Chapter 1

Introduction

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1.0 INTRODUCTION

`Dear Colleagues, leave the concept of large molecules well alone....there can be no such thing as a macromolecule'. It is said[1] that this advice was given to Herman Staudinger just 70 years ago after he delivered a major lecture devoted to his evidence in favour of the macromolecular concept. Today it seems almost impossible that this violent opposition to the idea of the existence of polymer molecules could have existed in relatively recent times. Now polymers have become a part of modern life. Being essential to clothing, shelter, transportation and communications as well as to the conveniences of modern living, they are truly indispensable to mankind.

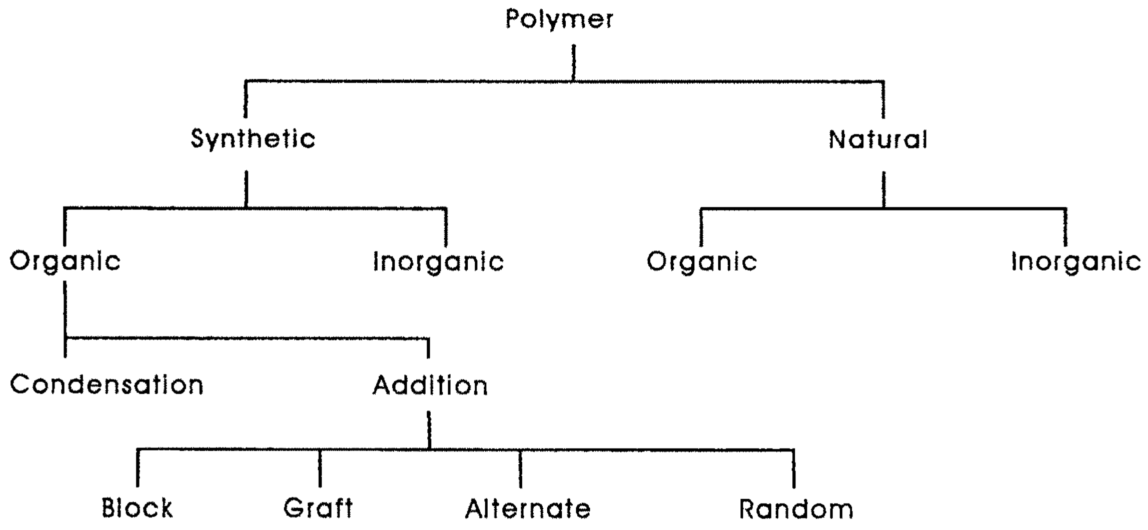
In 1909, the first ever commercial polymer `Bakelite' that could be moulded into hard infusible articles was prepared. In 1912, Jacques Brandenbarger introduced `cellophane' and since then scientific study and research in polymers have been ever growing.

1.1 What are Polymers ?

According to IUPAC definition `a polymer is a substance composed of molecules characterized by repeatation of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with addition or removal of one or a few of the constitutional units'. More simply a polymer is a long molecule built up by the repeatation of simple chemical units held together by primary covalent bonds along the molecules.

When the repeating units in a polymer are of one type, they are termed as homopolymers while if the repeating units are of two or more different types, they are termed as copolymers.

Polymers may be classified according to their origin, nature of polymeric backbone, mechanism of synthesis or according to the arrangement of monomeric units in them.



1.2 Polymerization

The process of synthesis of polymers is termed as polymerization. According to Carothers[2] `Polymerization is intermolecular combinations that is functionally capable of proceeding indefinitely'.

Polymerization processes can be divided into three subclasses based on the medium of polymerization :

(a) Polymerization in homogeneous medium

(b) Polymerization in heterogeneous medium and

(c) Polymerization in solid phase

1.2.1 Polymerization in Homogeneous medium

This can be carried out as bulk or solution polymerization.

(i) **Bulk Polymerization** : In this, monomer is initiated without using any solvent. This is practiced where the reactions are mildly exothermic and most of the reactions occur when the viscosity is low enough for ready mixing. The rate of reaction usually was found to be constant initially and then rises sharply. The increase in rate has been attributed to autocatalytic explosive or gel stage[3] of the reaction. The molecular weight is independent of the monomer concentration.

(ii) **Solution Polymerization** : In this, the polymerization is carried out in the presence of solvents. It is advantageous from the standpoint of heat removal and control. Like bulk polymerization it shows a definite period of induction, followed by linear rate of reaction in the initial stage but later the rate increases to a limiting value[4]. The degree of polymerization is related to the solvent[S]/monomer[M] molar ratio by the equation

$$P^{-1} = P_o^{-1} + K\,[S]/[M]$$

where P and P_o are the degrees of polymerization with and without solvent and K is a constant[5].

1.2.2 Polymerization in Heterogeneous medium

This can be carried out as gas phase, precipitation, suspension and emulsion polymerization.

(i) **Gas phase Polymerization** : In this type, as the polymer molecules grow in size they will cease to be subject to the laws of the kinetic theory and instead constitute a new phase in the system[6]. As a result, reactions which are initially truly homogeneous soon pass over to heterogeneous ones. The result of this is that instead of the monomer molecules merely colliding with the growing polymer, they are first adsorbed from the vapour onto the polymer particles, subsequently the reactions take place within the particles.

(ii) **Precipitation Polymerization** : In this type, the polymer being synthesized is insoluble in the monomer or polymerization is performed in the presence of non-solvent for the polymer. The kinetics deviates from that of homogeneous bimolecular termination and is not effective as a result of trapping or occlusions of radicals in the unswollen, tightly coiled precipitating polymer[7].

