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Solubility and activity of a phosphinosulfonate palladium catalyst in water with different surfactants†

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Water-soluble phosphinosulfonate palladium complexes were synthesized by coordination of a surfactant to the metal center. The ethylene polymerization activity of the corresponding catalyst was probed. The surfactant and pH of the solution are shown to influence the activity. A phosphated surfactant resulted in polymerization with the highest activity and stability.

The development of late transition metal-based catalysts for ethylene polymerization has enabled the synthesis of polyolefins with unprecedented structures and morphologies.[1–5] Two unique characteristics of these catalysts are their ability to copolymerize olefins with polar monomers and to remain active in water to produce polyethylene latex.[2,3,6] The direct production of semi-crystalline polyolefin latex is currently impossible using industrially relevant early transition metal catalysts, yet achieving this synthesis would greatly expand the processability of an important class of polymers. To this end, a series of different techniques to yield such polyolefin latexes has been developed in recent years, including a miniemulsion polymerization method that consists of encapsulating a pre-catalyst into nanometer-size hydrophobic droplets stabilized by large amounts of surfactant.[7–16] We recently reported an alternative encapsulation strategy wherein the catalyst is encapsulated within polymeric-based micelles.[17] A simpler strategy consists of implementing an aqueous soluble complex as a catalyst precursor. Upon initiation of the polymerization, the catalyst becomes insoluble and collapses into a micelle where the polymerization proceeds to yield a polyethylene (PE) particle. Amine-terminated PEG and sulfonated aryl phosphines are common hydrophilic ligands to provide water solubility for these catalyst precursors.[18–24] This method has been shown to be more successful with nickel than palladium catalysts presumably due to a higher sensitivity of the palladium complex toward water.[25,26]

Despite recent progress, commercialization of this technology has been hampered by the low catalyst productivity in water, the high cost of the encapsulation techniques and/or high cost of the water soluble labile ligands. Therefore, there remains a clear need for the development of less expensive and more robust strategies for the synthesis of semi-crystalline PE latex.

In this letter, we present a simple method for the solubilization of catalyst precursor in water *via* the coordination of a surfactant to the metal center. In our prior work focusing on a block copolymer encapsulation strategy, we established that coordination of PEG was inhibiting the catalyst and resulted in low activity.[17,27] Based on this observation, we hypothesized that inexpensive water soluble catalyst precursors could be synthesized using the coordination of PEGylated surfactant. In contrast to previous water-soluble pre-catalysts relying on strong σ-donor ligands, we hypothesized that the weak interaction between the palladium and the PEG would result in higher activity. We focused our study on a phosphinosulfonate palladium catalyst (Fig. 1a) as this catalyst was previously

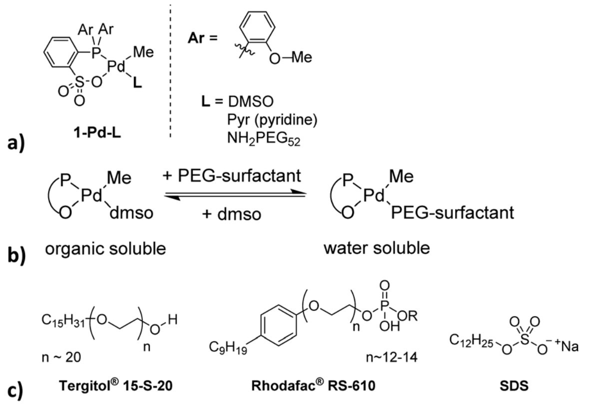

Fig. 1 (a) Structures of catalyst **1-Pd-L**, (b) labile ligand exchange, and (c) structure of surfactants: Tergitol®, Rhodafac® and SDS.

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shown to exhibit very high activity in organic solvent and to be stable toward water.[17,28] Lipshutz *et al.* reported several examples of successful Pd and Ru catalyzed reactions in water using this catalyst solubilization approach for small molecules functionalization.[29–32]

The water-soluble pre-catalysts were synthesized *in situ* by a simple ligand exchange (Fig. 1b). **1-Pd-DMSO** complex was used as the organic catalyst precursor. The weak coordination of the DMSO ligand was presumed to improve the yield of this ligand exchange. A UV titration method was developed to quantify the fraction of the phosphinosulfonate palladium complex solubilized in the aqueous phase using the absorption of the aromatic ligand (Fig. 2 and 3). A known water-soluble PEG-amine complex **1-Pd-NH$_2$PEG** dissolved in water/Rhodafac® was used to develop a calibration curve. The maximum absorbance of the complex was determined to occur at a wavelength of λ_{max} = 293 nm (presumably the aromatic rings of the ligand). Here, the aqueous solutions used to determine the calibration contain a surfactant (Rhodafac®) to faithfully represent the aqueous solutions used to synthesize the water-soluble catalyst precursor.

