CHAPTER 1

A brief overview of polymerisation in microemulsion medium.

1 .0 INTRODUCTION

[1 . 1] Polymers

A great thought of past can open the door for a bright present and an even brighter future. The birth and growth of polymer science is very much on the same lines. The idea of a macromolecule was first suggested by Herman Staudinger [1] in the year 1927, but was strongly opposed by the then scientific community. Since then polymer science has realized tremendous growth in both scope and applications. Most of the applications stem from the higher molecular weight, [typically millions] of a macromolecule; which is built up by the linking together of a large number of elementary units known as monomers. When same type of elementary units join, they are termed as homopolymers if they are of two or more types, they are termed as copolymers. Polymers are classified according to their origin, nature of polymeric backbone, mechanism of synthesis or according to the arrangement of monomeric units in them.

[1 . 2] Polymerisation Process

The process of synthesis of polymers is termed as polymerisation. Polymerisation process can be divided into three subclasses based on the medium of polymerisation.

- Polymerisation in homogeneous medium.
- Polymerisation in heterogeneous medium.
- Polymerisation in solid phase.

[1 . 2 . 1] Polymerisation in homogeneous medium

(i) Bulk or mass polymerisation

Bulk polymerisation is the simplest process, involving only the monomer and monomer - soluble initiator. The high monomer concentration leads to high rates of polymerisation and formation of high molar mass polymer. However, the viscosity of the reaction mixture increases rapidly with conversion, making stirring inefficient and heat removal difficult, which may lead to autoaccelaration. These problems can be avoided by restricting the reaction to low monomer conversions, though on an industrial scale, process economics necessitate the recovery and recycling of unreacted monomer. The major advantages of bulk polymerisation are simplicity and ability to produce high molar mass polymer of high purity [2].

[ii] Solution polymerisation

Many polymerization processes are carried out in solution by using solvent for the solubilisation of the reactants. They also allow higher reaction temperatures to be employed. Polymerisation of a monomer in a solvent overcomes many of the disadvantages of bulk process. The solvent acts as a diluent, aids efficient heat transfer, and allows efficient stirring and thermal control. However, the presence of solvents creates new difficulties like chain transfer to solvent, purity of the polymer and removal of the solvent [3].

[1 . 2 . 2] Polymerisation in heterogeneous medium

In order to circumvent the sudden rise in heat and viscosity encountered in bulk polymerisation, reaction can be performed in heterogeneous medium. The medium allows heat dissipation and also prevents sudden rise in viscosity. Polymerisation in heterogeneous medium can be carried out as gas phase, precipitation, suspension and emulsion polymerisation.

[i] Gas phase polymerisation

The term gas – phase polymerisation refers to a polymerisation reaction initiated on monomer vapors, generally by photochemical means. High molecular weight polymer molecules are not volatile, so a fog of polymer particles containing growing polymer chains quickly forms and a major portion of the polymerisation reaction proceeds in the condensed state. Gas phase polymerisation, in this sense is very similar to the mechanism of emulsion and precipitation polymerisation as the polymer particles in the fog can contain only one growing radical and fresh monomer diffuses into the particle from the gas phase. Some of the monomers that have been polymerized successfully in the gas phase include methyl methacrylate, vinyl acetate and chloroprene. Advantage is taken of the long life of the isolated polymer radicals in gas – phase polymerisation to prepare a block-copolymer of chloroprene and methyl methacrylate by alternatively exposing the particles to pure vapors of the two monomers [4].

[ii] Precipitation polymerisation

If a polymer is insoluble in its own monomer or in a particular monomer solvent combination, it will precipitate out as it is formed. If the polymer precipitates out in the form of compact small spheres while still containing living radical end group, an increase in the rate of polymerisation will be observed as the living end groups remain buried in the spheres and the termination between two growing polymer chains becomes extremely difficult or improbable. This phenomenon is termed precipitation polymerisation. Some of the polymerisation systems in which this phenomenon is believed to occur include styrene in alcoholic solvents, methyl methacrylate and acrylonitrile in water [5].

[iii] Suspension , dispersion and emulsion polymerisation

Suspension polymerisation is also referred to as bead or pearl polymerisation. It is carried out by suspending the monomer (disontinuous phase) as droplets (50 - 500μm in diameter) in water (continuous phase). The monomer droplets, subsequently converted to polymer particles are prevented from coalescing through agitation and the presence of suspension stabilizers or dispersants. Two types of stabilizers used are –

- Water soluble polymers often in the presence of electrolyte or buffer.
- Water insoluble inorganic powders.

The dispersants used in suspension polymerisation seldom form colloidal micelles as in emulsion polymerisation. Dispersion polymerization, carried out in the presence of high concentration (> 1%) of water soluble stabilizers is used to produce latex like dispersions of particles having small particle size in the range of 0. 5 - 10 μm.

In the case of emulsion polymerisation the surfactant concentration is above cmc. Polymerisation takes place in monomer swollen micelles as well as in aqueous phase. Generally water-soluble initiators are used. Further details are discussed in section 1.3.

[iv] Solid phase polymerisation

The term includes all types of polymerisation processes taking place in solid state such as crystalline and glassy states of pure monomers with other compounds [6, 7]. The development of solid state polymerisation was largely due to the high energy radiation which helped to carry out the reactions at lower temperature 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, ESR, DTA, X – Ray diffraction, IR and Raman spectroscopy to get experimental data on molecular structure, molecular packing and molecular vibrations in monomer crystals as well as in the configuration and conformation of the resulting polymers.

[1. 3] Emulsion

As we have carried out polymerisation in emulsion and microemulsion medium, the necessary details of both the polymerisation processes 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).

