# Articles

## Catalytic Polymerization of Ethylene in Emulsion

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ABSTRACT: Ethylene polymerization catalyzed by nickel(II) keto−ylide complexes has been performed in water to yield a latex of linear PE. Colloidal stability is highly enhanced by the use of a miniemulsion technique to disperse the catalyst prior contact with the monomer. Latex of typically 200 nm particle diameters and up to 10% solids are generated by this method. The influence of several factors (temperature, pressure, solids) onto the polymerization is studied in detail. The surfactant adsorption isotherms onto these highly crystalline and nonpolar particles are also presented.

### Introduction

Emulsion polymerization is a widely spread polymer manufacturing process (roughly 50% of the radical polymers are synthesized by this method).[1] Obviously, the use of water as a suspending medium is an environmental advantage. Moreover, because of its very high heat capacity, water can be safely used as a continuous phase or a solvent for carrying out very exothermic reactions such as polymerizations. Heterophase polymerizations (in water or any other medium) also benefit from the fact that even at high solids (up to 60% polymer volume fraction in the liquid), the viscosity remains low or moderate. Finally, the polymer, under the form of a latex, is free-flowing; therefore, it is easily formulated, and often it does not require further processing. Of course, these numerous advantages are counterbalanced by several drawbacks: generally the polymerization is not extremely reproducible (especially during the nucleation step), and the rheology of the product is complicated. The latex, under its colloidal form, needs to be stabilized by surfactants, and it is prone to aggregation due to several physical factors (freezing, increased ionic strength, presence of organics). Finally, it is nearly exclusively restricted to conventional radical chemistry[2] because of the poisoning effect of water on most nonradical active species (anionic, cationic, organometallic ones). Yet, the gap between the field of emulsion and organometallic chemistry is fast being filled, due to developments in atom transfer radical polymerization (ATRP) in emulsion[3−6] and to recent works on late transition metal catalyzed polymerization in water. For example, with the apparition of highly active water tolerant Ru Grubbs catalysts,[7−9] ring-opening metathesis polymerization (ROMP) is now easily performed in emulsion,[10−13] to yield nanoparticles of olefinic polymers with high conversions. Specific hydrosoluble alkylidenes bearing phosphines containing ammonium salts have been shown to polymerize with rapid and quantitative initiation in the presence of an organic acid (DCl).[10,11] Alternating copolymers of olefins and carbon monoxide can also be produced in water.[14] For this purpose, Sen has developed water-soluble palladium compounds stabilized by sulfonated dppp and 4,7-diphenyl-1,10-phenanthroline. An important decrease in the activity of these water-soluble catalysts is observed when compared to their organic analogues. Recently, Sheldon[15,16] and Bianchini[17] have reported very active water-soluble Pd(II) complexes containing sulfonated ligands. The productivities in water are almost as high as the ones obtained in MeOH (6−7 kg of C2/CO copolymer per gram of Pd).

In our laboratory, we have developed neutral nickel(II) complexes for catalytic α-olefin polymerization that we can use either in suspension/solution in organic solvents or in the presence of water.[18,19] For example, using some mononuclear and binuclear P,O-chelated nickel complexes,[18,20] derived from the complexes developed by Keim[21−24] and Klabunde,[25−28] we have synthesized linear PE with activities competing to those of metallocenes catalysts.[29−31] Especially striking were the results obtained with fluorinated P,O-chelated nickel complexes in the homopolymerization of α-olefins, since we have showed that these catalysts are very active in the presence of an aqueous medium, albeit with a loss of activity relative to anhydrous conditions. During our work, Mecking has reported a preliminary communication about the polymerization of ethylene in water[32] using Brookhart type catalysts[33,34] and Klabunde type catalysts.[35,36] The results confirm that it is possible to polymerize in an emulsion related process, in the presence of an acetone water mixture (5:95). Although pressures as high as 725 psi are used, activities and yields are low (0.17 kg/(g·h) and 2.2 g of polymer in 100 mL of water). In the present paper, we would