The water-soluble pre-catalyst solution was prepared by adding 0.1 mL of 0.02 μmol L^{-1} of **1-Pd-DMSO** complex in dichloromethane (DCM) to 10 mL of an aqueous Rhodafac® solution (8 g L^{-1}) heated to 85 °C, under vigorous stirring. Upon addition, gas evolved from the solution as the volatile organic solvent was flashed out, thereby yielding a clear solution. Upon cooling, the UV/Vis absorbance spectrum of this solution was determined. Using our calibration curve, we calculated that 99% of Pd complex was solubilized in water. This high yield motivated us to probe the limit of the titration method. Our original hypothesis relies on the coordination of the palladium complex to the PEG unit of the surfactant. Therefore, by removing the surfactant from the aqueous solution, we anticipated that a lower fraction of the catalyst precursor would be solubilized.

In a series of control experiments, we determined a new UV/Vis absorbance calibration in the absence of surfactant, and the solubilization of **1-Pd-DMSO** was repeated. The UV/Vis absorbance spectrum of the neat aqueous solution showed that 87% of the palladium complex was solubilized in the aqueous phase. This solubility was putatively attributed to the formation of an aqua complex.[25] However this experiment did not fully provide the validation for the UV titration. Therefore, we repeated the experiment using the corresponding pyridine complex (**1-Pd-pyr**) in place of the **1-Pd-DMSO** complex. The pyridine coordinates significantly more strongly than DMSO to the metal center, and therefore, formation of a water soluble aqueous complex was expected to be less favorable.[33] Indeed, only 40% of the pyridine complex was found to be dissolved in the aqueous solution. Moreover, the resulting aqueous solution was turbid, highlighting the low yield of the ligand exchange with **1-Pd-pyr**. Taken together, these experiments validate the UV/Vis titration method used to quantify the percentage of complex dissolved in water. Moving beyond solubility measurements, we further needed to determine the integrity of the catalyst precursor.

We next used the surfactant solubilization method to synthesize polyethylene latex upon exposure of the aqueous catalyst solution to ethylene (Table 1). In particular, we used three different surfactants to stabilize the polyethylene particles

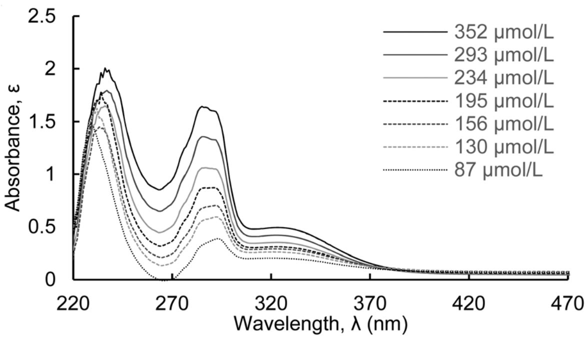

Fig. 2 Ultraviolet–visible (UV) absorbance calibration of **1-Pd-NH$_2$PEG** in water/Rhodafac® at different concentrations.

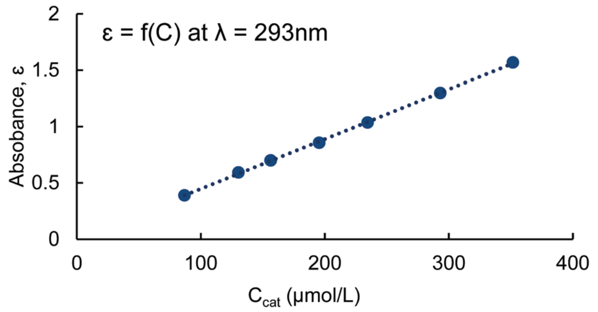

Fig. 3 Absorbance of **1-Pd-NH$_2$PEG** at λ_{max} = 293 nm as a function of concentration.

Table 1 Polymerization of ethylene with **1-Pd-DMSO** in water with different surfactants at different pH[a]

Trial	Surfactant	pH	TO (h^{-1})	PS[b] (nm)	% coag	M_n[c] (g mol^{-1})
1	None	3[e]	850	448	68	
2		7	850	193	52	2690
3		10[d]	315	90, 385	Traces	
4	SDS	3[e]	360	41	Traces	
5		7	330	54	0	560
6		10[d]	—	44, 164	0	
7	Rhodafac®	3	1300	135	18	
8		7[d]	560	24, 62	17	1710
9		10[d]	—	44, 474	Traces	
10	Tergitol®	3[e]	1015	41	25	
11		7	350	34, 481	63	2800
12		10[d]	—	50, 363	Traces	

