

# Living Aqueous Microemulsion Polymerization of Ethylene with Robust Ni(II) Phosphinophenolato Catalysts

Fei Lin, Tobias O. Morgen, and Stefan Mecking\*

**ABSTRACT:** Due to chain transfer events being competitive with chain growth, ethylene polymerization by P,O-chelated Ni(II) complexes usually affords low molecular weight polymers or oligomers. We now show that appropriately bulky substituted phosphinophenolato Ni(II) can polymerize in a living fashion, virtually devoid of chain transfer. Aqueous polymerizations with microemulsions of [ $\kappa^2$ -P,O-2-(2-(2',6'-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>)(Ph)P-6-(3',5'-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>O-NiMe(pyridine))] (3) at 30 °C yield polyethylenes with narrow molecular weight distributions ( $M_w/M_n$  1.02 to 1.34) and ultrahigh molecular weights (up to  $2 \times 10^6$ ) in the form of aqueous nanoparticle dispersions. Catalyst stability and activity are maintained up to 70 °C in water.

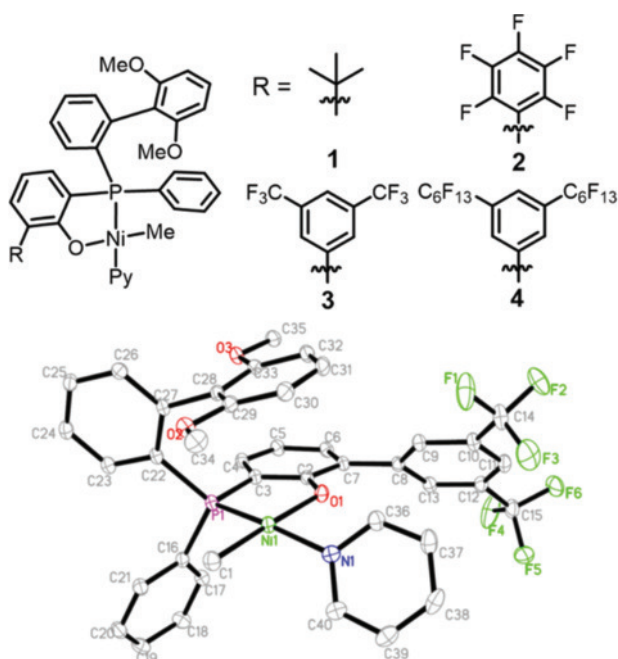
Traditional d<sup>0</sup>-metal catalysts are used on a vast scale for the production of polyolefins.<sup>1,2</sup> A limitation of these catalysts is their sensitivity to even trace amounts of heteroatom-containing polar compounds. This can be overcome by less oxophilic and more functional group tolerant late transition metal catalysts.<sup>3–6</sup> The ability to tolerate functional groups enhances the scope of both feasible monomers and reaction media beyond hydrocarbons.<sup>7</sup> Aqueous polymerizations are employed on a large scale in free-radical emulsion polymerization, which facilitate the removal of the heat of reaction and yield polymer dispersions, used in versatile applications. Polyolefin dispersions are produced today either by high-pressure free-radical emulsion polymerization<sup>8,9</sup> or by postpolymerization dispersion of catalytically produced copolymers.<sup>10</sup> Both these processes are energy consuming and limited to a certain range of branched microstructures.

