



Hydrophilic Catalysts with High Activity and Stability in the Aqueous Polymerization of Ethylene to High-Molecular-Weight-Polyethylene

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Abstract: Water-soluble synthetic transition metal catalysts have been studied extensively for many reactions, but for olefin polymerization such catalysts have been lacking. We report herein a straightforward synthesis of phosphinephenolato Ni^{II} catalysts endowed permanently with a hydrophilic sulfonate moiety bound to the chelating ligand. These catalysts' hydrophilic active sites promote aqueous ethylene polymerization with high activity (TOF up to $6.3 \times 10^4 \text{ mol}_{\text{Ethylene}} \text{ mol}_{\text{Ni}}^{-1} \text{ h}^{-1}$) to high molecular weight polyethylene (HDPE), with half-lives on the order of hours also at elevated temperatures. The obtained polyethylene dispersions feature narrow particle size distributions without any aggregates.

Synthetic aqueous catalysis by organometallic species has been demonstrated for numerous transformations, complementing those performed by enzymes.^[1] The perhaps most prominent example is aqueous hydroformylation with water-soluble rhodium catalysts, performed industrially.^[2]

The most important synthetic organometallic catalytic process is clearly olefin polymerization, which is carried out on a vast scale.^[3–7] Aqueous post-polymerization dispersions of polyolefins have recently evolved as key to environmentally friendly coatings,^[8] and also aqueous catalytic polymerizations have been demonstrated as a route to such dispersions.^[9–12] However, water-soluble olefin polymerization catalysts are scarce. Different from the approach of a water-soluble catalyst precursor that forms a water-insoluble active species,^[13,14] or the utilization of lipophilic catalyst precursors in the hydrocarbon droplet phase of mini- or microemulsions^[9–11,15] such permanently hydrophilic catalysts will be exposed to the aqueous phase throughout the entire catalytic reaction. Flood et al. reported an aqueous ethylene polymerization by the well-defined rhodium complex $[\text{CnRhMe}(\text{OH}_2)(\text{OH})^+]$ (Cn = 1,4,7-trimethyl-1,4,7-triazacy-

clononane) to yield a low molecular weight polyethylene ($M_w = 5 \times 10^3 \text{ g mol}^{-1}$) after 90 days of reaction at 60 bar ethylene pressure.^[16] Later, water-soluble sulfonated phosphineenolato Ni^{II} catalysts were shown to yield dispersions of low molecular weight linear polyethylene ($M_n = 970 \text{ g mol}^{-1}$) with moderate activity (360 TOF h^{-1} at 50 atm, 70 °C).^[10] Note a related in situ prepared water-soluble catalyst was more active, but also yielded low molecular weight polymer ($M_n = 1.4 \text{ to } 6.0 \times 10^3 \text{ g mol}^{-1}$).^[17] In contrast Brookhart's prototypical cationic Pd^{II} diimine catalysts^[18] are capable of aqueous polymerizations where the lipophilic catalyst is protected from the aqueous phase in the growing particles, but analogues rendered water soluble by sulfonation of the chelating diimine are completely inactive.^[19]

Here, we report a straightforward route to Ni^{II} catalysts rendered hydrophilic by a sulfonated phosphinephenolato chelating ligand. These are stable for hours under aqueous polymerization conditions and promote formation of high molecular weight HPDE high density polyethylene dispersions with high activities.

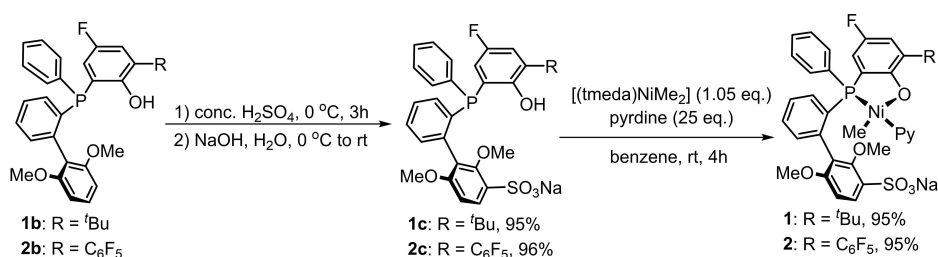
Traditional phosphinephenolato Ni^{II} catalysts have a high propensity for β -H elimination, such that this chain transfer reaction effectively competes with chain growth. This is the basis for oligomerization of ethylene to 1-olefins in the Shell Higher Olefin Process.^[20] Only recently, this picture was upset by Shimizu et al. and Li et al. finding that bulky substituents in *ortho*-position to the phenolate or on the phosphine can suppress chain transfer and yield high molecular weight polymers.^[21,22] Further development^[15,23,24] enabled a living chain growth.