Emulsion polymerisation is a free-radical initiated chain polymerisation in which a monomer or mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant to form a product, known as latex. Emulsions generally contain monomer, water, surfactant, initiator and in some cases chain transfer agents. Water , maintains low viscosity and efficient heat transfer. In addition, it serves to isolate the polymerisation loci. Surfactant (or emulsifier) provides sites for particle nucleation as well as provides colloidal stability to the growing particles due to adsorption at particle – water interface. Commonly used initiator is potassium persulphate. Apart from this redox initiators and oil-soluble initiators are also used. Chain transfer agents are mainly mercaptans, which are used to control the molar mass.

[1 . 3 . 1] The emulsion polymerization process

The procedure by which an emulsion polymerisation is carried out has profound effect upon the resulting latex and polymer properties. Latexes and polymers with quiet different performance characteristics can be prepared from the same reaction formulation by appropriate control of the addition of ingredients. If all the ingredients are added at the beginning of polymerisation it is referred as a **batch** ***or*** **continuous process**. One or more of the ingredients if added continuously or in increments process is known as a **semi – batch process** ***or*** **semi - continuous** . A semi – batch process allows control over polymerisation rate, particle number, colloidal stability, copolymer composition and particle morphology. In the third modification, the ingredients are fed continuously in a tank or in more than one tank connected in series. Latex is simultaneously removed at the same rate. It has the advantage of high production rate, steady heat removal and uniform quality of latexes.

[1 . 3 . 2] Description of emulsion polymerisation:

Harkins in (1947) [8] put forward original qualitative description of emulsion polymerisation, which was quantified by Smith and Ewart in (1948) [9] which was further modified by number of authors [10- 18]. According to Harkin's original picture, emulsion polymerisation is divided into three intervals encompassing the particle formation stage, termed as interval I , particle growth stages as interval II and III [Fig 1. 1 and Table 1.1]. During interval I, both particle number and polymerisation rate increase with time, and its end is marked by the disappearance of micelles, which are the main source of particle nucleation in Harkin's picture. During interval II , the particle number remains constant and monomer droplets provide the growing polymer particles the required monomer to maintain saturation swelling and support the propagation reaction. The polymerisation rate during this interval is classically considered to be constant. The beginning of interval III is marked by the disappearance of large monomer droplets and the polymerisation rate decreases due to decreasing monomer concentration inside polymer particles. The particle number also remains constant during this period incase coagulation is negligible. Since emulsion polymerization is a free – radical addition polymerization, all kinetic events, namely, initiation, propagation, termination and transfer reactions are applicable to describe the overall rate of the polymerisation and molar mass development of the polymer latex However, the heterogeneous nature of the polymerisation imparts some complications due to partitioning of the various ingredients between the phases namely, the micellar, aqueous phase, monomer droplet and the particle. The partitioning of ingredients leads to the possibility that in the initial stages the polymerisation takes place in all phases and then in the latter stages after the monomer droplets have disappeared, shifts mainly to the aqueous and the particle phase. Overall in emulsion, polymerisation in the polymer particles is generally predominant. Particle formation in emulsion polymerisation can be through micellar, homogeneous and droplet nucleation.

Table 1.1 : Qualitative description of an emulsion polymerisation system

Interval	% Conv range	Micelles	Monomer droplets	Particle number	Particle size	Comments
I	0 – 10	Present	Present	Increases	Increases	Nucleation Period
II	10 – 40	Absent	Present	Constant	Increases	Cp const
III	40 - 100	Absent	Absent	Constant	Roughly Constant	Cp increases

Cp : Monomer Concentration in particle

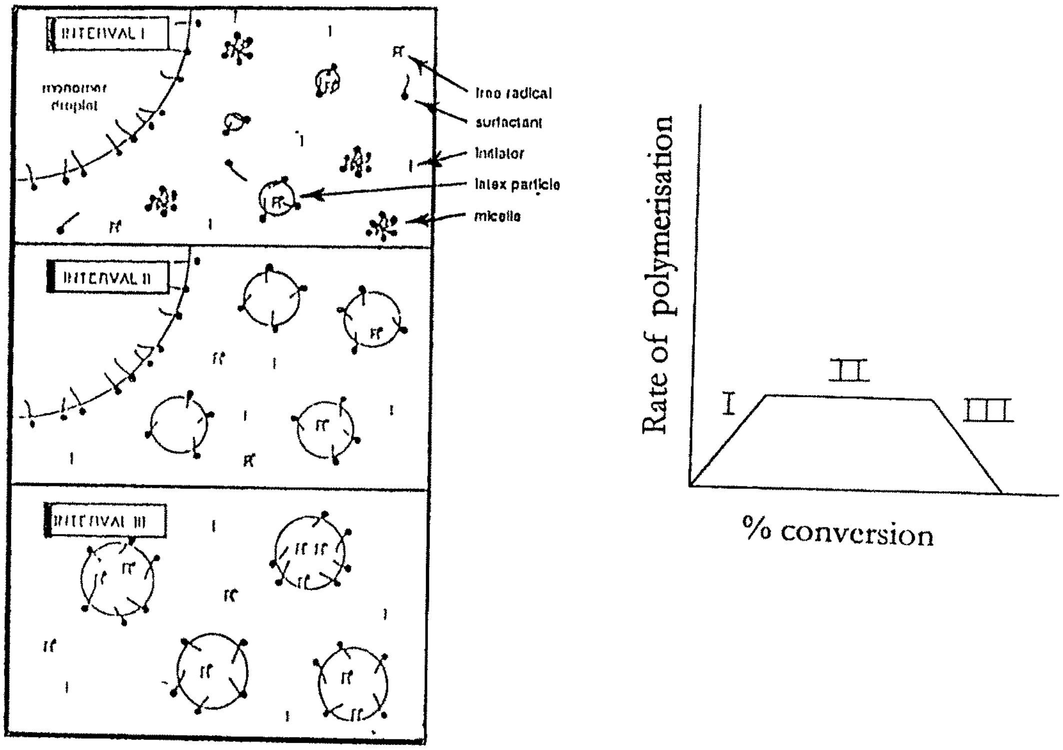

Fig 1 . 1 : Schematic representation of an emulsion polymerisation system.