The first examples of aqueous catalytic polymerization to linear polyethylene (high-density polyethylene, HDPE) dispersions were achieved with P,O-chelated Ni(II) catalysts.<sup>11–13</sup> The state-of-the-art in aqueous polymerizations employs N,O-coordinated catalysts, however, as these can provide very high molecular weights (e.g.,  $M_n = 3 \times 10^6$  g mol<sup>-1</sup> with  $M_w/M_n = 1.3$  at 15 °C polymerization temperature).<sup>14</sup> In the aforementioned studies with P,O-chelated Ni(II) catalysts, low molecular weights of several  $10^3$  g mol<sup>-1</sup>  $M_n$  result from the propensity of such catalysts for  $\beta$ -hydride elimination (BHE). In fact, the latter is the basis for the prominent use of P,O-chelated Ni(II) complexes for the industrial oligomerization of ethylene to linear 1-olefins in the Shell higher olefin process (SHOP),<sup>15</sup> where chain transfer competes effectively with chain growth ( $k_{\text{growth}}/k_{\text{elim}} \approx 5$  to 10). Considering this long-standing background,<sup>16</sup> seminal findings by Shimizu et al.<sup>17</sup> and further reports by Li et al.<sup>18</sup> and Agapie et al.<sup>19</sup> of bulky substituted P,O-chelated catalysts that afford high molecular weight polymers in hydrocarbon solvents and also can incorporate polar vinyl monomers were a surprising breakthrough (for example  $M_n = 10^5$  g mol<sup>-1</sup>,  $M_w/M_n \approx 2$ ).

We now report on aqueous polymerizations with robust Ni(II)phosphinophenolato catalysts virtually devoid of chain transfer to the extent that chain growth is living, and ultrahigh molecular weights are obtained.

Distinctive features of the P,O-chelated Ni catalysts that afford high molecular weight HDPE are a substitution in the *o*-position to the phenolato donor and a 2,6-dimethoxyphenyl (or 2-arylphenyl) substitution of the P-donor. These served as a guideline for our approach to aqueous polymerizations. Beyond complex 1<sup>18</sup> with *tert*-butyl substitution in the *o*-position, complexes 2,<sup>20</sup> 3, and 4<sup>21</sup> bearing different electron-withdrawing aryl groups were studied (Figure 1). X-ray diffraction analysis of the novel complex 3 shows that in the solid state one axial side of the Ni center is shielded by the 2-arylphenyl group, as also reflected by the C29–Ni distance of 3.28 Å. Possibly, this contributes in suppressing chain transfer (vide infra).<sup>22</sup>

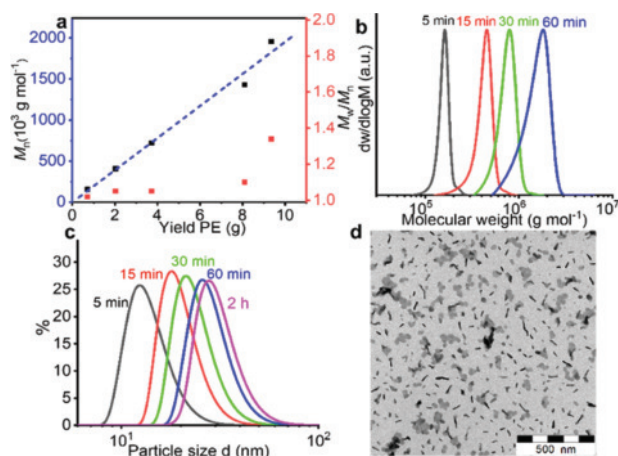
Microemulsions<sup>23</sup> were employed to achieve a high degree of dispersion of the initial catalyst precursor. Note that compared to a dispersion polymerization approach,<sup>14</sup> this concept does not require water-soluble catalyst precursors but can employ more prevalent lipophilic catalyst precursors. While microemulsions offer the benefit of forming spontaneously without the need for, for example, high shear and are highly disperse with length scales of the dispersed phase on the order of only 10 nm, reaching the microemulsion regime requires alcohol cosolvents (“cosurfactants”). Advantageously, complexes 1 to 4 are stable to such cosolvents, as evidenced by unaltered <sup>1</sup>H NMR resonances upon several hours of exposure to excess *n*-hexanol (Figures S3 to S6 in the Supporting



**Figure 1.** Catalyst precursors employed (top) and the crystal structure of precursor 3 (bottom).

**Information, SI).** As anticipated, solutions of the catalyst precursors in a small amount of toluene formed microemulsions with an appropriate excess amount of aqueous surfactant solution and cosolvent upon gentle stirring, as indicated by the formation of a single transparent phase (cf. SI for details). Exposure of these catalyst solutions to ethylene in a pressure reactor resulted in polymerization with high activity, to yield colloiddally stable and transparent to slightly opaque PE dispersions (Table 1). Notably, these contain substantial amounts (up to >20 wt %) of linear polyethylene with molecular weights in the ultrahigh molecular weight (UHMW-PE) regime ( $M_n > 10^6 \text{ g mol}^{-1}$ ).

