FEATURE REVIEW

Microemulsion Polymerization

Florentina M. Pavel*

Akcros Chemicals USA, New Brunswick, New Jersey, USA

ABSTRACT

Polymerization in microemulsions is reviewed. The effects of internal microstructure (oil in water, water in oil, bicontinuous) on resulting polymer morphology and characteristics are described. Aspects controlling latex particle size and composite closed cell and open cell length scales are discussed. Formulation effects on polymer functionalization are outlined.

Key Words: Microemulsion; Polymerization; Latex; Monomer; Surfactant.

INTRODUCTION

Polymerization in heterogeneous media generally leads to the formation of polymer colloids or latexes, which are dispersions of polymer particles (usually in water). These particles are almost always in the submicron range. In contrast to free-radical polymerization performed in surfactant-free solutions, this type of polymerization yields high molecular weights at rapid reaction rates due to the fact that the free radicals grow in relative isolation.[1] Millions of tons of polymer latexes are produced annually and include butadiene-styrene copolymers, poly(vinyl acetate), poly(vinyl chloride), acrylate ester copolymers, polyacrylamide and a wide variety of derivatives. These latexes find applications as coatings, binders in papers and textile products, adhesives, paints, additives, flocculants and rheological modifiers, and biomedical compounds. They are also used as size calibration standards for fundamental research.

Emulsion polymerization is certainly the most widely used process to prepare polymer colloids. The particle size of the latexes usually ranges between 0.05 to 0.5 μm and the mechanism and kinetics of the reaction have been extensively studied since 1930.[2]

The concept of polymerization in microemulsions appeared only around 1980, likely as a consequence of the numerous studies performed on microemulsion systems after the 1974 oil crisis. Since then, the field has developed rapidly as attested by the constant increase in the number of papers devoted to microemulsion polymerization. The interesting features of microemulsions, such as large internal interfacial area, optical transparency, thermodynamic stability, small domain

*Correspondence: Florentina M. Pavel, Akcros Chemicals USA, 500 Jersey Avenue, New Brunswick, NJ 08903, USA; E-mail: florentina_pavel@yahoo.com.

1

length scales, and great variety of structures, result in a unique microenvironments. Such microemulsions can be advantageously used to produce novel materials with interesting morphologies and polymers with specific properties.[1,3−5]

A primary goal of investigators has been to produce thermodynamically stable latexes in the nanosize range (<50 nm) not attainable with classical emulsion polymerization process.[3] Microlatexes with such characteristics are desirable in certain applications, such as in drug delivery or microencapsulation. It has also been of particular interest to prepare stable and uniform inverse latexes via inverse microemulsion polymerization, since the classical inverse emulsion technique is known to produce unstable latexes with broad particle size distributions. Another appealing aspect of microemulsion polymerization is the possibility to fix permanently the labile structure of these systems and to secure therein tightly solubilized molecules. In addition, the optical transparency and thermodynamic stability of microemulsions are advantageous for photochemical and other reactions.

A major difference between emulsions and microemulsions comes from the amount of surfactant needed to stabilize the respective systems. Much more surfactant is needed for microemulsions (≈10% of the total mass), due to the necessity of stabilizing a large internal interfacial area. This is a drawback that can considerably restrict the potential uses of microemulsion polymerization since high solid contents and low surfactant levels are desirable for most applications.[6] However, this limitation is being decreased by the increasing use of reactive or polymerizable surfactants.

Microemulsion polymerization of monomers may be achieved by incorporating a monomer in any of the water and oil phases of the system. Replacing dispersed phase by a monomer in an o/w microemulsion produces spherical latex particles of optimum diameter. However, solid materials may be produced if the continuous phase is polymerized, entrapping the dispersed phase in its matrix. This latter approach that has been successfully used for producing solid materials by microemulsion polymerization. Furthermore, copolymerization of monomers may also be achieved by placing monomers in both the water and oil phases. This opens the way for producing copolymers and nanocomposites with new characteristics.

The polymerization of microemulsions may be carried out by chemical, photochemical, and high-energy radiation techniques.[4] The variety of structures encountered in microemulsions offers great versatility in choosing the locus of polymerization.

An important characteristic of microemulsions is the transient character of the self-assembly aggregates. Surfactant molecules and other constituents are constantly exchanging among the interfacial, water, and oil pseudo phases. The droplets collide with lifetimes of the order of microseconds or longer, so it can be expected that polymerization of these dynamic structures will be accompanied by structural changes. Therefore, thorough research on appropriate formulation rules and characterization of the phase diagrams of the systems that contain the monomer should precede any study of microemulsion polymerization. Furthermore, the use of the materials obtained for different applications requires inexpensive formulations characterized by high monomer to surfactant ratios. An inappropriate choice of the nature and/or composition of the components can easily lead to phase separation or gel formation during the polymerization process.[1]

Polymerization reactions have been carried out in microemulsions of all types of structures and in particular in droplet containing microemulsions. Select studies done in this field are discussed in the following sections.

POLYMERIZATION IN OIL-IN-WATER MICROEMULSIONS

The polymerization of hydrophobic monomers in o/w microemulsions provides an attractive way for producing latex particles. Unlike conventional polymerization, polymerization in microemulsions occurs only in the monomer reservoir encapsulated in the particle, and the size of latex particles is often smaller than obtained with classical emulsion polymerization.[4]

The first attempts to combine the advantages of polymer chains with those of microemulsions were published in 1977.[7,8] The first papers that describe a polymerization process in globular oil-in-water microemulsions were published by Stoffer and Bone,[9,10] and by Atik and Thomas.[11−13] The latter authors polymerized styrene in an oil-in-water microemulsion using different initiating systems and obtained monodisperse latex particles with diameters in the order of 20−30 nm. Their system was based on hexadecyltrimethylammonium bromide and hexanol (as a cosurfactant), and it was found that the stability of such microemulsions is limited by the solubility of the polymer formed in the surfactant.[14,15] In 1979 Schauber and Riess worked on the polymerization of diverse methacrylates, microemulsified by sodium dodecyl sulfate (SDS)/alcohol mixtures, but published the data ten years later.[16] They

prepared crosslinked and non-crosslinked stable micro-latex particles with 5–10% solid content of polymer.

