

Water-Soluble Salicylaldiminato Ni(II)–Methyl Complexes: Enhanced Dissociative Activation for Ethylene Polymerization with Unprecedented Nanoparticle Formation

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Late transition metal catalysts for polymerization of olefins have been studied intensely recently.¹ Due to their functional group tolerance, polar monomers can be copolymerized.² Also, polymerizations can be carried out in aqueous emulsion to afford dispersions of submicron particles of polymers with controlled microstructures.^{3,4} Notably, particles with sizes <30 nm can be prepared.⁵ Such sizes are difficult to access for any given polymer microstructure, be it controlled or uncontrolled as from free-radical polymerization.⁶ A possible approach is polymerization starting from a homogeneous aqueous solution of a water-soluble catalyst (and surfactant). An easily accessible but ill-defined in situ prepared catalyst afforded ca. 20 nm particles of linear low molecular weight polyethylene.^{5a} The approach of water-soluble catalysts is attractive as the absence of water-immiscible organic solvents greatly simplifies the system in terms of the initial reaction mixture (single aqueous phase) and the dispersed particles obtained (no swelling with solvent).

We have reported the synthesis of polyethylene dispersions with (κ^2 -*N,O*)-salicylaldiminato Ni(II)–methyl complexes, such as **1-pyridine** or **1-tmeda** (tmeda = *N,N,N',N'*-tetramethylethylenediamine).^{3c,d} These lipophilic catalyst precursors were introduced to polymerization as aqueous mini- or microemulsions of a solution of **1** in a small amount of toluene.

Displacement of pyridine in complexes **1–4-pyr** by highly water-soluble ligands **L**, where **L** = TPPTS [tri(sodiumphenylsulfonate)-phosphine], TPPDS [di(sodiumphenylsulfonate)phenylphosphine], or H₂N-PEG [H₂N(CH₂CH₂O)_{*n*}Me; *n* = ca. 52], affords water-soluble complexes **1–4-L** (solubility > 200 μmol/L; for experimental details, see Supporting Information). In the absence of any organic solvent and using homogeneous aqueous solutions of, for example, complexes **1–4-TPPTS** and sodium dodecyl sulfate (SDS) under 40 bar ethylene, transparent high molecular weight polyethylene dispersions are formed.

Ethylene uptake by mass flow monitoring reveals that catalysts' lifetime is poor and deactivation occurs within less than 10 min at 50 °C. Decreasing the reaction temperature to 15 °C retards the deactivation process (ethylene consumption is observed for ca. 20–35 min) and allows for higher overall productivities and molecular weights (Table 1, entries 1–5).⁷ Slightly different polymer microstructures were obtained by varying the substitution pattern of the terphenyl moieties in **1–4-TPPTS**.⁸ At 15 °C, 40 bar ethylene, *tert*-butyl/hydroxy-substituted precatalysts **2** and **4** produce polyethylene with 18 (15, respectively) methyl branches (*T_m* = 107 and 118 °C, respectively) compared to ca. 5 methyl branches/1000 carbon atoms obtained with CF₃-substituted complexes **1** and **3** (*T_m* = 134 and 126 °C, respectively; see Supporting Information). Notably, the anthryl substituent^{2c} in **3,4-TPPTS**, which was thought to aid phosphine dissociation (i.e., without a phosphine scavenger), has no beneficial effect on the catalytic activity in water, when compared to the activity of diiodo-substituted **1,2-TPPTS** and **1,2-**

Chart 1. Lipophilic, Hydrophilic, and Amphiphilic Single-Component Polymerization Catalysts Used in This Study

