Polymers

Aqueous Dispersions of Extraordinarily Small Polyethylene Nanoparticles**

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Dedicated to Professor Wilhelm Keim on the occasion of his 70th birthday

Emulsion polymerization is among the most important polymerization processes.[1] As a product, polymer latices that are stable colloidal aqueous dispersions of polymer particles of about 50 nm to 1 μm in size are obtained. About ten million tons annually of polymer latices are used for a variety of applications, such as environmentally friendly coatings and paints.

To date, polymer latices are produced industrially by free-radical polymerization exclusively. Styrene–butadiene copolymers, acrylate homo- and copolymers, and vinyl acetate polymers are the major industrial products.[1,2] The range of polymer microstructures accessible by free-radical polymerization and corresponding materials properties is limited. For example, the synthesis of dispersions of saturated inert polymers, which do not bear hydrolyzable groups is a challenge.[1] It is desirable to synthesize dispersions from simple olefins obtained directly from cracking of hydrocarbon feedstocks. This process would avoid the need to convert the cracked products to monomers such as acrylates or vinyl esters, which consumes energy and raw materials.[3] We and the group of Claverie have recently reported the synthesis and properties of polyethylene dispersions by catalytic polymerization in emulsion.[4–6]

For traditional free-radical polymerization, the synthesis of very small particles is the subject of increasingly intense effort.[7,8] Microemulsion polymerization is a particularly suitable, albeit special, technique. Latices of, for example, polystyrene particles as small as 10 nm diameter have been prepared by microemulsion polymerization.[8] A strong limitation is that microemulsions only form under specific

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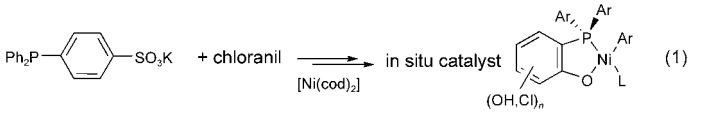
conditions that require large quantities of alcohols, or other organic solvents, and surfactants.

Concerning the aforementioned catalytic polymerization of ethylene in emulsion, a fine initial dispersion of the catalyst at the beginning of the reaction is a general prerequisite to obtain a large number of sub-micrometer polymer particles, that is, a polymer latex. This is usually achieved by using a miniemulsion technique. A solution of a liphophilic catalyst precursor (a nickel(II) complex) in a small amount of hydrocarbon solvent is dispersed in the continuous aqueous medium in the form of miniemulsion droplets.[9] Exposure to ethylene results in the formation of latices with the average sizes of polymer particle ranging from about 100 nm to 1 μm.[4,5] Although this technique enables the synthesis of polymer latices with lipophilic catalysts without the need for modifications to achieve water-solubility, a synthesis of much smaller particles would be desirable.[10] An aqueous solution of a hydrophilic catalyst clearly represents the highest possible initial degree of dispersion of the catalyst precursor, and therefore appears to be of interest for the synthesis of small particles.[11]

An active and easily accessible hydrophilic catalyst was obtained by the reaction of stoichiometic amounts of chloranil, potassium 4-(diphenylphosphino)benzene-sulfonate (TPPMS), and bis(1,5-cyclooctadiene)nickel ([Ni(cod)$_2$]).



possible structure of catalyst precursor
Ar = Ph, 4-$C_6H_4SO_3K$
L = solvent, monomer

As for a similar recently reported lipophilic catalyst,[4d] it can be speculated that a Ni^{II}-κ^2*P,O* phosphanylphenolate complex is the active species [Eq. (1)]. Catalyst preparation was performed in a small volume of 2-propanol (see the Supporting Information for experimental details). A careful choice of this solvent was found to be crucial to enable the reaction of the apolar chloranil with the polar TPPMS.

Figure 1. Optical appearance of a dispersion (2 wt% polyethylene).

Exposure of the catalyst in an aqueous solution that contained sodium dodecyl sulfate (SDS) as a surfactant to ethylene afforded clear or only slightly turbid products, despite an observed consumption of ethylene (Figure 1).