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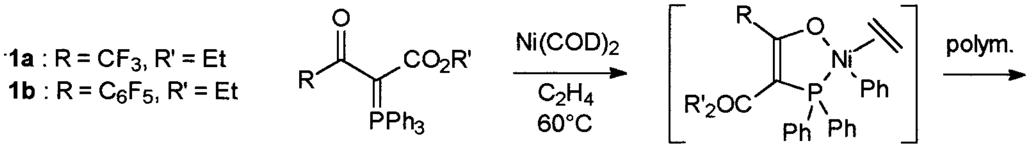
**Scheme 1. In Situ Catalyst Preparation**



**1** **2**

like to report the catalytic ethylene polymerization in emulsion using highly active fluorinated catalysts. It will be seen that, to reach reasonable solid contents and reasonable activities with no floc, it is not only necessary to use the most active catalysts, as a measurable loss of activities is observed under aqueous conditions, but also crucial to conveniently disperse the catalyst. The influences of pressure, temperature, and surfactant nature and concentration on colloidal characteristics of the latex are also analyzed in detail. Note that a similar latex cannot be prepared by free radical polymerization in emulsion, as it leads only to LDPE, with a substantial amount of surfactant grafting under drastic pressure and temperature conditions.[37]

## Experimental Section

Ligand **1a**, Ni(COD)$_2$, and surfactants were purchased from a commercial supplier. Other ligands were synthesized according to the literature.[18] All organic solvents and reagents were dried and degassed, according to standard Schlenk techniques. THF was distilled on sodium benzophenone prior use. Ultrapure water ($\sigma = 18.2$ MΩ·cm) was obtained from a Purite HP 50 analyst apparatus and filtered three times through a 0.02 $\mu$m filter. Water was heavily degassed and decarbonated with argon, in order for the pH to be between 6.8 and 7.2. NMR analysis was effected on a 400 MHz Bruker instrument. Polymer analyses were made in a mixture of $d_3$-trichloroethane and $d_6$-benzene at 90 °C. GPC was determined in 1,3,4-trichlorobenzene at 145 °C, using a Waters AlC instrument. Particle size measurements were effected on a LoC Malvern QELS instrument and a 4800S autosizer from Malvern equipped with a 50 mW laser. Particle size distribution was also followed on a FlowFFF (flow field flow universal fractionation) from FFF Corp., equipped with a static light scattering detector, MiniDawn from Wyatt Technology.[38]

TEM measurements were effected on Philips 120-GM$_2$ ($V = 80$ kV). Negative staining agents (uranyl acetate) were sometimes used to increase the contrast.[38] Surface tension measurements were effected on Krüss K12 interfacial balance, using the Wilhelmy method.

**Typical (Mini)emulsion Polymerization Procedure.** In a Schlenk tube, 33 mg of Ni(COD)$_2$ is dissolved in 10 mL of toluene. This solution is added to 13.3 mg of ligand **1a**. The solution is stirred for 15 min and then added to 300 mL of water containing 5 g/L of surfactant in a flask. In the case of miniemulsion experiment, hexadecane is added to the biphasic mixture (concentration 10 g/L), and the mixture is then emulsified with an 600 W ultrasonic Branson sonifier for 2 min under magnetic stirring (and under argon). Alternatively, homogenization with an ultraturrax can be effected for 10 min. Finally, the mixture (colloidal dispersion in minemulsion and biphasic in emulsion) is cannula transferred into a 1 L stainless steel reactor, equipped with a mechanical stirrer (magnetic induction), a thermocouple, a sampling valve, and a external jacket heated at 70 °C. Ethylene is immediately introduced at 20 bar. Ethylene is continuously fed into the reactor at the set pressure from a high-pressure 5.5 L reservoir. The pressure drop in the reservoir is recorded, to assess activity and productivity measurements. The reaction medium (300 mL) is collected after having vented the remaining ethylene through a micrometric manifold slowly enough to prevent latex flocculation through creaming. The latex is filtered to determine the floc content, and the liquid residue is analyzed by DLS and gravimetry.

