

Miniemulsion Polymerization: An Overview*

V. Mittal

BASF SE, Polymer Research, 67056 Ludwigshafen, Germany

Abstract

Miniemulsion polymerization exhibits distinct advantages over the conventional emulsion polymerization. The polymerization of monomer droplets is directly achieved when the diffusion of the monomer from the droplets to polymer particles is not required. This helps to polymerize water insoluble monomers. It also allows the presence of various system components like initiators, costabilizers, etc. directly at the site of the polymerization thus allowing better control. Conventionally, volatile hydrophobes or costabilizers like cetyl alcohol or hexadecane have been used. A number of advances have been reported in recent years on the use of costabilizers which are more compatible to the polymerization system. Use of polymers as costabilizers was reported to be very effective even though the polymer forms a poor costabilizer. Similarly, the comonomers and initiator have also been used as costabilizers. The use of chain transfer agents as costabilizers also opens the opportunities for molecular weight control in the polymer particles. These advances ensure that the particles are free from any low molecular weight impurity or volatile components. The living polymerization techniques like nitroxide mediated polymerization, atom transfer radical polymerization and reversible addition fragmentation chain transfer are also well suited for miniemulsion processes in order to generate specific morphologies in polymer particles and to control the molecular weight and its distribution in the particles.

Keywords: diffusion, monomer droplet, costabilizer, surfactant, initiator, micelles, chain transfer, comonomer, miniemulsion, conversion, colloidal stability, controlled living polymerization.

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1.1 Introduction to Polymerization Techniques

Free radical polymerization can be carried out by using a number of different techniques. The simplest of these techniques is the bulk polymerization. In this technique, monomer is in the liquid form and the generated polymer is in solid form. Though the reaction mixture is free from any unwanted impurities or contamination leading to clean polymer, however, the viscosity of the system increases significantly due to the generation of polymer chains during the course of polymerization and thus the mixing of the system becomes extremely difficult leading to very broad molecular weight distributions in the polymer chains. Additionally, the polymer chains do not diffuse freely in the highly viscous medium leading to the accumulation of radicals at particular sites causing the polymerization rate to increase exponentially. Solution polymerization is an alternative method in which a solvent is used in which the monomer and polymer are soluble. The use of solvents eliminates the problems of higher viscosity and heat dissipation associated with bulk polymerization and allows one to stir the reaction medium easily. However, the choice of solvents must be proper; otherwise extensive chain transfer to solvent can take place resulting in only low molecular weight polymer chains. Precipitation polymerization is another form of polymerization in which the polymer is not soluble in the monomer or the reaction medium and precipitates out soon from the solution. Thus, precipitation polymerization starts as homogenous polymerization, but is soon turned into a heterogeneous polymerization. Dispersion polymerization is also similar to precipitation polymerization that the polymer formed is not soluble in monomer or organic solvent. After the formation of polymer particles, these particles are stabilized by added particle stabilizer and the polymerization proceeds in the polymer particles by the absorption of monomer into the polymer particles. Suspension or bead polymerization is a method in which monomer droplets are directly polymerized to generate high molecular weight polymers. In this method, water insoluble monomer is suspended in water with the aid of suspension stabilizers. The initiator used is also water insoluble or monomer soluble. The size of monomer droplets can be controlled depending on the ratio of monomer to the dispersion medium, i.e., water, the speed of agitation to generate droplets as well as by the amount of stabilizing agents.

During the polymerization, the monomer droplets polymerize independently and each droplet can be visualized as a bulk polymerization happening inside the droplet. Inverse suspension polymerization is also possible in which a water soluble monomer is used and its droplets are generated in an organic solvent. Initiators used are also water soluble and the monomer droplets are stabilized similarly by using suspension stabilizers. Emulsion polymerization is the one of the most versatile technique to generate small particles. With this technique, water insoluble monomers are polymerized by suspending them in water in the form of emulsion droplets stabilized by surfactants. The initiators used are water soluble in contrast to suspension polymerization where water insoluble initiators are used, the most common being potassium persulphate (KPS). Polymerization of extremely low water soluble monomers is very difficult with conventional emulsion polymerization. The low solubility of the monomer would not allow its diffusion to the polymer particles through the aqueous medium. Miniemulsion polymerization has been developed for such purposes, in which the monomer droplets generated by using high shear in the presence of an ionic surfactant and a co-surfactant or hydrophobe like hexadecane, are directly polymerized. The droplets and hence resulting polymer particles are generally in the size range of 50–500 nm. There are other forms of polymerization techniques like microemulsion, melt polycondensation and solution polycondensation etc. Figure 1.1 lists the large number of polymerization techniques used to synthesize a variety of polymers [1].

