Coordination polymerization of ethylene in water by Pd(II) and Ni(II) catalysts

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Ethylene is polymerized in water as a reaction medium by Pd(II) and Ni(II) complexes to afford branched or linear homopolymer.

Water possesses unique properties as a reaction medium. It is highly polar and immiscible with most organic compounds, has a high heat capacity and also features a strong propensity for micelle formation. In addition, water is an ideal medium from an environmental and safety perspective. Thus, emulsion and suspension polymerization of olefinic monomers is employed on a vast scale, *e.g.* for the direct production of water-based lattices, used for coatings and paints. In contrast to these free radical polymerizations, transition metal catalyzed coordination polymerization reactions in water have received less attention, as the early transition metal catalysts[1] used predominately are extremely sensitive to moisture.

Late transition metal complexes are generally less sensitive to polar media due to their less oxophilic nature. Due to the propensity of late transition metal alkyl complexes for β-hydride elimination, dimers or oligomers are usually obtained in C–C linkage of ethylene.[2] Only a limited number of catalysts for polymerization to high molecular weight products are known. Most of them are based either on neutral Ni(II) complexes[3,14a] of formally monoanionic bidentate ligands or on cationic Fe, Co, Ni or Pd complexes[4] of neutral multidentate ligands with bulky substituted N donor atoms.[5] The aforementioned stability of late transition metal complexes is demonstrated by the tolerance of some of these polymerization catalysts towards polar function-alized comonomers[3d,4b,c] and polar organic solvents.[3c,d,4c,6]

In the context of possible side reactions in transition metal catalysis in aqueous media[7] (such as hydrolysis of metal alkyl species, attack of water on coordinated substrates or coordination of water to the metal center as a ligand), regarding polymerization reactions a conceivable effect of water on chain transfer[8] is of specific interest as small (absolute) changes in the overall chain transfer rate will strongly influence product molecular weight.

A very slow (*ca.* 1 turnover per day) coordination polymeri-zation of ethylene in water catalyzed by a Rh complex has previously been investigated.[9] We now report on the homo-polymerization of ethylene in water by neutral Ni(II) and cationic Pd(II) complexes.

Exposure of an aqueous suspension of Pd complex **1**[4c] to ethylene at elevated pressure results in formation of high molecular weight, highly branched polyethylene (Table 1). The reaction is effective under mild conditions (7 bar, room temperature), an increase of the ethylene pressure to 40 bar resulting in a doubling of productivity (entry 1 *vs.* 3). Comparison of 3 and 16 h experiments reveals no significant deactivation of the cationic catalyst in the presence of water (entry 2 *vs.* 3). In comparison to polymerization employing a homogeneous solution of **1** in CH_2Cl_2 as a non-aqueous solvent

2a: M⁺ = Na⁺
2b: M⁺ = $H_{33}C_{16}NMe_3^+$
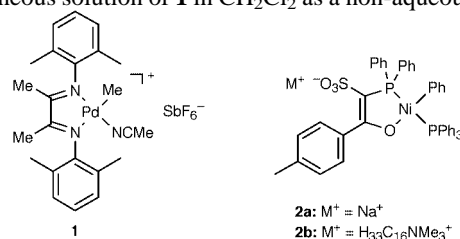
(entry 3 *vs.* 4), activities are similar. However, branching is reduced in comparison to reaction in CH_2Cl_2 (69 to 83 branches per 1000 C atoms in runs 1 to 3 *vs.* 109 branches per 1000 C in run 4; determined by ^{1}H NMR). Also, GPC analysis reveals a much higher molecular weight of the polymers obtained in water (Table 1). These findings correspond to the physical appearance of the polymers: whereas the material obtained in CH_2Cl_2 is a highly viscous oil, the polymers obtained in the aqueous reaction medium are rubbery solids. In preliminary

Table 1 Polymerization results

Entry No.	Catalyst	n(cat.)/ μmol	Ethylene pressure/bar	Reaction medium	Reaction time/h	Polymer yield/g	Productivity/ mol(ethylene) mol(cat.)$^{-1}$	Average activity/ mol(ethylene) mol(cat.)$^{-1}$ h^{-1}	$M_w{}^a$/g mol^{-1}	$M_n{}^a$/g mol^{-1} (M_w/M_n)
1	**1**	81	7	H_2O	23	7.4	3 260	140	160 000	70 600 (2.3)
2	**1**	61	40	H_2O	3	2.3	1 340	450	181 100	63 500 (2.8)
3	**1**	61	40	H_2O	16	10.9	6 380	400	179 400	77 700 (2.3)
4	**1**	61	50	CH_2Cl_2	14	14.4	8 430	600	32 300	14 500 (2.2)
5	**2a**^{b}	130	50	acetone:H_2O 50:50	1.5	2.5	680	450	^{c}	^{c}
6	**2a**^{b}	121	50	acetone:H_2O 50:50	3	3.2	940	310	^{c}	^{c}
7	**2a**^{b}	108	50	acetone:H_2O 5:95	2	2.2	710	360	2 230	970 (2.3)
8	**2a**^{b}	89	50	toluene:H_2O 5:95	2	5.9	2 360	1 180	3 030	960 (3.1)
9	**2b**^{b}	116	50	toluene:H_2O 5:95	1.5	1.0	310	210	^{c}	^{c}
10	**2b**^{b}	104	50	toluene:H_2O 5:95	3	1.6	550	180	^{c}	^{c}
11	**2a**^{b}	12	50	toluene	2	9.0	26 680	13 340	580 000	13 900 (42)
12	**2a**^{b}	26	50	acetone	2	22.2	30 440^d	15 220^d	94 000	3 770 (25)
13	**2b**^{b}	9	50	toluene	1.75	5.2	20 600	11 780	28 800	5 440 (5.3)

