[16] An even shorter Si–Li bond of 2.644 Å (average of 2.614 Å and 2.673 Å for two crystallographically independent molecules) was reported for **3**.[6b]

[17] The Li–O bond length in **1** (1.976 Å)is slightly longer than in **3** (av. 1.945 Å[6c]).

[18] In both dimers **2** and **4** the two central silicon and the two lithium atoms form a planar four-membered ring. In **2** the Li ··· Li distance of 2.641 Å is 0.12 Å shorter than that in **4**. The formally negatively charged Si1 atom is more strongly pyramidalized in **2** than in **4**; that is the Si2-Si1-Si2′ bond angles are 102.6° in **2** and 107.5° in **4**. Agostic Li ··· CH interactions are probably responsible for the relatively short Li ··· C4″ distance of 2.70 Å in **2**. These Li ··· C agostic interactions are stronger in **4** (r(Li ··· C) = 2.49 Å).[8]

[19] This factor is 1.4 for alkyllithium compounds. P. von R. Schleyer, J. Chandrasekhar, A. J. Kos, T. Clark, G. W. Spitznagel, *J. Chem. Soc. Chem. Commun.* **1981**, 882.

[20] For $[(H_3SiH_2Si)_3Si–Li]_2$ and $[(H_3Si)_3Si–Li]_2$ only constrained geometries could be studied as full-geometry optimizations lead to rearrangements (e.g., hydrogen atoms migrate to silicon). Therefore, a comparison of the structures of these model dimers with the corresponding complexed lithium silanides **8b** and **9b**, as shown for **1**–**4** in Scheme 2, was not possible.

[21] a) Another example is the observation that the Si–Li distance in **3**[6b,c,16] and in **4**[8,21b] is elongated by about 0.03–0.10 Å as a function of the crystallographic unit; b) personal communication from Dr. K. W. Klinkhammer.

[22] In **2** the Si1 ··· Si1* distance of 4.766 Å is longer than that in **4** (4.40 Å), which may also indicate steric repulsion between the $(Me_3SiMe_2Si)_3Si$ fragments.[18]

[23] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry—Principles of Structure and Reactivity, 4th ed.*, HarperCollins, New York, **1993**, p. 292.

[24] a) NBO4.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **1996**; b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899; c) E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593.

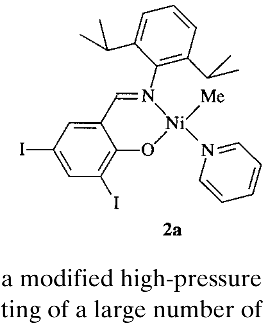
High Molecular Mass Polyethylene Aqueous Latexes by Catalytic Polymerization**

Florian M. Bauers and Stefan Mecking*

Emulsion polymerization of olefinic monomers is one of the most important and also versatile polymerization processes.[1] Polymer latexes are obtained, that is, stable aqueous dispersions of surfactant-stabilized polymer microparticles in the range of 50 to 1000 nm diameter. Numerous applications of latexes (for example, in coatings) involve the formation of films upon evaporation of the dispersing medium, and the environmental friendliness and nonflammability of water is particularly advantageous. To date, polymer latexes are produced by free-radical processes exclusively.[2] Transition metal catalyzed coordination polymerization has received comparatively little attention, as the early transition metal catalysts[3] used commercially for polyolefin production are extremely sensitive to moisture. Carrying out such reactions in water is a highly attractive goal, however, as many polymer microstructures are not available by means other than catalytic polymerization. We[4] and others[5] have recently reported the successful polymerization of ethylene in water by neutral nickel(II) complexes.[6, 7] However, dispersions consisting of low molecular mass material with a degree of polymerization of less than 100 (M_n values typically 1000 $\mathrm{g\,mol^{-1}}$) were obtained. The formation of higher molecular mass polymers (with chain length considerably above the entanglement limit) is a crucial prerequisite to fully exploit the unique property profile of latexes. At the same time, the complex steps of microparticle formation during polymerization must afford stable dispersions of these high molecular mass polymers.