1.2 Emulsion and Miniemulsion Polymerization

The common mode of particle synthesis in emulsion polymerization is achieved by micellar nucleation method, though there is also the presence of homogenous nucleation especially in water soluble monomers. The surfactants like sodium dodecyl sulphate are added which at a concentration higher than the critical micelle concentration in the aqueous phase form micelles. These micelles owing to their hydrophobic nature inside the inner space are an ideal site for the radical entry as well as propagation of polymerization. The structure of surfactant is generally amphiphilic, with one part hydrophobic and the other part hydrophilic. These

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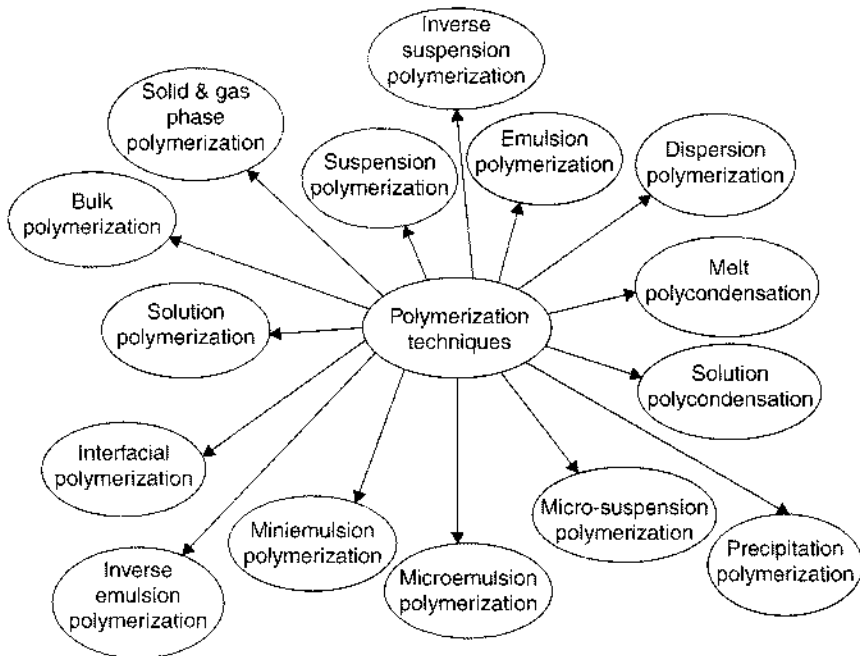


Figure 1.1. Various polymerization techniques to generate a wide spectrum of polymers. Reproduced with permission from Nova Science Publishers [1].

molecules thus arrange themselves in a way that their hydrophilic parts are in interface with water. Every surfactant has a different critical micelle concentration value and it should be considered carefully while using different kinds of surfactants. The micelles generally have a size of 10 nm and generally 100–200 surfactant molecules form a micelle [2,3]. It is generally known that the surface tension of the solution decreases with the addition of surfactant at critical micelle concentration. However, it is not only the surface tension that is affected by the surfactant, rather a host of other properties of the solution are affected at critical micelle concentration.

Once the monomer is added to the system, a small amount of monomer enters the micelles and some gets dissolved in the aqueous phase owing to the partial solubility in water. However, the majority of the monomer is generally present in the form of monomer droplets. These droplets are stabilized by the adsorption of surfactant molecules on the surface. The number of micelles is much

larger than the number of droplets and the droplet size may fall in the range of tens of micrometers [2,4]. When the polymerization is initiated by the addition of the initiator and after achieving the required polymerization temperature, the radicals are generated in the aqueous phase. The generated radicals have two possibilities to propagate further: to enter either the micelles or the monomer droplets. However, the experimental studies report that it is very rare that the radicals enter the monomer droplets. This is because of very large number of micelles present in the system as well as the architecture of the micelles provides ideal conditions for the monomer polymerization. When the radicals enter the micelles and start polymerizing the monomer contained in these micelles, the polymer particles form. These growing polymer particles are then supplied by the monomer molecules from the monomer droplets by diffusion through the aqueous phase. The termination of the radicals is quite slow as at a particular time during polymerization, there is rarely more than one radical per particle.

The conventional emulsion polymerization is thus divided into three intervals as shown in Figure 1.2. On addition to the aqueous phase, the monomer enters the micelles as well as forms the monomer droplets apart from dissolution in water to some extent based on the solubility of the monomer as shown in Figure 1.2a [2]. The first interval, also termed as particles formation phase, is then initiated. The radicals re generated in the aqueous phase due to the decomposition of initiator. These radicals enter the micelles and initiate monomer polymerization leading to the generation of polymer particles. The number of particles keeps on increasing in this interval which also results in the continuous enhancement in the polymerization rate. The system, as shown in Figure 1.2b, thus consists of polymer particles, monomer droplets, and the inactive micelles. The particles keep on increasing in size, thus requiring more and more surfactant to stabilize the increasing surface area. This leads to the adsorption of the dissolved surfactant in the aqueous phase on the surface of the particles and the surfactant concentration thus falls much below the critical micelle concentration. This results into the destabilization of the remaining micelles and they provide their surfactant to stabilize the growing particles. The number of particles generated from total micelles in the beginning is generally in the range of 0.1%. At the end of first interval, all of the micelles either are polymer particles or are destabilized to lose the surfactant. In the second interval, the particles keep on growing in size and no new particles are nucleated