[i] Micellar nucleation

The radicals generated in the aqueous phase enter monomer swollen micelles as oligomeric radicals to initiate polymer particles . Usually one out of every 100 – 1000 micelles captures a radical to become a polymer particle[19].

[ii.] Homogeneous nucleation

Radicals generated in the aqueous phase propagate by adding monomer units from water-soluble oligomers until they reach the limit of their solubility in aqueous phase and precipitate out of the solution. The precipitated oligomeric radicals form primary particles which adsorb surfactant molecules, bringing about their stabilization and diffusion of monomer from larger droplets contributes to further propagation and growth of the particle [20]. These primary particles can persist or coagulate with themselves or with growing stable particles. Thus, the profile of change in particle size and number during the course of the polymerisation and the final particle size and number are governed by the amount of surfactant and its effectiveness in stabilizing the primary and the growing particles. Particle formation by coagulative nucleation has also been proposed by Napper and Gilbert [21] wherein small size "precursor" particles are initially formed through homogeneous nucleation, followed by their aggregation to form stable, mature particles.

[iii] Droplet nucleation

In this type the smaller droplets are produced by intensive mechanization.The small size of the droplets competes effectively for radical capture with the larger droplets [22]. This mechanism is predominant in miniemulsion polymerisation [23]. These systems generally require the use of a cosurfactant like hexadecane or cetylalcohol (having low molar mass and low water solubility) in addition to the surfactant.

In principle, all three-particle formation processes may operate simultaneously. However their relative contribution to particle formation varies depending on surfactant concentration, monomer solubility in aqueous phase and level of subdivision of monomer droplets. Particle formation by droplet nucleation is considered to be insignificant in conventional emulsion polymerisation.

Once the latex particles form they grow mainly by diffusion of monomer from the monomer droplets. Most of the polymer generated in the latex particles is generated by the above-mentioned processes. Emulsion polymerisation generally employs a water-soluble initiator like potassium persulphate. The complexity of particle nucleation in emulsion polymerisation comes from the various physical processes and chemical reactions which follow the formation of these ionic radicals and determine their destiny. Fig 1. 2 illustrates the possible fate of these radicals generated in aqueous phase.

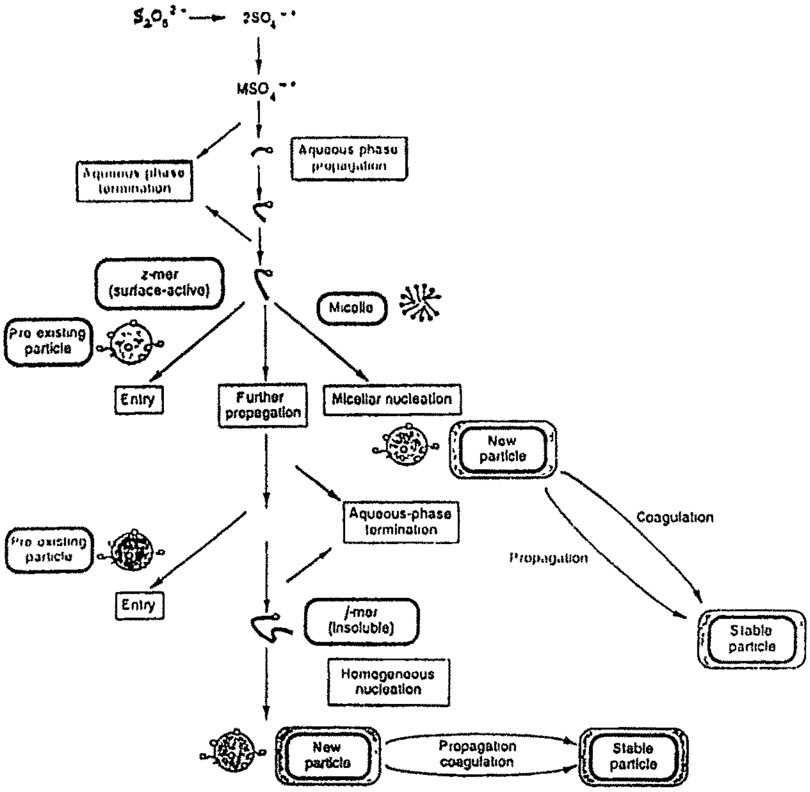

Fig 1. 2 : The events involved in particle formation.

[iv] Termination

In an emulsion polymerization, a particle is born with a weight fraction of polymer, [Wp] typically of 0.3 - 0.4, rather than zero as happens at the start of bulk or solution polymerisation. Over a range of polymer fraction applicable to an emulsion polymerization (say, 0.3 < Wp < 1) termination is always diffusion controlled [24]. Therefore, the rate coefficient for termination will depend on the degrees of polymerization of the two terminating chains. This chain length dependent termination has a major effect on kinetics. As Wp increases, the diffusion coefficients of oligomeric radicals decrease, "short – long" termination still dominates, but the mobile short chains are slightly longer than at lower Wp. If the polymer system becomes glassy at high Wp , motion of a radical of any degree of polymerization by center – of – mass diffusion is very slow, and hence the dominant mode of motion of radical end is by reaction diffusion [25].The dominant events in termination for emulsion polymerization are shown in Fig 1 . 3.