(iii) **Suspension Polymerization** : In this type, polymerization is carried out in an aqueous medium by dispersing the monomer into fine droplets of 0.01 - 0.5 cm diameter using surface active reagents. The polymer formed also remains as a dispersed phase. In this type initiator is dissolved in the monomer phase and kinetics of polymerization resembles more to bulk polymerization process.

(iv) Emulsion Polymerization : The polymerization is carried out in an aqueous medium by dispersing the monomer to droplets using surface-active agent, the concentration of which is above critical micellar concentration. The polymerization nucleation takes place in monomer swollen micelles. The initiator is located in the aqueous phase and the monomer-polymer particles are of the order of 10^2 nm in diameter. The kinetics of emulsion polymerization differs significantly from that of bulk polymerization.

Further details are discussed in 1.3.1

1.2.3 Solid Phase Polymerization

The term includes all types of polymerizations in the solid state such as crystalline and glassy states of pure monomers with other compounds[8,9]. The development of solid state polymerization was largely due to the high energy radiation which helped to carry out the reactions at lower temperatures at which monomers exist in the solid state, and led to the production of new types of polymers. Solid state reactions are followed by non-destructive techniques such as optical and electron microscopy, electron spin resonance, DTA, X-ray diffraction, IR and Raman spectroscopy and high resolution NMR spectroscopy to get experimental data on molecular structure, molecular packing and molecular vibrations in monomer crystals as well as on the configuration and conformation of the resulting polymers.

1.3 Emulsion

As we have carried out polymerization in microemulsion medium which is a further extension of emulsion system the necessary details of emulsion and emulsion polymerization are discussed here.

A liquid phase dispersed as fine droplets in another immiscible liquid phase is known as emulsion. Emulsions are of two types : oil dispersed in water (o/w) and water dispersed in oil (w/o). For stabilization of emulsions either very small droplets with a charge on the drops is needed or a third `stabilizing agent' that would prevent coalescence of the droplets coming in contact is needed. The stabilizing agent forms an oriented interfacial film at the liquid-liquid interface. This oriented film performs two functions:

(i) It reduces the interfacial tension between the liquids and
(ii) It decreases the rate of coalescence of the liquid particles by forming mechanical, steric and/or electrical barriers between them[10].

Based on the size of the dispersed particles, three different types of emulsions have been distinguished. They are :

(i) Macroemulsions which are opaque with particles >400 nm; generally in μm size.
(ii) Miniemulsions, transparent or transluscent dispersions with particles between 100 - 400 nm and
(iii) Microemulsions, transparent dispersions with particles < 100 nm in size, ideally between 10 - 40 nm.

All these types of emulsions are being used as polymerizing media.

1.3.1 Emulsion Polymerization

Emulsion polymerization is a reaction technique which is used to produce polymer colloids from monomers via free radical reactions. In the initial stage of the reaction three types of particles are observed in the reaction medium[11] :

(i) emulsified monomer droplets of size 10^3 - 10^4 nm range,

(ii) soap micelles containing solubilized monomer of size ~10 nm and

(iii) growing emulsifier stabilized polymer particles swollen with monomer and having 50 - 100 nm size.

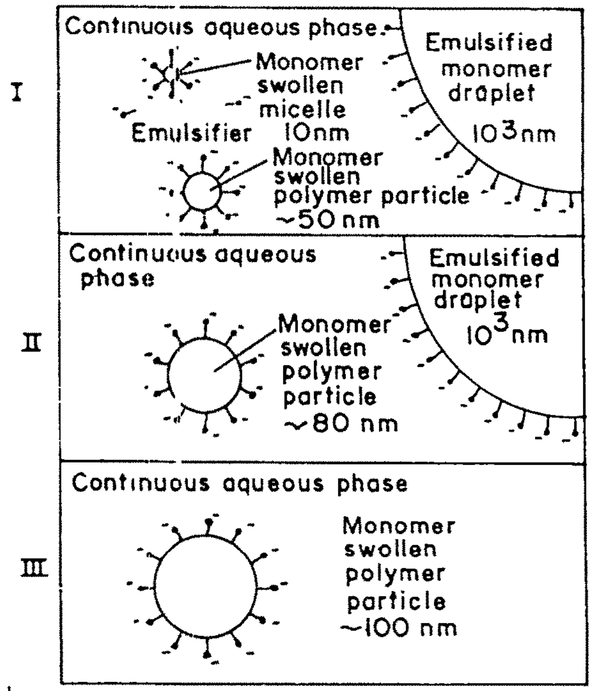


Fig.1. Schematic representation of an emulsion polymerization system.

The initiator is usually present in the continuous phase. Polymer latex particles are generated by two simultaneous processes. One is the entry of the free radicals from the external medium into the micelles (micellar nucleation)[12]. The other involves the polymer formation in the continuous phase of soluble oligomeric radicals (homogeneous nucleations)[13].

Three distinct intervals are observed in emulsion polymerization (Figure 1)[14-16]. Interval I corresponds to the initial period of polymerization where the particles are nucleated. As the particles grow, they are stabilized by absorbing surfactant from surrounding micelles. By the end of interval I, the micelles have either been nucleated to form new polymer particles or depleted to stabilize those particles. Most of the polymerization occurs in interval II where the nucleated polymer particles continue to grow due to diffusion of monomer molecules from the monomer droplets through the continuous medium and into the particles. Finally, at interval III all of the monomer in the monomer droplets is consumed and only the monomer in the still-swollen particles remains to be polymerized.