With complexes $[(\mathrm{X}^\frown\mathrm{O})\mathrm{Ni^{II}R(L)}]$, where X = P (type **1**) or X = N (type **2**, $\mathrm{N}^\frown\mathrm{O}$ = salicylaldimine), materials of relatively similar maximum weight-average molecular mass (M_w) are accessible by traditional ethylene polymerization in apolar organic media.[8, 9] By contrast, in water, the latter offer access to polymers with much higher M_w and M_n values than the low molecular weight materials obtained in water with complexes of type **1**.[4b] In regard to particle formation, a comparison with free-radical emulsion polymerization is instructive.[10] In classical emulsion polymerization, water-soluble initiators are used. Chain growth initially affords water-soluble oligomeric radicals, which nucleate particles by collapsing upon themselves after reaching a certain chain length or by entering a surfactant micelle. Similar considerations appear reasonable for the aforementioned emulsion-type catalytic polymerization by a hydrophilically modified water-soluble complex of type **1**, which affords stable latexes of low molecular mass material.[4] However, a certain water-sensitivity[4b, 9c] of salicylaldimine-substituted complexes (type **2**) can be problematic to an analogous approach.

As a different concept to enable formation of a large number of latex particles during polymerization, a very fine dispersion of the catalyst precursor was achieved in the form of a solution of a lipophilic complex (**2a**) in submicron-size compartments of a hydrocarbon solvent, dispersed in the continuous aqueous phase.[14] A mixture of water, surfactant, and a solution of the complex in a small amount of hydrocarbon (toluene and a small portion of hexadecane as a hydrophobic additive[11]) was subjected to high shear, generated either by ultrasound or by means of a modified high-pressure homogenizer. Mini-emulsions consisting of a large number of small hydrophobic droplets (diameter about 100 nm, 10^{16}–10^{17} droplets $\mathrm{L^{-1}}$) containing the catalyst resulted. Exposure of the mini-emulsions to ethylene in a pressure reactor resulted in polymerization to form stable polyethylene latexes



2a

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Table 1. Polymerization conditions[a] and results.

Entry	n(cat.) [µmol]	Toluene [vol%]	$C_{16}H_{34}$ [vol%]	Surfactant type[b]	Surfactant c [mmol L^{-1}]	Emulsification method[c]	TON[d]	M_n [g mol^{-1}]	M_w [g mol^{-1}]	M_w/M_n	$\bar{d}$[e] [nm]
1	25	1	2	SDS	17	US	2515	1.4×10^5	3.2×10^5	2.3	330
2	23	1	0.3	SDS	35	US	1206	1.2×10^5	3.3×10^5	2.7	220
3	36	1	0.3	SDS	17	US	1135	8.5×10^4	2.6×10^5	3.1	260
4	29	1	0.3	SDS	5	US	1230	1.0×10^5	4.5×10^5	4.5	(485)[f]
5	36	1	0.3	Trit	11	US	959	8.9×10^4	1.9×10^5	2.1	100
6	32	1	0.3	K30	18	US	990	9.0×10^4	2.5×10^5	2.8	240
7	63	2	1	SDS	17	HP	165	9.5×10^4	2.1×10^5	2.2	135
8	32	1	0.3	SDS	17	HP	75	2.0×10^4	3.4×10^4	1.7	90
9	44	4	1	Lut	5	HP	265	1.6×10^4	2.4×10^4	1.5	250

[a] 30 °C, 45 bar constant ethylene pressure, 2 h reaction time. Total volume of water and organic solvents: 100 mL. [b] SDS = sodium dodecylsulfate, Lut = Lutensol AT80 (C_{16}–C_{18} fatty alcohol–ethoxylate with an average of 80 ethylene oxide units; BASF), Trit = Triton X-100 (*iso*-octylphenololigoethoxylate), K30: Emulgator K30/40 (Bayer, sodium alkylsulfonates). [c] US = ultrasound, HP = high-pressure homogenizer (for details see Experimental Section). [d] Mol of ethylene per mol of Ni. [e] Average size of latex particles, determined by light scattering. [f] Latex unstable, partial coagulation occured.