Catalyst precursor 3 stands out in polymerizing in a living fashion as evidenced by (1) a linear relationship between yield and molecular weight (Figure 2a); (2) very narrow molecular



**Figure 2.** (a) Number average molecular weight and polydispersity vs yield in microemulsion polymerization with 3 (30 °C, 40 bar of ethylene). (b) GPC traces of PE obtained in a microemulsion at different polymerizations times. (c) DLS traces of PE dispersions obtained in a microemulsion at different polymerization times. (d) TEM image of PE nanocrystals (entry 9, Table 1).

weight distributions with an  $M_w/M_n$  as low as 1.02 (Figure 2b); and (3) chains per Ni ratios close to unity (Table 1, entries 5–9). Precursor 3 is highly active in water especially at elevated temperatures ( $5.8 \times 10^4 \text{ TO}$  at 30 °C,  $6.3 \times 10^4 \text{ TO}$  at 50 °C, and  $7.5 \times 10^4 \text{ TO}$  at 70 °C.  $\text{TO} = \text{mol}_{\text{ethylene}} \text{ mol}_{\text{Ni}}^{-1} \text{ h}^{-1}$ ) and features a half-life of ca. 2 h at an elevated temperature of 50 °C (Figures S18–S20). By comparison, state-of-the-art water-soluble salicylaldiminato Ni(II) catalysts can promote living aqueous polymerizations to yield UHMWPE, ideal conditions being 15 °C (with  $M_w/M_n = 1.5$  at 30 °C, 40 atm<sup>24</sup>).<sup>14</sup> The high melting points observed by differential scanning calorimetry (DSC) evidence a highly

**Table 1. Ethylene Polymerization Results in Microemulsion**

entry <sup>a</sup>	precat.	<i>t</i> [min]	yield [g]	$M_n^b$ [ $\times 10^3$ ]	$M_w/M_n^b$	chain / [Ni]	$T_m^c$ [°C]	cryst. <sup>c</sup> [%]	particle size [nm] (DLS) <sup>d</sup>	PDI (DLS) <sup>d</sup>	particle size [nm] (TEM) <sup>e</sup>	chains/particle
1	1	15	4.52	1334	1.60	0.7	142/138	78/46	29	0.10	22.1 ± 0.4	0.8
2	1	120	23.85	1660	1.81	2.9	149/141	79/45	46	0.11	30.1 ± 0.4	1.1
3	2	15	1.58	391	1.33	0.8	141/139	75/55	25	0.10	20.1 ± 0.3	2.8
4	2	120	11.47	1295	1.65	1.8	146/139	78/51	36	0.10	27.2 ± 0.3	1.2
5	3	5	0.72	155	1.02	0.9	139/138	74/61	15	0.11	7.4 ± 0.1	1.2
6	3	15	2.03	406	1.05	1.0	141/139	75/55	24	0.09	12.6 ± 0.2	1.3
7	3	30	3.73	720	1.05	1.0	141/139	77/53	28	0.09	15.3 ± 0.2	1.1
8	3	60	8.10	1428	1.10	1.1	142/138	79/48	35	0.09	21.4 ± 0.4	1.0
9	3	120	9.35	1955	1.34	1.0	146/139	78/51	38	0.10	27.1 ± 0.5	1.0
10	3 <sup>f</sup>	120	17.59	667	1.60	5.3	146/141	76/57	33	0.11	n.d.	n.d.
11	3 <sup>g</sup>	60	10.46	327	1.65	6.4	136/140	39/52	31	0.10	n.d.	n.d.
12	4	15	2.07	585	1.34	0.7	141/140	74/55	20	0.09	11.7 ± 0.2	0.6
13	4	120	13.50	1678	1.54	1.6	144/139	76/47	33	0.12	31.3 ± 0.5	1.3