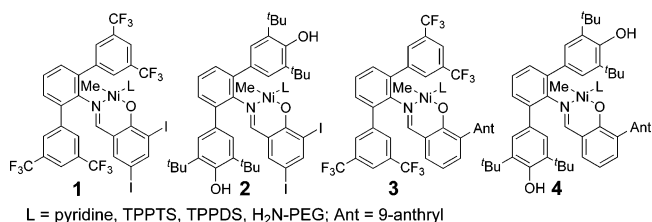


Table 1. Polymerization Results

entry	catalyst	solvent	T (°C)	yield (g)	TON ^d (×10 ³)	<i>M_w</i> /PDI ^e (×10 ⁵ g mol ⁻¹)	Φ ^g (nm)
1	1-TPPTS	H ₂ O ^a	50	0.61	2.18	1.1/(2.5)	12
2	1-TPPTS	H ₂ O ^a	15	1.82	6.48	1.8/(1.9)	4
3	2-TPPTS	H ₂ O ^a	15	1.80	6.40	0.9/(1.9)	5
4	3-TPPTS	H ₂ O ^a	15	1.26	4.50	1.5/(2.0)	4
5	4-TPPTS	H ₂ O ^a	15	1.35	4.80	3.5/(2.0)	4
6	1-TPPDS	H ₂ O ^a	15	2.34	8.36	0.6/(7.0) ^f	4
7	1-TPPDS	tol ^b	15	0.37	1.31	3.7/(2.5) ^f	n/a
8	1-TPPDS	tol ^b	50	8.55	30.5	0.6/(2.0)	n/a
9	1-TPPDS	H ₂ O ^a	50	1.01	3.60	0.6/(2.2)	5
10	2-TPPDS	H ₂ O ^a	15	2.22	7.93	1.5/(6.0) ^f	6
11	2-TPPDS	tol ^b	15	0.22	0.79	2.1/(3.2) ^f	n/a
12	1-H₂N-PEG	H ₂ O ^a	15	1.75	6.25	1.2/(2.1)	15
13	1-H₂N-PEG	tol ^b	15	c	c	c	n/a
14	1-H₂N-PEG	tol ^b	50	0.37	1.33	0.7/(2.5)	n/a
15	3-H₂N-PEG	H ₂ O ^a	15	1.78	6.36	2.1/(2.5)	15
16	3-H₂N-PEG	tol ^b	15	c	c	c	n/a
17	4-H₂N-PEG	H ₂ O ^a	15	2.33	8.32	5.9/(1.9)	8
18	4-H₂N-PEG	tol ^b	15	c	c	c	n/a
19	1-pyr	tol ^b	15	0.09	0.32	0.8/(2.1)	n/a
20	1-pyr	tol ^b	50	5.66	20.2	1.0/(5.0)	n/a

^a Polymerization conditions: 10 μmol precatalyst, 100 mL of H₂O, 750 mg of SDS, 40 bar C₂H₄, 30 min, polymer obtained as latex. ^b Polymerization conditions: 10 μmol precatalyst, 100 mL of toluene, 40 bar C₂H₄, 30 min. ^c No polymer obtained. ^d Mol [C₂H₄] × mol⁻¹ [Ni]. ^e From GPC versus linear PE standards at 160 °C. ^f Bimodal distribution. ^g Volume average particle size determined by DLS.

TPPDS (entries 4 and 5 vs 2, 3, 6, and 10). Likewise, phosphine scavenger-free ethylene polymerization is also observed with diiodo-substituted **1-TPPDS** in toluene with activities exceeding those of **1-pyr** (entries 8 vs 20).

Most noteworthy, while lipophilic **1-pyr** is a highly active and stable polymerization catalyst at 50 °C in toluene (entry 20),^{3c,d} its productivity at 15 °C in toluene is significantly lower than that of hydrophilic **1-TPPTS** or **2-TPPTS** at 15 °C in water (entries 2 and 3 vs 19), even though deactivation of **1-pyr** is not observed. A similar drop in productivity (and activity) when changing from aqueous to toluenic polymerization conditions was observed for **1,2-TPPDS** and **1,3,4-H₂N-PEG**, which are soluble in both toluene and water; that is, **1-TPPDS** is highly active and stable at 50 °C,

40 bar in toluene (30.5×10^3 TO in 30 min), while under otherwise identical aqueous conditions, 3.6×10^3 TO in ethylene and fast deactivation within 5 min were observed. In stark contrast, at 15 °C, 40 bar ethylene, **1-TPPDS** produces 6.5 times the amount of PE within 30 min in water when compared to toluene (8.4×10^3 TO in water vs 1.3×10^3 TO in toluene), even though deactivation in water is still evident (entries 6–9). An even more dramatic decrease in activity was observed for **1,3,4-H₂N-PEG**, which are not active at 15 °C in toluene while high activity is observed in water (entries 12–18). Complex **1-H₂N-PEG** even at 50 °C in toluene exhibits only a very minor activity when compared to the activity in aqueous conditions at 15 °C (entries 12 and 14).

