

PLA- and PCL-based Pd(II)-Pyridine Macrocomplexes

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Abstract. Pyridine end-capped L-poly(lactide), L,D-poly(lactide) and poly(ε-caprolactone) were synthesized by 4-hydroxymethyl-pyridine initiated ROP and employed as macroligands for the square-planar coordination of Pd(II) ions. PdCl₂ macrocomplexes with *trans*-stereochemistry were obtained and further reacted to give homo- and heteroleptic star-shaped products. Palladium bis-acetate macrocomplexes were synthesized and employed as recyclable homogeneous catalysts for aerobic oxidation reactions. (Homo- and heteroleptic V-shaped Pd(II)(allyl) macrocomplexes were synthesized via a suitable Pd(II) intermediate. All new compounds were characterized by ¹H- and ¹³C-NMR, UV/Vis-spectroscopy, GPC and DSC analyses.

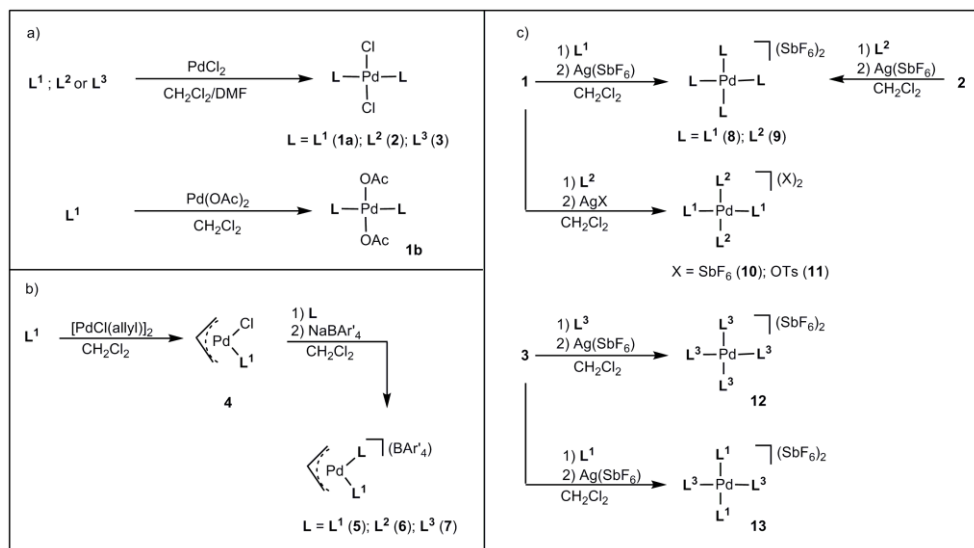
1. INTRODUCTION

The synthesis of metallo-supramolecular block-copolymers with new tunable physical and chemical properties (e.g. light absorption/emission, viscosity/adhesion) is gaining increasing interest.¹⁻³ In particular, metallo-supramolecular block copolymers linked by a metal-ligand complex have seen important progresses, exploiting: (i) the coordination geometry of the metal centre to impart new polymer architectures;¹⁻⁹ (ii) the electronic property of the metal centre characterized by its oxidation state;¹⁰⁻¹³ (iii) the much lower stability of coordination bonds compared to covalent bonds in order to reversibly control the macroligand dissociation and association to the metal centre.^{1-3,14} Generally, metallo-supramolecular polymers are accessible by either the coordination of preformed macroligands to a metal ion, or by the use of a suitable metal complex as the initiator for the polymerization reaction.¹⁻³ The most employed ligands in metallo-supramolecular chemistry are terpyridine-^{1-5,12,14} or bipyridine-based,^{6,10} while pyridines are rarely used.¹³ The nitrogen ligand end-capped polymers were mostly coordinated to Fe(II) and Ru(II), leading to linear or star-shaped polymer architectures.¹⁻³

