# Aqueous Dispersions of Polypropylene and Poly(1-butene) with Variable Microstructures Formed with Neutral Nickel(II) Complexes

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Polymerization of 1-olefins and the polymer microstructures formed have been studied intensly with early transition metal catalysts, and more recently with late transition metal cationic Ni(II) and Pd(II) diimine complexes.[1,2] In contrast, while neutral Ni(II) polymerization catalysts are of general interest due to their specific functional group tolerance, they have been little studied for 1-olefin polymerization.[3−5] The only notable study is Fink's polymerization of $C_4$ to $C_{20}$ 1-olefins (in a nonaqueous system) with an in situ catalyst $[Ni^0(cod)_2]/(Me_3Si)_2N\text{-}P\{=NSiMe_3)_2$ that most likely contains neutral Ni(II) active sites. 2,ω-incorporation was observed exclusively.[3−5]

Polymer dispersions, that is aqueous dispersions of polymer particles with sizes of ca. 50 nm to 1 μm, are employed on a large scale e.g. for environmentally friendly coatings and paints.[6] Catalytic synthesis of polymer dispersions is an attractive aim, as it can enable control of polymer microstructures, by contrast to currently practiced free radical emulsion polymerization.[7−11] Moreover, 1-olefins in particular are not susceptible to radical polymerization due to stable radical formation.

Complexes $[\{\kappa^2\text{-}N,O\text{-}6\text{-}C(H){=}NAr\text{-}2,4\text{-}R'_2C_6H_2O\}NiMe(L)]$ (Ar = 2,6-$\{3,5\text{-}R_2C_6H_3\}_2C_6H_3$; **1**: L = tmeda, R = $CH_3$, R′ = I; **2**: L = tmeda, R = $CF_3$, R′ = 3,5-$(F_3C)_2C_6H_3$; **3**: L = tmeda, R = $CF_3$, R′ = I; tmeda = *N,N,N′,N′*-tetramethylethylenediamine) in ethylene polymerization afford a range of microstructures depending on the remote substitutents R (**1**, highly branched polymer; **3**, nearly linear).[12] **1** has a high capability for chain running, and for insertion of ethylene into secondary metal alkyls, which prompted us to study 1-olefin polymerization.

Exposure of **1**−**3** to 1-butene indeed resulted in the formation of low-molecular-weight polymers (Table 1). Productivities up to $10^3$ TO (TO = turnover = mole monomer converted per mole of Ni) are observed, vs $10^5$ TO in ethylene polymerization. The question arises whether catalyst deactivation occurs (intrinsically or, e.g., by impurities in the monomer) or whether chain growth is slow. Monitoring a reaction by continuously drawing samples reveals that polymerization continues for hours (Figure 1). By comparison to ethylene polymerization, insertion of the bulky 1-olefin into a Ni(II) alkyl bond slows down chain growth. Accordingly, **1** which has a pronounced capability for chain running (vide supra) to form a less hindered species after 1-olefin insertion is the most active. Molecular weight is time-independent, that is chain transfer controls molecular weights. In accordance with this, the calculated number of chains formed per nickel(II) center present in the reaction mixture is ≫1, on the order of $10^2$.

To prepare polymer dispersions, a high degree of dispersion of the catalyst in the intial reaction mixture is a prerequisite.[7,8,11] To a mixture of an aqueous surfactant solution and a solution of **1**, **2**, or **3** in a small amount of toluene a metered amount of liquid monomer was added (vapor pressure of 1-butene at 20 °C, 2 bar; vapor pressure of propylene, 9 bar). The mixture was sheared intensly by an ultrasound device in the pressure reactor, to form a miniemulsion. Colloidally stable dispersions were obtained (entries 7−9). Polymer solids content of entry 7 was 2.6 wt %. Volume average particles sizes, as determined by dynamic light scattering, are 50−100 nm. Catalyst activity is somewhat lowered by comparison to nonaqueous polymerizations. This is likely due to a partial, reversible or irreversible, deactivation of the catalyst by water[13] (note that reaction conditions in terms of monomer concentration in the organic phase are similar in aqueous and nonaqueous polymerizations). However, half-lifes for deactivation in the aqueous system must be on the order of at least an hour.[14]