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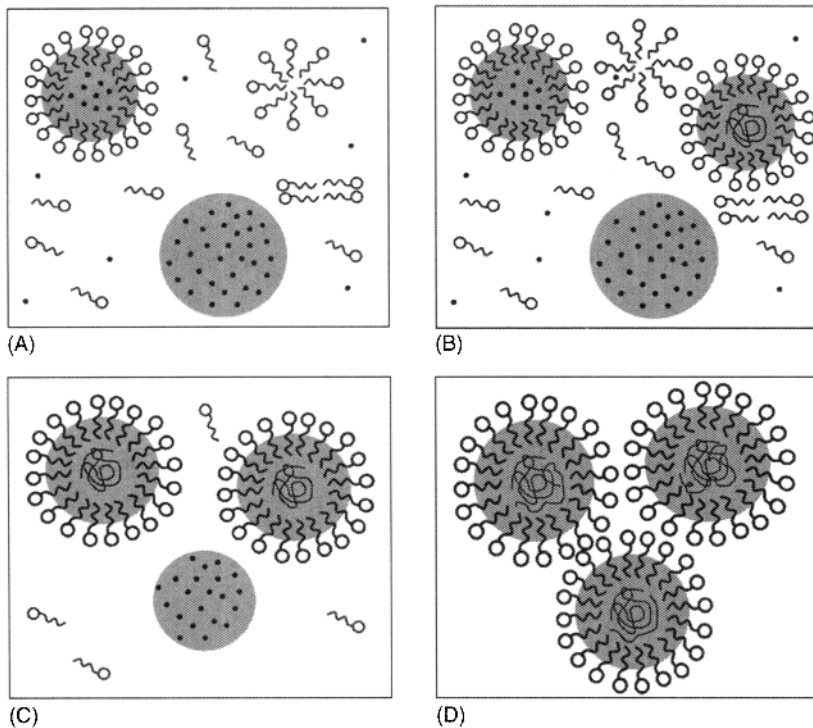


Figure 1.2. Representation of various intervals of emulsion polymerization [1].

thus leading to the constant rate of polymerization. As the particles grow in size during the course of polymerization, they deplete the monomer content present in them. This depletion is continuously replenished by the absorption of more monomer from the water phase, which has been dissolved in it. The water phase in return absorbs more monomer from the monomer droplets resulting in the reduction of the size of the monomer droplets as shown in Figure 1.2c. After a certain conversion of the monomer is achieved, the monomer droplets also disappear which forms the transition period between the second and third interval. As shown in Figure 1.2d, the particles in this interval keep on polymerizing the monomer enriching them. Thus, concentration of the monomer in the particles decreases, and subsequently the polymerization rate also decreases in this interval. The number of particles thus also remains the same as the second interval and after the monomer has been completely depleted, the polymerization rate climbs down to zero.

Miniemulsion polymerization exhibits several advantages over conventional emulsion polymerization also called macroemulsion polymerization [5-8]. The most prominent advantage is the elimination of the need of the monomer to diffuse through the aqueous phase from the monomer droplets to the polymer particles during the course of polymerization. It is due to the reason that the monomer droplets are directly polymerized in this mode of polymerization. The monomer droplets are generated by shearing the system with high energy along with the addition of costabilizer (with the surfactant) which is needed to be hydrophobic in order to avoid the collapse of the monomer droplets by Ostwald ripening when the shearing of the system is stopped. Thus, in this mode of polymerization, it is of importance to avoid the micellar nucleation, therefore, the amount of surfactant is below the critical micelle concentration. Thus, miniemulsion polymerization differs from the macroemulsion polymerization significantly in the mechanism of particle nucleation. In fact, this difference also acts as an advantage of miniemulsion polymerization as micellar nucleation in conventional emulsion polymerization is extremely sensitive to a large number of factors such as amount of surfactant, amount of initiator, agitation speed, temperature of the polymerization reaction, mode of addition of the monomers, etc. The number of particles in miniemulsion polymerization is thus dependant on the shearing forces as well as the amount of surfactant and costabilizer, and is independent on the initiator amount. A significant advancement has been achieved in the living polymerization methods in miniemulsion polymerization. The colloidal stability is also much better in miniemulsion polymerization as compared to the conventional emulsion polymerization, which makes it a technique of choice.

Figure 1.3 demonstrates the mechanism of miniemulsion polymerization [1]. The costabilizer and the surfactant are added along with monomer in the aqueous medium. The miniemulsion is then achieved by the action of shear. The application of shear breaks the bigger monomer droplets into the droplets of size range 10-500 nm which also forms the range of polymer particles generated by miniemulsion polymerization. However, as mentioned above, the size of the monomer droplets and hence polymer particles can be tuned by the amount of surfactant and costabilizer in combination with shearing forces. The surfactant is required in the system to eliminate the droplet coalescence by the action of Brownian motion or settling, whereas the costabilizer prevents the

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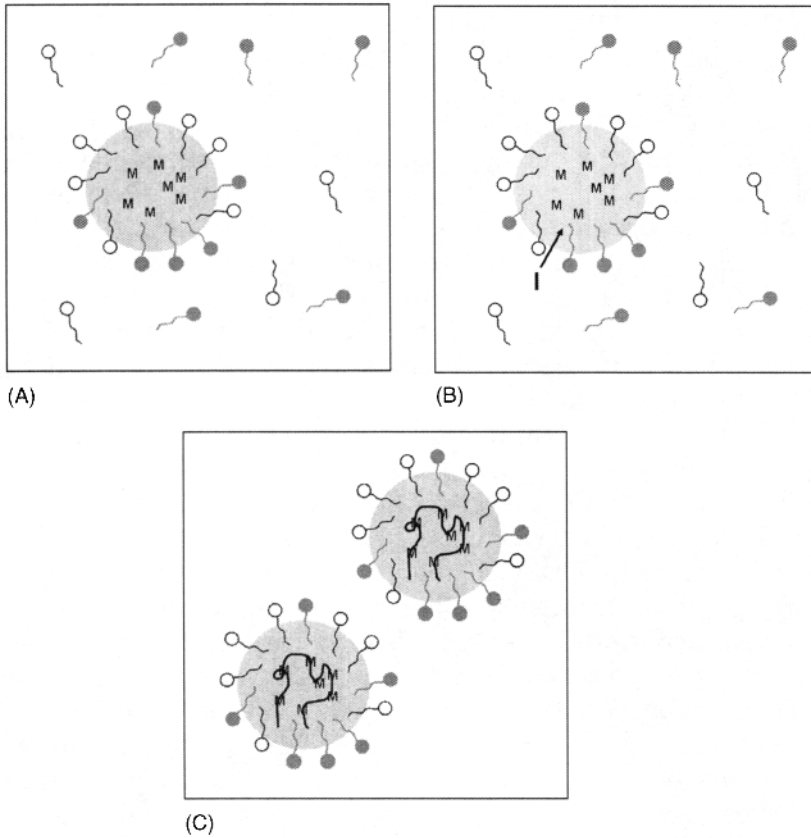


