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POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

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Progress in controlled/living polymerizations (CLP) in aqueous media***)

Part II: CONVENTIONAL POLYMERIZATION IN AQUEOUS MEDIA

Summary — A review with 66 references covering homogeneous and heterogeneous polymerization, classification of heterogeneous radical polymerizations, suspension, emulsion and mini-emulsion polymerizations, non-radical polymerizations in heterogeneous aqueous media including ionic polymerization, coordination polymerization and ROMP. Water used in place of organic solvents as medium is environmentally advantageous and economic and this fact inspires researchers to develop not only radical but also non-radical polymerization in aqueous media. The polymers prepared by conventional polymerization techniques are poorly defined in terms of *M* and *MWD*, composition and architecture. The controlled/living polymerization techniques (*cf.* Part I) allow potentially to remove this demerit.

Key words: aqueous dispersed polymerization, suspension polymerization, emulsion polymerization, mini-emulsion polymerization, aqueous anionic and cationic polymerizations, aqueous ring-opening metathesis polymerization.

The polymerization carried out in aqueous media has been receiving increasing attention for a number of reasons. The rising environmental concern and the sharp growth of pharmaceutical and medical interest in hydrophilic polymers are presumably the most important reasons. In contrast with numerous polymerization methods in organic media, the aqueous polymerization is mainly focused on radical polymerization. Nevertheless, several non-radical polymerization processes have also been accomplished in aqueous media. This part, covers conventional non-living systems.

HOMOGENEOUS POLYMERIZATION

An essential requirement for the aqueous solution polymerization is that the monomer and the resulting polymer should be sufficiently soluble in water. Some typical water-soluble monomers are listed in Table 1.

Free-radical polymerizations in aqueous systems [1] basically follow the same rules as those in the organic systems. Various initiation techniques, including ther-

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T a b l e 1. **Typical water-soluble monomers**

Monomers with heterocyclic functions	Monomers with basic functions
N-vinyl-2-pyrrolidone	acrylamide
2-vinylpyridine	methacrylamide
3-vinylpyridine	*N*-hydroxymethylacrylamide
4-vinylpyridine	*N*,*N*-dimethylacrylamide
4-methylenehydantoin	2-aminoethyl methacrylate
4-vinyl-3-morpholine	*N*,*N*-dimethylaminoethyl methacrylate
1-vinyl-2-methyl-2-imidazoline	
Monomers with acidic functions	Monomers with neutral hydroxyl functions
acrylic acid	allyl alcohol
itaconic acid	2-hydroxyethyl acrylate
methacrylic acid	2-hydroxyethyl methacrylate (polymer is insoluble in water)
allenesulfonic acid	
ethylenesulfonic acid	2-hydroxypropyl methacrylate
styrenesulfonic acid	
2-sulfoethyl methacrylate	

mal, redox, photochemical, electrochemical and radiolytic have been employed. There are, however, a few unique features of the aqueous-solution polymerization. For example, monomers with ionizable pendant groups are often seen to polymerize faster in aqueous solutions than in the bulk or in organic solvents. This is generally attributed to the increased ionic dissociation of the pendant group that produces greater electrostatic repulsion between the two growing radicals, thus remarkably increasing the k_p/k_t ratio [2]. In addition, the existence of polymer-water interactions that produce a strongly bound hydration shell also helps to protect the propagating radical center from termination [3]. Therefore, modifications of pH and ionic strength have a remarkable influence on the polymerization of these basic and acidic monomers. One of the consequences is that, in copolymerization, the reactivity ratios of two monomers, of which one or both are ionizing monomers, vary with the degree of ionization. In contrast, monomers containing neutral hydroxy groups are less sensitive to pH and ionic strength variations. Such a stability of the water-structuring center makes the hydrogels derived from these monomers very attractive for biomedical applications.

Contrary to radical polymerization, ionic polymerization and transition metal catalyzed polymerization in general are intolerant to even traces of water. A small amount of water is enough to deactivate the propagating ions by participating in the chain transfer and termination processes, or to destroy the active catalyst complexes. As a consequence, the documentation on ionic polymerizations and transition metal catalyzed polymerizations conducted in aqueous solutions is rare. Among a few exceptions, vinylpyridine salts were found to undergo spontaneous polymerization anionically in an acidic aqueous solution at room temperature [4]. The active center consisting of a zwitterion was protected by the association of the monomer through hydrophobic interactions, which explained why the anionic polymerization could proceed. Any disturbance of the association, such as dilution or rise of temperature, led to the reduction of both polymerization rate and polymer molecular weight. The anionic polymerization through carbonyl group was also achieved in aqueous solution, mainly because of the relatively weak basicity of the alkoxide anion, which suppressed the chain transfer to water. An example of such systems is the polymerization of disodium salt of ketomalonic acid in a basic aqueous solution [5]. Similarly, it is also possible to conduct cationic polymerization in aqueous solution if the monomer is more nucleophilic than water. This is the case with the ring-opening polymerization of aziridine derivatives in water [6].