Reaction temperature: room temp. (entries 1 to 4), 70 °C (entries 5 to 13). Total volume of water and/or organic solvent: 100 mL.

^{a} Determined *vs.* polystyrene (entry 1 to 4) resp. linear polyethylene (entry 5 to 13) standards. ^{b} Phosphine scavenger [Rh(CH₂=CH₂)₂(acac)] (Ni:Rh 2:1). ^{c} Not determined. ^{d} Probably mass transfer limited.

experiments, the water ligand of the cationic complex [(ArN=C-(Me)C(Me)=NAr)PdMe(OH$_2$)]$^+$SbF$_6^-$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$)[10] was found to be displaced completely upon addition of ethylene in low temperature NMR experiments. This result implies that in catalysis in aqueous media with cationic complexes of this type no severe blocking of coordination sites by water should be expected, in accordance with the above polymerization experiments.

In ethylene polymerisation by a neutral Ni(II) complex with a P,O ligand, introduction of a sulfonate substituent has been reported to enhance formation of higher molecular weight products (toluene as reaction medium).[3c,d] At the same time, the sulfonate group affects water solubility. In order to produce higher molecular weight polymer the absence of strongly coordinating phosphine ligands is required.[3d,11] For this reason we have employed complex **2a**,[12,13] utilizing [Rh(H$_2$C=CH$_2$)$_2$(acac)] as a phosphine scavenger. For comparison to water-soluble **2a** with respect to aqueous polymerization in the presence of a water-immiscible solvent (*vide infra*) the novel complex **2b** was prepared by oxidative addition of 4-MeC$_6$H$_4$C(O)C(SO$_3^-$H$_{33}$C$_{16}$NMe$_3^+$)=PPh$_3$ to [Ni(cod)$_2$] in the presence of PPh$_3$, or by addition to [Ni(PPh$_3$)$_4$].[13] Introduction of the large H$_{33}$C$_{16}$NMe$_3^+$ cation results in a strong increase in lipophilicity: whereas **2a** dissolves in the aqueous phase upon addition of water to a toluene solution of the complex, **2b** remains in the organic phase.

The stability of C–C linkage catalysts based on Ni complexes with anionic bidentate ligands towards protic media, including water, had been noted early on by the original inventors.[14] However, successful polymerization to afford higher molecular weight products in water has not been reported, to the best of our knowledge. The complex [{κ^2P,O-Ph$_2$PC(Ph)=C(OEt)O}NiPh(PEt$_3$)] (removal of PEt$_3$ by phosphine scavengers) was reported to be completely inactive for ethylene polymerization in organic media in the presence of 1000 eq. water.[3d,15] For this reason, we were somewhat surprised to observe formation of linear polyethylenes employing catalysts **2a** and **2b** in an aqueous environment, utilizing only a small amount of water-miscible (acetone) or -immiscible (toluene) organic solvent to enable injection of the phosphine scavenger or the scavenger and **2b**, respectively (Table 1, entries 7 to 10). By comparison to polymerization in neat toluene or acetone[16] (entries 11 to 13), polymer molecular weight is significantly reduced and productivity is lowered in aqueous media. From the data presented, no dramatic effect of water on chain transfer reactions is evident, the lowering of polymer molecular weight also being attributable to a slower chain growth (as reflected by the lower productivity) caused by the lower solubility of ethylene in water. Considering catalyst stability, comparison of entries 5 *vs.* 6 and 9 *vs.* 10 shows that the catalysts are still active for polymerization after several hours in water. A preliminary comparison of the hydrophilic **2a** and the lipophilic **2b** in the multiphase system water/toluene/insoluble polymer (entries 8 and 9) reveals that phosphine abstraction from **2a** is not significantly hampered by the different solubilities of **2a** and [Rh(H$_2$C=CH$_2$)$_2$(acac)].

Interestingly, when performing the Ni(II)-catalyzed polymerization in the presence of ionic or non-ionic surfactants (SDS, Triton X-100), stable polyethylene emulsions are obtained. Typically, emulsions with particle sizes in the range of ϕ 80 to 300 nm are obtained at a catalyst productivity of, *e.g.* 1300 mol(ethylene) per mol(Ni) (conditions of run 7, surfactant added).

In conclusion, high molecular weight polymers can result from the coordination polymerizaton of ethylene in water at high catalyst activities. Branched or linear polymers are accessible in water as a reaction medium.

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