(Table 1). Analysis of the isolated polymer by gel-permeation chromatography (GPC) reveals these dispersions to contain only high molecular mass polyethylene with M_w values of up to 4×10^5 g mol^{-1} and narrow molecular mass distributions. The average latex particle sizes are in the range of 90 to 350 nm, as observed by light scattering measurements.[12] It should be noted that the polymerization reaction of ethylene reported here differs from typical free-radical polymerization in a preformed mini-emulsion of a liquid monomer. Gaseous ethylene monomer is fed continuously into the reaction mixture after mini-emulsification of the catalyst solution. Thus, polymerization of preformed mini-emulsion droplets of monomer to particles of the same size, as the typical feature of "mini-emulsion polymerization", does not apply.

The polymer latexes obtained are stable for weeks or longer. As a surfactant, various anionic and nonionic compounds were found to be suited, that is, compatible with the catalyst in the mini-emulsion system employed and capable of forming stable latexes (Table 1). As expected, a decrease in the surfactant concentration under otherwise identical conditions resulted in an increase in the average size of the latex particles (entries 2–4). The lower activities observed on employing the high-pressure homogenizer (entries 7–9) relative to ultrasonification are probably related to deactivation of the catalyst precursor, as the former method required more time for mini-emulsification.

The latex particles were visualized by transmission-electron microscopy (TEM; Figure 1). In comparison to smooth, spherical latex particles of amorphous polystyrene, as a well-studied hydrocarbon polymer prepared by free-radical emulsion polymerization, the ruggedness of the particles shown can be rationalized by their high degree of crystallinity (39 to 51 % by differential scanning calorimetry (DSC); T_m = 120–130 °C).[13]

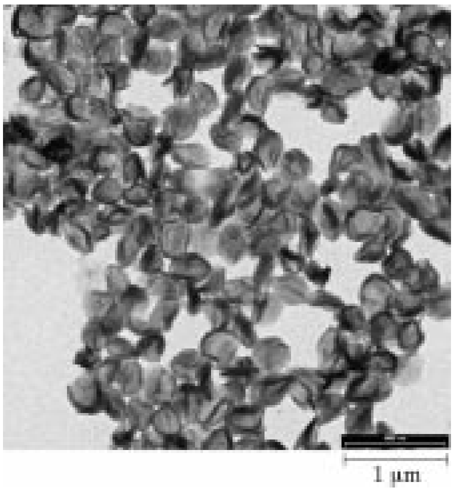

Figure 1. TEM micrograph of latex particles.

Experimental Section

General: Complex **2a** was prepared as described previously.[4b] The compound was manipulated by standard Schlenk techniques under argon. Deionized water was degassed prior to use. High-temperature GPC was performed in 1,2,4-trichlorobenzene at 140 °C using a PL-220 instrument equipped with mixed-bed PL columns. The data reported was referenced to polyethylene standards (universal calibration). Dynamic light scattering measurements on the dispersions were performed on a Malvern particle sizer after dilution. TEM investigations were carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. The DSC data reported were recorded in the second heating cycle at 10 K min^{-1}.