In emulsion polymerization both the polymerization rate, Rp and the number average degree of polymerization , DP are proportional to the number of polymer particles N, according to :

$$Rp = K_p N \bar{n} [M]_p / N_A$$

$$DP = 2 K_p N \bar{n} [M]_p / R_i$$

where K_p is the propagation rate constant, $\bar{n}$ is the average number of radicals/particles, R_i the rate of radical generation, $[M]_p$ the monomer concentration in the particles and N_A the Avogadro number. Thus an increase in N leads to a simultaneous increase in R_p and DP.

Emulsion polymerization is carried out in batch, semicontinuous and continuous reactors. The type of reactor system and the way it is operated can have significant effects on the polymerization kinetics and the characteristics of the latex produced.

Particle size distribution (PSD) is expected to be narrow for a batch reactor products as all the particles have the same age. In a semicontinuous system if the nucleation period is short, the PSD can be narrow. If however, nucleation period is expanded, broad PSD's are produced.

Higher molecular weight can be obtained if semi continuous reactor is operated in monomer starved mode. The high viscosity within monomer starved particles reduces the rate of termination and higher molecular weights are resulted.

1.3.2 Miniemulsion Polymerization

If polymerization is carried out in the emulsions with smaller droplet sizes (100 - 400 nm) it is termed as miniemulsion polymerization. This was studied by Ugelstad et al[17] who pioneered the research in monomer droplet nucleation, and showed experimentally that by dispersing the monomer into submicron size stable monomer droplets the area available for radical capture was increased drastically and monomer droplet became the main locus for particle formation.

Chamberlain et al[18], Choi et al[19] and Delgado et al[20] studied miniemulsion polymerization using water soluble initiator and showed that radicals entry to miniemulsion droplets and the subsequent particle formation was a process of low efficiency and that only a fraction of the original number of droplets gets initiated.

Chamberlain et al[18] studied polymerization of styrene in miniemulsion droplets and found that polymerization rate is higher for a system designed to give smaller droplet size than one with larger one. It was found that for the system with smaller droplet, particle size distribution is less than one with larger particle size. The latex produced from former was reasonably monodisperse. Similar observations were made by Hansen and Ugelstad[21] that droplet initiation leads to more monodisperse latexes if a water soluble initiator is used for initiation.

1.3.3 Microemulsion Polymerization

As the present work is in microemulsion polymerization all relevant aspects of it have been discussed here.

(i) Microemulsion

The term `microemulsion' was introduced by Schulman[22,24] in 1959. It has been defined as `a thermodynamically stable, isotropic clear dispersion of two immiscible liquids, consisting of microdomains of one or both liquids stabilized by an interfacial film of surface active molecules[23]'.

The formation of microemulsion has been attributed to the development of very small or even negative interfacial tension[24-26] which results due to the free energy decrease associated with the entropy of dispersion far outweighing the increase in interfacial energy accompanying the creation of interfacial area. Thus the free energy change due to mixing, ΔG_m , is negative resulting in spontaneous formation of microemulsion[27].

Role of short chain alcohols is well known in microemulsions: It helps to

- fluidize the interface
- decrease interfacial viscosity
- destroy the lamellar liquid crystalline structures,
- provide additional interfacial area
- reduce electrical repulsion between droplets by decreasing surface charge density.
- induce appropriate curvature changes.

On polymerization of microemulsions containing short chain alcohols, phase separation occurs. This instability can be attributed to the complex effect of entropic increase of free energy as a result of conformational limitations and the limited solubilities of polymers in cosurfactant. Hence, recently number of workers[28-30] have reported microemulsions without cosurfactants.

Contrary to emulsions which are w/o or o/w type, microemulsions can adopt a large variety of structural organizations. Figure 2 gives an illustration of the most common structures encountered in microemulsions.

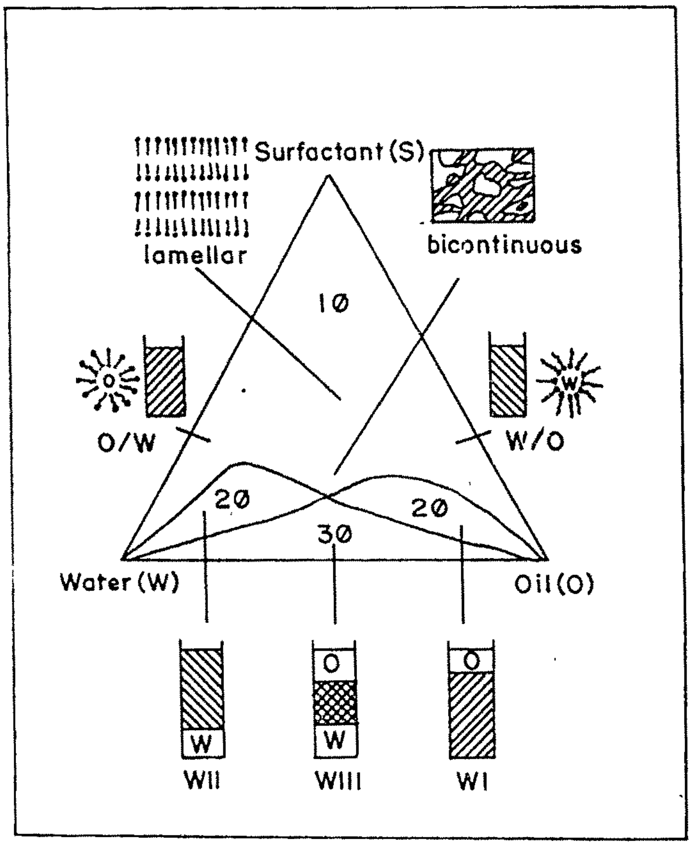


Fig. 2 : Illustration of some phase equilibria encountered in multicomponent systems