To enable a straightforward access to sulfonated phosphinephenols with a suitable substitution pattern, we sought a regioselective sulfonation of only one of the multiple aryl rings of the substrate. To this end, the *tert*-butyl- or C_6F_5 -substituted phenol ring was blocked for sulfonation by introduction of a fluorine substituent in the *para*-position of the phenol motif in **1b** and **2b**, respectively, to allow for selective incorporation of a water-solubilizing sulfonate sodium moiety on the electron-rich 2',6'-dimethoxyphenyl group.^[25] Treatment of **1b** and **2b** with concentrated H_2SO_4 at 0 °C for 3 hours resulted in exclusive monosulfonation at the 3'-position, to afford after neutralization **1c** and **2c**, respectively, in virtually quantitative yield. Ni^{II} complexes **1** and **2** were obtained by reaction of the respective sulfonated phosphinephenols with $[(\text{tmeda})\text{NiMe}_2]$ in the presence of excess pyridine (Scheme 1).

The complexes **1** and **2** dissolved readily in C_6D_6 to give transparent solutions, but different from non-sulfonated analogues ¹H NMR spectra show very broad peaks, possibly

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Scheme 1. Synthesis of sulfonated phosphinephenols and their Ni^{II} complexes.

due to ionic agglomeration^[26] via the sulfonate moieties. By contrast in CD₃OD as a polar protic solvent, well-resolved spectra are obtained (Figures S7 and S8 in the Supporting Information for **1**; Figures S14 and S15 for **2**. For full characterization data of all compounds cf. the Supporting Information).

Exposure of aqueous solutions of complex **1** containing sodium dodecyl sulfate surfactant to ethylene under pressure reactor conditions afforded colloiddally stable dispersions of HDPE nanoparticles (Table 1). Polymerization at 30 °C afforded HDPE with a molecular weight of M_n 220 kg mol⁻¹, with an average activity corresponding to a turnover frequency of TOF = 11.6 × 10³ TOh⁻¹. Monitoring of the reaction via the mass flow of ethylene uptake during the polymerization indicated observable catalyst deactivation (Figure S17). For other aqueous polymerizations, protolysis of growing Ni-polymeryl species was identified as the most likely and relevant cause of catalyst deactivation, as also indicated by a dependency of catalyst deactivation rates on the pH of the aqueous system.^[27] Indeed, the presence of added NaOH base resulted in a higher productivity as reflected by TOFs of 18.9 × 10³ TOh⁻¹ and 26.0 TOh⁻¹ with 0.063 M and 0.125 M base, respectively, in one hour experiments (Table 1, entries 2 and 3, Figure S18). Even higher base concentration resulted in only slightly higher productivities (Table 1, entry 4). Remarkably, the catalyst is stable at these extremely basic conditions of pH ≈ 13. This stability is

retained over hours under polymerization conditions, as evidenced by polymer yields in polymerization experiments over longer times of 2 h and 4 h (Table 1, entries 5 and 6) and by monitoring of these reactions via the ethylene uptake (Figure S19).

Polymer molecular weights of ca. M_n 400 kg mol⁻¹ are obtained independent of the polymerization time, showing that the molecular weights are determined by chain transfer in the time regime of these polymerization (≥ 1 h). This is further underlined by observed molecular weight distributions of M_w/M_n ≈ 2, which also demonstrate the well-behaved single-site nature of the polymerization. At an elevated temperature of 50 °C catalyst **1** stays active for more than one hour and polymerizes with high activity to yield HDPE dispersions with solids contents > 10 %. (Table 1, Entries 7 and 8, Figure S20). Polymerization also commences at 70 °C but catalyst deactivation over time results in lower overall productivity in a one hour experiment (Table 1, entry 9 and Figure S21).

Complex **2** bearing the electron-withdrawing C₆F₅-group adjacent to the *O*-donor showed a lower activity than complex **1** under identical polymerization conditions (entries 10 to 12). Notably, **2** retained polymerization activity over extended times even at a temperature of 70 °C (Figure S22).