Apparently, latices consisting of extremely small particles with sizes far below the wavelength of visible light are formed. Dynamic light scattering (DLS) reveals volume average particle sizes < 20 nm (Table 1). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) confirm these findings. TEM images of microtome cuts of latex particles embedded in a solid matrix[12] show very small particles (Figure 2) in accordance with AFM images of samples obtained by drying

Table 1: Polymerization results.[a]

Entry no.	Ethylene pressure [bar]	T [°C]	Solids content [%]	Average activity[b]	$\bar{M}_n$ [g mol^{-1}][c]	$\bar{M}_w/\bar{M}_n$	T_m [°C]	Average size of particles [nm][d]
1	40	25	0.4	70	6.0×10^3	5	139	n.d.
2	40	50	6.0	1070	2.0×10^3	7	n.d.	18
3	40	60	9.4	1675	2.6×10^3	5	130	n.d.
4	40	70	13.3	2370	1.9×10^3	5	129	28
5	40	80	6.8	1210	1.4×10^3	4	126	18
6	20	60	3.4	605	1.7×10^3	6	127	17
7	10	60	0.8	145	1.6×10^3	6	125	n.d.

[a] Reaction conditions: 90 mL of water, c(SDS) = 34.7 mmol L^{-1}, catalyst prepared in 10 mL of 2-propanol (100 μmol chloranil, 100 μmol TPPMS, 110 μmol [Ni(cod)$_2$]), polymerization time 2 h. [b] [mol(ethylene) mol(Ni)$^{-1}$ h^{-1}]. [c] Determined by GPC versus linear polyethylene (PE) standards. [d] Volume-average particle sizes determined by DLS. n.d. = not determined.

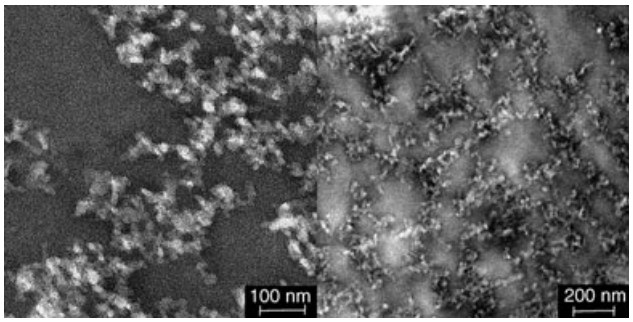


Figure 2. TEM micrographs of microtome cuts of latices.

the dispersions at room temperature (Supporting Information).

The course of the polymerization reaction was followed by using a mass flowmeter at a constant ethylene pressure of 40 bar at different polymerization temperatures (Table 1, entries 1–5; Figure 3). Although the reaction is sluggish at room temperature, satisfactory activities are observed at elevated temperatures of 50 to 70 °C, and the catalyst retains activity over the duration of the experiments (2 h).[13] Average catalyst activities over two hours range up to 2370 mol(ethylene) mol(Ni)$^{-1}$ h^{-1}. Further studies revealed that the polymerization continues for more than seven hours at 60 °C (see the Supporting Information). At 80 °C substantial catalyst deactivation within one hour is observed. Catalyst activities increase strongly with ethylene pressure in the range investigated (Table 1, entries 3, 6, and 7).

Incidentally, the results clearly demonstrate that efficient catalytic latex synthesis can be carried out without any water-immiscible liquid hydrocarbon phase. This offers some clear advantages for applications and for fundamental studies in comparison to the aforementioned miniemulsion technique. The simplification of the system, that is, the absence of

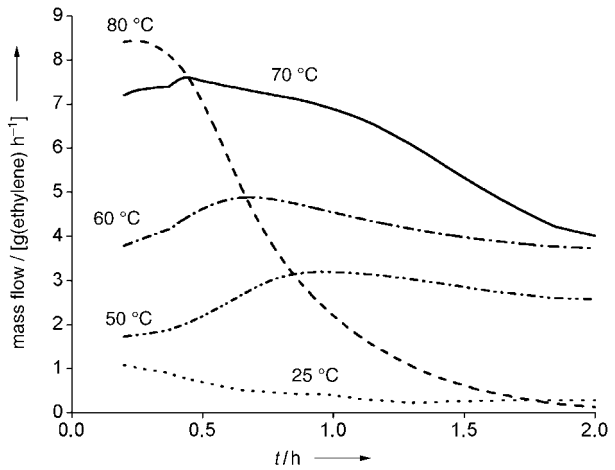


Figure 3. Temperature dependence of catalyst activity and stability over time (40 bars constant ethylene pressure, for the conditions see Table 1).

additional organic droplets, enables future studies of, for example, particle-formation processes.