Figure 1.3. Process of miniemulsion polymerization. The molecules with open and filled circles represent the surfactant and costabilizer, respectively.

Ostwald ripening [5]. When the emulsion is subjected to shear by sonicator or mechanical homogenizer, the generation of small droplets is achieved in the liquid medium. As the droplets have a distribution in the sizes, the monomer tends to diffuse from the smaller droplets into the large ones if the monomer is even slightly soluble in the continuous phase. The surface area of the monomer droplets is quite high and most of the surfactant is adsorbed on the particle surface. As no micelles exist in the system therefore the particle nucleation takes place by radical entry into the droplets. The initiators used for the miniemulsion polymerization can be both water soluble as well as monomer soluble. Figure 1.4 is another representation of the comparison between the emulsion and miniemulsion polymerization processes.

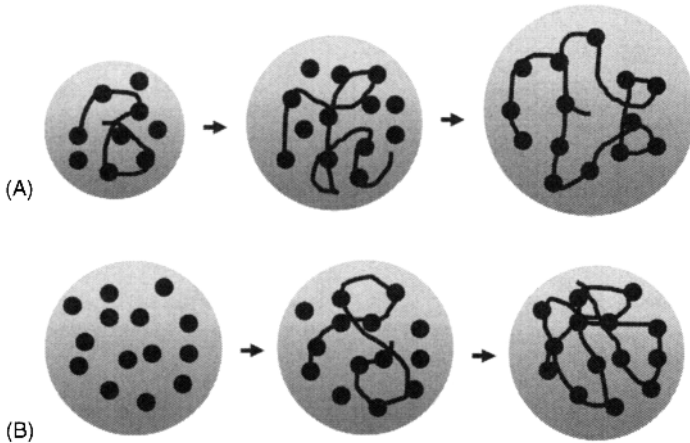


Figure 1.4. Comparison of (a) emulsion and (b) miniemulsion polymerization.

Owing to the differences in the mechanism of particle nucleation as well as propagation, the rates of polymerization in both macroemulsion and miniemulsion polymerization are also different. As described above, the conventional emulsion polymerization has initiation of polymer particles in micelles followed by the diffusion of monomer from the monomer droplets to the polymer particles through the aqueous phase. The polymerization rate, therefore, first grows till the micelles are present in the system owing to the increase in the number of the particles. Subsequently, the rate of polymerization becomes constant as the polymer particles grow only in size and not in number owing to the use of all the surfactant to stabilize the polymer particles. The monomer in this interval is diffusing continuously to the polymer particles and is, therefore, getting depleted in the monomer droplets. When the droplets cease to exist, the rate starts to fall and becomes zero when all the monomer enriching the polymer particles is also consumed. However, in the case of miniemulsion polymerization, there is no diffusion of the monomer through the aqueous phase owing to direct polymerization of monomer droplets, therefore, there is no constant polymerization rate period in this mode of polymerization. This is, however, only true if the monomer is not diffusing from the small droplets to the large ones even in small extents. The rate initially grows owing to the increasing number of polymer particles by the entry of radicals in the droplets, and then drops down as the monomer in the droplets is depleted. One limitation of miniemulsion polymerization is

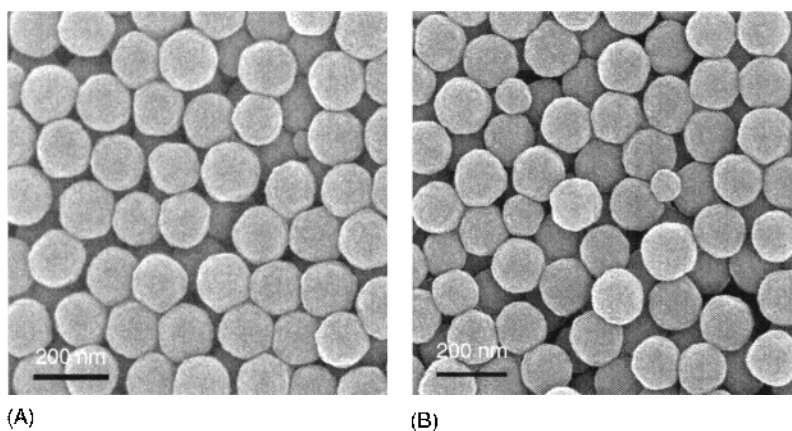


Figure 1.5. SEM micrographs of polystyrene latex generated by miniemulsion polymerization.

the use of hydrophobe which can be volatile in nature, the use of which thus limits the applications of the polymer particles generated by miniemulsion. Figure 1.5 shows the representative scanning electron microscopy (SEM) micrographs of polystyrene particles synthesized with miniemulsion polymerization.