2. RESULTS AND DISCUSSION

The Sn(Oct)₂ (Oct = 2-ethylhexanoate)-catalyzed ring opening polymerization (ROP)¹⁵ of L- and *rac*-lactide and ε-caprolactone carried out in bulk in the presence of 4-PyCH₂OH gave the 4-pyridinemethylene-end-capped L-poly(lactide) macroligand **L**¹ (*M*_n = 3280 g/mol, PDI = 1.33); the *rac*-poly(lactide) macroligand **L**² (*M*_n = 3700 g/mol, PDI = 1.54) and the PCL macroligand **L**³ in 84, 75 and 60% yield, respectively. The esterification of 4-PyCH₂OH has been proved by a ¹³C NMR singlet centered at 64.97 ppm, which was

assigned to the 4-PyCH₂O carbon atom. In addition, the absence of the ¹³C NMR singlet assigned to the carboxylic acid carbon atom at ca. 171.60 ppm combined with the lack of a ¹H NMR singlet at 4.74 ppm assigned to PyCH₂OH is a further valuable prove of the occurred end-capping of poly(lactide). The 1:2 stoichiometric reaction between PdCl₂ and L¹ or L² carried out in a 3:1 solvent mixture of CH₂Cl₂ and DMF gave *trans*-[PdCl₂(L¹)₂] (**1a**) and *trans*-[PdCl₂(L²)₂] (**2**), respectively as light brown powders with ca. 80% yield. The 1:2 stoichiometric reaction between PdCl₂ and L³ carried out in a 1:1 solvent mixture of CH₂Cl₂ and DMF gave *trans*-[PdCl₂(L³)₂] (**3**) as a brown powder with ca. 85% yield. The 1:2 stoichiometric reaction between Pd(OAc)₂ and L¹ carried out in CH₂Cl₂ gave *trans*-[Pd(OAc)₂(L¹)₂] (**1b**) as a beige powder with 95% yield (Scheme 1a).



Scheme 1: Synthesis of Pd(II) macrocomplexes.

¹H NMR and ¹³C{¹H} NMR spectra of **1a**, **1b**, **2** and **3**, acquired in CD₂Cl₂, showed for the *ortho*-hydrogen atoms of the pyridine moiety a coordination shift of ca. 0.2 ppm. GPC-measurements carried out on CHCl₃ solutions of **1a**, **1b**, **2** and **3** proved a two-fold increase of the molecular weight compared to the corresponding uncoordinated macroligand. The coordination of the pyridine moieties *trans* to each other in **1a**, **1b**, **2** and **3** has been confirmed by acquiring UV/Vis spectra of the latter macrocomplexes in CHCl₃ and using *trans*-[PdCl₂(4-EtPy)₂] and *trans*-[Pd(OAc)₂(4-EtPy)₂] (4-EtPy = 4-ethylpyridine) as reference compounds. The X-ray structure of these reference compounds confirmed the *trans*-coordination of the pyridine ligand to palladium. The 1:1 stoichiometric reaction between [PdCl(η³-allyl)]₂ and L¹ gave **4** as beige powder with 68% yield (Scheme 1b). ¹H and ¹³C NMR spectra for **4**, acquired in CD₂Cl₂ at room temperature and -60 °C confirmed the asymmetric coordination of the allyl-moiety, due to the presence of different ligands (i.e. chloride and pyridine moiety) coordinating *trans* to it.¹⁶ The reaction of **4** with either L¹, L² or L³ in the presence of NaBAR'₄ (Ar' = 3,5-bis(trifluoromethyl)phenyl) gave the