Compared with the ionic polymerizations, transition metal catalyzed polymerization is more successful in aqueous media thanks to the discovery of a few water-resistant catalysts that involve late transition metals. However, most monomers and their corresponding polymers in these polymerizations are not soluble in water, real aqueous solution polymerizations are very rare, except for monomers bearing hydrophilic functional groups.

HETEROGENEOUS POLYMERIZATION

Although aqueous-solution polymerizations are of considerable interest, the number of water-soluble monomers and polymers available limits their applications. On the other hand, heterogeneous polymerization processes are applicable to a much wider range of monomers. Additionally, they offer many invaluable practical advantages in industrial applications such as low viscosity at high conversion, ready control of heat transfer and the possible direct use of the water-based product. Today, heterogeneous radical polymerization in aqueous media has become one of the most important industrial processes for synthetic polymers.

Radical polymerizations

A number of terms have been used to describe different heterogeneous radical polymerizations, such as suspension, emulsion, mini-emulsion, micro-emulsion, inverse emulsion, dispersion, and precipitation. The criteria to classify these systems depend on (*i*) the initial state of the polymerization mixture; (*ii*) the kinetics of the polymerization; (*iii*) the mechanism of particle formation; and (*iv*) the shape and size of the final polymer particles. The details have been well reviewed in the literature [7, 8]. The following is a brief introduction to three systems that are most widely applied, *i.e.* suspension, emulsion and mini-emulsion systems. It has to be noted, however, that many terms used in the literature do not follow these strict definitions. For example, the so called "emulsion" polymerization does not necessarily mean "emulsion" according to the description below, but rather a polymerization carried out in a mixture involving monomer, water and surfactant. This confusing terminology partially exemplifies the complex nature of the heterogeneous systems.

Suspension polymerization [9]

A relatively water-insoluble monomer is dispersed in the continuous aqueous phase as liquid droplets by vigorous stirring. An oil-soluble initiator is employed to initiate polymerization inside the monomer droplets. During the course of polymerization, the coalescence of monomer droplets and the adhesion of partially polymerized particles are hindered by a small amount of stabilizers. The latter may be either water soluble polymers, such as poly(*N*-vinylpyrrolidone) (PVP) and poly(vinyl alcohol-co-vinyl acetate), or insoluble inorganic salts such as talc, calcium and magnesium carbonates, silicates and phosphates.

The average number of radicals per particle ($\bar{n}$) is on the order of 10^2—10^6, therefore each particle behaves as an isolated micro reactor and the kinetics resembles that of bulk polymerization (or solution polymerization if the monomer phase contains a diluent). Consequently, the droplet size and the amount of stabilizer do not affect the polymerization rate. The continuous aqueous phase serves only to decrease the viscosity and to dissipate the heat generated in the polymerization.

The diameters of the particles obtained from suspension polymerization are usually in the range of 20—2000 μm, depending on the stirring speed, volume ratio of the monomer to water, concentration of the stabilizer, the viscosities of both phases, and the design of the reaction vessel. With a properly designed reactor and a well-stabilized suspension, monodisperse particles can be produced in agreement with theoretical predictions.

Another important property that is directly related to the application is the surface and bulk morphology of the individual particles. Particles with the polymer soluble (or swellable) in its own monomer have a smooth surface and a relatively homogeneous texture, like polystyrene and poly(methyl methacrylate). When the polymer is not soluble (or swellable) in its own monomer, the particles will have a rough surface and a porous morphology, like poly(vinyl chloride) and polyacrylonitrile. A suitable monomer diluent can control the degree of porosity and the pore structure of the particles, which is of particular interest in the production of crosslinked ion exchange resin and polymer supports.

Some typical polymers produced by suspension polymerization include polystyrene, poly(vinyl chloride), polyacrylates, poly(vinyl acetate) and their copolymers.