Most studies have dealt with the free radical polymerization of hydrophobic monomers, e.g., styrene, methylmethacrylate (MMA) within the oily core of o/w microemulsions. Polymerization can be initiated thermally,[9,11,14,17] photochemically[15,18] or under γ-irradiation.[11,19] Beside conventional dilatometry and gravimetry techniques, polymerization kinetics have been monitored by Raman spectroscopy,[20,21] pulsed UV laser source,[22,23] the rotating sector technique,[24,25] calorimetry and internal reflectance spectroscopy.[26]

For both o/w and w/o systems, the amount of monomer is usually restricted to 5–10wt% with respect to the overall mass, and that of the surfactant(s) lies within the same range or even above. Nevertheless, there are a few reports for which the formulation deviates from these conditions (surfactant concentrations less than 2 wt%).[11–13,27]

The main difficulty encountered lies in retaining optical transparency and stability of the microemulsions upon polymerization. In addition to entropic factors contributing to the destabilization of microemulsions during polymerization, the compatibility between polymer and cosurfactant also influences the system.[14] This is especially true when styrene is polymerized within o/w microemulsions containing an alcohol, because the latter is a non-solvent for the polymer. There are some other drawbacks that make alcohols undesirable hosts in monomer-containing microemulsions: alcohols partition between the interfacial film and the other phases which complicates considerably the dilution procedure required for the determination of the droplet or particle size, they may modify monomer partitioning,[28] and they act as chain-transfer agents, thus lowering the polymer molecular weight.[1]

Despite these difficulties, most of the earliest studies used alcohols as cosurfactants in the formulation of o/w microemulsions, and it was only in 1989 that the polymerization of hydrophobic monomers in a three-component o/w cationic system was reported.[27] This spurred new interest and systematic studies on ternary microemulsions based on cationic surfactants with different alkyl chain lengths. Nonionic surfactants were also used in ternary o/w microemulsions for the polymerizations of styrene and methylmethacrylate[29] and anionic (AOT: sodium 1-4*bis*(2-ethylhexyl)sulfo-succinate) surfactants for the polymerization of tetra-hydrofurfuryl methacrylate.[26,30]

The comprehension of the mechanism of polymerization in ternary and quaternary oil-in-water micro-emulsions had slow progress, due to the onset of turbidity upon polymerization and the lack of stability with time observed by most of the authors and more particularly for MMA monomer. Only slight changes in the formulation are sufficient to significantly affect the polymerization process and to induce particle coagulation at any stage of the reaction. This may explain the disparity in the experimental and kinetic data reported by some authors for very similar systems. It can however be concluded that the model that is now well accepted is that of a continuous particle nucleation mechanism.

Styrene has been polymerized in a series of cationic microemulsions containing alcohols of different alkyl chains lengths.[31] The distributions of styrene and cosurfactants in both disperse and continuous phases were analyzed by dialysis. The concentration dependence of styrene and potassium persulfate initiator (KPS) on the polymerization rates were roughly constant in the systems and quite similar to the values found for other ternary or quaternary microemulsions. The polymer molecular weights were found to depend on the alcohol used in the formulation, due to an indirect effect of the interfacial fluidity, which affected the termination rate in the particles.

Comparative mechanistic studies on the microemulsion polymerization of styrene and methylmethacrylate have been carried out by several groups.[20,21,32–43] The results were coherently interpreted in terms of the relative monomer solubilities in water. In the case of styrene, which has a very weak solubility in water (0.031%), it was postulated that initiation takes place in the microemulsion droplets. The polymer particles grow by recruiting monomer and surfactant from uninitiated droplets. Homogeneous nucleation in styrene systems may be relatively insignificant due to the large number of microemulsion droplets which will capture most of the radicals generated in the aqueous phase before they reach a critical size for precipitation. The continuous particle nucleation and growth during the polymerization in a system containing styrene was also determined by using a water-insoluble dye, and measuring the increasing weight percentage of dye incorporated into latex particle with the progress of the polymerization reaction.[44]

The experiments performed in MMA systems suggest that homogeneous nucleation can compete with monomer droplet initiation because of the non-negligible solubility (1.56%) and the more polar and cosurfactant character of MMA in water. It was proposed[42] that homogeneous nucleation occurs at early stages of the reaction when the increase in conversion is very slow. In the second stage, which has a much faster polymerization rate, nucleation proceeds via a micellar entry mechanism. An increase in total number of particles with conversion was also found and provided good evidence for continuous nucleation.

The growth of polymethylmethacrylate (PMMA) and polystyrene (PS) particles in ternary cationic microemulsions were compared.[43] Different growth patterns were observed which were attributed to a different redistribution of the components during the reaction. The strong interactions between the polar MMA-monomer and the cationic surfactant at the water/oil interface reduce the swelling of monomer-swollen polymer particles. In contrast, interactions are weak for styrene and maximum swelling is already reached at the early stages of the reaction.[33,34]

The dependence of the polymerization rate on monomer concentration exponent was found to vary from about 1[31,36] to 1.3,[41] close to the theoretical value of 1 for emulsion, solution, or bulk polymerization.