In the water and oil rich regions of the monophase domain (over a macroscopic scale) of the phase diagram, microemulsions consist of uniform and spherical droplets surrounded by a surfactant layer and dispersed in a continuous medium. The particle size is 10-40 nm, which explains the optical transparency of these systems. In the intermediate regions, the structure is no more globular (droplets) and the surfactant film has a spontaneous curvature close to zero. It is commonly described as disordered bicontinuous in which aqueous and oily domains are interconnected over macroscopic distances or locally lamellar.

Microemulsions form numerous equilibria. The well known Winsor phase equilibria are illustrated in figure 2. In Winsor I (W-I) systems, an oil/water microemulsion is in equilibrium with excess oil. While W-II systems consists of a microemulsion (surfactant dissolved in the oil) in equilibrium with excess water. In W-III systems, a middle phase microemulsion coexists with both oil and water excess phases. W-I and W-II microemulsions are of globular form while the W-III middle phase is bicontinuous[31].

(ii) Polymerization in Microemulsion

As a consequence of the extensive studies performed on microemulsion systems after 1974 oil crisis, in early eighties, a new interest developed for the polymerization in microemulsions. A primary goal of the investigators was to produce thermodynamically stable latex in the nanosize range (<50 nm) which are not attainable with the classical emulsion polymerization process.

Microemulsion polymerization of monomers may be achieved by incorporating a monomer in any of the water or oil phases of the system. Replacing dispersed phase by a monomer in a o/w microemulsion spherical latex particles of optimum diameter are produced. However, solid material may be produced if the continuous phase is polymerized entrapping the dispersed phase in its matrix.

Mechanism of Polymerization : Various studies[32-35] have shown that the diameter of the final latex particles during microemulsion polymerization ranges between 25 to 50 nm, which is much larger than that of the initial micelles 5 - 10 nm. These results indicate that nucleated particles grow by addition of monomer from other micelles, either by coalescence with neighbouring micelles or by diffusion of monomer through the continuous phase. Both mechanisms can be operative when droplet is mainly of steric origin[36]. Monomer diffusion from inactive micelles towards active particles should be the dominant process in aqueous microemulsions which are electrostatically stabilized.

In microemulsion polymerization each final microlatex particle contains a very low number of polymer chains of high molecular weight. The determination of the number of polymer molecules/particles, N_p is made from the final latex particle size and the polymer weight. The unusual finding of $N_p=1$, which does not follow the Smith-Ewart theory, and number of polymer particle increasing steadily led Candau et al[37] to suggest that microemulsion polymerization kinetics are characterized by a continuous particle nucleation.

Two main factors control particle nucleation in general :

(i) the ratio of monomer mass over surfactant mass and

(ii) the overall rate of radical capture (entry rate) over particle number R_c/N.

Kinetics of o/w microemulsion polymerization : Kuo et al[33] and Guo et al[34,38,39] studied the variations of the rate of polymerization, Rp and the degree of polymerization DP as a function of initiator concentration and light intensity on styrene/SDS + 1-pentanol/water microemulsions.

In conventional emulsion polymerization (initiator is in the aqueous phase) R_p and DP_n follow scaling laws of initiator concentration accordingly[40-42].

$$Rp \propto [I]^X$$

$$DP \propto [I]^{-Y}$$

Emulsion polymerization of styrene gave x = 0.4 and y = 0.6 values for the above exponent. In miniemulsion polymerization of styrene the same value of x (x = 0.4) was obtained when a water soluble initiator was used. But smaller value x = 0.2 was observed when the oil soluble initiator was used[19].

A more complex behaviour was observed for the polymerization of styrene in microemulsions. It was observed that the values depend on the type of initiator used and on whether the initiation is thermal or photochemical[33,34]. The polymerization rate conversion curves show only two intervals with no constant rate interval in microemulsions. Interval I is attributed to the nucleation stage; it increased to a maximum which marked the onset of Interval III, which is attributed to termination stage.

A lower rate of polymerization was observed for acrylates[29,30,43] in microemulsions than in conventional emulsions. This type of results are expected for solution polymerization while the opposite trend should be obtained in microemulsion due to large number of micelles present in the medium ($Rp \propto N$). Most of the kinetic studies on o/w microemulsion polymerization are very recent and are still under extensive investigations by various groups. It is expected that considerable progress with regard to the mechanism will be brought about in the near future and will provide better insight in the understanding of these complex systems.

Work carried out in this area of microemulsion polymerization is discussed in brief here. A part of the work is referred earlier while explaining microemulsion polymerization, whereas, selected references are discussed in text and others are listed in the Table 1.1for easy referencing.

1.4 Review of work done in microemulsion polymerization

From the literature survey it is seen that work has been carried out for the microemulsion polymerization using thermal, photochemical and high energy radiation initiation in the dispersed medium and in the continuous medium of oil/water, water/oil microemulsion and in bicontinuous microemulsion. The monomers studied were mainly styrene, acrylates, acrylamides and vinyl acetate.