Emulsion polymerization [8, 10]

Typical emulsion polymerization employs two different ingredients from suspension polymerization: (*i*) The surfactant (or emulsifier) used to impart colloidal stability is composed of both hydrophilic and hydrophobic parts. Stabilization comes either from electrostatic effect (anionic and cationic surfactants), or steric effect (nonionic surfactans), or both (polyelectrolytes). The monomer is present in the micelles (5—15 nm) as well as in large droplets (10^3—10^4 nm). (*ii*) The initiator is water-soluble and the radicals are produced in the continuous aqueous phase. Accordingly, emulsion polymerization is distinguished from suspension polymerization by nucleation proceeding outside of monomer droplets (in micelles or in aqueous phase) and $\bar{n}$ on the order of 10^{-1}—10^0 owing to the small size of the particles (50—300 nm). The polymerization takes place in the monomer-swollen particles, and monomer droplets serve primarily as reservoirs to supply the consumed monomer within particles.

The number of polymerization sites (10^{17}—10^{18} cm^{-3}) is usually much larger than the number of radicals continuously generated (10^{13}—10^{15} cm^{-3} s^{-1}); therefore, the radicals tend to remain isolated in separated particles with no direct access to each other. This compartmentalization effect has a profound influence on the kinetics and the nature of the polymers formed in emulsion polymerization. A resultant distinctive feature is that both polymerization rate and degree of polymerization can be simultaneously increased, which is of particular interest for industrial applications. However, in homogeneous or suspension systems, the enhancement of the polymerization rate is always accompanied by a reduction of the molecular weight.

The kinetics of emulsion polymerization is characterized by three intervals. Interval I is the particle formation stage, represented by the increase of both the number of particles and the polymerization rate. The end of Interval I is usually marked by the disappearance of micelles, i.e. all of the surfactant has been absorbed by the polymer particles. The duration of Interval I varies in the range of 2—10% conversion, depending on the type and the concentration of surfactants, initiation rate, solubility of monomers in water, *etc.* Polymerizations starting with Interval I are called the "*ab initio* emulsion polymerizations". Because the nature of nucleation has been poorly understood so far, it is often preferable to bypass Interval I by starting an emulsion polymerization with preformed polymer particles. Such polymerizations beginning directly with Interval II are called the "seeded emulsion polymerizations". During Interval II, both the particle number and the monomer concentration inside the particles remain approximately constant. Accordingly, the polymerization rate is relatively constant, whereas the particles increase in size as the monomers continue to diffuse from the droplets to the particles through the aqueous phase. Interval II may extend from 5—10% to 50—70% conversion, ending with the disappearance of monomer droplets. Interval III commences with a reduction of polymerization rate, resulting from the decreasing monomer concentration inside the polymer particles in spite of the unchanged number of particles. Thus, a first-order kinetics is expected to hold true in this final stage until a gel effect takes over, where the polymerization rate starts to increase again. The various phases presented in each of the three intervals and the corresponding kinetics are depicted in Fig. 1.

polymerization. This is basically due to the fact that, rather than the rate of chain termination, it is the entry rate of the radicals into the particles that controls the lifetime of each growing chain. Hence in many cases, chain transfer agents are intentionally added to the system in order to adjust the molecular weight to a desired range. The molecular weight distribution is generally larger than in homogeneous systems by theory. However, the opposite is also observed due to the large deviation from the theoretical behavior in the homogeneous systems [13].