**Table 1. Polymerization Results**[a]

| no. | mon. | cat. (μmol) | yield [g] | TON[d] | $M_n$ ($M_w/M_n$)[e] [$10^3$ g mol$^{-1}$] | 1,2[f] | 2,ω[f] | 1,ω[f] |
|---|---|---|---|---|---|---|---|---|
| 1[b] | B | **1** (40) | 1.5 | 670 | 0.5 (3.3) | n.d. | n.d. | n.d |
| 2[b] | B | **1** (42) | 3.2 | 1360 | 1.0 (3.5) | 10% | 65% | 25% |
| 3[b] | B | **2** (60) | 1.5 | 450 | 1.4 (1.9) | 50% | 22% | 28% |
| 4[b] | B | **3** (80) | 1.5 | 340 | 1.2 (1.9) | 73% | 13% | 14% |
| 5[b] | P | **3** (80) | 1.5 | 450 | 0.6 (1.3) | 90% |  | 10% |
| 6[b] | H | **1** (40) | 0.3 | 90 | 0.5 (1.7) | 27% | 41% | 32% |
| 7[c] | B | **1** (80) | 3.2 | 710 | 1.6 (1.9) | 11% | 66% | 23% |
| 8[c] | B | **3** (94) | 0.7 | 130 | 1.1 (1.6) | 65% | 13% | 21% |
| 9[c] | P | **3** (94) | 0.4 | 100 | 0.4 (1.7) | 79% |  | 21% |

[a] 5 °C (entry 1: 20 °C); reaction time: 16 h (entry 1), 64 h (entries 2 and 3), 120 h (entries 4 and 8), 200 h (entry 5), 83 h (entry 6), 41 h (entries 7), 167 h (entry 9). [b] 10 mL of toluene; monomer = 30 g (entry 1), 50 g (entries 2−4), 40 g (entry 5), 65 g (entry 6). [c] 120 mL of water; 0.9 g of SDS; 2 mL of toluene; 0.1 mL of hexadecane (entry 9: 200 mL water; 1.5 g of SDS); monomer = 7.7 g (entry 7), 6.3 g (entry 8), 8.0 g (entry 9). [d] mol [1-olefin] × $mol^{-1}$ [Ni]. [e] From GPC vs linear PE standards at 160 °C. [f] Incorporation mode.

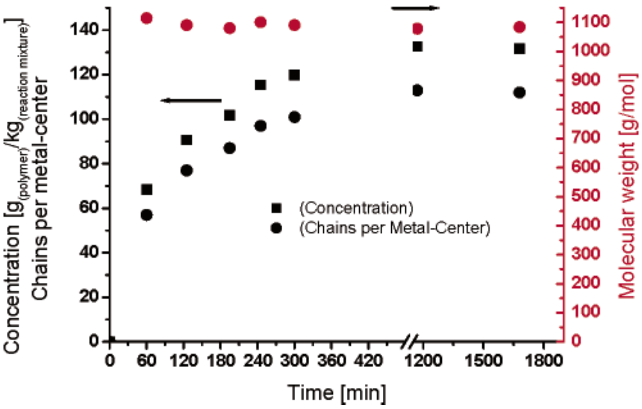

**Figure 1.** Polymer formation over time; time-dependent molecular weights and calculated number of polymer chains per Ni center present in the reaction mixture (99 μmol of **1**, 80 g of 1-butene, and 9 g of toluene, at 5 °C).

Microstructures of the poly(1-olefins) were studied by $^{13}C$ NMR spectroscopy. Unexpectedly in view of Fink's findings, 1,2-, 2,ω-,[15] and also 1,ω-incorporation are found (Table 1 and Figure 2; cf. Supporting Information for NMR details). Concerning the underlying insertion steps, 1,2-insertion is well documented for catalytic polymerization, and observation of 2,ω-incorporation shows it to occur also with these neutral Ni(II) complexes. 1,ω incorporation shows that 2,1-insertion of olefin also occurs to a significant extent. The absence of ethyl and propyl branches in poly(1-hexene) shows that after a 1,2-