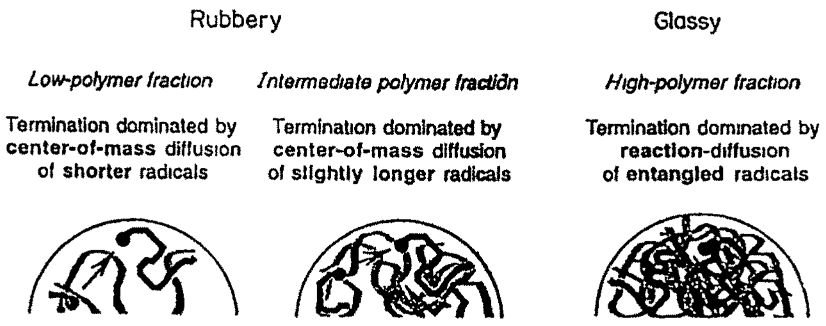

Fig 1. 3 : The dominant events in termination for emulsion polymerization.

[1.4] Microemulsion

On increasing the surfactant concentration an emulsion system can be transformed into a transparent microemulsion [26]. Increase in the surfactant concentration leads to the reduction in interfacial tension. A point is reached when the interfacial tension is so low that **spontaneous emulsification** results [27 , 28]. The oil in such a situation is solubilised in aqueous phase. The very small size of the droplets makes the solution appear transparent. The term microemulsion was introduced by Schulman in 1959 [29]. 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 [30]. The formation of microemulsion has been attributed to the development of very small or even negative interfacial tension which results due to free energy decrease associated with the entropy of dispersion outweighing the increase in interfacial free energy accompanying the creation of interfacial area. Thus the free energy change due to mixing, ΔGm , is negative resulting into a spontaneous formation of microemulsion [31].

Contrary to emulsions which are w / o or o / w type, microemulsions can adopt a large variety of microstructures [32]. Fig 1. 4 illustrates most of the common structures encountered in microemulsion. In water and oil rich regions of the monophase domain (over a macroscopic scale) of the phase diagram , microemulsions consists 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 intermidiate regions, the structure is no more globular 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.

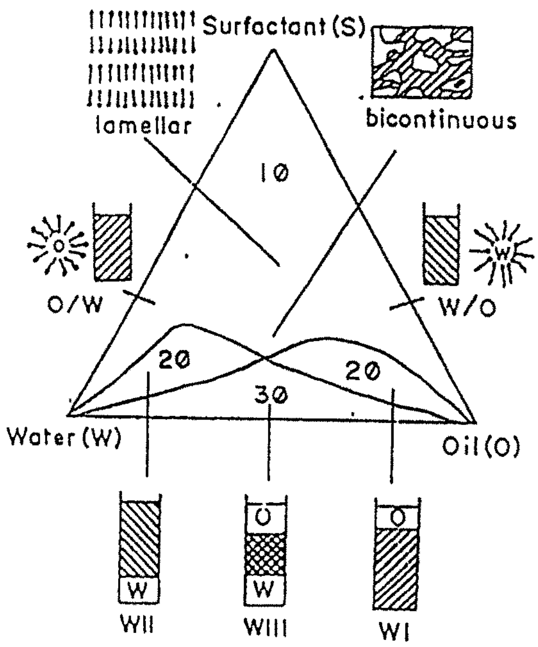

Fig 1. 4 : Illustration of some phase equilibria in multicomponent systems.

Microemulsions form numerous equillibria ,The well known Winsor phase equllbria are illustrated in Fig 1. 4. In Winsor I (W – I) systems, an oil/water microemulsion is in equllibrium with excess oil. Whereas W II systems consist of a water / oil microemulsion 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 composed of spherical droplets whereas W – III middle phase is a bicontinuous one. [33].

[1 . 4 . 1] Polymerisation in microemulsion

Due to well defined nature of the mesophases and the enormous inner surface of these structures, it is very attractive to perform polymerization reactions inside these systems, either to stabilize the three dimensional structures or to synthesise polymer materials which are not accessible by other techniques, such as special copolymers. The concept of polymerization in microemulsion is still young and was first reported in 1980. Nevertheless, it has developed into a rapidly growing field of research and features a wide variety of different complex applications ranging from colloidal drug carriers to the development of highly functional polymer particles.

There are however, still very contradictory sets of data reported in literature and a consistent picture is missing. A few specific reports pertaining to the kinetics of polymerization in oil- in -water and water- in-oil microemulsion are briefly discussed here.

[i] Polymerisation in oil / water microemulsion

[a] Styrene

As early as 1977, Riess et al. [34 , 35] first attempted to combine the advantages of polymer chains with those of microemulsion. However, the first paper, which described a polymerization process in oil-in-water microemulsion, was published by Stoffer and Bone in 1980 [36]. In 1981 Atik and Thomas [37] polymerized styrene in an oil-in-water microemulsion using different initiating systems and obtained narrowly distributed latex particles with diameters in the order of 20 - 30 nm. Their system however, was based on the use of hexadecyltrimethylammonium bromide (CTAB) and hexanol as a cosurfactant.

The polymerization of styrene in o/w microemulsions at 50 ^{0}C was reported to take a very long period of eight days by Tang et al [38]. They reported bimodal distribution of molecular weight through photon correlation spectroscopy (PCS) and time average intensity measurement of polystyrene latex.

Jhonson and Gulari [39] using PCS found a good correlation between the size of the latex particles and the droplet size of o/w microemulsion of styrene indicating the transformation of droplets into polymer particles.

Gou et al. [40 - 42] examined the kinetics of styrene with SDS as surfactant and pentanol as cosurfactant. They showed that the growth of the microdroplets during polymerization is independent of initiator type. They found continuous nucleation over the complete duration of reaction and consistency with Smith – Ewart case II kinetics.