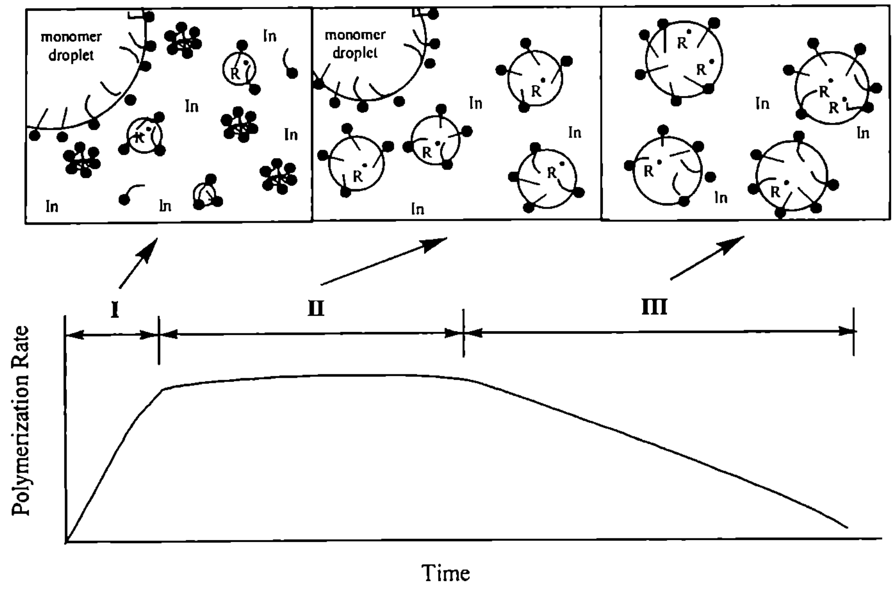


Fig. 1. The three intervals of an ab initio emulsion polymerization and their kinetics

Many theoretical descriptions concerning the unique kinetics of emulsion polymerization have been developed [11, 12]. The most commonly applied is the one established by Smith and Ewart [12], who classified all emulsion polymerizations into three cases: (*i*) Case 1, $\tilde{n} < 0.5$. This is applicable when radicals easily escape from the particles (*i.e.*, significant transfer reaction) without re-entry (*i.e.*, termination in aqueous phase), such as vinyl acetate and vinyl chloride radicals that have a high chain-transfer constant to monomer. In this case, the polymerization rate is little affected by the number of particles. (*ii*) Case 2, $\tilde{n} = 0.5$. This case is also referred to as the "zero-one" system, and is applicable to most emulsion polymerizations. The polymerization rate shows strong dependence on the number of particles, hence the surfactant and initiator concentrations are of critical importance. (*iii*) Case 3, $\tilde{n} > 0.5$. This occurs when the particle size is sufficiently large (0.1—1 μm) or the viscosity inside the particle is high enough (at high conversion) so that two or more radicals can coexist within a single particle without instantaneous termination. This case leads to a "pseudo-bulk" kinetics, which is indistinguishable from that of the equivalent homogeneous system. (pseudo-bulk kinetics can also be observed with $\tilde{n} \leq 0.5$ under certain circumstances, therefore, pseudo-bulk system ≠ Case 3) [8].

The molecular weights of the polymers obtained from emulsion polymerization (usually in the range of millions) are significantly higher than those obtained from bulk

Emulsion polymerization has been the dominant process in the synthesis of poly(vinyl acetate), poly(chloroprene), acrylic copolymers, and diene-based synthetic rubbers. It is also widely used in polymerization of other monomers such as methacrylates, vinyl chloride, acrylamide, fluorinated ethylenes, *etc.*

Mini-emulsion polymerization [14, 15]

The concept of mini-emulsion polymerization is to produce a latex which is a 1:1 copy of the original droplets so as to achieve a direct control over the number of particles. This is accomplished by reducing the monomer droplets to submicronic size (50—500 nm) by using a strong shear force such as ultrasonication. An enhanced stabilization of these tiny monomer droplets comes from the addition of the so called "co-surfactant" (usually ultra hydrophobes such as hexadecane and hexadecanol). The function of the co-surfactant is to retard the diffusion of the monomer out of the monomer droplets (Ostwald ripening) with a balanced osmotic pressure and the Laplace pressure.

Because of the dramatically reduced sizes, the total interfacial area of droplets is significantly increased, which allows droplets to compete readily with monomer-swollen micelles for radical capture. In fact, most mini-emulsion polymerizations are carried out with a surfactant concentration below the critical micellar concentration (cmc), so that the monomer droplets become the principal locus of particle nucleation (homogeneous nucleation is still possible).

Technically, mini-emulsion polymerization offers some unique advantages over an emulsion polymerization. Both water-soluble and oil-soluble initiators can be used to generate stable latexes with small particles (50—500 nm). This process is especially useful for polymerizations involving an ingredient highly insoluble in water, which transports slowly through the aqueous phase in an emulsion polymerization. It is also superior in encapsulating various inert materials (such as dye or pigment) in the final particles, in preparing latexes with a high solids content, or in conducting copolymerizations of monomers with remarkably different water solubilities. In the final case, an increased control over the copolymer composition can be achieved, which is not affected by variations other than monomer reactivities.