The effect of water-soluble (KPS) and oil-soluble (2,2′-azo*bis*isobutyro-nitrile: AIBN) initiators on the microemulsion polymerization of styrene and methyl-methacrylate in ternary and quaternary microemulsions has been investigated by several groups.[20,35–37,39,41] The polymerization mechanism does not seem to depend on the nature of the initiator used: both KPS and AIBN initiated systems produced microlatexes with similar hydrodynamic radi, number of polymer particles, molecular weight of polymer and number of macromolecules per particle.[37] However, the polymerization rates were generally faster with KPS than with AIBN[20,36,37] and the latex parameters showed stronger dependencies on the concentration of KPS than on that of AIBN. This behavior was discussed in terms of different efficiencies of the initiators in producing effective radicals for the polymerization. At an equimolar concentration of initiators, KPS generates more radicals in the aqueous phase than AIBN. These radicals are thus more effective for initiation (in the continuous phase, in the monomer droplets or at their interfaces) than AIBN radicals, due to a significant autotermination of AIBN radical pairs in the small droplets (cage-effect) and the low solubility of AIBN in water. In this case, initiation is believed to occur essentially via micellar entry of single radicals arising either from the very small portion of AIBN dissolved in water or desorbed from other swollen micelles.

Both AIBN and a cationic water-soluble initiator (2,2′azo *bis*(2-amidinopropane)dihydrochloride: V50) were used for MMA polymerization in ternary cationic microemulsions.[42] Contrary to the case of the anionic KPS initiator, the free radicals produced by V50 decomposition have the same sign as the microemulsion droplets. The repulsion between these two species favors homogeneous nucleation rather than micellar entry during the first stages of the reaction. This accounts for the longer homogeneous nucleation regime observed with V50. Moreover, homogeneous nucleation is known

to yield primary particles prone to limited flocculation. This is likely the reason for the higher number of polymer chains per particle found at the end of the reaction (three times more chains than with AIBN initiator).

In the case of thermal initiation of styrene[31,36] the polymerization rate was found to be proportional to [AIBN]^{0.39} and [KPS]^{0.47}, in good agreement with other data in three or four component microemulsions.[37,45] The exponential dependency on [AIBN] is consistent with the prediction of 0.40 based on the micellar nucleation theory in emulsion polymerization. The exponent dependency on [KPS] lies between this case and the value of 0.5 for solution or bulk polymerization.

In addition to electrostatic stabilization, steric stabilization was found to be an important factor in the microemulsion polymerization of MMA. A comparative stability study has been performed on MMA polymerization in tetradecylammonium bromide (TTAB) or stearyltrimethylammonium chloride (STAC) microemulsions.[43] A strong increase in particle size was observed above 50% conversion for the former systems whereas the size remains rather constant up to 98% conversion for the latter, offering clear evidence of the occurrence of particle coagulation in MMA systems based on TTAB surfactants. Surfactants with longer carbon chain lengths form thicker interfacial layers that prevent latex flocculation. It should be noted that the stability of PS microlatexes is not affected by the alkyl chain length of cationic surfactants due to a stronger surfactant adsorption on the surface of PS particles compared to that on PMMA particles.[43] It is known that surfactant adsorption at a latex/water surface decreases upon increasing the polarity of a polymer.[46]

The kinetic studies performed on the polymerization of MMA in the emulsion and microemulsion regions of ternary systems based on cetyltrimethylammonium bromide (CTAB) confirmed the difference in mechanism between the two processes.[40,47] The following kinetic laws were obtained:

Emulsion regime $\quad R_\mathrm{p} \propto [\mathrm{CTAB}]^{0.31}[\mathrm{KPS}]^{0.82}$

Microemulsion regime $\quad R_\mathrm{p} \propto [\mathrm{CTAB}]^{0.58}[\mathrm{KPS}]^{0.33}$

The low value of 0.31 found in emulsion polymerization for the dependency of rate of polymerization (R_p) on the surfactant concentration indicates a significant contribution by homogeneous nucleation, as already quoted for this monomer.[48] On the other hand, the micellar nucleation mechanism is likely predominant in microemulsion polymerization due to the large number of micelles and large overall surface areas

available for capturing free or oligomeric radicals generated in the aqueous phase. The exponent of 0.58 found in microemulsion systems supports this view.

Similar studies were conducted for the polymerization of styrene.[47,49] They led to a single dependency of R_p on surfactant concentration for both emulsion and microemulsion systems, which confirms that when surfactant concentrations are well above the CMC (>3 wt%) in emulsion or microemulsion systems, the micellar nucleation mechanism prevails in both cases due to the very low solubility of this monomer in water.

In general, research in o/w systems is focused towards applications based on the properties of the latex particles obtained after polymerization. One of the challenges that remains is the search for new types of surfactants, which will allow the formation of microemulsions using much lower amounts of surfactant. Another challenge is the formation of non-spherical latex particles that will exhibit interesting rheological features.

POLYMERIZATION IN WATER-IN-OIL MICROEMULSIONS

The polymerization of water-soluble monomers (e.g., acrylamide (AM)) within the aqueous core of w/o microemulsions has been investigated in detail.[24,25,50−69] In the case of AM the monomer is a powder, which has to be first dissolved in water (1:1 mass ratio), so that the resulting polymer particles are swollen by water and dispersed in the organic continuous phase, in contrast with o/w latex particles where the polymer is in a "bulk" state.