The miniemulsion polymerization of hydrophobic monomers in the aqueous phase is achieved owing to no or insignificant dissolution of monomer in the aqueous phase which leads to the droplet stability in the system. However, if the monomers are water soluble, one can use inverse miniemulsion polymerization. Here, a hydrophobic reaction solvent or dispersion medium like cyclohexane is used instead of water, and the process is exactly similar to miniemulsion polymerization. Instead of a hydrophobe as a costabilizer, one must use a lipophile such as sodium chloride, and the stabilizer is also different.

1.3 Properties of Miniemulsion Polymerization

If the Ostwald ripening is allowed to occur continuously, the monomer from the smaller particles would diffuse into the larger particles and extensive creaming would result. Costabilizers are therefore added as they help to stop the Ostwald ripening by stopping the diffusion of the monomers from monomer droplets. Therefore, they

should be very hydrophobic in nature and should be soluble in the monomers. As the costabilizers generally have a little water solubility therefore the Ostwald ripening still occurs but the time required for the destabilization of the miniemulsion runs in the range of months which thus allows enough time to achieve polymerization using stable miniemulsions. As mentioned earlier, the miniemulsions are generated by the combination of the high shear to break the bigger monomer droplets into the sub-micron monomer droplets in the presence of costabilizer to stop the diffusion of monomer from these particles. One must be clear that the addition of a costabilizer stops the conversion of a miniemulsion into a conventional emulsion; however, the addition of a costabilizer to conventional emulsion does not automatically convert it into a miniemulsion. It is only after addition of high shearing energy that it becomes a stable miniemulsion. The mechanical shear is generated by stirring, ultra-turrax or by ultrasonication. The mechanism of ultrasonication is primarily cavitation. Sonication is an attractive method for the laboratory scale miniemulsion generation, however, it is not suitable for the large scale processes and more efficient shearing devices are needed.

In most of the reported studies over the use of miniemulsion polymerization, the use of anionic surfactant is most common. Sodium dodecyl sulphate is one the most commonly used anionic surfactant used for emulsion polymerizations. Therefore, it has also been automatically used for the majority of the miniemulsion polymerization reactions. These anionic surfactants are also attractive choices owing to their compatibility with the majority of the monomers and the initiators. However, the use of anionic surfactants is not suitable in controlled living polymerization achieved by the atom transfer radical polymerization and in such cases, non-ionic surfactants are mostly used. However, some studies have also reported the use of cationic surfactants like cetyltrimethylammonium bromide and dodecyltrimethylammonium chloride [9,10] and the resulting particles were reported to be similar to the particles achieved by using anionic surfactants. Some studies have also reported the use of non-ionic surfactants. Wang et al. reported the use of poly(vinyl alcohol) as stabilizer with hexadecane as co-stabilizer [11]. The authors also reported that the use of hexadecane costabilizer was important as the use of poly(vinyl alcohol) was not sufficient to control the polymerization reaction.

The costabilizer is conventionally required to be monomer soluble, water insoluble and with a low molecular weight. The insolubility

in water leads to the elimination of the diffusion of monomer into the aqueous phase from the monomer droplets. The low molecular weight, on the other hand, allows to increase the weight ratio of costabilizer molecules as compared to monomer molecules in the monomer droplets. In the early studies cetyl alcohol and hexadecane have been used as costabilizers as they fit well to the characteristics required from an ideal costabilizer. However, these costabilizers are volatile in nature and their presence in the product may not be desirable for a number of applications. To circumvent these limitations, a number of studies have reported the use of various costabilizers which are not volatile in nature and help to achieve better acceptability of the polymer particles. Reimers et al. [12] reported the use of polymer as a costabilizer. The authors reported that using the polymer which is soluble in its own monomer would also fulfill the requirements of the costabilizer. The high molecular weight of the polymer was reported to make the polymer as poor costabilizer, but still the use of polymer as costabilizer was reported to reduce the diffusion of the monomer from the monomer droplets owing to high water insolubility of the polymer. The miniemulsion in such cases were reported to be thermodynamically unstable, but kinetically stable which still allowed the miniemulsions to be stable for the time scale suitable for the polymerization. The miniemulsions generated by using polymer as costabilizer were observed to be not true miniemulsion as they did get destabilized after a period of time, however, the polymer particles generated from these systems were similar to the systems where cetyl alcohol or hexadecane were used as costabilizers. This, therefore, completely eliminates the use of volatile hexadecane or other low molecular weight costabilizers in these miniemulsion polymerizations. The low molecular weight components are not desirable in the final latex, as these can easily migrate to other materials owing to their low molecular weight, thus causing health and safety concerns.

Reimers et al. [12-13] reported on the effect of the amount of polymeric hydrophobe and its molecular weight on the generated size and size distribution of the monomer droplets. It was reported that the droplets diameters could range between 19.5 nm to 141.2 nm using polymeric costabilizer. These values were reported to be similar when the miniemulsion had hexadecane as co-stabilizer. The size of the droplets was generally observed to decrease on increasing the concentration of hexadecane, such phenomenon was also observed when polymer stabilizers were used. Though polymeric

costabilizer acted only as a poor costabilizer, the generated latexes with polymeric costabilizer were observed to have much lower polydispersity of 1.006 as compared to the 1.049 for the emulsion polymerization and 1.037 for the alkane stabilized miniemulsion. As the solubility parameter of PMMA is $19.3 \text{ MPa}^{1/2}$, which is very similar to $18.9 \text{ MPa}^{1/2}$ value for the MMA monomer, therefore, indicating, using polymers as co-stabilizers in the polymerizations of its monomers ensures its solubility with monomer and elimination of diffusional degradation of monomer droplets owing to the water insolubility. Similarly, other monomer/polymer systems were reported to be effective. The polymeric costabilizers were also reported to be stable against the presence of small amount of inhibitors, retarders or other monomer impurities, which is generally not the case for low molecular weight co-stabilizers. Other similar studies have also been reported [14].