[a] Polymerization was carried out with 20 μmol catalyst loading at 85 °C in 100 mL of water at 40 bar ethylene for 0.5 h. [b] Particle size, determined by dynamic light scattering (DLS). [c] Determined by ^{1}H-NMR in $Cl_2CDCDCl_2$ at 90 °C. [d] pH adjusted with CsOH. [e] pH adjusted with H_3PO_4 (1 M).

during polymerization (Fig. 1c): sodium dodecyl sulfate (SDS), an alkyl sulfonated surfactant; Tergitol®, a non-anionic PEGylated surfactant; and Rhodafac®, a phosphated PEGylated surfactant. These surfactants were chosen to illustrate the solubilization protocol. Presumably changing the hydrophobic-hydrophilic balance of the surfactant would also influence the solubility and activity of the catalyst. As a control, we also performed polymerization reactions in absence of surfactant. Without surfactant, a polyethylene latex was formed with broad particle size distribution and a large amount of coagulated polyethylene (52% of the PE formed) was observed floating at the top of the latex. Despite this colloidal instability, the catalyst reached a turnover (TO) rate of 850 TO h^{-1}. Note that the activities reported here do not include the polymer isolated as coagulate. As illustrated by the lower amount of coagulate formed, the addition of surfactants significantly improves the colloidal stability of the latex. The activity of the catalyst is also dependent on the surfactant, with SDS and Tergitol® resulting in lower activity than Rhodafac®. The pH of all polymerization reactions were set to be identical (~7), such that a small amount of cesium hydroxide was added to neutralize the Rhodafac® solution.[20]

We were further interested in studying the impact of the pH on the activity of the catalyst. Mecking and coworkers recently demonstrated that the stability and activity of a nickel catalyst was improved when the pH was increased.[20] A series of polymerization reactions at pH 3 and pH 10 was performed using the different surfactants.

The activity of the phosphinosulfonate palladium catalyst is lower at higher pH with all three surfactants. We observed the highest activity with the Rhodafac® surfactant at pH 3. The stability of the catalyst was also probed in presence of Rhodafac® and SDS (Fig. 4). With both surfactants, the catalyst did not show any decay in activity for over 1.5 hours. In the case of Rhodafac®, we observed only a 35% loss of activity after 6 hours of polymerization. Interestingly, the stability but low activity observed with SDS suggests that SDS is strongly inhibiting the catalyst. This inhibition could explain the low activity previously reported for the same catalyst when implemented in miniemulsion polymerization and with water soluble precursors.[34] Dynamic light scattering (DLS) analysis of the latex made with Rhodafac® showed that the volume of the polyethylene particles formed increases linearly with time, which is consistent with the absence of new nucleation or any coagulation. We also noticed that the ratio between the mass of PE formed in water and the mass of PE collected as coagulum remain constant over time (see ESI†). Both of these observations suggest that the particles are stable throughout the polymerization and the coagulation is caused by the presence of an insoluble catalyst fraction that remains active throughout the experiments.

We further studied the effect of surfactant concentration on the activity of the catalyst (Table 2). The addition of larger amounts of surfactant resulted in higher activity and lower amounts of coagulum, which is consistent with the coagulum being caused by a non-solubilized catalyst. Rather than continuously increasing the surfactant loading to fully solubilize the catalyst and reach a maximum activity, we lowered the catalyst loading. A polymerization reaction containing 7 μmol of catalyst (33% of the original loading) exhibited an impressive activity of 4040 TO h^{-1} without formation of coagulum. This activity is ~5× higher than the activity achieved in block copolymer micelles and >50× higher than previous miniemulsion attempts using the same catalyst.[17,34]

Isolated polyethylene samples made in the aqueous emulsions were analyzed by NMR spectroscopy and differential scanning calorimetry (DSC). We observed a broad melting temperature around 110 °C and a crystallinity reaching 70%, as determined by DSC. These thermal properties are consistent with the low molecular weights determined by ^{1}H-NMR. The appearance of olefinic protons in NMR spectra implies that the ratio of the rates of chain transfer to propagation is larger in water than in organic solvents. Again, this observation generally contrasts with the polymerization behavior using salycilaldimine nickel catalysts that rarely undergoes any chain transfer in water.[20] This higher propensity for chain transfer in water than in organic solvent could be caused by the coordination of water or by the lower solubility of ethylene in water, as both are known to lower the molecular weight of the polyethylene formed. Transmission electron microscopy (TEM) images were collected to observe the morphology of the par-

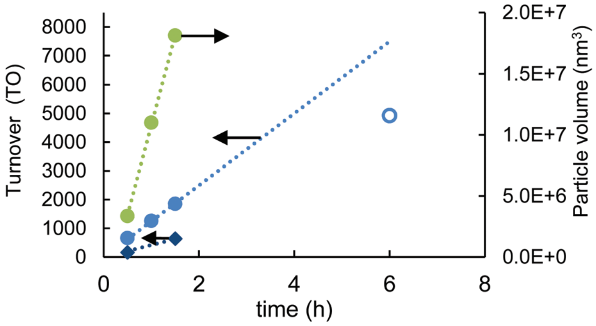

Fig. 4 Study of the catalyst activity in blue (● 0.8 g mL^{-1} Rhodafac®, ○ 1.6 g mL^{-1} Rhodafac® and ◆ 0.75 g mL^{-1} SDS) and particle size as a function of time in green (● Rhodafac®).