Incorporation of monomers can considerably modify the structure of microemulsions and the phase diagram. This was shown for water-soluble monomers and more particularly for acrylamide (AM).[70−79] Acrylamide has been investigated most thoroughly because of the numerous applications of the corresponding polymer.[80] It was found that water-soluble monomers act as cosurfactants leading to a considerable extension of the microemulsion domain in the phase diagram. The cosurfactant role of various hydrophilic monomers was confirmed by surface-tension experiments.[73,74,81] These results gave clear evidence that the monomer molecules partially locate at the w/o interface between the surfactant molecules. In the case of the widely studied AOT/water−acrylamide/toluene systems (AOT: sodium 1-4bis(2-ethylhexyl)sulfo-succinate), the interfacial localization of the AM molecules induces attractive interactions between the droplets as seen by light scattering, small angle neutron scattering and viscometry experiments.[76,77,82] It should be noted that

without acrylamide, the systems display essentially a hard sphere behavior. Upon further addition of acrylamide, the interaction potential becomes so attractive that transient clusters form. Above a threshold volume fraction, a large increase in the electrical conductivity is observed, which is a signature of a percolation phenomenon.[82] The percolation threshold decreases upon increasing AM/H_2O ratio, i.e., upon increasing the attractive interactions, in good agreement with theoretical analyses[85] and data obtained for other microemulsions containing alcohols as cosurfactants.[86,87] This percolating structure has an effect upon the formation of polymer latex particles and the polymerization mechanism.

The polymerization in w/o microemulsions can be initiated thermally,[87,88] photochemically[24,25,53,82] or under γ-irradiation.[89] The problem of particle nucleation was first addressed in the eighties in the case of water-in-oil microemulsions.[52,76] The studies concerned the polymerization of acrylamide inside water-swollen micelles stabilized by AOT and dispersed in toluene. A thorough investigation of the structures prior to and after polymerization by elastic and quasi-elastic light scattering (QELS), viscometry and ultracentrifugation yielded two key experimental results. The first is that the particle size of the final microlatex ($d \approx 20-40$ nm) was much larger than that of the initial monomer-swollen droplets. This leads to a final number of polymer particles circa 2 or 3 orders of magnitude smaller than that of the monomer droplets. The second key result was the number of polymer chains contained in each particle, which was 1, on average.

From these results, it was postulated that particle nucleation was continuous throughout the process,[52] in strong contrast with emulsion polymerization. A continuous particle nucleation mechanism was further confirmed by TEM experiments performed on polyacrylamide samples taken at various degrees of conversion.[83] The number of polymer particles was shown to increase proportionally with conversion, whereas the size remained roughly constant.

To account for the particle growth, it was proposed that only a small fraction of the overall number of droplets is nucleated. The nucleated particles grow, the monomer being supplied from the non-nucleated reservoir droplets either by diffusion through the continuous phase or by "sticky" collisions between droplets. As a result of this growing process and because of the large amount of surfactant involved in the formulation, small micelles are always present in the reaction mixture. Owing to their high overall interfacial area compared to that of the nucleated polymer particles, these micelles capture, preferentially, the primary
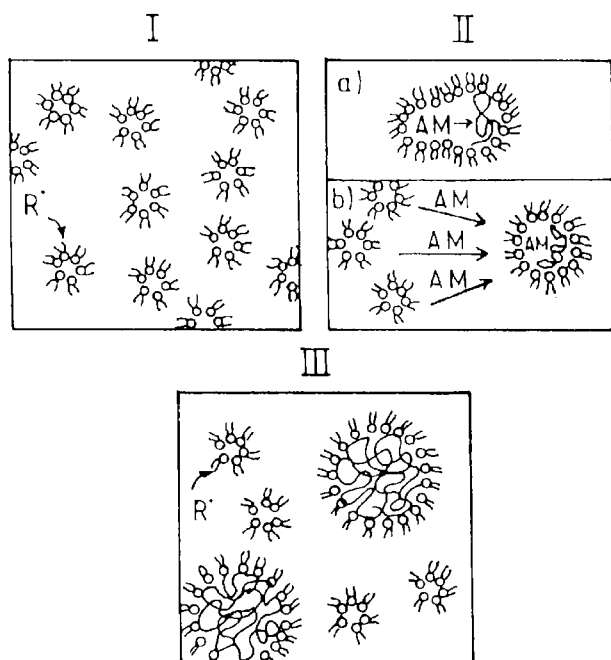
Figure 1. Polymerization mechanism in AOT w/o microemulsions: I-Before polymerization: water swollen AOT droplets ($d \approx 6$ nm), II-polymer particle growth a) by collisions between particles; b) by monomer diffusion through the toluene phase. III-end of polymerization: polymer particles ($d \approx 40$ nm) + small micelles ($d \approx 3$ nm).

radicals generated in the organic phase. Hence, each particle is entered once on average (Fig. 1).[81]

Dilatometry and rotating sector techniques were combined to follow the photopolymerization of acrylamide in AOT reverse micelles with AIBN as the initiator (and toluene as the organic phase).[24,25] Very high polymerization rates were observed with total conversion to polymer achieved in a few minutes. The reaction likely occurs at the water–oil interface by transfer of the growing polymer radical to toluene.

A detailed study of the loci of initiation and propagation of AM (co)polymerization in the same AOT systems was performed using initiators and inhibitors of various solubilities.[55–59,90] Initiation with AIBN was shown to take place predominantly in the water/oil interfacial layer, where the encounter with acrylamide-cosurfactant is facilitated. With water-soluble ammonium persulfate, initiation occurs, as expected, in the droplet water-pools.

Steady-state fluorescence of indolic probes quenched by AM and selectively located at the various loci of the microemulsion (toluene, interfacial layer and water phase) was used to follow the depletion of monomer during polymerization.[64] The results showed

that AM is evenly consumed from all parts of the microemulsion system, independently of the initial composition and of the nature of the initiator.