Styrene

Extensive studies have been carried out on microemulsion polymerization of styrene since 1981 when Atik and Thomas[44] first reported o/w microemulsion polymerization using AIBN as initiator. Monodisperse spherical latex particles having diameter in the range of 350 ± 30 A° were produced. They also reported that when photopolymerization is carried out using Cs radiation source the latex particle size went down to 200 ± 20 A° [44]. Tang et al[45] reported styrene polymerization at 50 °C which took very long period (8 days) and showed bimodal distribution of molecular weights. Johnson and Gulari[46] found a good correlation between the latex particle size and droplet size when oil soluble initiator AIBN was used. Rabagliati et al[47] studied the polymerization using anionic - non-ionic surfactant mixture and AIBN and KPS as initiator and found inverse dependence of the DP on initiator concentration. Qutubuddin et al[48] have shown that polymerization of styrene in W-I, W-II or W-III systems can lead to novel porous solid materials with interesting morphology and thermal properties. Guo et al[34,38,39] carried out a detailed study on the polymerization of styrene microemulsions prepared from water/SDS and 1-pentanol as cosurfactant, using KPS and AIBN initiators at 70°C. A kinetic investigation of polymerization was carried out to determine the polymerization rate, latex particle size and molecular weight and its distribution. A mathematical model was developed to simulate the polymerization kinetics of styrene.

Graetzel et al[49] studied photopolymerization of styrene microemulsion and found that Rp was similar to radical initiated emulsion polymerization. Kuo et al[33] have reported photochemical polymerization using dibenzyl ketone and UV light of 313±10 nm. The particle size of produced latex was in the range of 30-60 nm and polydispersity was 1.6 - 2.2. It was found that Rp and DP depended on DBK initiator and light intensity.

$$Rp = [DBK]^{0.2}\ L^{0.2}$$

$$DP = [DBK]^{-0.4}\ L^{-0.2}$$

Holdcroft and Guillet[50] using pulsed UV lasers polymerized microemulsions of styrene.

Jaykrishnan and Shah[43] reported the polymerization of both styrene and MMA and observed lower rate of reaction, for both the monomers, than classical emulsion using the same surfactant. Feng and Ng[51] studied styrene and MMA polymerization using Raman spectroscopy. AIBN and KPS initiators were used. KPS initiated systems resulted in higher initial rates though AIBN resulted with higher total conversions. They reported that polymerization rate for MMA is higher than that of styrene. Number of other workers[52-67] carried out various studies on different aspects of polymerization of styrene in microemulsion.

Methyl methacrylate and other Acrylates

Thermal polymerization of methyl methacrylate and acrylate in microemulsion was originated in 1980 when Stoffer and Bone first reported it for MA and MMA[68,69]. Since then extensive work is being carried out especially since 1990 onwards. The use of cosurfactant is being avoided by large number of workers[29,30,70,71].

In the pioneering work Stoffer and Bone[68,69] studied the phase behaviour of SDS/pentanol/methyl methacrylate or methyl acrylate/water systems before and after polymerization. In the polymerization of the continuous phase of microemulsions phase separation occurs.

Gan et al[70,73-76] have carried out extensive work on microemulsion polymerizations of MMA and other acrylate monomers, using various type of surfactants. On polymerizing a system of MMA/CTAB/water with KPS it was found[70] that turbid emulsions can be changed progressively to transport microemulsion by merely increasing surfactant concentration. Two rate intervals were observed for microemulsion and an additional rate interval was observed for emulsion polymerization. Microparticles obtained ranged from 16 to 30 nm and molecular weight of PMMA was observed to be 5.7×10^6. Micro emulsion polymerization using STAC surfactant[76] resulted in transparent latex, stable for ~ 1 year and a constant rate of polymerization was observed with low initiator concentration. Bicontinuous microemulsion polymerization of MMA using DDAB resulted in microporous material with high surface area[78].

Bleger et al[71] studied the particle nucleation in microemulsion polymerization of MMA using DTAB and DDAB. The reaction was reported to follow two stage polymerization with nucleation mainly on the water phase irrespective of the type of initiator. Nucleation was reported to be continuous through out and occurs mainly in microemulsion droplets. Lusvardi et al[77] studied the phase behaviour and microstructure of polymerizable microemulsions of alkyl methacrylates using mixed surfactants DTAB/DDAB. Polymerization of tetrahydrofurfuryl methacrylate by Full et al[79] at 60°C using KPS with AOT resulted in particles with 25-34 nm and molecular weights of order 10^7. Gupta and Eicke[80] carried out polymerization of cyclohexylmethacrylate monomer as an oil phase in water-in-oil microemulsion in the presence of AIBN initiator and allyl methacrylate cross linker. Characterization of latex was done by using SEM and showed that the products were porous in nature.

Schauber and Riess[81] polymerized cyclohexyl methacrylate with tetramethylene dimethacrylate cross linker by photoinitiation to stable microlatexes containing 5-10% solid and particle size of 10-30 nm. Chieng et al[82] studied polymerization of MMA and 2-HEMA using ethylene glycol dimethacrylate crosslinker and SDS as surfactant by photochemical initiation with dibenzyl ketone which resulted in microporous polymer.

Gan et al[83] replaced SDS by a polymerizable surfactant, sodium acrylamideoundecanoate in the polymerization of MMA and acrylic acid. It was found that the polymerization of MMA and acrylic acid (AA) in these microemulsions produced transparent solid polymers. Number of other workers[72,84-95] has carried out polymerization in microemulsion using acrylate and methacrylate monomers.