## Catalytic Ethylene Polymerization in Emulsion

**Catalyst Synthesis.** We have recently developed very active nickel catalysts for the polymerization of ethylene that are also active in the polymerization of α-olefins and in the presence of water.[18] These catalysts are based on very electron-deficient fluorinated ligands which induce a high acidity to the metal. The keto–ylide ligands described in Scheme 1 selected for their high electron-withdrawing properties can be easily synthesized in two steps.[39]

The mechanism described in Scheme 1 has been discussed in length by Keim and Klabunde.[26,40] With fluorinated ylides, we have found that the complexation of the fluorinated ligands onto Ni(COD)$_2$ was more difficult than with more electron-rich keto–ylide ligands, as proven by a NMR study.[18] We have also shown that the synthesis of the active complex **2** can be done in situ by mixing the ligand with one or more equivalents of Ni(COD)$_2$ in toluene or in benzene upon addition of ethylene at temperatures of 50 °C or more.

**Direct Emulsification and Miniemulsion.** In emulsion polymerization, the initiator (preferably water-soluble) is mixed with water, surfactant, and a hydrophobic monomer. During the nucleation step, particles are formed through micellar nucleation or through precipitation of polymer grown in water (homogeneous nucleation). In our case, when the catalyst, dissolved in a small amount of toluene, is stirred in the presence of surfactant, high amounts of floc are generated (entries 1–6, Table 1). Most of the product is constituted of large particles ($>1$ $\mu$m) of polyethylene suspended in water: these particles sedimentate rapidly when the stirring is stopped (creaming), due to the density difference between water and polyethylene. They are floating on the surface of the aqueous phase (when stirring is stopped), and they can be collected by filtration through a 25–50 $\mu$m fritted filter. The white milky filtrate contains an extremely low amount of polymer ($\ll$1%). The particles constituting the filtrate can be characterized by light scattering, as typical colloidal objects. Usually, dynamic light scattering measurement indicates that the filtrate is constituted of particles between 250 and 750 nm (very broad particle size distribution). In summary, the product of the reaction (before filtration) looks like a latex (because of the white milky aspect) but is indeed predominately a suspension of large PE particles. This behavior is independent of surfactant choice (sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide, nonylphenol ethoxylated 30, nonylphenol ethoxylated 40, Dowfax 2A, poly(vinylpyrrolidone) (MW 340 kg/mol)) and surfactant concentration (entries 2 and 3, Table 1).

In miniemulsions, a high shear is applied to the reaction medium before the polymerization, using an ultraturax homogenizer or an ultrasonic processor, to

**Table 1. Representative Emulsion Polymerization Results Carried Out Using Catalyst 1a; Experiments 2−6 Were Performed Using the Emulsion Technique, Whereas Experiments 7−13 Using the Miniemulsion One**

| | catalysts | | | | | | emulsion | | | | | | PE | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no. | $N$ ($\mu$mol) | toluene (mL) | $P$ (bar) | $T$ (°C) | activity (kg/($g_{Ni}$ h)) | prod[a] (kg/$g_{Ni}$) | $V_{H_2O}$ (mL) | $c_{SDS}$ [b] (g/L) | $c_{C16}$ [b] (g/L) | part. size[c] | sc[d] (%) | floc (%) | $M_w$ [j] | Ip |
| 1[e] | 2 | 400 | 3 | 70 | >2000 | 272 | 0 | 0 | 0 | | | | 3.5 | 2.7 |
| 2 | 21 | 32 | 25 | 65 | 23 | | 500 | 2 | | | 0.35 | | 4.2 | 3.2 |
| 3 | 23 | 36 | 25 | 65 | 40 | | 500 | 20 | | | 1.98 | | 4.1 | 3.0 |
| 4 | 25 | 12 | 20 | 75 | 70 | | 500 | 5 | | 850 | 0.95 | 98 | 3.9 | 3.7 |
| 5 | 20 | 10 | 20 | 45 | 3 | | 500 | 5 | | | 0.52 | | 3.8 | 2.8 |
| 6 | 30 | 24 | 5 | 65 | 5 | | 500 | 5 | | | 0.50 | | 3.2 | 3.8 |
| 7 | 31 | 20 | 25 | 70 | 23 | 3 | 500 | 5 | 12 | 606[h] | 2.2 | nm[i] | 4.1 | 3.5 |
| 8 | 31 | 10 | 25 | 70 | 40 | 7 | 500 | 5 | 8 | 242 | 3.7 | nm[i] | 4.0 | 3.4 |
| 9 | 32 | 10 | 25 | 65 | 45 | 49 | 800 | 5 | 10 | 242 | 8.5 | nm[i] | 4.1 | 3.2 |
| 10 | 31 | 20 | 25 | 65 | 83 | 46 | 500 | 5 | 10 | 208 | 10.2 | nm[i] | 3.9 | 3.2 |
| 11 | 16 | 15 | 25 | 70 | 56 | 13 | 500 | 3 | 6 | 366 | 1.5 | nm[i] | 3.8 | 3.3 |
| 12 | 22 | 3[g] | 25 | 65 | 6 | 6 | 300 | 1.5 | 3 | 410 | 2.2 | nm[i] | 3.9 | 3.1 |
| 13[f] | 32 | 10 | 25 | 65 | 8 | 9 | 300 | 1.5 | 3 | 467 | 3.9 | nm[i] | 4.1 | 3.1 |