It was also reported that the used of a comonomer can also be employed to act as costabilizer. The comonomer can also subsequently get polymerized along with the monomer during the course of polymerization. [15]. Vinyl hexanoate, p-methyl styrene, vinyl stearate etc. were used as comonomers with MMA and the reported system had stable miniemulsions with droplets diameters between 150 and 230 nm. The advantage of the comonomer as stabilizer is that it would reinforce the polymer chains, thus removing any concerns regarding the diffusion of low molecular weight costabilizer molecules out of the particles. Dodecyl methacrylate was also reported as a comonomer as well as costabilizer in the miniemulsion polymerization of styrene [16]. Figure 1.6 demonstrates the conversion as well as diameter evolution in the miniemulsion particles as a function of time as well as the concentration of costabilizer. Low water solubility of the costabilizer and better solubility with styrene monomer helped to achieve stable miniemulsions. Use of imitator has also been similarly reported to act also as costabilizer. Schork et al. [17] reported the use of lauroyl peroxide as initiator as well as costabilizer. The molecules first act as costabilizers helping to stabilize the monomer droplets and subsequently during the course of polymerization yield radicals by the thermal decomposition. The droplet sizes were also reported to be in the similar range as observed in miniemulsion polymerization and the ratio of polymer particles to the monomer droplets was also observed to be near unity thus confirming the efficiency of lauroyl peroxide molecules to act both as initiator as well as monomer costabilizer.

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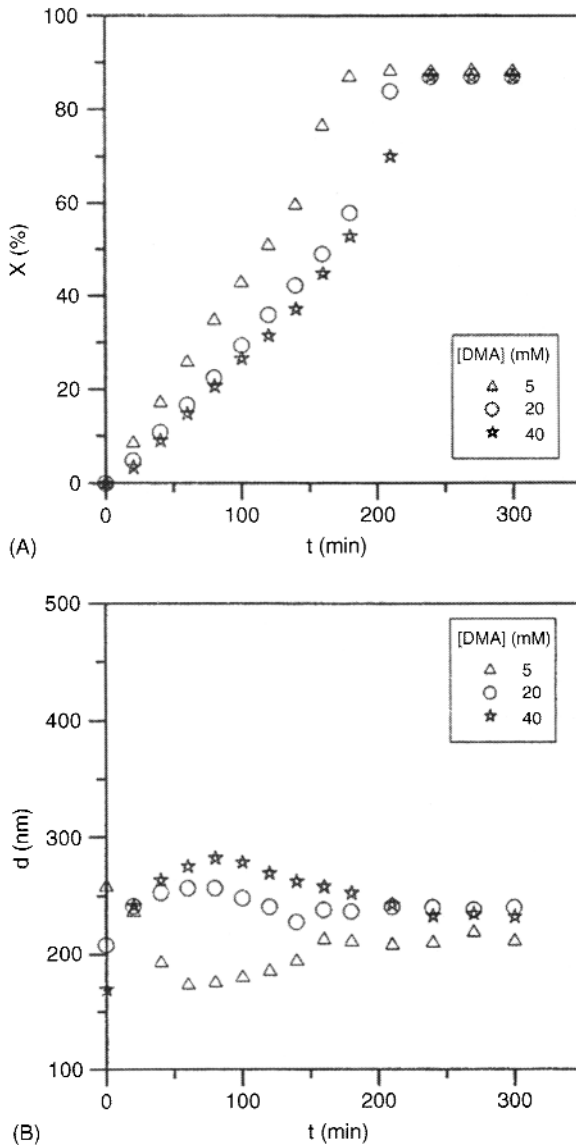


Figure 1.6. Use of comonomer as a costabilizer [15]. Monomer conversion and (b) average particle size as a function of the reaction time: [DMA] . (Δ) 5; (\circ) 20; (\star) 40 mM. Reproduced from reference 16 with permission from Elsevier.

In this process, similar to the use of comonomer as costabilizer, the initiator moieties are chemically incorporated in the polymer chains, thus leaving no low molecular weight residue in the polymer particles.

