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 $[Ni^0(cod)_2]/(Me_3Si)_2N-P\{=NSiMe_3)_2$ that most likely contains neutral Ni(II) active sites. $2,\omega$-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 $[\{\kappa^2-N,O-6-C(H)=NAr-2,4-R'_2C_6H_2O\}NiMe(L)]$ (Ar = 2,6-$\{3,5-R_2C_6H_3\}_2C_6H_3$; **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 $\gg1$, 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

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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.
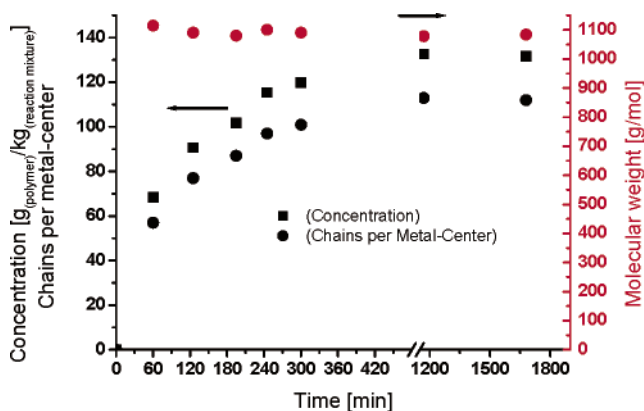

Figure 1. Polymer formation over time; time-dependent molecular weights and calculated number of polymer chains per Ni center present in the reaction mixture (99 μmol of **1**, 80 g of 1-butene, and 9 g of toluene, at 5 °C).

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]

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-
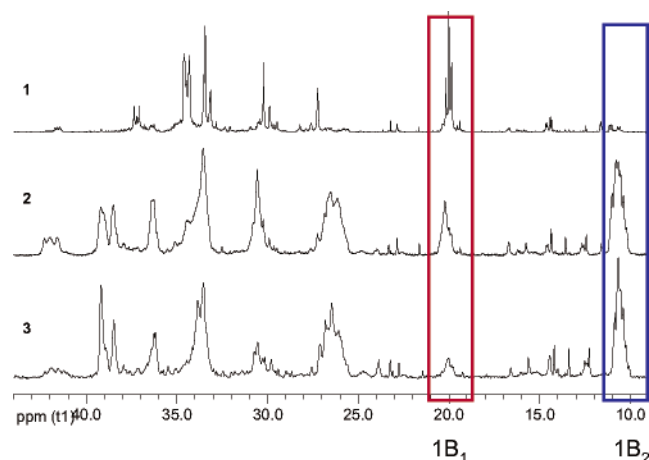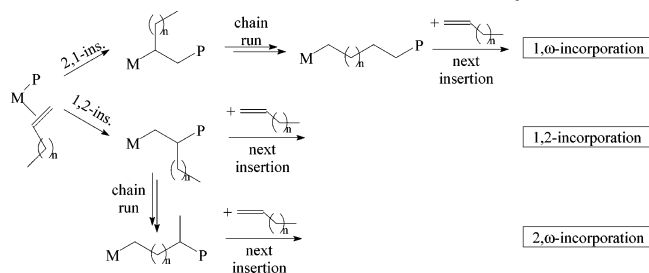
Figure 2. ^{13}C NMR spectra of poly(1-butene)s prepared with different catalyst precursors (1B$_1$, −CH$_3$ of a methyl branch; 1B$_2$, −CH$_3$ of an ethyl branch). For full assignments see the Supporting Information).

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$_2$CH=CH$_2$, trisubstituted −CH=CMe$_2$, internal olefin −CH=CH− and vinylidene groups −CH$_2$C(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 κ^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.

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).