[a] Productivity in the aqueous phase (floc not taken into account). [b] Concentrations in the volume of water. [c] Particle size in nm determined by dynamic light scattering at low concentrations. [d] Solid content determined by gravimetry of the filtered latex. [e] Experiment in organic phase (activity and productivity in organic phase). [f] Catalysts used is **1b**. [g] Benzene was used instead of toluene. [h] Very low power used for this emulsification. [i] Non measurable (less than 3% of the total solid polymer). [j] In kg/mol, determined by GPC at high temperature vs polyethylene standards uncorrected.

disperse the monomer into small thermodynamically stable droplets (size between 50 and 500 nm) where the polymerization will take place.[41−45] A hydrophobic agent (usually hexadecane) is added to the organic phase to prevent the Ostwald ripening leading to droplet coalescence. In radical miniemulsion polymerization, it is usually the monomer that is dispersed, and after polymerization, the latex particles have a final size that corresponds to the initial monomer droplet size. In our case, the catalytic solution is miniemulsified. As our catalysts are very active in emulsion polymerization, the amount of catalytic solution to disperse is very small compared to the amount of polymer generated at the end of the polymerization: as a result, the amount of VOC in the latex is low. Obviously, the best alternative would be to disperse the catalyst in the absence of organic solvent, and we are currently investigating methods to achieve it. We have observed a drastic effect on the stability of the latex, when we use a miniemulsified catalytic solution. In all cases, the amount of floc generated (mostly due to splattering of the latex on the upper wall of the reactor and the stirrer) is so low that it is not possible to quantitate it accurately. With this method, lattices of linear PE at 10% polymer content could be generated. We will now embark on a detailed analysis of the influence of different parameters on the catalytic activity and colloidal stability.

**Polymerization in Water: Influence on Catalyst Activity.** As we can expect, in the presence of a very large excess of aqueous phase (from 94 to 99.3% in volume), the activity is decreased by up to 2 orders of magnitude compared to organic phase polymerizations (entry 1 vs all other entries, Table 1). But, the reported activities are still high for late transition metal catalysts and exceptional considering the polarity of the reaction medium. More surprisingly, the presence of a surfactant, in concentration of 2−30 g/L, is not influencing the activity although this component is highly polar. As for an organic phase polymerization, lower activities for catalyst **1b** compared to **1a** are observed in emulsion (entries 9 and 13). The emulsion polymer molecular weight is comparable to the solution or heptane suspension molecular weight: for example, 3000 g/mol for a PE synthesized in organic phase and 3500 g/mol for the emulsion one. $^1$H and $^{13}$C NMR analyses indicate that essentially linear PE is made by the emulsion process. 0.15 long chain branching, 0 methyl branching, and 0.2 internal vinyl unsaturations are found for 1000 carbons (entry 9 of Table 1).[46] It appears that in the presence of water the mechanism of chain transfer and termination is quite similar to the ones observed in organic solution.