Acrylamide

Leong and Candau[96] first reported microemulsion polymerization of acrylamide in 1982, to obtain inverse latex of <500 A° in diameter by the photopolymerization of acrylamide microemulsion by dispersing a water-acrylamide mixture in toluene with AOT as surfactant. Since then extensive work was carried out and reported by Candau et al[37,42,97,100-104]. Candau et al[101] carried out polymerization of acrylamide and sodium acrylate microemulsion in Isopar M. stabilized by a non-ionic emulsifier blend of sesquioleate sorbitan (Arlacet 83; HLB 3.7) and polyoxyethylene sorbitol hexaoleate with 40 ethylene oxide units (HLB 10.2) to result in the appearance of turbidity and increase in the viscosity of the medium. A detailed study[97] on the kinetics of the acrylamide polymerization in microemulsion using AIBN and $K_2S_2O_8$ showed that clear and highly stable latexes were produced in the system. The recent studies of Carrer et al[98,99] showed a detailed kinetic analysis of polymerization of acrylamide inverse microemulsions. In three different systems (i.e. toluene, heptane and benzene) the rate of polymerization R_p was found to be 1.06, 0.73 and 0.55 respectively[99]. Number of other workers[105-119] have studied microemulsion polymerization of acrylamide studying its various aspects. Several patents have been listed to Candau et al[120-122] in inverse microemulsion polymerization.

Vinyl Acetate

Donescu et al[123,124] reported polymerization of vinyl acetate in SDS-propanol microemulsion system and observed slower polymerization rate than for regular emulsions. Structure of polymers was studied using viscometry and conductometry. Anghel et al[125] studied phase behaviour of vinyl acetate-water systems in the presence of various surfactant and cosurfactant mixtures during their polymerization. Donescu et al[126,127] studied the kinetics with respect to the initiator ammonium persulphate to be first order using ethoxylated nonyl phenol/propanol surfactant system. The polymerization rate and molecular weight decreased with increasing SDS and propanol concentrations in polymerizing microemulsions of vinyl acetate/SDS-propanol/water and APS as initiator[128].

Aniline was polymerized in microemulsion to yield conducting polyaniline of 10-35nm diameter[129]. Corpart et al[130] synthesized ampholytic copolymers of high molecular weight and charge density by free radical polymerization.

1.5 Proposed Work

Microemulsion polymerization is an upcoming technique having wide ramifications in future industrial quality product development. One of its applications will be in the field of surface coatings. It was proposed to study microemulsion polymerization, the properties of the polymers synthesized as it is dependent on the polymerization process and its relevance to surface coatings.

The proposed work is as follows :

1. Determination of the phase diagrams of MMA, MMA-BA (1:1 w/w) and BA using SDS as surfactant.

2. Optimization of various reaction conditions for the copolymerization of MMA-BA (1:1 w/w) in microemulsion in batch process using SDS.

3. Kinetic study of MMA, BA and MMA-BA (1:1 w/w) in emulsion and microemulsion medium with respect to temperature, KPS concentration and monomer concentration.

4. Semicontinuous copolymerization of MMA-BA (1:1 w/w) using disodium diphenyl oxide disulphonate (Dowfax 2A-1) and sodium dodecyl sulphate. Optimization of reaction conditions using disodium diphenyl oxide disulphonate (Dowfax 2A-1).

5. Characterization of the products synthesized in batch and semi continuous process for tacticity, molecular weights, thermal properties and solution properties through NMR, GPC, TGA-DSC and viscosity studies respectively.

6. Characterization of the latexes for their particle size, film forming property and their use in paint formulation.

Table 1.1 : Microemulsion Polymerization.

MONOMER	SURFACTANT	INITIATOR	GENERAL INFORMATION	REFERENCE
STYRENE				
1. Styrene & Acrylonitrile	TTAB	KPS	Monomer reactivity ratio from C^{13} NMR data, Tg of SAN decrese with increasing mol. fraction of Styrene.	65
2. Styrene	-	-	Effect of water soluble cosurfactants.	55
3. Styrene	-	-	Comparision of oil-sol. and water-sol. initiation of styrene polymerization.	56
4. Styrene	CTAC		Microparticles,radius 10-60 nm.	59
5. Styrene	(I)Hexadecyl trimethyl ammonium bromide (II)SDS-Butyl Carbitol	(I) KPS (II) AIBN	Stable for one year,kinetics investigated.	60
6. Styrene	SDS-Pentanol	(I) KPS (II) AIBN	Particle nucleation and monomer partitioning Modeling o/w Microemulsion polymerization.	38 39

7. Styrene	SDS-pentanol; NaCl	-	Thermodynamic Model	64
8. Styrene	-	KPS	Av. diameter 50-70 nm; Tg for o/w & w/o products were 103°C and 143°C respectively.	63
9. Styrene	SDS,NaCl, NaSCN, 2-pentanol,5-hexane diol, Sod.Styrene sulfonate.	Photoinitiation	Photopolymn. of Middle phase Microemulsions	62
10. Styrene-Acrylic Acid	Anionic & Cationic surfactant.	AIBN	Inverse Microemulsion	61
11. Styrene	SDS	KPS AIBN	Polym. by Raman spectroscopy	67
12. Styrene	-	KPS	Polymn.resulting 2-reaction intervals $5 - 10 \times 10^6$, particle diameter 20-40 nm.	52
13. Styrene, MMA, vinyl acetate	Nonylphenol with 5,6 or 7 mol. ethylene oxide + nonyl phenol with 15 or 16 mol. ethylene oxide unit + SDS/AOT/SDBS	KPS AIBN	37-100 nm diameters with broad distribution.	57