The use of chain transfer agent as costabilizer was reported to open opportunities for molecular weight control [5]. The chain transfer agent is generally difficult to transport to the polymer particles from the monomer droplets in the conventional emulsion polymerization, however, when the chain transfer agent is present at the site of polymerization as is possible in the case of miniemulsion polymerization, various possibilities of control of polymer reaction can be achieved. Dodecylmercaptan was reported to be used as a chain transfer agent as well as costabilizer for the miniemulsion polymerization of methyl methacrylate [18]. Sodium lauryl sulfate was used as surfactant and potassium persulphate as initiator. Stable monomer droplets were observed to form and the nucleation of the polymer particles proceeded by droplet polymerization owing to the presence of surfactant below the critical micelle concentration. When the surfactant concentration was held constant, the size of the droplets was observed to decrease on increasing the concentration of dodecylmercaptan, which is similar to the behavior as observed in the miniemulsion polymerization using hexadecane as costabilizer. The rate of polymerization was observed to be dependant upon factors such as the concentration of surfactant, co-surfactant as well as initiator. The authors reported that at low concentrations of initiator and surfactant (below CMC), the ratio of number of particles to number of droplets was 0.80 indicating that all the droplets were not nucleated. On the other hand, at higher concentrations of surfactant and initiator, the ratio was 13.56 indicating that nucleation of the polymer particles occurred not only by droplet nucleation but also by micellar nucleation. The surfactant concentration below CMC and initiator concentration at intermediate levels was observed to result a ratio near to unity indicating that the droplet nucleation resulted in the formation of polymer particles. It was observed by the authors that the value of chain transfer coefficient for the system of dodecylmercaptan as chain transfer agent and methyl methacrylate as monomer was in the range 0.6–0.8, which indicated that the chain transfer agent reacted only slightly more than the monomer thus ensuring its presence and effect throughout the course of polymerization. On the other hand, in the system with dodecylmercaptan as chain transfer agent and styrene as monomer, the chain transfer coefficient lies in the range of 15–20, indicating that it would be consumed very early in the polymerization reaction. Thus, its role as costabilizer would end very shortly in the polymerization

the initiator also acted as costabilizer so that no additional costabilizer was added to the polymerization medium. The second case was more conventional miniemulsion polymerization where hexadecane was used. Figure 1.8 demonstrates the time evolution of the droplet diameters. It was observed that the miniemulsions containing LPO had droplet sizes similar to those of the classical miniemulsion polymerizations and the size of these miniemulsions remained roughly constant for more than two hours after the sonication. The average size of the miniemulsions containing BPO and AIBN was, on the other hand, very large suggesting that these miniemulsions suffered a quick partial degradation after sonication. In the presence of hexadecane, however, the size distributions were almost similar irrespective of any initiator used. BPO and AIBN, on their own, are not water insoluble enough to avoid the Ostwald ripening of small particles. Figure 1.9 also represents the mechanism by which the three initiator systems work in the absence and presence of hexadecane. Figure 1.10 also represents the time evolution of conversion of the monomer when oil soluble initiator lauroyl peroxide was used [20]. As can be seen, the polymerization rate was not affected by the presence of hexadecane also confirmed by the particle size analysis. The conventional emulsion polymerization was also carried out for

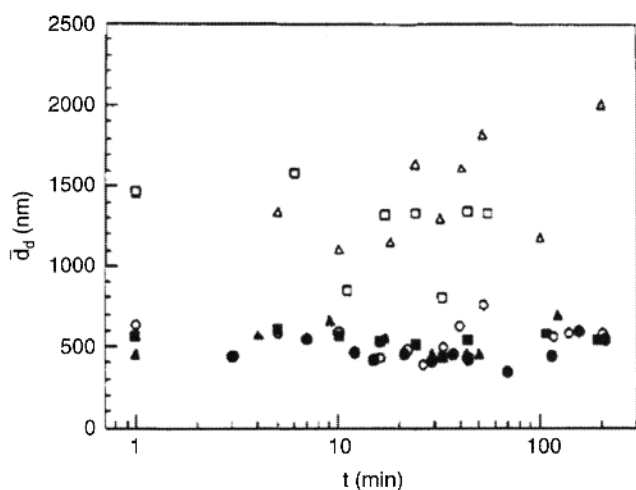


Figure 1.8. Time evolution of the droplet diameter for the different miniemulsions. (O) LPO, (●) LPO+HD, (Δ) BPO, (▲) BPO+HD, (□) AIBN, (■) AIBN+HD. Reproduced from reference 19 with permission from American Chemical Society.

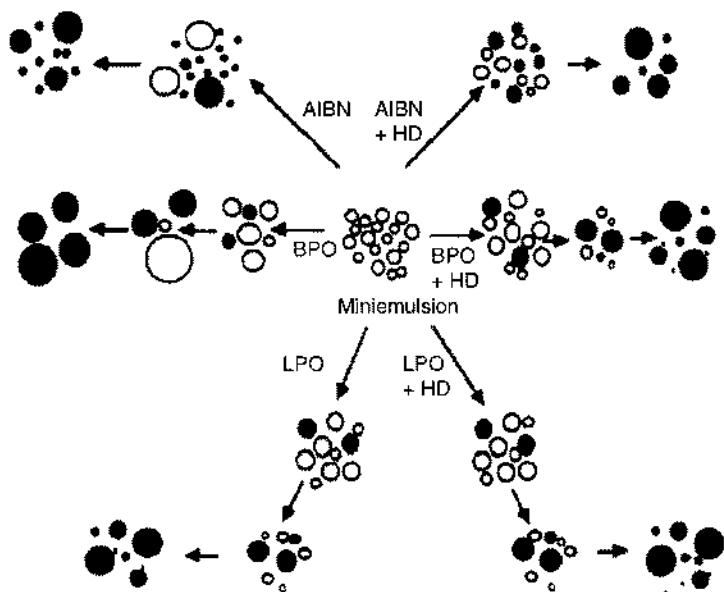


Figure 1.9. Schematic of various processes occurring during the miniemulsion polymerization with different oil soluble initiators. Reproduced from reference 19 with permission from American Chemical Society.