Dispersions with a solids content of up to 15 wt% polymer were obtained without optimization. Up to about 6 wt%, the latices were transparent. The latices obtained were colloidally stable for more than six months. As for the amount of alcohol used in catalyst preparation, reduction from the usual 10 mL to 2 mL, which corresponds to only 2 vol% relative to the aqueous phase, had no significant effect on polymerization rate or otherwise. Increasing the scale of reaction from 0.1 L to 0.6 L did not result in a decrease in catalyst activity or dispersion stability (conditions of entry 3 in Table 1; 600 μmol Ni; dispersion obtained: 10.5% solids content).

A very simple picture of particle formation would involve initial chain growth on active sites dissolved in the aqueous phase and subsequent nucleation of one polymer particle per active catalyst molecule as continued chain growth results in increased hydrophobicity; the (surfactant-stabilized) particles thus formed continue to grow. However, further possibilities to be considered are, for example, the coalescence of already-existing particles (well-known from free-radical polymerization in general), the entry of a growing chain into an already-existing particle before nucleating a new particle, or the catalyst leaving an existing particle to nucleate a new one. In addition to the obvious possible complexity of particle-formation processes, it is not trivial to verify the number of active sites, particularly for the in situ catalyst system investigated. Nonetheless, it is interesting to know as a rough guideline the number of latex particles versus the number of metal centers to within an order of magnitude. From the number-average sizes of the latex particle, a ratio of Ni center:particle of only around 20 to 30 has been calculated. This high number of particles translates to a very efficient particle formation and stabilization in the polymerization investigated (particularly when keeping in mind that not all nickel added is necessarily present as an active site).

Concerning the microstructure of the dispersed polymer, ^{1}H and ^{13}C NMR spectroscopy demonstrate the formation of linear polyethylene as expected (see the Supporting Information). Number-average molecular weights ($\bar{M}_n$) of polyethylenes determined by high-temperature gel-permeation chromatography (GPC) are in the range of $\bar{M}_n = 1.4 \times 10^3$–$6 \times 10^3\ g\,mol^{-1}$. This is in accordance with $\bar{M}_n$ calculated from ^{1}H NMR spectra as well as T_m values.[14] As expected, molecular weights decrease with increasing reaction temperature due to an increase in β-hydride transfer. Interestingly, preliminary investigations by differential scanning calorimetry (DSC) on the polymer dispersions demonstrate stability of the colloids up to 140 °C and reveal high supercoolings of 55 °C due to an independent crystallization of individual droplets during the cooling cycle (cooling rate $10\ K\,min^{-1}$),[4e,15] which differs greatly from classical heterogeneous nucleation in bulk samples ($T_m - T_c = 18$ °C).

In summary, stable aqueous polyethylene dispersions consisting of extraordinarily small particles are reported. To our knowledge, such small stable polyethylene particles are not accessible by any other means. An easily prepared, robust catalyst is utilized for their synthesis.

Experimental data given in the Supporting Information: Catalyst preparation and polymerization procedure; ^{1}H and ^{13}C NMR spectra of polyethylene; DSC of latex and of bulk polymer; AFM images.

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[9] Please note that the catalytic polymerization reactions of ethylene discussed differ from typical free-radical miniemulsion polymerization of a preformed miniemulsion of a liquid monomer. Gaseous ethylene monomer is fed continuously to the reaction mixture subsequently to miniemulsification of the catalyst solution.
[10] The water-immiscible hydrocarbon solvent introduced with the miniemulsion can be disadvantageous. Claverie and co-workers even suggested that swelling of the polymer by the added liquid hydrocarbon is mandatory to enable polyethylene formation at all; the amount of polymer attainable is limited to about 60% of the overall organics content, which would prohibit any commercial application.[5c] While we can not support this suggestion quantitatively from our experience,[4,11] the necessity of a certain amount of liquid hydrocarbon for any efficient ethylene polymerization remains questionable.
[11] Ethylene polymerization by water-soluble complexes has been demonstrated:see reference [4a] and F. M. Bauers, PhD thesis, University of Freiburg (Germany), **2003**. However, low polymer yields in combination with the synthetic effort for the catalyst precursors hampered any further studies.
[12] Microtome cuts were investigated, as in regular TEM aggregation of the sample during preparation hampered its analysis.
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