The polyethylenes obtained are highly linear, as evidenced by exemplary ¹³C NMR analysis (< 1 branch per

Table 1: Aqueous ethylene polymerization by hydrophilic complexes **1** and **2**.^[a]

Entry	Precat.	T [°C]	c _{NaOH} [mol L ⁻¹]	Yield [g]	TOF ^[b]	M _n ^[c] [kg mol ⁻¹]	M _w /M _n ^[c]	T _m ^[d] [°C]	Cryst. ^[d] [%]	Particle size ^[e] [nm]	PDI ^[e]
1	1	30	0	1.62	11.6	220	2.2	139/138	74/58	17	0.098
2	1	30	0.063	2.65	18.9	349	2.1	139/138	74/57	20	0.103
3	1	30	0.125	3.64	26.0	400	2.0	144/141	71/55	20	0.084
4	1	30	0.250	3.69	26.4	378	2.0	140/139	73/59	21	0.095
5	1 ^[f]	30	0.125	5.12	18.3	362	1.9	144/141	74/53	23	0.153
6	1 ^[g]	30	0.125	7.59	13.6	369	2.0	143/139	76/57	27	0.113
7	1	50	0.125	8.85	63.2	101	2.2	137/136	73/62	20	0.120
8	1 ^[f]	50	0.125	10.80	38.6	104	2.2	136/136	69/59	22	0.117
9	1	70	0.125	3.97	28.4	61	2.5	137/137	62/69	14	0.123
10	2	30	0.125	0.57	4.1	185	1.6	142/142	79/63	14	0.306
11	2	50	0.125	2.67	19.1	51	2.8	141/142	67/65	16	0.244
12	2	70	0.125	3.46	24.7	24	2.2	135/135	63/68	15	0.258

[a] Polymerization conditions: 5 μmol of **1** or **2**, respectively, in 100 mL of water, 40 bar ethylene pressure, 4 g sodium dodecyl sulfate, 1 hour polymerization time. [b] Given in 10³ mol_{Ethylene} mol_{Ni}⁻¹ h⁻¹. [c] Determined via GPC at 160 °C in 1,2-dichlorobenzene. [d] Determined by DSC on nascent polymer powder, isolated by precipitation from the nanoparticle dispersion, measured with 10 K min⁻¹ heating/cooling rate, first and second heating cycle reported. [e] Determined by DLS; volume mean given. [f] Polymerization run for 2 hours. [g] Polymerization run for 4 hours.

1000 carbon atoms for entry 7, cf. Figure S23) and the high melting points observed by differential scanning calorimetry (DSC) (Table 1 and Figures S24–S29).

Dynamic light scattering (DLS) analyses of the obtained polyethylene dispersions revealed small particles with sizes on the order of only 20 nm, with relatively narrow particle size distributions and devoid of any aggregates (Table 1 and Figure 1a). With increasing polymerization time, larger average particle sizes are observed which already indicates that formed particles continue to grow during the polymerization (Table 1, entries 3, 5 and 6). Elucidation of the shapes of the particles and of their growth by transmission electron microscopy (TEM) revealed a disk-like particle shape and narrow size distributions in all cases (Figure 1b and Tables S1 and S2, Figures S36 to S39). Within experimental error, the TEM data correspond to one particle formed per Ni present in the reaction mixtures. An estimation of the number of chains per particle from their volume and the polymer molecular weight indicates 1.2 (1 h polymerization time at 30°), 2.3 (2 h) and 3.5 (4 h), respectively, and 14 for a polymerization at 50°C. That is, also upon chain transfer the particle number density is unaltered, new particles are not formed to a significant extent. This suggests the picture of the catalyst not leaving a particle upon a chain transfer event, rather the new chain is grown on the same particle.

In summary, sulfonated phosphinephenolato Ni^{II} complexes can be accessed cleanly in a straightforward way. These catalysts endowed permanently with a water-solubilizing moiety via the chelating ligand are capable of aqueous polymerizations, and in fact are stable over long reaction times and at elevated temperatures. They yield high molecular weight polymer and do so with high activities, unlike previous examples of ethylene polymerization with water-soluble catalysts. These insights provide new perspectives for both environmentally friendly polymerization processes and polyolefin coatings with low emission of volatile organic compounds.

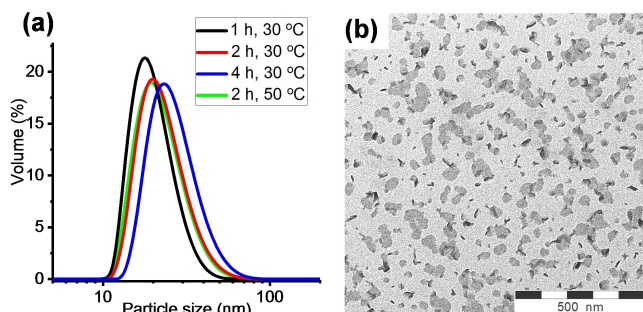


Figure 1. a) DLS traces of PE dispersions obtained by complex 1 at different polymerization times and temperatures. b) TEM image of PE nanoparticles from Table 1, entry 6 (4 h, 30°C).