The emulsification process does not have a drastic effect on the catalytic activity (entries 4−10 and 3−11), but it seems that the miniemulsion method gives better results in terms of activity. In miniemulsion, the catalyst droplets are more hydrophobic than in emulsion thanks to the addition of a hydrophobic compound. Thus, the deactivating effect of water may be slightly reduced. Another explanation could be that the catalyst is more dispersed with miniemulsion as the surface offered by the organic phase is 3 orders of magnitude greater in the case of miniemulsion compared to our emulsion process; thus, ethylene transfer through water from gas phase to particles is easier: this limits the problem of ethylene diffusion inside the particle. Activity in emulsion and miniemulsion is strongly dependent on the polymerization temperature. For example, at 40 °C, the catalyst is not active at all, whereas activities are important at 65 °C (entries 3 and 4). We believe that the active species are formed in significant amounts only by heating above 50 °C.[18] In addition, an increase in pressure translates into an increase in the activity (entries 4 and 6). Clearly, at higher pressure, more ethylene is dissolved in water and in polymer particles.

There is no obvious trend between activity and the volume of organic solvent used for catalyst dissolution. We believe that there are two antagonistic factors influencing activity: because the solubility of ethylene is important in the organic solvent, the activity may increase with the volume of solvent (entries 11 and 12). Yet, initial dispersion, after miniemulsification, leads to a droplets size that increases with solvent volume (entries 7 and 8). Thus, because of poorer dispersion, larger particles are created, and active sites are less accessible.

**Latex Characteristics.** We have looked at the influence of the surfactant concentration on colloidal stability: larger, less stable particles are obtained in the case of low concentration of surfactant (entries 10, 12, and 13). Note that, with small amount of surfactants, initial dispersion after miniemulsification consists of large particles. However, we have not found any direct

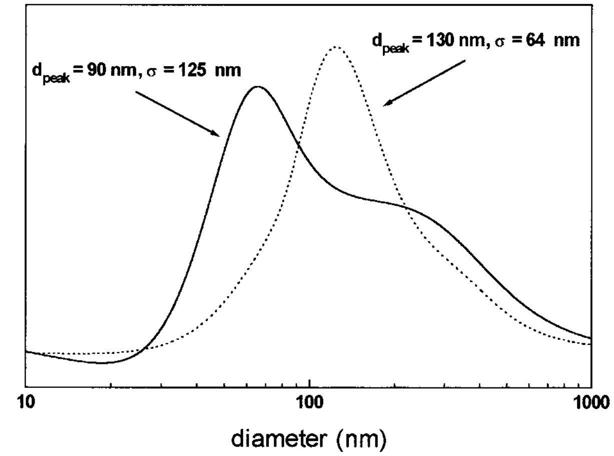


**Figure 1.** f-FFF fractograms of the initial miniemulsion (doted line) and of the final latex (plain line).

correlation between the initial droplet size and the final particle size. In general, the number of polymer particles is much larger than the initial number of emulsion droplets. For example, the number of particles for entry 10 of Table 1 is 1.07 × $10^{16}$ part/L, whereas the initial number of droplets was 4.29 × $10^{14}$ (size of the droplets: 487 nm). Very precise results can be harvested through the use of f-FFF.[47] Figure 1 displays the fractogram for the initial emulsion of catalyst, benzene, and water and for the final latex in a typical experiment. Clearly, the two distributions (starting and final) are highly polydispersed, but there is no obvious relationship between both, as the initial distribution is quite symmetrical whereas the final is displaced toward smaller particle size. Note that a benzene or toluene droplet distribution is only slightly affected when exposed to 25 bar ethylene pressure: in the case of distribution shown in Figure 1, the average is shifted from 130 nm to 120 nm right after exposure to ethylene. At this stage, the mechanism of particle formation is still not elucidated. But it seems that the nucleation mechanism needs to include a step in which the catalyst, although extremely hydrophobic, is transferred from the initial droplet to a new site. To our knowledge, such a behavior is never encountered in radical emulsion polymerization.[48]