14. Styrene & acrylic acid	DTAB	AIBN	Anionic Inverse Microemulsion polymn.	66
15. Styrene & MMA	SDS-pentanol	KPS	Polymn. by in situ Raman spectroscopy	51
16. Styrene	DTAB	-	20-30 nm particle size	28
17. Styrene	SDS-pentanol	Pulsed, UV lasers,AIBN	Oil, Benzene	50
18. Styrene	SDS and nonionic surfactant/pentanol Butyl cellsolve	AIBN KPS	Polymn. in Middle phase Micro - emulsions, Porous, mol.wt. $(0.2 - 1.0) \times 10^6$	48
19. Styrene	-	KPS AIBN	Particle size 20-30 nm, mol.wt. 1.2×10^6	34
20. Styrene	-	water-sol. & oil-soluble initiator	Kinetics of Microemulsion; Radical polymerization	54

21. Styrene	SDS/pentanol	Photochemical Initiation DBK; UV 313+10 nm	Transparent; 30-60 nm; PDI 1.6-2.2	33
22. Styrene	Anionic & non-ionic surfactant	AIBN KPS	Inverse dependence of the degree of polymerization on initiator concn. (as in bulk polymerization)	47
23. Styrene	-	Photopolymerisation	Rp was similar to radical-initiated emulsion polymn.	49
24. Styrene	Ethoxylated polypropylene glycol	-	Microemulsion polymerization.	53
25. Styrene, MMA	Aerosol MA-30, pluronic L 31	BPO AIBN	For MMA the rate of polymn. is less for microemulsion than emulsion	43
26. Styrene	-	-	o/w microemulsion, Thermal polymn. at 50°C for very long time	45
27. Styrene	SDS-pentanol	KPS AIBN	In oil soluble initiator the droplet size in the microemulsion seems to have correlation to the size of the product.	46

28. Styrene	SDS-pentanol	g-radiation	In pyrene -	58
29. Styrene	CTAB, Hexanol	AIBN Cs Γ-ray	Spherical particles	44
ACRYLATES AND METHACRYLATES				
30. Butyl Acrylate	SDS	APS DBP	o/w microemulsion and emulsion polymerization	29
31. Alkyl Methacrylates	DTAB DDAB	-	Phase behaviour and microstructure of polymerisable microemulsions	77
32. MMA and N-Methylol acrylamide	AOT	-	Microemulsion polymerisation	84
33. MMA and Iso butyl methacrylate	-	-	Emulsion and Microemulsion copolymn.	72
34. MMA and Ethylene glycol dimethacrylate	[{(acryloloxy) undecyl} dimethylamino] acetate	Photoinitiation	Zwitterionic microemulsion polymerization., microporous material.	73

35. MMA	DDAB	-	Bicontinuous microemulsion polymerization. Microporous material with high surface area.	78
36. MMA	TTAB STAC	-	Cationic microemulsion polymerization, stable latexes with traces of PMMA particles.	74
37. MMA and 2-HEMA Ethylene glycol dimethacrylate	SDS	Dibenzyl ketone photochemical initiation	Morphology of microporous material was studied.	82
38. Butyl acrylate	-	APS DBP	Rate of polymn. shows nucleation and termination intervals	85
39. MMA and Styrene	TTAB OTAC	-	The rate of polymn. in microemulsion was slower than in emulsion for MMA.	75
40. Butyl acrylate	-	APS BPO AIBN	Polymn. faster with APS than with BPO or AIBN. The polymn. rate shows two intervals-initiation & termination	86
41. MMA and BA	SDS	AIBN	Microemulsion and emulsion Copolymn;	87

		BPO	polymn. rate higher in emulsion.	
42. MMA	DDAB : DTAB (1:3)	AIBN KPS V-50	Particle nucleation during Microemulsion polymerization.	71
43. MMA	DTAB	AIBN KPS	Initiation and termination rate Intervals observed. No constant rate interval.	88
44. MMA and Ethylene glycol dimeth-acrylate acrylic acid	SDS	-	Control of microstructure and morphology Bicontinuous microstructure	89
45. MMA	CTAB	KPS	Stable PMMA latexes, emulsion and microemulsion polymn. mol.wts. 5.7 x 10^6	70
46. MMA	STAC	-	Transparent and stable ~1 yr. A constant rate of polymn. for 1st time with low initiator concentration.	76

47. n-Butyl meth-acrylate Ethylene dimethacrylate camphor,Quinone and $CH_2 = CH COOCH_2CH_2 NMe_2$	$CH_2 = CH (Me(CH_2)_{11} NMe_2 [(CH_2)_{11} Me]+ Br-$	Photopolymn	Polymn. in microemulsion using polymerisable surfactant	90
48. Tetrahydrofurfuryl methacylate	AOT	$Na_2S_2O_8$/ $NaHSO_3$	Latex particle size 37-39 nm Tg 67°C	91
49. Tetrahydrofurfuryl methacrylate	AOT	KPS	Microlatex diameter 25-34 nm polymer mol. wt. ~107	79
50. MMA and Styrene	CTAC DTAB	-	Particle size 10-60 nm, polymn. and copolymn. in microemulsions, m-diisopropylbenzene was used.	92
51. Cyclohexyl meth-acrylate, Allyl methacrylate	-	AIBN	Porous membrane material polymerization in inverse microemulsions	80
52. MMA, Acrylicacid Ethyle glycol dimethacrylate	SDS	-	Porous polymeric structure, polymerization. in inverse microemulsions.	93