Polymerization: The catalyst precursor was dissolved in the given amount of toluene and hexadecane (Table 1). The surfactant and about 100 mL of water were added with mechanical stirring. Homogenization was performed under an argon atmosphere by means of a high-pressure homogenizer directly connected to the polymerization reactor (modified version of the EmulsiFlex®-C5 apparatus from Avestin Inc.; 500–1000 bar) or by ultrasound (Bandelin HD2200 with KE76 tip; 2 min at 120 W). The resulting mini-emulsion was transferred to a mechanically stirred 250-mL pressure reactor equipped with a heating/cooling jacket and a constant ethylene pressure (45 bar) was applied. The reaction temperature was controlled (30 °C) by means of a thermocouple dipping into the reaction mixture. After the specified reaction time the ethylene was vented. The resulting latex was filtered through glass wool. For the determination of yields and for further polymer analysis a specified portion was precipitated by pouring into methanol.

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opening polymerization of cyclic siloxanes); b) K. Landfester, F. Tiarks, H.-P. Hentze, M. Antonietti, *Macromol. Chem. Phys.* **2000**, *201*, 1–5 (polyaddition).

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[10] It should be noted that the different mechanisms of chain initiation, growth, and transfer in free-radical versus coordination polymerization can clearly affect the delicate steps involved in particle nucleation and growth. Nonetheless, the general comparison drawn here is reasonable.

[11] For background information on mini-emulsions and the function of the hydrophobe, see a) E. D. Sudol, M. S. El-Aasser in *Emulsion Polymerization and Emulsion Polymers* (Eds.: P. A. Lovell, M. S. El-Aasser), Wiley, Chichester, **1997** pp. 699–722; b) K. Landfester, N. Bechthold, F. Tiarks, M. Antonietti, *Macromolecules* **1999**, *32*, 5222–5228, and references therein.

[12] In regard to the development of particle numbers during polymerization, a comprehensive interpretation of the data is complicated by the necessity of extensively diluting the turbid emulsion for light-scattering analysis. Deviations from the original state may result in analyses of the catalyst mini-emulsion (liquid/liquid dispersion).

[13] Like the polymers obtained in traditional polymerization in organic media with these catalysts,[9] the polyethylenes prepared in water are moderately branched. For the material isolated from dispersions, about 20 branches/1000 carbon atoms (predominantly methyl branches) were observed by ^{1}H and ^{13}C NMR spectroscopy. By comparison to linear polyethylene, a moderate decrease in crystallinity results.

[14] Note added upon revision of this manuscript (May 23, 2001): after submission of this manuscript, the preparation of latexes of low molecular mass materials by the polymerization of ethylene employing mini-emulsions of water-stable nickel(II) complexes was reported: R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* **2001**, *34*, 2022–2026.

Formal Enantioselective Michael Addition with Umpolung of Reactivity**

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Dedicated to Professor Dieter Seebach

The conjugate addition of nucleophiles to unsaturated carbonyl derivatives is an important reaction,[1] and its enantioselective variant has received much attention over the last few years.[2] Several general methods such as copper-catalyzed additions of organolithium or organomagnesium derivatives,[3] or the addition of diorganozinc compounds[4] have been described in detail. Recently, a rhodium-catalyzed addition of boronic acids has also been reported.[5] Although satisfactory results have been obtained in many cases, several classes of organometallic compounds, such as alkynyl,[6] allylic, and allenyl organometallic compounds still cannot be added enantioselectively. Herein, we report a new synthetic approach to conjugate additions in which an umpolung[7] of the Michael acceptor reactivity occurs. Whereas the usual reactivity of an enone of type **1** (a^{3}-reactivity)[7] requires a reaction with a nucleophile (Nu^{-}) and leads to the addition product of type **2** (Scheme 1), we envisioned an umpolung of the enone reactivity by successive protection of the carbonyl function and formal hydrometalation, leading to the chiral organometallic species **3**. After the reaction of **3** with an electrophile (E^{+}) and deprotection, products of type **4** would be produced. If an asymmetric hydrometalation and a stereoselective reaction with the electrophile (E^{+}) is possible, then this would correspond, after deprotection, to a formal enantioselective Michael addition with umpolung of the normal reactivity pattern (Scheme 1).

Recently, we developed a reaction sequence involving an asymmetric hydroboration followed by a boron–zinc ex-

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