In this system, it was found that the synthesis of secondary amine functional, individual and spherical microparticles was possible under certain polymerization conditions. As the stirring speed, and the concentrations of initiator, amine, and $Al_2(SO_4)_3$ increased, average particle size decreased. However, as the crosslinking agent concentration increased, average particle size decreased. Particles within the size range of 50 – 200 μm were obtained.

In the third method, a proper amount of $Al_2(SO_4)_3$ was added to the aqueous dispersion medium as a co-stabilizer, again individual and spherical microparticles were obtained within the size range of about 130 - 250 μm. Average particle size decreased with increasing amine, stabilizer, and initiator concentrations. Average particle size increased with increasing crossliking agent concentration.

Future studies should be done with other stabilizers (e.g; polyvinylpyrrolidone), and sparingly soluble inorganic salts (e.g.; Al_2O_3) to explore the preparation of uniform particles. Also the effectiveness of these microparticles in biomedical applications (cell culturing, etc) should be investigated.

CHAPTER 6

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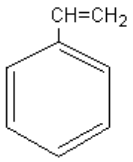
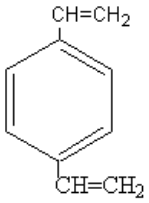
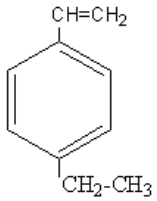
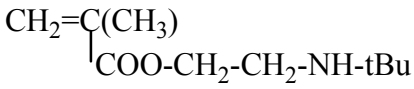
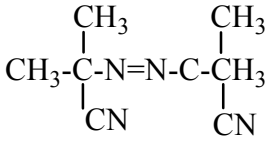
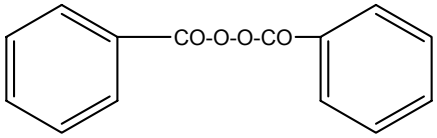
APPENDIX-I

ABBREVIATIONS and CHEMICAL FORMULAS

Monomers

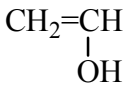
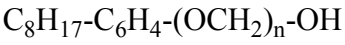
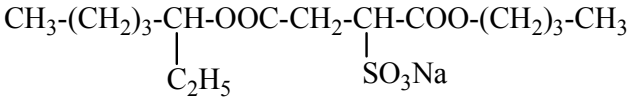
Name	Abbreviation	Structure
Styrene	STY	
Divinylbenzene	DVB	
Ethylvinylbenzene	EVB	
2-(tert-Butylamino)ethyl methacrylate	tBAEMA	

Initiators

2,2′-azobisisobutyronitrile	AIBN	
Benzoylperoxide	BPO	

Surfactants

Sodium dodecylsulfate	SDS	CH_3-(CH_2)11-OSO_3Na

Poly (vinyl alcohol)	PVA	
Polyoxyethylene(10) isooctyl phenyl ether	Triton X-100	
Sodium dioctyl sulfosuccinate	SDSS