To find a suitable surfactant for the stabilization of the polymer particles, we have determined the adsorption energy of different surfactants on a surfactant-free linear PE latex. For this purpose, a 2% in weight latex has been repetitively washed over a mixed bed $H^+$ and $OH^-$ exchanging resin until the conductivity is under 10 $\mu$S/cm and the surface tension measurement close to 72 mN/m. Surfactant is then gradually added, and the drop of surface tension is recorded. The amount of surfactant adsorbed onto the latex particle surface can be deduced from the difference of cmc in the presence and in the absence of latex.[49−51] Two anionic surfactants were used (SDS and DOWFAX-2A). In the case of SDS, the specific surface coverage per surfactant molecule is 38 $Å^2$ and for Dowfax it is 58 $Å^2$. For the nonionic NP30 surfactant, a very high and unrealistic specific surface coverage has been found (~350 $Å^2$). This seemingly indicates that the surfactant has a very low affinity for this polymer surface, and this is also confirmed by a very low adsorption energy (−12 kcal/mol for SDS). For Dowfax, the adsorption energy is typical of an hydrophobic latex adsorption energy (−21 kcal/mol).

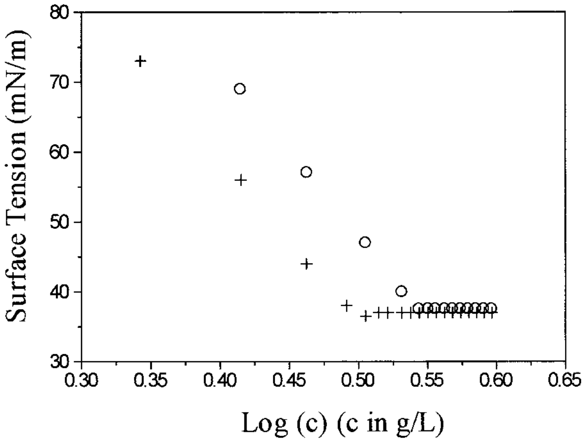


**Figure 2.** Surface tension = $f(\log(c))$ curves for the addition of SDS to a solution of water (crosses) and to a latex (hollow circles).

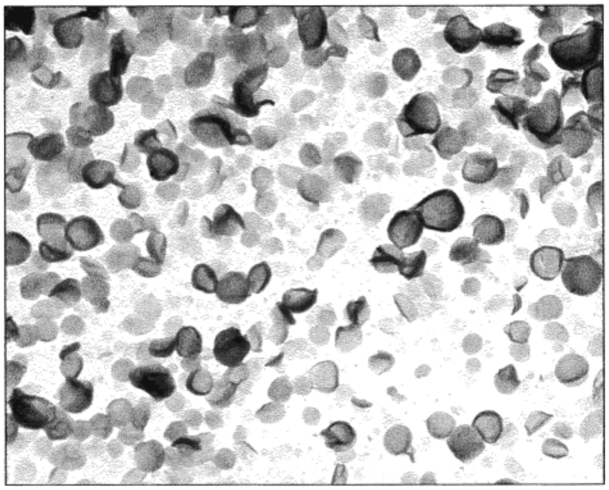


**Figure 3.** Transmission electron microscopy of a PE latex (entry 10 in Table 1).

DSC measurements of the polymers synthesized in emulsion indicate a crystallinity between 60 and 70% as determined by the ratio of the enthalpy of the melting polymer to the one of a 100% crystalline PE. The crystallinity of these polymers confers a nonspherical shape to the particles as shown by the rugged surface (Figure 3). Usually, one expects to see latex particles made of homopolymers to be perfectly spherical as they tend to minimize the ratio surface to volume. Nonspherical particles occur when the crystallization rate is faster than the particle growth. Notably, the melting point of our particles as determined by DSC is comprised between 125 and 130 °C, as expected for a low MW linear PE. Therefore, despite the fact that these particles have a totally nonpolar surface, they cannot minimize their surface with water. In this regard the linear PE latex differs completely from a typical radical made latex. In radical ethylene polymerization, grafting to the surfactant is observed, thus generating a high amount of sulfate or carboxyl groups onto the surface.[37]

## Conclusion

We have reported the synthesis of stable lattices of linear PE by a nonradical route. The water-resistant organometallic catalysts used are P,O-chelated nickel(II) complexes. The stability of the lattices is strongly dependent on the dispersion of the catalytic homogeneous organic solution. Only miniemulsion, obtained by ultrasonification, leads to stable polymer particles of size ranging from 100 to 500 nm. Future work on copolymerization and on core–shell particles is in progress.

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