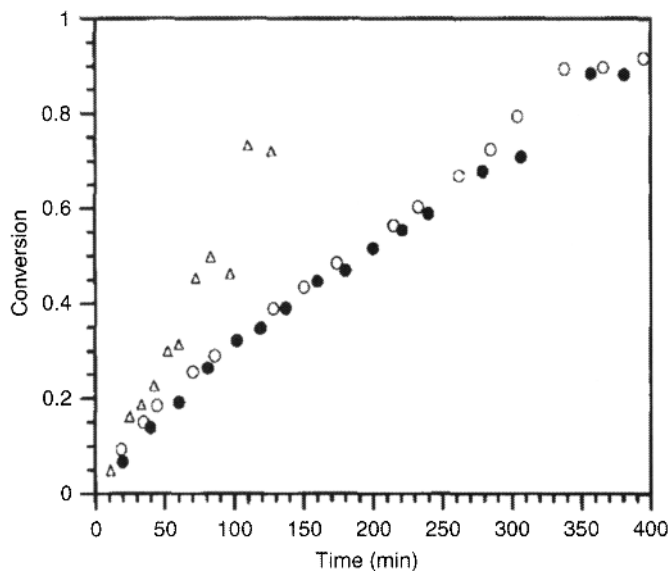
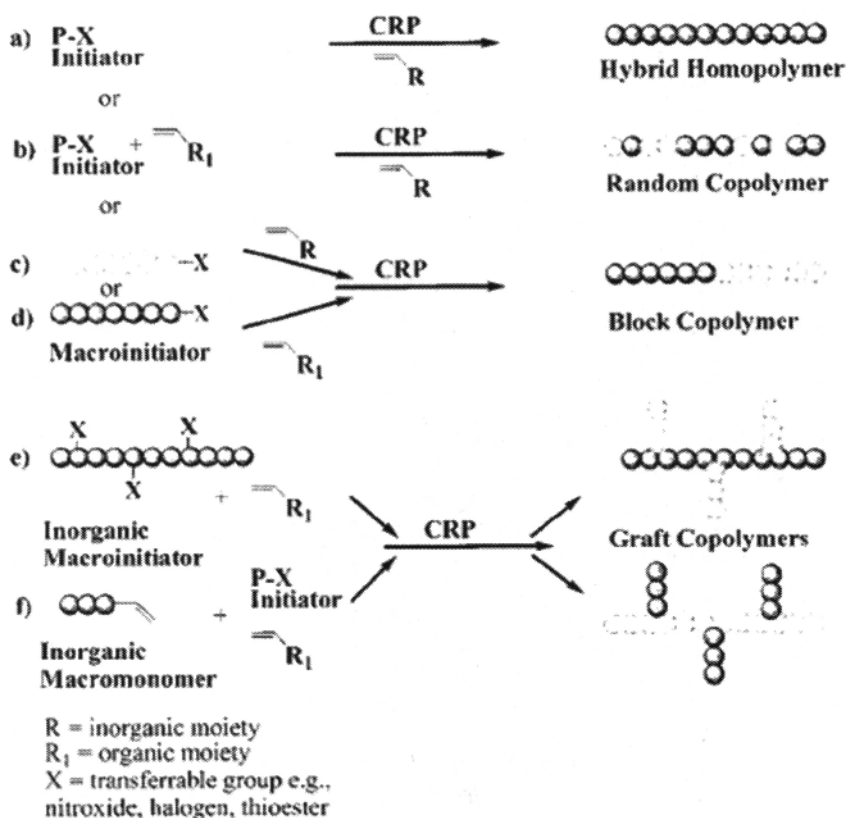


Figure 1.10. Time evolution of the conversion in the polymerizations initiated by LPO: (O) LPO, (●) LPO+HD and (Δ) conventional emulsion polymerization. Reproduced from reference 20 with permission from Elsevier.

The process involves an organic halide which reversibly terminates the polymer chains and generates reversibly active chains and the redox process is catalyzed by a transition metal compound such as cuprous chloride or bromide complexed with a ligand. Scheme 1.1 (Relation 2) shows the schematic of ATRP process. The limitation of ATRP process is the presence of transition metal compounds in the end product. Another limitation of this method is the possible interaction of copper compounds with the emulsifiers used in emulsion polymerization. The polymerization in emulsion phase can though work when no surfactant is used in the system or non ionic surfactants are used.

Reversible addition fragmentation chain transfer (RAFT) is another form of controlled polymerization (Scheme 1.1, Relation 3)



Scheme 1.2. Systematic approach to synthesize hybrid polymers. Reproduced from reference 31 with permission from American Chemical Society.

which operates by reversible transfer mode thus not similar to the reversible termination performed in ATRP or nitroxide mediated polymerization. The core of this process is a RAFT agent which contains dithioester groups. The living polymerization takes place as the transferred end group in the polymeric dithioester is as labile as the dithioester group in the starting RAFT agent. The disadvantage of the techniques operating by reversible termination is the partitioning of the deactivating species in the aqueous phase as well as organic phase. It complicates the concentration of active and dormant species in the polymer particles. However, the techniques based on reversible transfer do not suffer from these disadvantages, as the number of free propagating radicals in these polymerization methodologies practically remains unchanged. The initiator for the polymerization can be the conventional initiators like AIBN or benzoyl peroxide. Important advantage of this technique is the possibility of polymerization reaction to be carried out at lower temperatures. However it also suffers from the presence of excess or remainder RAFT agent which owing to the presence of sulphur also leads to color and odors to the product. Synthesis of hybrid polymers can also be achieved by using these methods as depicted in Scheme 1.2 [31].

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