53. BA	Dowfax 2A-1 Acrylamide	APS	Solid content 41 %, particle size 520 Ao, polydispersity 0.124	94
54. Cyclohexylmeth- Stable micro- latexes methylene di- methacrylate (cross-linker)	- -	Photoinitiation	Solid content 5-10 %, particle size 10-30 nm.	81
55. MMA, Sodium acrylamide stearate	-	AIBN	Gel effect when % conversion around 36%	83
56. MMA	SDS Acrylic acid	High energy radiation	Confirm the studies made by Friberg that the entropic effect is not only factor contributing to the destabilization of microemulsion during polymerization. Solubility of polymer is an important factor.	95
57. Me acrylate	SDS, pentanol	KPS,BPO,AIBN	Linear dependence revealed 1/Dp- Vs [S]/[M] comparision of mol.wt. behaviour by various classical methods of polymerization.	68
58. MMA	SDS, pentanol	KPS,BPO,AIBN	Addition of KPS did not influence phase stability region.	69

ACRYLAMIDE

59. Acrylamide	AOT	APS BPO KPS	Percolating Inverse phase microemulsion polymn.	105
60. Acrylamide	Non-ionic surfactant HLB 6-10		Temp $< 100^{\circ}$C Polymer solids > 15 %	106
61. Acrylamide & MMA	-	APS AIBN	Tolvene continuous medium, inverse microemulsion, locus of initiation by APS was waterpool and AIBN was interphase between water micro pool and tolvene macrophase.	107
62. Acrylamide, MMA and Styrene	-	-	Copolymn. of water and oil soluble monomer in inverse microemulsions.	108
63. Acrylamide MMA and Styrene	-	AIBN	Inverse microemulsions,typical `dead end'polymerization.	110
64. Acrylamide	-	-	Microemulsion within near & supercritical continuous phase	109

65. Acrylamide	AOT	-	Toluene continuous medium; particle nucleation occurs throughout the polymerization.	102
66. Acrylamide	Polyethylene glycol-monoalkyl ether	-	Polymn. in inverse microemulsions near and super critical continuous phase, C_2H_6 and C_3H_8.	112
67. Acrylamide, MMA & Styrene	-	APS BPO AIBN	Inverse microemulsion in Toluene/water	111
68. Acrylamide	-	-	$C_6H_5CH_3$, C_7H_{16} & C_6H_6 continuous phase, termination mechanism in acrylamide w/o microemulsion polymn. Non-radical termination in toluene, Biradical in Benzene.	99
69. Acrylamide	AOT	AIBN	Kinetic analysis	98
70. Acrylamide (A) -MADQUAT (B)	-	-	Reactivity ratio calculated;	114
71. Acrylamide & Sodium Acrylate	Ethoxylated Surfactant	-	Solid content < 25% particle diameter 450-700 A°.	103

72. Acrylamide	Sorbitan sesquioleate polyoxy ethylene, Sorbital Hexaoleate, NaoAC, Isopar M.	-	Polymn. in non-ionic microemulsion Isoparaffin oil.	117
73. Acrylamide & Sod. acrylate	Blend of emulsifiers	-	Isoparaffinic oil Bicontinuous Cht.	100
74. Acrylamide	Hydrocarbon dispersants	-	3-pentane in benzene and toluene	113
75. Acrylamide (A) Sodiumacrylate (B)	-	-	Relativity ratio calculated; $r_A = 0.95 + 0.15$ $r_B = 0.89 + 0.15$	101
76. Acylamide		Benzophenone Photoinitiation	Decane as continuous phase; w/o inverse microemulsion	115
77. Acrylamide	AOT	AIBN	Toluene/water; <500 A°, polydispersity 1.45	104
78. Acrylamide	AOT	KPS, AIBN	Clear and highly stable latexes	97
79. Acrylamide	-	Photoinitiation UV-radiation	< 500 A° particle size, mol.wt. ~ 3.0×10^6	96

VINYL ACETATE

80. Vinyl acetate	Ethoxylated, Nonyl-phenol ethanol.	APS	The interdependence between the scission rate of APS initiator and polymn. rate of monomer studied.	127
81. Vinyl acetate	-	APS	Polymn. rate increased with increasing monomer concn.	128
82. Vinyl acetate	SDS, propanol	APS	The polymn. rate and mol.wt. deceased with increasing SDS and propanol concentration.	124
83. Vinyl acetate	Propanol, ethoxylated nonyl phenol	APS	1st order kinetics with respect to the initiator	126
84. Vinyl acetate	SDS, polyethylene glycol Nonyl phenyl ether, MeOH, 2-ethyl Hexanol, 1 % NaCl.	-	Phase behavious of vinyl acetate-water system in the presence of various surfactant and cosurfactant mixtures studied.	125
85. Vinyl acetate	SDS-propanol	-	Polymn. rate slower than regular emulsions. Structure and polymerization studied using viscometry and conductometry.	123

MISCELLANEOUS

86. Aniline	-	-	Conducting polyaniline, 10-35 nm diameter	129
85. Na-2 acrylamide-2-Me(propane sulfonate) 2-(methacryloloxy) Et-tri-Me-ammonium chloride.	-	Radical polymerization	Free radical copolymn. high mol.wt. and high charge ampholytic copolymers.	130

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