An ideal mini-emulsion polymerization, *i.e.*, every droplet is nucleated and transformed into a polymer particle, displays a kinetics different from that of an emulsion polymerization [16]. After reaching a maximum polymerization rate, the particle formation stage (Interval I) is immediately followed by Interval III (same definition as in emulsion polymerization) with a steadily dec- reasing rate. In emulsion polymerization Interval II, which is characterized by a constant polymerization rate, is missing in the mini-emulsion system. This is so because the transportation of monomer is negligible in mini-emulsion polymerization. The polymerization rate is affected by the surfactant concentration but not by the initiator concentration, because the latter does not change the number of particles.

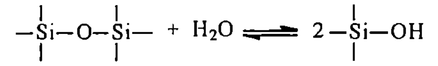
In reality, however, not all monomer droplets are successfully nucleated. The efficiency of droplet nucleation ranges from 20% [17] to 95% [18]. This presumably originates from the slow rate of radical absorption by monomer droplets, which also results in an unusually long nucleation stage. Accordingly, the kinetics is disturbed from the ideal case, as diagnosed by the influence of the initiator concentration on both the polymerization rate and the number of particles. This incomplete droplet nucleation undermines the advantages expected for mini-emulsion systems, *i.e.*, direct control over the particle size and composition. El-Aasser *et al.* [19] found that adding a small amount (≤2 wt % *vs.* monomer) of preformed polymer to the monomer phase prior to the forming mini-emulsion, allows to achieve a 100% nucleation efficiency.

The research on mini-emulsion polymerization has been conducted for styrene (S), butyl acrylate (BA), methyl methacrylate (MMA), vinyl acetate (VAc), vinyl 2-ethylhexanoate (V2EH), as well as a number of copolymerization systems [14].

Non-radical polymerizations

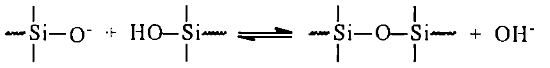
Ionic polymerization

The first example of ionic polymerization in aqueous emulsion was reported by Hyde and Wehrly [20]. Permethylcyclosiloxanes were polymerized *via* the cationic mechanism in the presence of a cationic emulsifier. Stable latexes were obtained with the particle size much smaller than that of the initial monomer dispersion. The surfactant served partially as a source of the active catalyst of the polymerization upon addition of a water-soluble base. Water, no longer an inert suspending medium, participated in the reaction and consequently affected the molecule weight of the resulting polymer (eq. 1). Accordingly, both temperature and the substituent attached to the silicon have a significant influence on the final molecular weight.

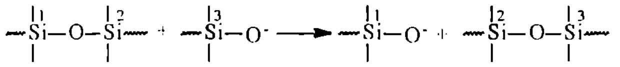


$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O} \rightleftharpoons 2-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} \qquad (1)$$

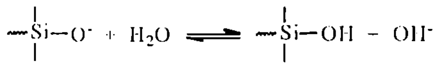
Later, a number of anionic emulsion polymerizations have also been reported for cyclic siloxanes [21] in the presence of anionic surface active catalysts; and for cyclic sulfides initiated by zinc or cadmium salts [22]. The former polymerizations could result in polymers with narrow molecular weight distributions ($1.1 < M_w/M_n < 1.4$) up to high yields (70%), accompanied by increasing molecular weights as conversion was increased. However, these are not CLPs, because the increase in molecular weight was caused by the condensation reaction between the anionic growing species and the OH-ended polymeric silanol (eq. 2), leading to a decrease in the number of polymer chains. This was particularly obvious at conversions higher than 70% when the concentration of silanol became significant. Meanwhile, chain transfer to polymers (eq. 3) and water (eq.4) also took place.



$$\sim\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O^-} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}\sim \rightleftharpoons \sim\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}\sim + \mathrm{OH^-} \qquad (2)$$



$$\sim\overset{|1}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|2}{\underset{|}{\mathrm{Si}}}\sim + \sim\overset{|3}{\underset{|}{\mathrm{Si}}}-\mathrm{O^-} \longrightarrow \sim\overset{|1}{\underset{|}{\mathrm{Si}}}-\mathrm{O^-} + \sim\overset{|2}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|3}{\underset{|}{\mathrm{Si}}}\sim \qquad (3)$$



$$\sim\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O^-} + \mathrm{H_2O} \rightleftharpoons \sim\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} - \mathrm{OH^-} \qquad (4)$$