Leong et al. [43] showed that addition of alcohols as cosurfactant to microemulsion leads to the chain termination due to chain transfer reactions during polymerization which also limits the molecular weight of the resulting polymer.

Jaykrishnan and Shah [44] first demonstrated that the polymerization of styrene and methylmethacrylate (MMA) can be performed in ternary o/w – microemulsions containing SDS without cosurfactants using benzoyl peroxide as initiator. They have reported longer polymerization time and both the microemulsion latexes of styrene and methylmethacrylate were no longer transparent and stable during polymerization.

Gan et al. [45] investigated the kinetics of microemulsion polymerization of styrene initiated by water-soluble initiator KPS. Two reaction rate intervals were observed. The final latexes contained high molecular weight ~ 10^6 polystyrene particles with 20 - 40 nm diameter. Each latex particle was reported to contain 2 - 4 polymer chains.

Mendizabal et al. [46] modelled microemulsion polymerization predicting a large desorption rate and occurrence of both homogeneous and micellar nucleation mechanisms in microemulsion polymerization of styrene. In ternary microemulsions the amount of surfactant used for the stabilization of the system is generally very high.

To overcome this drawback Dreja and Tieke [47] polymerized styrene in ternary microemulsions by using gamma radiation. The microemulsions were stabilized by a polymerisable surfactant 11 – (acryloyloxy) – undecyl trimethyl ammonium bromide. Core shell type structure morphology was suggested for the particles formed. Gemini surfactants are known to be new generation surfactants. Dreja and Tieke [48] for the first time reported synthesis of polystyrene from microemulsions, which were stabilized by Gemini surfactants having hydrophilic and hydrophobic spacers. These surfactants showed better solubilisation of styrene as well as stabilization of polystyrene latex when compared with conventional surfactant CTAB.

Xu et al. [49] reported high polymer / surfactant wt. ratios (up to 15 : 1) for polystyrene microlatex formed through microemulsion polymerisation using a mixture of CTAB and polymerizable surafctant , omega – methoxypoly (ethylene oxide) (40) undecyl alpha – methacrylate macromonomer (PEO – R – MA – 40). Semicontinuous mode of addition was followed for a period of four hrs at room temperature. Nearly monodispersed latex particles with diameters ranging from 50 – 80 nm were obtained. The dependency of the number of particles per ml of the microlatex , the latex particle size and the copolymer molar mass on the polymerisation time was discussed in conjunction with the effect of macromonomer concentration.

In another report Xu et al. [50] increased the solid content of the latex through a modified microemulsion polymerization of styrene. A water - soluble redox initiator was used to obtain nanosized latexes ranging from 15 to 65 nm. The monomer starved latex particles were first generated in the initial microemulsion containing 0.5 wt % styrene stabilized by 1.5 wt % SDS or 1.0 wt % CTAB. The subsequent supply of monomer to the prepolymerised microemulsion proceeded via hollow – fiber feeding from the external monomer reservoir. The polymerization produced nearly uniform (Dw / Dn < 1.15) latex particles having high molar masses (10^6 g / mol) and high polymer / surfactant weight ratios up to 15.

[b] Alkyl acrylates

Polymerisation of alkylacrylates and methacrylates has also been studied in the o / w microemulsions. These alkylacrylates due to their partial water solubility partition between two phases and depending on the degree of partitioning the nucleation mechanism varies.

Using electron microscopy Texter et al. [5 1] reported that the parent droplets of highly hydrophobic tetrahydrofuryl methacrylate / AOT / water . o / w microemulsion system had diameters of the order of 5 nm. However, in polymerisation using redox system sodium persulphate / sodium metabisulphite the resulting latexes were observed to be of 39 nm diameter.

In a report on o / w microemulsion polymerisation of methylmethacrylate in a cationic microemulsion using AIBN or KPS Rodriguez – Guadarrama et al. [52] reported the absence of the constant rate interval with respect to monomer conversion. Activation energies for the microemulsion polymerisation of methylmethacrylate with AIBN (10.3 kcal / mol) and KPS (13.4 kcal / mol) were reported to be smaller than that for bulk polymerisation using AIBN (20 kcal / mol).

Gan et al. [53] noted a constant rate interval for the first time for o/w microemulsions containing a lower concentration of initiator and / or at a lower polymerisation temperature. The system studied was MMA / STAC / water. This was attributed to the generation of lesser number of polymerisation sites resulting into particle growth and the observed constant rate interval. Gan et al. [54] also compared o / w emulsion and microemulsion polymerisation of MMA using CTAB as surfactant and KPS as initiator. The activation energies for the polymerisations of both the systems were similar, 81 and 85 KJ / mol respectively for STAC and CTAB.

Bleger et al.[55] reported two rate intervals for the polymerisation of MMA in ternary water / MMA/ DTAB:DDAB (3:1) o/w microemulsion system. The conversion of monomer to polymer was monitored by direct on line densitometry. Two rate interval kinetics was reported.

In a significant contribution Kaler and coworkers [56–58] tested the mechanistic assumptions for the microemulsion polymerization of non-polar hexylmethacrylate in DTAB / DDAB stabilized buffered/unbuffered microemulsions using water soluble initiator, 2,2' – azobis 2 – amidinopropane dihydrochloride, better known as V50. The rate maximum was expected to occur at 39% conversion and was found in good agreement with the experimental results. Small angle neutron scattering was employed to evaluate particle size distributions.

In a recent report, David et al. [59] used a functional macromer poly (N – acetylethylenimine) [PNAEI] in oil – in – water microemulsion polymerisation of MMA and butylmethacrylate stabilised by SDS. The average diameter of latex particles was in the range of 17 – 200 nm. Presence of PNAEI into polymer nanoparticles was confirmed through FTIR and ^{1}H NMR studies.