The mechanistic scheme and kinetics described above for polymerization in w/o AOT/(water-AM)/ toluene microemulsions become more complex when these systems are initially percolating. QELS and TEM techniques were used to monitor changes in particle size with conversion for both types of systems.[83] Different behaviors were observed at early stages of the reaction ($<10–15\%$ conversion). In particular, a large initial rise in size observed for percolating systems was attributed to the formation of a necklace of connecting beads. A comparative study of the kinetics of polymerization of AM in percolating and non-percolating systems[60,61] yielded different orders of reaction rates with respect to AM. Also, for a given AM/water mass ratio, the polymerization rate is higher in a non-percolating system. It was proposed that some local AM concentration gradients could occur in the propagation loci, thus altering the kinetic behavior. In the case of water-soluble monomers, much effort has been devoted to an optimal formulation, compatible with an economical process.[71]

In the preceding studies, it is the monomer in water phase that is polymerized, and the oil phase remains intact, producing latex particles. In contrast to these studies, Menger et al.[91] replaced the oil phase with a polymerizing monomer, styrene, using AOT as the surfactant. Photopolymerization was carried out in the presence of AIBN as initiator. Solid materials were produced within 10 h. In this study it was shown that the pore size in the material was highly dependent upon the water/surfactant ratio in the microemulsion. The size of pores in the solid material was always larger than the radii of the original water droplets in the microemulsions. This may be due to the collision of water droplets during the process of polymerization, which leads to their growth as they become encased in the polymer matrix. The authors found that the pore size is larger by 1 order of magnitude in the polymerized matrix. An increase in the surfactant concentration (for constant water), that is decreasing the value of $[H_2O]/[AOT]$ resulted in a decrease in the surface area of the pores in the material. In general, a small number of large microemulsion droplets was more effective than a large number of smaller droplets. In another study Menger et al.[92] reported the polymerization of a w/o microemulsion system consisting of styrene, the cross-linker divinylbenzene, water, and AOT. The polymerization was initiated by benzoyl peroxide/UV light, and a sponge-like polymer was obtained. Although the reacting systems were optically clear mixtures, after polymerization opaque polymers were obtained. The

existence of porosity reflects the tendency for water pools to assemble within the polymer composite.

The synthesis of transparent polymeric solids in w/o microemulsions has been attempted by using polymerizable surfactants. These surfactants have an advantage over nonpolymerizable surfactants in that the templating effect of the amphiphilic interface may be better preserved during polymerization.[93] Extensive studies are currently underway in this field.

POLYMERIZATION IN BICONTINUOUS MICROEMULSIONS

The variety of structures encountered in microemulsions offers great versatility for choosing the locus of polymerization. Beside polymerization in o/w and w/o microemulsions, several studies have dealt with polymerization of monomers in irregular bicontinuous microemulsions. One of the main goals motivating these studies was to utilize the microstructure of microemulsions as a template to produce solid polymers with similar characteristics. For example, incorporation of large amounts of hydrophobic monomers in the continuous phase of w/o microemulsions should yield solid polymers with a swiss-cheese-like structure capable of encapsulating the disperse phase (water). This would allow inclusion of materials (e.g., metallic colloidal particles as catalysts) in the disperse phase that would otherwise be insoluble in the polymer.

In the case of bicontinuous microemulsions, both hydrophobic and hydrophilic monomers have been considered. The morphology of the final product depends on the microemulsion composition and on the nature of the monomer. In some studies polymerization of hydrophobic monomers led to porous materials, whereas polymerization of water-soluble monomers yielded transparent and stable microlatexes. The incentive in these two kinds of studies was different. In particular, the aim of the research on water-soluble monomers was to prepare high molecular weight polymers at large contents that can be used as flocculants.[1]

Microemulsions Based on Hydrophobic Monomers

In their pioneering work, Stoffer and Bone, studied the phase behavior of sodium dodecylsulfate (SDS)/pentanol/methylmethacrylate or methyl acrylate/water systems before and after polymerization.[9,10,94] In polymerizing the continuous phase of microemulsions, phase separation occurs. A typical composition of the

system was: MMA (41.7%), pentanol (27%), SDS (14.6%), and water (16.7%).

Polymerization degree (DP) dependencies on initiator concentration were shown to follow solution kinetics (DP $\propto$ [I]$^{-1/2}$) for water and oil soluble initiators. Such a behavior could be expected since the monomer is located in a continuous medium and not in the micellar dispersed phase. The pentanol present in large amounts (27%) acts as a chain transfer agent.

The kinetics of the homopolymerization of methylmethacrylate in the continuous phase of AOT reverse micelles was studied,[90] and strong turbidity was observed in the course of polymerization although MMA was highly diluted with toluene ($C_{MMA} \approx 6\%$). The MMA polymerization in AOT systems was compared to that in pure toluene and to that in toluene in the presence of AOT. A very low polymerization rate was found with water-soluble ammonium persulfate. This indicates that only a small amount of MMA is present in the AOT water pools and that the APS radicals remain trapped inside.

The problems of stability were examined in a series of papers related to the polymerization of styrene in water-in-oil microemulsions stabilized by SDS and pentanol.[14,95–97] Their conclusions were that entropic conformational factors were not the only ones of importance in the mechanism of destabilization. A correlation was established between polymer solubility in the cosurfactant compared to that of monomer by using another cosurfactant, butylcellosolve. The higher solubility of polystyrene in butylcellosolve gave better stability than pentanol-containing microemulsions.