We believe that an incipient compartmentalization in the polymer particles formed of the lipophilic, highly active species generated by dissociation of the hydrophilic **L** (TPPTS, TPPDS, or H₂N-PEG) from complexes **1–4-L** in water retards the recombination of the hydrophilic/amphiphilic phosphine (or H₂N-PEG, respectively) and the hydrophobic (κ^2 -*N,O*)-salicylaldiminato nickel alkyl fragment. That is, water serves as phosphine scavenger (amine scavenger, respectively) by solvation of the hydrophilic (or amphiphilic) ligand. Further, hydrophobic solvation of the catalytically active Ni fragment preferentially occurs by the surfactant, ethylene, and the formed polymer when compared to water, and thus enhances ethylene insertion.^{9,10} Evidence for this proposal is provided by NMR spectra of **1-4-TPPTS** in CD₃OD, DMSO-*d*₆, and D₂O/SDS, which indicate a solvent-dependent dissociation of **TPPTS** from the catalytically active Ni–methyl fragment. In CD₃OD solution, **1-TPPTS** exhibits two ³¹P NMR resonances at δ 32.3 (Ni-bound TPPTS) and –3.1 (free TPPTS) in a ca. 11:1 ratio. Correspondingly, the ¹H NMR spectrum exhibits a doublet (δ –1.50, ³J_{PH} = 8.4 Hz) for the Ni–methyl resonance of **1-TPPTS** and two additional singlets for phosphine-free Ni–methyl complexes at δ –1.28 and –1.31 in a ca. 40:2.4:1 ratio. In DMSO-*d*₆, **1-TPPTS** is much more dissociated as evidenced by (a) one singlet (δ –1.19) and one doublet (δ –1.69, ³J_{PH} = 7.2 Hz) for the nickel–methyl resonances in a ca. 1:2 ratio, and (b) the two signals in the ³¹P NMR spectrum at δ 31.4 and –3.9 in a ca. 2:1 ratio. Finally, the respective ¹H NMR spectrum in D₂O/SDS is dynamically broadened with respect to the salicylaldimine– and the Ni–methyl resonances, while sharp signals for free TPPTS are observed. The respective ³¹P NMR spectrum exhibits a single resonance at δ –4.9 indicative of free TPPTS. Similar effects are observed for **2-TPPTS** and **4-TPPTS** (see Supporting Information).

Solvation effects are assumed to enhance dissociation of amphiphilic TPPDS also in toluene. The low solubility of TPPDS in toluene may account for a less effective recombination of active sites with TPPDS. Thus, polymerization with TPPDS complexes in toluene is enhanced when compared to polymerization of complexes of H₂N-PEG which is highly soluble in toluene.

Preliminary analyses of obtained polyethylene dispersions by dynamic light scattering (DLS; single-angle 173° backscattering) reveal unprecedented small sizes of as low as ca. 4–6 nm (Table 1). An order of magnitude estimate based on the observed particle volumes and *M_n* values indicates that the average particle contains ca. one polyethylene chain (see Supporting Information).¹¹ Note that these sizes are close to those of the thinnest polyethylene lamella observed to date, that is, the smallest hierarchical structures known to be responsible for crystallinity of polyethylene.¹²

An estimation of the number of particles generated per nickel center present in the reaction mixture yields values of *N_{part}/Ni* of 0.2–10.¹¹ The molecular weight distributions clearly show that chain transfer occurs. Calculated numbers of chains formed per nickel center present in the reaction mixture of, in some cases, *N_{chain}/*

Ni < 1 thus indicate that not all nickel centers are active. With this in mind, the aforementioned *N_{part}/Ni* rather indicates that one or several particles are formed per active site. The latter would imply that an active site can leave an existing particle by recoordination of water-soluble **L** and nucleate a new particle. In any case, the data demonstrate that a single active site can nucleate and grow a given polymer particle.

In conclusion, we have prepared (κ^2 -*N,O*)-salicylaldiminato nickel–methyl complexes for the polymerization of ethylene featuring water-soluble labile ligands. Under conditions where catalyst deactivation is retarded, the activity in water is higher than that in toluene. This unusual behavior is presumably due to effective scavenging of the hydrophilic labile ligand by solvation in water. Extremely small particles of high molecular weight polyethylene are formed under organic solvent-free aqueous conditions. The observed generation of a given particle by a single active site is an unprecedented formation mechanism for aqueous particle dispersions.

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Supporting Information Available: Synthesis and characterization of **1–4-L**, polymerization procedures, additional polymer data, including *N_{part}/Ni*, *N_{chains}/Ni*, *N_{chains}/N_{part}*, GPC and DLS traces, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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