[c] Copolymerisation in Microemulsion

Microemulsion copolymerisation is much more complex process than homopolymerisation. Kinetic and colloidal parameters depend on the complex structure of the o/w microemulsion containing monomer pair of dissimilar polarity. Some of these studies involving monomer pairs of different polarity provided interesting information on the reactivity ratios of different monomers in microemulsions. In addition kinetics of some systems has also been investigated.

The reactivity ratios of styrene and MMA in o/w microemulsion were determined from ^{1}H NMR spectra by Gan et al. [60]. The obtained values of $r_S = 0.74 \pm 0.09$ and $r_{MMA} = 0.38 \pm 0.04$ were different from those determined for solution , bulk or emulsion polymerization. The results were discussed in terms of partitioning of monomers in the microemulsions.

However , Kluperman and Aerdts [61] recalculated the reactivity ratios for styrene and MMA in microemulsion using Gan's data by Error – in – variable method and found that reactivity ratios in microemulsions hardly deviate from earlier reported bulk polymerization values.

Reactivity ratios for styrene and acrylonitrile o/w microemulsion copolymerisation were evaluated from ^{13}C NMR analysis by Lee et al. [62] who have considered microemulsion droplets as copolymerisation loci. They observed that the reactivity ratios were strongly dependent on the monomer feed ratios and reported a range of the reactivity ratios for styrene , $r_S = 0.61 - 2.98$ and acrylonitrile , $r_{AN} = 0.009 - 0.039$ which were very different than the values reported for the homogeneous polymerization.

Mendizabal et al. [63] compared the copolymerisation of styrene – acrylonitrile in both cationic (DTAB stabilized) and anionic (dodecyl benzenesulphonic acid stabilized) emulsion and microemulsions using water soluble KPS and oil soluble AIBN as initiators. Polymerisation initiated with AIBN in DTAB containing microemulsions was faster and resulted into higher conversions than with KPS. However, opposite effect was reported for emulsion polymerization.

In another report on the kinetic investigation of the copolymerisation of a partially water soluble monomer acrylonitrile and hydrophobic monomer butylacrylate in SDS stabilized o/w microemulsions Capek and Juranicova [64] reported that the Rp was proportional to the 0.48 th and 0.65 th power of KPS and BZ_2O_2 concentrations.

Recently Zhu et al.[65] reported the o/w microemulsion co-polymerisation of styrene-octadecyl ester / cetyl pyridine bromide / t -butanol system by laser light scattering method. The mechanism of nucleation of latex particles was discussed. The most probable locations of nucleation of the acrylic octadecyl ester and styrene latex particles were thought to be monomer swollen micelles and monomer droplets.

Core – shell polymers of styrene – butylacrylate were synthesized by two stage microemulsion polymerization [66]. The effect of the addition of a functional monomer (itaconic acid) on the mechanical properties of the microemulsion based products was also studied. Microemulsion based polymers were reported to be more rigid and harder than core – shell polymers of similar compositions prepared by emulsion polymerization.

Santhanalakshmi and Anandhi [67 – 70] in a series of papers studied the polymerization of vinyltoluene or / and styrene / MMA. Smith- Ewart case II hypothesis was reported to be followed in the vinyltoluene microemulsion polymerization. They also synthesized poly (vinyltoluene – co – styrene) and poly (vinyltoluene – co – MMA) copolymers in SDS / carbitol or butylcellosolve cationic o/w microemulsions using , KPS, APS or AIBN, BZ_2O_2 initiators. Detailed kinetics of vinyltoluene polymerization in o/w cationic microemulsions was examined by using Laser Raman spectroscopy and dilatometry. Each latex particle was reported to contain 1- 3 polymer chains.

Co et al.[71] revisited the particle nucleation in the microemulsion polymerisation of styrene , n – butylmethacrylate and n – hexyl methacrylate with dodecyl trimethyl ammonium bromide surfactant. Polymerising microemulsions were simulated by equilibrium mixtures of unpolymerised and fully polymerised microemulsions for which the monomer partitioning was accurately measured using SANS. Experimental results were semiquantitatively reproduced by modelling the monomer partitioning as a competition between the Flory – Huggins bulk polymer free energy and the Helfrich curvature elastic energy of the surfactant monolayer.

[ii] Polymerisation in w/o microemulsion

Polymerisation in w / o type microemulsions results in the formation of the materials with nanosized pores. These materials can be utilized as membranes for separation of solubilizates and the technique can be used for microencapsulation. In most of the initial reports of polymerization in w/o microemulsions acrylamide and methylmethacrylate have been used as monomers. However, random reports on the polymerization of styrene in w/o are also available.

Leong and Candau [72] prepared inverse polyacrylamide latexes by photo-polymerising w/o microemulsion formulated by dispersing water-acrylamide mixture in toluene with AOT as surfactant. Polymerisation was carried out using AIBN / UV irradiation.

In an extension of this study by Candau et al. [73] the polymerization of acrylamide and sodium acrylate was carried out in Isopar M, stabilized by a non-ionic emulsifier blend of sesquioleate sorbitan and POE sorbitol hexaoleate. Continuous nucleation mechanism was proposed to explain the experimental results. The authors also proposed that polymerization in microemulsion exhibits a bi-continuous structure at higher monomer contents (~25w %). The polymerization of acrylamide in inverse microemulsions has been studied extensively [74 - 76].

Vaskova et al. [74] carried out homopolymerisation of acrylamide and methylmethacrylate in inverse microemulsions . The interphase between the aqueous phase and the oil phase was proposed as the polymerization site. This report [75] was followed by another one in which co – polymerisation of acrylamide was carried out with MMA or Styrene using AIBN. The co – polymerisation was reported to be a typical dead end polymerisation. The locus of initiation for the co-polymerisation of acrylamide and methylmethacrylate was reported to be the water micro-pool by Vaskova et al. [76] when the reaction was carried out using APS, whereas it was reported to be the interphase between water micro-pool and toluene macro-phase, in case of AIBN.