Gan and Chew reproduced the previous experiments of Stoffer and Bone, and confirmed that transparent PMMA mixtures could not be fully polymerized in situ by using pentanol as cosurfactant in which PMMA is insoluble.[89] They subsequently improved appreciably the procedure by replacing 1-pentanol by the polymerizable cosurfactant acrylic acid (AA).[89] This monomer is soluble in water and dissolves up to 32% PMMA. Transparent solid copolymers could be obtained by fully polymerizing 54% MMA, 34% AA, 10% H$_2$O and 2% SDS or with other lower water contents. The copolymers are very heterogeneous in composition and have high molecular weight ($\approx 10^6$). Scanning electron microscopy (SEM) observations did not reveal any particular pattern of the structure, indicating that water is isotropically distributed in the polymeric matrix.

Gan and Chew extended their studies to microemulsions in which all the components except water were polymerizable. Polymerization in microemulsions containing a polymerizable surfactant (sodium acrylamidoundecanoate[98] or acrylamidostearate,[99] a

cosurfactant (acrylic acid) and methylmethacrylate as the continuous phase, led, under certain conditions, to transparent solid terpolymers with up to 10–20% water dispersed in the polymer matrices. As in the case of copolymers, these terpolymers did not present any particular structure by SEM.

Porous solids were obtained by copolymerization of styrene-divinyl-benzene[92,100] and cyclohexylmethacrylate-allylmethacrylate[101] in the continuous phase of the microemulsions. It was shown that the pore size of the material, always larger than the initial droplet size, is highly dependent upon the water/surfactant ratio in the microemulsion.[92] The same authors have prepared porous materials with chemically active groups on the surface.[91]

The preparation of solid porous materials by polymerization of styrene in Winsor I, II, III microemulsions stabilized by an anionic surfactant (SDS) and 2-pentanol or by nonionic surfactants has also been reported.[87,88] The porosity of materials obtained in the middle-phase was greater than that obtained with either w/o or o/w microemulsions. This is related to the structure of middle phase microemulsions, which consist of oily and aqueous bicontinuous, interconnected domains. A major difficulty encountered during the thermal polymerization was phase separation. A solid and opaque polymer was obtained in the middle phase with excess phases at the top (essentially 2-pentanol) and bottom (94% water). The nature of the surfactant has a profound effect on the mechanical properties of polymers. The polymers formed from nonionic microemulsions are ductile, non-conductive and exhibit a glass transition temperature lower than that of normal polystyrene. The polymers formed from anionic microemulsions are brittle, conductive and exhibit a higher T_g. This was attributed to strong ionic interactions between polystyrene and SDS.

Thermal polymerization of styrene was also carried out in a three phase Winsor III (microemulsion) styrene-brine system.[102] The system exhibited features of a solution polymerization process and no mention was made of the morphology of the final product.

Porous polymeric structures were obtained by photopolymerization of monomers in single-phase microemulsions.[103–107] The systems consisted of methylmethacrylate (MMA), acrylic acid (AA), a cross-linking agent, ethylene glycol dimethacrylate (EGDMA), water and sodium dodecylsulfate (SDS) as the surfactant. Large amounts of monomer were used in the formulation (up to 70% in some cases). The structures of the initial microemulsions were determined from conductivity, viscosity and QELS experiments. A close correlation was found between the microstructure

of the polymeric material and the nature of the initial microemulsion. SEM, thermogravimetry, adsorption studies, swelling and permeability measurements, and differential scanning calorimetry characterized the polymeric materials obtained. The main conclusions reached by these authors were that polymerization in microemulsions with a water/oil droplet structure yields closed cell porous polymeric solids, having a morphology characterized by a disjoined cellular structure where the water pools are distributed as discrete pockets throughout the solid, and that polymerization in microemulsions with a bicontinuous structure results in a polymer with an open-cell structure, i.e., an interconnected porous structure with water channels through the polymer. The surface area increased steadily upon increasing water content in the precursor microemulsion.

The above morphology assignments were clearly supported by means of scanning electron microscopy and thermogravimetric analysis. A distinction between open cell and closed cell porous structures was made, based on the strong difference in the shape of the drying rate curve for the two structures. In closed cell structures, the drying process is diffusion limited, resulting in an exponential decrease in drying rate with decreasing moisture content. In open cell structures, the drying process is dominated by transport of moisture from the interior of the solid to its surface (capillary forces). In this case, a linear decrease in drying rate was observed down to a certain threshold of water content.

These results indicate that the morphology of the polymer keeps some memory of the initial structure since this structure is retained to a certain extent. However, the length scale of the porous structure obtained (1–4 μm) was considerably larger than the length scale characteristic of microemulsions (less than 0.1 μm), due to phase separation effects or structural changes during polymerization. This instability can be related to the complex effect of entropic increase of free energy as a result of conformational limitations. The incorporation of the cross-linking agent EGDMA was found quite effective in minimizing the occurrence of phase separation. Microemulsions with EGDMA concentrations below 10% by weight of monomer content yield, upon polymerization, transparent polymeric solids.[103] The porous polymers have good mechanical stability and their rigidity can be varied according to their composition and especially to the amount of cross-linking agent used.

Other authors[108,109] confirmed these results, i.e., the morphology of the resulting polymeric material strongly depends on the composition of the precursor microemulsions. These authors have also attempted to preserve to a greater extent the initial bicontinuous structure of microemulsions by varying the nature of the

surfactant and the polymerization conditions.[110–112] The reaction has to be carried out as fast as possible (photoinitiation at 35°C) in order to reduce the rearrangements of the microemulsion at the early stages of the reaction. The use of bicontinuous microemulsions based on a polymerizable surfactant seems the key parameter for obtaining transparent solid polymeric materials with an open-cell microstructure.[108,110,112]

The preparation of novel solid materials is a huge field for applications such as microfiltration, separation membranes or their supports, microstructured polymer blends and porous microcarriers for the culture of living cells and enzymes. The considerable progress made over the years permits one to envision many future developments.