Coordination polymerization and ROMP

Highly stereoregular polydienes can be synthesized in aqueous emulsions *via* coordination polymerizations. For example, crystalline *trans*-1,4-polybutadiene was obtained in the presence of Rh and Ir containing catalysts [23]. Synthesis of *trans*- and *cis*-1,3-polypentadiene was achieved also with a rhodium salt catalyst [24]. Syndiotactic 1,2-polybutadiene was obtained by using a cobalt catalyst [25]. The success of these polymerizations was attributed to the stability of the noble metal catalysts toward water (and air). On the other hand, water did participate in the polymerization by acting as a hydrogen donor either in the termination step or in some side reactions [26]. The active catalyst was a π-allylic complex formed between olefin and Rh(I), Ir(I) or Co(0) [25—27]. The double bond character between the monomer and the metal provided an explanation for the stereospecificity of the insertion. Interestingly, in the Rh catalyzed polymerizations, the emulsifiers acted as ligands for the metal and therefore influenced the stability of the propagating chain, possibly by changing the environment of the complex against termination by water. Both the concentration and the chemical structure of the emulsifiers were important. Only two types of surfactants were effective, *i.e.*, sodium lauryl sulfate and sodium alkyl benzene sulfonates with alkyl chains greater than C_5 [28]. No latex properties have been reported in any of these polymerizations.

The coordination polymerization of ethylene in aqueous media is more challenging. The polar medium requires the use of late transition metal complexes, but these complexes in general favor β-hydride elimination, yielding dimers and oligomers. The first success was achieved by using a palladium/*bis*-phosphine complex as the catalyst to obtain alternating copolymers of ethylene and/or propylene with carbon monoxide [29]. However, the catalyst productivity in water was much lower than usually observed in organic solvents on account of poor solubility of the monomers in water as well as the coordination of water to the catalyst center. A rhodium based catalyst was also used to polymerize ethylene in water, but the rate was extremely slow (1 turnover/day) [30]. More active catalysts were later found by Brookhart *et al.* (Pd) [31] and Tomov *et al.* (Ni) [32]. However, all of the above polymerizations were carried out in the absence of surfactants and no latex was formed. The first aqueous emulsion polymerization of ethylene, catalyzed by an organometallic catalyst and in the presence of an anionic surfactant, was discovered by Tomov *et al.* [33]. The oil-soluble catalysts, binuclear nickel(0)-ylide complexes, display high productivity under emulsion or mini-emulsion conditions. HDPE latex was produced with average particle sizes in the range of 130—280 nm (emulsion) or 620—730 nm (mini-emulsion). The solid contents, were very low (~1%), however. The molecular weights ($\overline{M}_w$) are on the order of 10^4—10^5. Slightly later, Mecking *et al.* [34] reported another nickel(II) catalyzed ethylene emulsion polymerization in the presence of ionic or nonionic surfactants. Emulsions with particle size in the range of 80—300 nm were obtained at a catalyst productivity of 1300 mol(ethylene)/mol(Ni) in 2 h.

Other examples of coordination polymerizations include the polymerization of isocyanides catalyzed by nickel complexes [35] and the 1,2-addition polymerization of norbornene catalyzed by $PdCl_2$ complexes [36]. The latter system is very interesting, since nanoparticles with a size range of 10—17 nm were obtained at 3—6% surfactant (SDS) level. Such small particles are usually observed in micro-emulsions where a large quantity of surfactant in combination with a cosurfactant is used [37]. The particle formation was strongly affected by pH, and the latex bearing functional groups such as alcohol or sugar residues were also prepared. However, the molecular weights of the polymers were low ($\overline{M}_n \approx 1000$). This was attributed to the coordination of the emulsifiers to the palladium and thus resulted in numerous chain terminations.

The earliest report on ROMP in an aqueous emulsion appeared in 1965. Norbornene and derivatives were polymerized by using iridium, osmium and ruthenium catalysts [38]. The problem, however, was that both the polymer yields and the tolerance of the catalysts toward functionality were low. More than twenty years later, Novak and Grubbs [39] discovered much more active ruthenium(II) catalysts for the polymerization of 7-oxanorbornenes. The polymerization was initiated even faster in water than in organic solvents. Polymers bearing a variety of functionalities were obtained in almost quantitative yields, with high molecular weights and relatively low polydispersities [40]. No surfactant was used in these polymerizations, and the polymers precipitated out from the reaction mixture. Later, more catalysts such as ruthenium, iridium and osmium complexes were found successful in polymerizing functionalized norbornenes and 7-oxanorbornenes in water, with or without surfactant [41, 42]. When a surfactant was used, the latex particle diameters were typically 40—100 nm and decreased with the increasing surfactant concentration [42].

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