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Aqueous Polymerization · Ethylene Polymerization · P₂O Ligand · Polyethylene Dispersion · Water-Soluble Catalyst

- [1] *Applied Homogeneous Catalysis with Organometallic Compounds*, 3rd ed. (Eds. B. Cornils, W. A. Herrmann, M. Beller, R. Paciello), Wiley-VCH, Weinheim, **2018**.
- [2] “Oxo Synthesis”: H. Bahrman, H. Bach, G. D. Frey, *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2013**.
- [3] M. Stürzel, S. Mihan, R. Muelhaupt, *Chem. Rev.* **2016**, *116*, 1398–1433.
- [4] A. Keyes, H. E. Basbug Alhan, E. Ordenez, U. Ha, D. B. Beezer, H. Dau, Y.-S. Liu, E. Tsogtgerel, G. R. Jones, E. Harth, *Angew. Chem. Int. Ed.* **2019**, *58*, 12370–12391; *Angew. Chem.* **2019**, *131*, 12498–12520.
- [5] C. Tan, C. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 7192–7200; *Angew. Chem.* **2019**, *131*, 7268–7276.
- [6] D. J. Walsh, M. G. Hyatt, S. A. Miller, D. Guironnet, *ACS Catal.* **2019**, *9*, 11153–11188.
- [7] A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.* **2009**, *109*, 5215–5244.
- [8] A. C. Neubauer, A. Quaranta, N. W. Dunchus, M. J. Kalinowski, G. M. Strandburg, K. D. Maak, US2010255207 (A1), **2008**.
- [9] R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* **2001**, *34*, 2022–2026.
- [10] A. Held, F. M. Bauers, S. Mecking, *Chem. Commun.* **2000**, 301–302.
- [11] A. Tomov, J.-P. Broyer, R. Spitz, *Macromol. Symp.* **2000**, *150*, 53–58.
- [12] C. Boucher-Jacobs, M. Rabnawaz, J. S. Katz, R. Even, D. Guironnet, *Nat. Commun.* **2018**, *9*, 841.
- [13] I. Göttker-Schnetmann, B. Korthals, S. Mecking, *J. Am. Chem. Soc.* **2006**, *128*, 7708–7709.
- [14] M. Schnitte, A. Staiger, L. A. Casper, S. Mecking, *Nat. Commun.* **2019**, *10*, 2592.
- [15] F. Lin, T. O. Morgen, S. Mecking, *J. Am. Chem. Soc.* **2021**, *143*, 20605–20608.

- [16] L. Wang, R. S. Lu, R. Bau, T. C. Flood, *J. Am. Chem. Soc.* **1993**, *115*, 6999–7000.
- [17] L. Kolb, V. Monteil, R. Thomann, S. Mecking, *Angew. Chem. Int. Ed.* **2005**, *44*, 429–432; *Angew. Chem.* **2005**, *117*, 433–436.
- [18] L. K. Johnson, C. M. Killian, M. S. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.
- [19] A. Held, F. Weiss, S. Mecking, *Polym. Prepr.* **2001**, *42*, 466–467.
- [20] W. Keim, *Angew. Chem. Int. Ed.* **2013**, *52*, 12492–12496; *Angew. Chem.* **2013**, *125*, 12722–12726.
- [21] B. S. Xin, N. Sato, A. Tanna, Y. Oishi, Y. Konishi, F. Shimizu, *J. Am. Chem. Soc.* **2017**, *139*, 3611–3614.
- [22] Y. Zhang, H. Mu, L. Pan, X. Wang, Y. Li, *ACS Catal.* **2018**, *8*, 5963–5976.
- [23] S. Xiong, M. M. Shoshani, X. Zhang, H. A. Spinney, A. J. Nett, B. S. Henderson, T. F. Miller, T. Agapie, *J. Am. Chem. Soc.* **2021**, *143*, 6516–6527.
- [24] M. Baur, F. Lin, T. O. Morgen, L. Odenwald, S. Mecking, *Science* **2021**, *374*, 604–607.
- [25] K. W. Anderson, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2005**, *44*, 6173–6177; *Angew. Chem.* **2005**, *117*, 6329–6333.
- [26] Z. Shen, R. F. Jordan, *J. Am. Chem. Soc.* **2010**, *132*, 52–53.
- [27] A. Godin, I. Göttker gen Schnetmann, S. Mecking, *Macromolecules* **2016**, *49*, 8825–8837.

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