Novel conductive composite films were developed using a two-step process. The porous film coated on an electrode was prepared by polymerizing a bicontinuous microemulsion containing acrylamide and styrene monomers followed by electropolymerization of pyrrole.[113] The copolymer matrix was found to improve the mechanical behavior of the pyrrole composite film.

Microporous silica gels were prepared by polymerization of partially hydrolyzed tetramethoxysilane gels present in the aqueous phase of bicontinuous microemulsions stabilized with didodecylammonium bromide.[114] When vacuum dried, the gels made in microemulsions have about twice the specific surface area of conventional vacuum dried silica gels.

Microemulsions Based on Water-Soluble Monomers

The polymerization of water-soluble monomers in the aqueous domains of nonionic bicontinuous microemulsions has been studied. Microemulsions containing up to 25 wt% monomers dissolved in the same amount of water and around 8 wt% surfactant[1,115] have been prepared.

Various water-soluble monomers have been investigated: neutral monomer (acrylamide),[70,71,116,117] anionic monomers (sodium acrylate (NaA)[72,118–120] and sodium 2-acrylamido-2-methyl-propanesulfonate (NaAMPS)[73,114,121–125]) or cationic monomer (methacryloyloxyethyltrimethyl-ammonium chloride (MADQUAT),[73–75,121–126]) and copolymers of the above combinations.

During the polymerization of hydrophobic monomers in the bicontinuous phase of microemulsions, the initial structure is not preserved upon polymerization. Several factors are responsible for the structural change observed upon polymerization, such as the fact that microemulsions have flexible and fluctuating interfaces, which undergo easy deformations, and the monomer consumption from the interfacial layer (cosurfactant effect) modifies the film curvature energy. The formation of water-swollen spherical polymer particles dispersed in the oily phase corresponds to the minimum free energy of the system.

The correlation between the composition of the initial system and the stability of the final microlatex for copolymers of AM-NaAMPS has been examined.[115] A comparison between the domain of stability of microlatex and that of microemulsion indicated that the former is slightly shifted towards lower HLB values of the nonionic surfactant blend. The best area for carrying out the polymerization reaction is likely located at the interface of these two domains.

CHARACTERISTICS OF THE FINAL PRODUCTS

The characteristics of both particle latexes and polymers formed depend critically on the formulation. The composition chosen for the system depends on whether the ultimate goal of the formulator is to prepare specific polymers or to produce small-sized latex particles. As a general trend, research in o/w systems is focused towards applications based on the properties of latex particles whereas studies in w/o systems are aimed at producing water-soluble polymers of high molecular weights. As a rule, the higher the surfactant/monomer ratio, the smaller the particles size.[16,49,75,116] Therefore, high solid contents and small-sized particles can hardly be achieved simultaneously.

Polymers

The polymers formed by this process can be recovered from the latexes by precipitation in a large excess of non-solvent and dried under vacuum. They may further be characterized in dilute solutions by means of techniques such as light scattering, GPC or viscometry.

The polymer molecular weights are high, usually ranging from 10^6–10^7, as expected for polymerization in dispersed media. In some cases, exceptionally high molecular weights have been reported ($M_w \approx 2.5$ to 3.3×10^7).[36,37] but there is a question about the structure and linearity of the polymers thus formed. When alcohols are used in the formulation, chain transfer reactions can occur which reduce the molecular weight.[18,65,127] The distribution of molecular weights

in o/w systems is usually very broad ($M_w/M_n \approx 2-7$ and up to 12 in some cases).[47] With regard to the effect of monomer/surfactant ratio, a trend similar to that obtained for particle size was observed: the higher the molecular weight, the larger the monomer/surfactant ratio.[75,122] The few polymer chains of high molecular weight confined in the microlatex particle must be strongly collapsed in order to fit such small dimensions ($d < 40$ nm).[1,76]

The large differences observed between the kinetics and mechanism of microemulsion polymerization and other polymerization processes (solution, emulsion, and bulk) can account for differences observed in some polymer characteristics like the molecular structure, the microstructure or molecular weight. These effects can be especially important in the case of water-soluble polymers whose efficiency as flocculants depends on their characteristics. A comparative study of the microstructure of copolymers prepared by polymerization in microemulsion, emulsion, and solution[118,122] indicated that microemulsion polymerization seems to improve the structural homogeneity of the copolymers with reactivity ratios close to unity. For example, microemulsion polymerization leads to almost random ampholytic polymers whereas those prepared in solution exhibit a strong tendency to alternation.[122] It was shown both theoretically[128] and experimentally that the conformation and solution properties of these ampholytic polymers were directly related to the monomer sequence distribution.[124] At equimolar proportions of anionic and cationic monomers, a random polyampholyte (micro-emulsion process) is insoluble in water whereas an alternated one (solution process) is soluble. These results are accounted for by the marked differences between the microemulsion process and others, in terms of micro-environment (charge screening and preferential orientation of the monomers at the w/o interface) and mechanism (interparticular collisions with complete mixing).[1,118]

In the above studies, both ionic monomers are exclusively located in the aqueous disperse phase so that monomer partitioning between oil and water can be neglected in the calculation of the reactivity ratios. This does not hold anymore when styrene is copolymerized with methylmethacrylate[129] or acrylonitrile (AN)[130] in o/w microemulsions. The difference in reactivity ratio values observed between microemulsion and solution polymerizations was attributed to the partitioning of MMA or AN in the droplets and the aqueous phase of the microemulsions. Furthermore, in the case of AN, whose water solubility is higher than that of MMA, the monomer reactivity ratios were found to vary not only with the initial monomer composition, but also with the

molar ratio of monomers in the microenvironment of the polymerization loci. In the system styrene, acrylic acid, and in dodecyltrimethylammonium bromide (DTAB) microemulsions initiated by KPS,[131] the styrene is solubilized within the droplets while acrylic acid is distributed between the aqueous phase and the w/o interphase. This resulted in copolymers with acrylate units randomly distributed among PS blocks. Initiation was assumed to take place at the micelle surface followed by polymerization in the micellar core.