Polymerisation of acrylamide in percolating / non-percolating inverse microemulsions, in the presence or absence of retardant potassium nitrosodisulphonate was studied by Barton [77]. The dependency of Rp and M_n on acrylamide concentration was reported to be 1.8th and 1.4th power of acrylamide concentration in non-percolating microemulsions and of 1.1th and 0.4th order of acrylamide concentration for percolating microemulsion [78].

Copolymerisation of styrene-acrylamide in inverse microemulsions was studied by Barton and Juranikova [79]. The overall copolymerisation rate was found to increase with increasing volume fraction of the dispersed (water + acrylamide) phase. They also reported decrease in copolymerisation rate irrespective of the nature of the initiator employed for a given volume fraction of increase in styrene / toluene ratio.

Gan and co-workers [80 – 88] in a series of papers reported the synthesis of micro-porous polymeric materials by polymerizing bicontinuous microemulsion containing mainly MMA as a monomer.

Microemulsion polymer latexes have always been discarded due to the requirement of high surfactant concentration which leaches out during their application. This problem was solved by using polymerisable surfactants. Gan and Chew [80 - 88] polymerized methylmethacrylate and acrylic acid w / o microemulsions stabilized by polymerisable surfactant sodium acrylamidodecanoate, using AIBN. Though polymerization produced transparent solids, the polymers could hardly tolerate only 10 - 12 wt % water at lower surfactant concentration. This study was followed by another one using sodium acrylamidostearate [81] as surfactant. In these microemulsions, acrylic acid was proposed to act as a cosurfactant.

Photo – polymerization of a bicontinuous microemulsion system consisting of water / MMA / EGDMA / 2 – HEMA and sodium 11 – (N – ethylacrylamido) undecanoate produced transparent polymeric networks [82]. Open – cell type porous materials were synthesised by photo – polymerization of Zwitter-ionic microemulsions consisting of [(acryloyloxy) undecyl) di – methylamino] acetate / MMA / water with or without EGDMA. The widths of bi – continuous structures were reported to be 50 – 70 nm by Gan et al. [83].

Morphological study of the micro-porous polymeric materials of MMA, 2-HEMA and EGDMA was also done by Chieng et al. [84] through microscopic analysis. From the bi-continuous microemulsions [85] the morphology showed a transition from worm like oval shape to globular on decreasing the alkyl chain length of the surfacant (C_{12} – C_{16} alkyltrimethylaminobromide) at a particular concentration.

Transparent ultrafiltrtion membranes of MMA, 2-HEMA, EGDMA and maleic acid with pore size of 1-5 nm were synthesized successfully by Li et al. [86] using a polymerisable cationic surfactant AUTMAB and redox initiator system at 30 ^{0}C. The separation of different molecular weight polyethylene glycols by using synthesized membranes was successfully demostrated.

Microporous membranes of poly (MMA – co – HEMA) of pore size < 100 nm were also synthesized by Gan et al. [87] using polymerisable non-ionic surfactant. Ionic membranes of poly 4 – vinyl benzene sulphonate with conductance 2 – 3 x 10^{3} S / cm were synthesised by Chow et al. [88] by polymerising 4 – vinyl benzene sulphonate / (- methoxy – (PEO) – 40 – Undecyl – (- methacrylate) / acrylonitrile / MMA / water / EGDMA bi-continuous microemulsion system containing 2 , 2 – dimethyl – 2 phenyl – acetophenone , photo – initiator at 35 ^{0} C.

Raj et al. [89] studied the effect of cross-linking agent ethylene glycol dimethacrylate on the microstructure of porous solids prepared by polymerization of an inverse/ bicontinuous microemulsion comprising of methylmethacrylate , acrylic acid , SDS and water.

Qutubbudin et al. [90] reported the polymerization of styrene in w/o microemulsions containing SDS / 2 – pentanol and KPS and AIBN initiators. Phase separation during polymerization was observed. However, incorporation of butylcellosov as a cosurfactant in place of 2-pentanol was found to increase the stability of polystyrene latexes during polymerization.

Donescu et al. [91 – 99] reported systems which are neither o / w nor w / o microemulsions. But as the organic phase volume is very large they are being discussed here. Donescu et al. throughly explored the vinyl acetate polymerisation in homogeneous systems. Authors used viscometry and conductometry to follow polymerisation of vinyl acetate / SDS / PrOH microemulsons. The polymerisation rate was found lower in microemulsions than in regular emulsions When a non – ionic surfactant nonyl phenyl ethoxylate (d . p . 30) was used in place of SDS , the induction period was found to increase with increase in surfactant concentration. In another report on the polymerisation of vinyl acetate in SDS / PrOH stabilised microemulsions the polymerisation rate followed 0.9 th [SDS] and 0. 5 th [APS] orders. This report was followed by another one in which effect of vinyl acetate concentration on polymerisation and initiator decomposition rate was studied.

W / O microemulsion polymerisation of vinyl acatate using APS was reported by Donescu et al. in systems which were stabilised by ethanol / sodium salt of sulphosuccinic acid semiester / nonyl phenyl ethoxylate (20) emulsifier blend. Reaction order was found to be one with respect to APS concentration.