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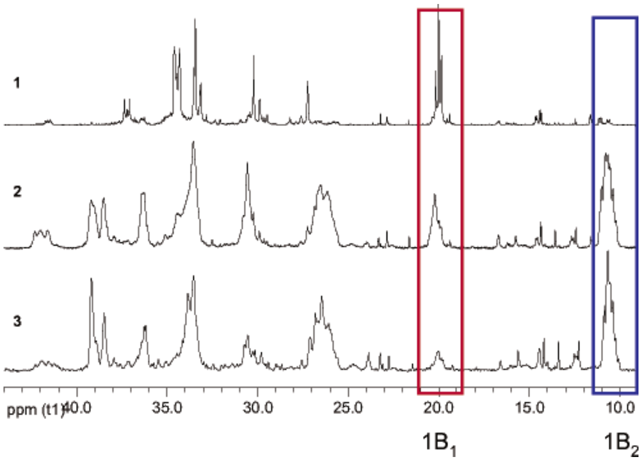
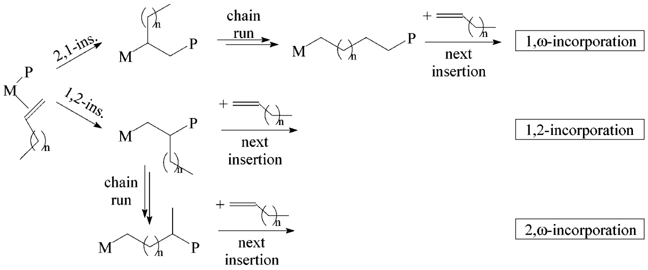


**Figure 2.** $^{13}$C NMR spectra of poly(1-butene)s prepared with different catalyst precursors (1B$_1$, $-CH_3$ of a methyl branch; 1B$_2$, $-CH_3$ of an ethyl branch). For full assignments see the Supporting Information).

**Scheme 1. Mechanism of Chain Growth (*P* = Polymer Chain)**



insertion either the next insertion occurs (1,2-incorporation; Scheme 1), or chain running will go all the way to the end of the branch to form a primary alkyl prior to the next insertion (2,*ω*−incorporation) The latter makes it seem likely that 2,1-insertion will also be followed by chain running to form a primary metal-alkyl, that is result in 1,*ω*-incorporation exclusively. Overall, insertion occurs only in primary metal alkyls. $^1$H NMR spectra of polypropylene show vinyl end groups $-CH_2CH{=}CH_2$, trisubstituted $-CH{=}CMe_2$, internal olefin $-CH{=}CH-$ and vinylidene groups $-CH_2C(Me){=}CH_2$ (the latter two predominating), confirming both 1,2- and 2,1-insertion to occur. Poly(1-butene) possesses analogous end groups (Supporting Information). That 2,1-insertion does not occur in Fink's system can be due to the high steric crowding of the Ni center by the $\kappa^2$-*N,N* ligand.[5b]

Remarkably, the microstructures are dependent on the catalyst (Table 1 and Figure 2). Whereas 1,2-incorporation prevails in poly(1-butene) prepared with **3** (73%), **1** affords 2,*ω*-incorporation preferentially (65%). As outlined, 1,2-insertion prevails with all catalysts, and the preference for 2,*ω*-incorporation of **1** is due to a high propensity to run even past a tertiary carbon. The high capability of **1** to chain run to a less hindered M-CH$_2$-CH$_2$R is also in accord with the higher activity observed in 1-butene polymerization (Table 1).[16] It also agrees with the high chain running capability of **1** observed in ethylene polymerization.[12]

In summary, 1-olefins are polymerized by the neutral Ni(II) complexes studied. Polymerizations in aqueous emulsions, starting from a monomer miniemulsion, afford dispersions of poly(1-olefins). Microstructure analyses reveal that insertion occurs in primary alkyls exclusively, formed by 1,2- and 2,1-insertion, and subsequent chain running. 2,1-insertion has been unambiguously shown for a neutral Ni(II) polymerization catalyst for the first time. Microstructures can be varied by control of the chain running capability of the catalyst via remote substituents of the salicylaldimine ligand.

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**Supporting Information Available:** Text giving general methods and materials and figures showing NMR spectra of polymers and assignments and DSC plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Monitoring polymerization in emulsion by drawing of samples was hampered by foaming and clogging of the valve.
(15) For propylene, 2,*ω* incorporation is identical to 1,2-incorporation.
(16) This applies to chain running after a 1,2- as well as 2,1-insertion, cf. Scheme 1. The observed inactivity of **1** towards propylene indicates that also insertion into M-CH$_2$CH(Me)P is slower than with **2** or **3** (a M-CH$_2$CH$_2$ species cannot be formed in the case of propylene).

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