The applications of polymers formed by micro-emulsion polymerization concern essentially porous polymers and water-soluble polymers. Most of the applications known for high-molecular weight water-soluble polymers prepared by inverse emulsion can be extended to processing in w/o microemulsions.[1] The use of a microemulsion rather than an emulsion enables one to overcome some of the problems encountered in the latter process such as poor colloidal stability, broad particle size distribution and excessive amount of aggregates formed during the reaction. In spite of their stability, inverse microlatexes are self-inverting and can be used as such in oil-recovery processes, as flocculants in paper manufacture, mining, and water treatment. The preparation of polypyrrole[132] and polyaniline[133] conducting polymers in inverse microemulsions have also been reported.

Microlatexes

The size of microlatex particles has usually been determined by QELS and TEM. As a general rule, the particles prepared in microemulsions are much smaller than those obtained by emulsion polymerization, although they still significantly exceed those of the precursor microemulsion droplets. These diameters are typically 20–60 nm when the starting microemulsions are globular (o/w or w/o). They are bigger and around 50–150 nm if the microemulsions are initially bicontinuous simply due to the larger monomer incorporations ($\approx 25\%$). As can be expected, the particle size increases upon increasing the monomer content or decreasing the surfactant[16,31,32,40,45,47,49,116] and/or the initiator concentration.[33,35,45]

The polydispersity is characterized by the analysis of the monoexponentiality of the auto-correlation function of the scattered intensity (QELS), which gives only a rough estimate of this parameter. The index of polydispersity of the particle diameter d_w/d_n is between 1.05–1.15, but some higher values (1.40) have also been reported.[31,134] If we consider w/o microlatexes, their polydispersity is thus considerably lower than that of

inverse latexes prepared by a conventional emulsion process, which have a polydispersity index around 2.[81]

Some efforts have been made to control particle size by using appropriate formulations. In one study a new class of metallosurfactants (tetradecyldiethanolamine-copper: TDEA-Cu) was used, which allowed the reduction of both particle size and surfactant concentration.[135] With this class of surfactants, the authors succeeded in getting a particle diameter as low as 14 nm (width of the distribution = 0.38).

The effect of the nature of surfactant on particle size was investigated for poly(AM-NaAMPS) microlatexes obtained by polymerization in bicontinuous microemulsions.[115] By using different nonionic surfactant blends at the optimal HLB conditions the authors showed a significant effect of this parameter on particle size. The relative proportions of ionic monomers in copolymerization reactions also have a direct effect on the particle size. The dimensions of poly(acrylamide-co-sodium acrylate) microlatex particles were shown to decrease linearly with the acrylate content in the comonomer feed.[72]

Functionalized Microlatex Particles

The large internal surface area of microemulsions can be easily modified and functionalized by simple copolymerization reactions or embedding reactions.[5,138–141] Microemulsion copolymerization of styrene with functional monomers acting as cosurfactants and in the presence of a cross-linker resulted in spherical microgels, where most of the functional groups were located at the particle surface.[138,139] The functional additives were shown to stabilize or destroy the initial microemulsions depending on their nature. Successful additives were based on methacrylate derivatives such as (dimethylamino)ethyl methacrylate (DAMA).

For most applications, it is desirable to produce particles as small as possible, but this requires a large amount of surfactant. Several procedures have been devised for the applications described below.

Metal-Complexing Microlatexes

These materials were synthesized via copolymerization of styrene in microemulsions using two comonomers,[141] which led to stable microemulsions and microlatexes, by improving the matching between surfactant and comonomer.

Another way to functionalize the surface of microlatex particles is to incorporate amphiphilic block copolymers (for example polystyrene/polyvinylpiri-dine) as cosurfactants together with the classical surfactants used in the formulation.[138,139] These block copolymers were shown to stabilize the oil–water interface and to effectively bind ions of transition and heavy metals via complexation.

Functionalized Microlatexes for Biological Applications

The use of microlatexes for biological applications is also very attractive. Conventional latexes prepared from emulsion polymerization are already classically used for such purposes, as for example in immune-assays, adsorbants for proteins, immobilization of enzymes, and antibodies and for controled release in drug delivery. The latex particle size is in the range 0.1 to 10 μm. Stable microlatexes in the nanosize range (20–30 nm) may be preferred and some procedures based on inverse microemulsion polymerization have been proposed for the preparation of nanocapsules.[1,140–143]

In immune-assay experiments, the size of particles is obviously a critical parameter for the detection sensitivity. For medical or pharmaceutical applications, attention must be paid to the problems which can be caused by the possible toxicity of the surfactant remaining in the final product. Natural, non-toxic and nondenaturating surfactants based on mixtures of lecithin and sodium chlolate were proposed for the formation of globular microemulsions.[138]

CONCLUSIONS

The field of microemulsion polymerization is a fast developing field that continues to grow. Microemulsions used as polymerization media offer new prospects for colloidal physical chemistry by yielding materials with novel and interesting properties. Future work should be directed towards (co)polymers exhibiting specific properties and microstructures resulting from micro-environment effects. The main limitation arises from the rather high surfactant levels needed. Nevertheless, thanks to careful optimization of formulations, industrial polymers derived from microemulsions are now commercially available.

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