<sup>a</sup>Polymerization conditions: 5  $\mu\text{mol}$  of pre-catalyst, 40 bar of ethylene pressure, 10.0 g of sodium dodecyl sulfate, 4.0 mL of hexanol, 1.0 mL of toluene, 100 mL of water, 30 °C. <sup>b</sup>Determined via GPC at 160 °C in 1,2-dichlorobenzene. <sup>c</sup>Determined by DSC on nascent polymer powder, isolated by precipitation from the nanocrystal dispersion, measured with a 10 K  $\text{min}^{-1}$  heating rate, first and second heating cycle reported. <sup>d</sup>Volume mean given. <sup>e</sup>Lateral particle size determined from TEM statistics (equivalent diameter and standard error reported). <sup>f</sup>At 50 °C. <sup>g</sup>At 70 °C.

linear polymer microstructure, which was also confirmed by exemplary  $^{13}\text{C}$  NMR analysis (Figure S7). The observation of significantly decreased melting points upon slow heating ( $1\text{ K min}^{-1}$ ) hints at a disentangled nature of the nascent polymer (Figures S8–S12).<sup>25,26</sup> Considering the origin of the outstanding catalytic properties of **3**, the numbers of chains per Ni and the molecular weight distributions suggest that **3** is very efficiently activated in this aqueous system (entry 5). This can be due to a facilitated pyridine dissociation in **3**, but also to physical differences in the initial catalyst microemulsions promoted by the nature of the dissolved catalyst precursor molecules (like droplet size or solvent nature of the droplet phase, which influences, for example, partitioning coefficients).

In view of the living nature of polymerizations with **3**, the process of particle growth was investigated. According to dynamic light scattering (DLS) analysis, all dispersions feature narrow particle size distributions without any aggregates. With increasing polymerization time from 5 min to 120 min, the average particle size of the obtained dispersion grows from 15 nm to 38 nm (Figure 2c; note the analysis of DLS data assumes a spherical particle shape). The narrow size distributions are confirmed by transmission electron microscopy (TEM), which further reveals a disk-like particle shape in all cases (Figure 2d and Figure S21). With reaction time, the average diameter of the particles increases from 7.4 nm to 27.1 nm. The thickness is independent of the duration of the polymerization and only 8.0 nm, which corresponds to the expected value for a single lamella particle (Tables S2 and S3).<sup>27</sup> A comparison of the average mass of particles (derived from the size) with the molecular weight of the formed PE suggests that a particle consists of a single chain. That is, in polymerizations with microemulsions of **3**, a controlled particle growth is also realized, which also is reflected by a linear increase of particle volume with yield (that is, the number of particles remains constant over time) and the aforementioned narrow particle size distributions (Table S3).

We show that the established robust nature of P,O-coordinated Ni catalysts in aqueous systems can go along with achieving useful polymer molecular weights in the range of typical HDPEs and even ultrahigh molecular weight polyethylenes. Further, Shimizu et al. and Li et al. have only recently broken the long-lasting paradigm that frequent BHE chain transfer events with P,O-coordinated catalysts invariably result in limited molecular weights ( $<M_n 10^4\text{ g mol}^{-1}$ ). Our findings of living polymerization take this to yet another level. Overall, this provides novel perspectives for the generation of polyolefin dispersions as well as the generation of desirable block copolymers.

## ■ ASSOCIATED CONTENT

Synthesis, characterization, and X-ray structure data of complex **3**; polymerization procedure; interactions between Ni complexes and 1-hexanol; NMR spectra, DSC traces, and GPC data of the obtained polymers; mass flow of ethylene consumed in microemulsion polymerizations; particle size data analysis of nanoparticle dispersions (PDF)

## Accession Codes

CCDC 2111789 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

F.L. is grateful to the Alexander von Humboldt Foundation for a postdoctoral research fellowship. Dr. Inigo Göttker-Schnetmann is gratefully acknowledged for assistance with single-crystal analysis and for helpful discussions. The authors also thank Lars Bolk for DSC measurements and Manuel Schnitte and Florian Wimmer for GPC measurements. Support by the ERC (Advanced Grant “DEEPCAT”) is acknowledged.

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