Table 2 Polymerization of ethylene with **1-Pd-DMSO** with different amounts of Rhodafac®[a]

Trial	Rhodafac® (g L^{-1})	TO (h^{-1})	M_n[c] (g mol^{-1})	PS[b] (nm)	% coag
1	4	400	1900	191	56
2	8	1300	2300	135	18
3	16	1650	1900	145	11
4	30	1900	—	119	6
5	30[d]	4040	—	148	Traces

[a] Polymerization was carried out with 20 μmol catalyst loading at 85 °C in 100 mL of water at 40 bar ethylene for 0.5 h. [b] Particle size, determined by DLS. [c] Determined by ^{1}H-NMR in $Cl_2CDCDCl_2$ at 90 °C. [d] With 7 μmol of catalyst.

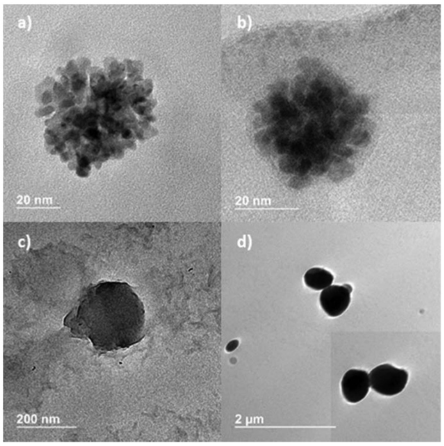

Fig. 5 TEM images of polyethylene at pH 3 (a) with Tergitol® (Table 1, entry 10) (b) with SDS (Table 1, entry 4) (c) with Rhodafac ® (Table 1, entry 7) (d) with no surfactant (Table 1, entry 1).

ticles. The sizes of the particles observed by TEM are in good agreement with the size determined by DLS even though aggregation occured during the sample preparation process. Zoomed in images of latex samples show that the particles synthesized with Tergitol® and SDS appear as an agglomeration of small particles with a rounded shape (Fig. 5). The volume of these sub-particles (assuming a sphere) is in the same order of magnitude as the volume of a single polymer chain based on its molecular weight (see ESI† for calculation). By analogy to radical emulsion polymerization where polymer chains are initiated in water, the morphology observed lead us to postulate that the catalyst shuttles between the aqueous phase and the particle. The water solubility of the palladium methyl complex (in absence of surfactant) suggests that the corresponding palladium hydride is also water soluble, and thus, upon chain transfer, the palladium complex becomes water soluble until it inserts multiple units of ethylene and collapses into a PE particle (Fig. 6). This morphology was not observed for Rhodafac®. We hypothesize that this difference could be caused by the coalescing of the sub-particles with the Rhodafac® and/or by the faster rate of polymerization (the fast polymerization with Rhodafac prevents the catalyst from diffusing out of the particle and initiate the growth of a new sub-particle).

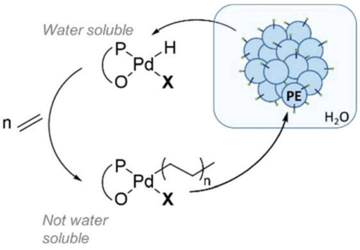

Fig. 6 Schematic of proposed mechanism showing shuttling of catalyst between the water phase and the polymer particle.

Conclusions

In summary, we developed a simple strategy for the production of semi-crystalline polyethylene latex in water. The catalyst precursors were solubilized in water by coordination to a water-soluble surfactant. Moreover, the catalyst generally exhibited high activity and high stability, with activity for over 6 hours. The chemistry of the surfactant as well as the pH of the aqueous solution were found to play a significant role in the rate of polymerization. The palladium catalysts studied here performed best under acidic pH with a phosphated surfactant. A common sulfonated surfactant, SDS, was shown, however, to strongly inhibit the catalyst, which explain the low activity observed with this catalyst in miniemulsion. Overall this approach enables the easy strategy for the synthesis *in situ* of water soluble catalyst precursor active for ethylene polymerization.

Conflicts of interest

There are no conflicts to declare.

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