Donescu and Fusulan also reported the copolymerisation of vinyl acetate with di – 2 – ethyl – hexyl – maleate in microemulsions using n – propanol as cosurfactant and APS and AIBN as initiators. n – Propanol was used in copolymerisation as cosurfactant and NP (25) as a surfactant. Rp was found to be proportional to vinyl acetate concentration. Poly vinyl acetate hydrogels were sysnthesised by Donescu etal. from bicontinuous microemulsions using diethylene glycol bis – maleate cross – linker . Acrylic acid was also used as co – monomer and NP (25) ethylene oxide monomaleate as a surfactant. The water absorption capacity of hydrogels was reported to be a function of cross – linked monomer content and the organic / aqueous phase ratio. Authors also studied the microemulsion polymerisation of styrene using NP (25) ethylene oxide monomaleate as surfactant and various alcohols such as methanol , iso – propanol as cosurfactants.

De – Buruaga et al. [100] modeled inverse microemulsion polymerization and the values obtained for inverse microemulsion polymerization of MADQUAT initiated by UV light in the presence of AIBN were simulated in the model

Recently De and Hoffman [101] successfully prepared polyacrylic acid nanoparticles using a reverse microemulsion polymerization process and used them for sustained drug delivery. They obtained narrow particle size distribution averaging 50 nm and latexes were stable in buffer. The drug timolol maleate was loaded into the nanoparticles from aqueous drug solutions. Slow release over several hours was observed when the particles were dispersed in a phosphate buffer.

[iii] Micellaneous reports and patents

In a distinct report Schubert et al. [102] have reported successful polymerization of hexylmethacrylate or styrene in a non – aqueous microemulsion stabilised with AOT , which resulted into a bluish dispersion of ~ 80 nm size particles. In these systems the aqueous phase was replaced by dimethylformamide.

Though polymerisation in microemulsions has been studied extensively for kinetics and mechanism of polymerisation , stability , synthesis of high – solid content latexes , nanoparticles and micro – porous materials , the number of patents obtained by using this polymerisation technique to produce commercial products are very limited [103 – 114]. Patents cover polymerised microemulsions as binders / adhesives , high solid content polyacrylamide micro – latex , impact and weather resistant articles , micro – porous styrene polymers , finely dispersed teterafluoro ethylene particles , useful dewatering dispersions containing polyacrylamide , polymer composites , polyvinylidine fluoride particles with improved resistance to heat induced de – coloration , pesticides , flocculants , associated acrylic polymers and poly tetrafluoroethylene polymers.

The review articles [115 – 125] are highly recommended for referencing of microemulsion polymerisation.

[1. 5] Recent Developments and Future Scope

It has been shown that polymerization in microemulsion allows the synthesis of ultrafine polymer lattices in a size ranging between 5 nm to 50 nm [126]. These lattices are well defined with respect to their size and their chemical composition. The large interface of such lattices can be modified by simple copolymerisation with functional monomers, thus ending in surfaces with high densities of functional groups [127]. In a recent report, Amigonigerbier et al. [128] synthesized ultrafine selective metal complexing nanoparticles through the microemulsion copolymerisation of styrene and vinylbenzylcyclam (cyclam : 1,4,8,11 – tetraazacyclotetradecane). These nanoparticles exhibited a very high selectivity for cupric ions with binding capacities of up to 0.65 mmol of Cu / g as well as a remarkable ligand accessibility, deduced from spectrophotometric titration, with about 75 % of the cyclam residues located near the surface for nanoparticles in the 12 – 13 nm range.

The microemulsion, however, has to accept the incorporated functionalities. In case of incompatibility between surfactant and functional comonomer or an induced fragility, the microemulsions break during polymerization [126]. The functional groups may be polymers themselves, such as block copolymers or proteins, a technique called as modular fictionalization and which results into complex polymer superstructures [129]. Such systems may be involved in complex operations such as catalysis. Selective ion binding or detoxination, and development of tailor-made combination can be a topic of future research.

Another challenge is the formation of non-spherical latex particles with axial ratios exceeding the value for liquid crystallinity (or the polymerization of hexagonal phases). Such latex particle in principle enable the examination of ordering effects in colloidal dispersions and exhibit some interesting rheological features [130]. There is also a great demand for polymerized cubic bicontinuous phases as materials containing the maximal number of well – defined pores with a controllable size in nanometer range [131]. Therefore the phase behavior and microstructure of a microemulsion has gained a lot of attention. Nyden et al. [32] investigated the microemulsion phase for didodecyldimethylammonium sulphate /hydrocarbon/ water system using self-diffusion NMR and time resolved fluorescence quenching technique. They observed a transition in the microstructure from discrete spherical micelles to bicontinuous network formation with an increase in the surfactant to oil volume ratio.

.In another report Silas and Kaler [132] reported changes in bicontinuous microstructure as a function of added charge for a didodecyldimethylammonium bromide (DDAB), n – alkyl polyglycol ethers decane and water system. The results were explained on the basis of change in bending modulus as ionic surfactant is added.

[1. 6] Proposed Work

A serious drawback of polymerisable microemulsions, at least of the oil – in – water types, is the requirement of large amounts of surfactant. One of the challenges in microemulsions is therefore the search for new surfactants, which allows the formation of sturdy microemulsions with a large stabilized area per surfactant molecule. Such surfactants may be found in the class of functional oligomers of amphiphatic monomers. An alternative approach is to employ a different polymerization techniques, keeping intact the advantages of microemulsion polymerization like low particle size and narrow polydispersity albeit at a much lower surfactant concentration. In a recent report [133], El – Aasser et al. reported 50 nm polystyrene particles through miniemulsion polymerization of 20 wt % styrene and 2 % SDS as surfactant.

The present work is an attempt to further reduce the surfactant concentration inorder to produce high solid, stable, translucent nanolatex through the emulsion polymerization of polar monomers ethyl acrylate (EA) and methylmethacrylate (MMA). For polar monomers their partitioning between aqueous and organic phase plays an important role in deciding the kinetics, colloidal parameters, monomer reactivity which has been studied in detail. Microemulsion polymerization has been used as a reference system for comparing the results.

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