monocationic, V-shaped, homo- and heteroleptic macrocomplexes **5**, **6** and **7**, respectively. The substitution of the chloride atom in **4** by L^1 , L^2 or L^3 was confirmed by 1H and $^{13}C\{^1H\}$ NMR spectra, acquired at room temperature and at $-60\text{ }^\circ C$. The homoleptic star-shaped Pd(II) macrocomplexes (i.e. **8**, **9** and **12**) were obtained upon reaction of **1**, **2** and **3** with two molequiv. of L^1 , L^2 and L^3 , respectively in the presence of $Ag(SbF_6)$; the heteroleptic PLA-based macrocomplexes (i.e. **10**, **11**) were obtained by the reaction of **1a** with two molequiv. of L^2 in the presence of either $Ag(SbF_6)$ or $Ag(OTs)$ ($OTs = p$ -Toluenesulfonate), while the heteroleptic PLA/PCL macrocomplex **13** was obtained by the reaction of **3** with two molequiv. of L^1 in the presence of $Ag(SbF_6)$ (Scheme 1c). All star-shaped macrocomplexes were obtained as light brown powders with not yet optimized yields ranging from 45 to 60%. 1H and $^{13}C\{^1H\}$ NMR spectra acquired for the star-shaped macrocomplexes confirmed the symmetric coordination of the pyridine moieties to the metal centre. The successful coordination of four macroligands to the same Pd(II) centre has been proved by: (i) the 1H NMR integral ratio between the aromatic tosylate and pyridine hydrogen atoms in **11**; (ii) the reaction of **8** with two molequiv. of 1,2-bis(diphenylphosphanyl)ethane (dppe) in CD_2Cl_2 leading to uncoordinated L^1 and $[Pd(dppe)_2](SbF_6)_2$, which was the only phosphorus containing compound. Unfortunately, the charged complexes proved to be not stable during GPC-analysis, due to the presence of strong shear forces stemming from high-performance packing in size exclusion chromatography.¹⁷ The stepwise de-coordination of macroligands from V- and star-shaped macrocomplexes has been studied by means of NMR-spectroscopy. To this purpose, **5** was reacted with one molequiv. of $[N(n-Bu)_4]Cl$ in CD_2Cl_2 to give a 1:1 mixture of **4** and uncoordinated L^1 . The corresponding 1H NMR spectrum, acquired at room temperature, showed for the pyridine-moiety two broad singlets centred at 7.35 and 8.72 ppm, due to a dynamic equilibrium between **4** and L^1 at room temperature. Accordingly, the corresponding 1H NMR spectrum, acquired at $-70\text{ }^\circ C$, showed for the *ortho*-hydrogen atoms of **4** and L^1 two distinct 1H NMR doublets at 8.77 and 8.62 ppm, respectively. Upon reaction of **5** with one molequiv. of dppe, $[Pd(\eta^3\text{-allyl})(dppe)]BAR_4^+$ was formed under the quantitative release of L^1 as proved by the corresponding 1H NMR spectrum. The addition of two molequiv. of $[N(n-Bu)_4]Cl$ to a CD_2Cl_2 solution of **8** led to a 1:1 mixture of **1a** and uncoordinated L^1 . The successive addition of two molequiv. of PPh_3 to the latter NMR solution brought about the quantitative transformation of **1a** into *trans*- $[PdCl_2(PPh_3)_2]$ and uncoordinated L^1 . From a perusal of DSC results arises that: (i) the homoleptic macrocomplexes containing L^1 (i.e. **1**, **5** and **8**) showed a higher melting (T_m) and crystallization temperature (T_c) compared to L^1 , due to an increase of the molecular weight; (ii) **8** showed the lowest crystallinity (χ_c), which is mainly due to the higher number of end groups compared to **1a** and **5** and to the presence of two counter-anions; (iii) the heteroleptic macrocomplexes **6**, **10** and **11** showed a significantly lower value of crystallinity compared to the corresponding homoleptic counterpart, confirming the influence of L^2 on the crystallization behaviour of L^1 in the macrocomplexes; (iv) L^2 and **9** were found to be completely amorphous; (v) **7** and **13** show crystallinity of both PLA and PCL, each with its own characteristic transition temperatures. The acetate-containing macrocomplex **1b** was tested as catalyst precursor under homogeneous catalytic conditions (i.e. 4bar of air; toluene; $70^\circ C$; precat/substrate ratio = 1:1600) for the aerobic oxidation of primary and secondary alcohols and its catalytic activity was compared with that of the reference compound *trans*- $[Pd(OAc)_2(4-EtPy)_2]$. Due to the solubility properties of PLA, **1b** was easily separated from the reaction solution by precipitation, thus combining the advantages of homo- and heterogeneous catalysis.

Experiments aiming at the formation of macroligand-stabilized Pd(0)-nanoparticles and their use in C-C coupling reactions are in progress in our laboratory.

3. CONCLUSIONS

In summary, we successfully synthesized 4-pyridinemethylene-end-capped L- and LD-poly(lactide) and poly(caprolactone), which was coordinated for the first time to Pd(II) forming neutral linear, monocationic V- and bis-cationic star-shaped macrocomplexes. The occurred metal coordination has been proved in solution by NMR-, UV/Vis-spectroscopy and in the solid state by DSC. The reversibility of the macroligand coordination was demonstrated upon reactions of the macrocomplexes with appropriate ligands (i.e. chloride and phosphanes). The easy stepwise synthesis of the Pd-macrocomplexes allowed the formation of heteroleptic species, which combined poly L-poly(lactide) with LD-poly(lactide) and poly(caprolactone). The Pd acetate-based macrocomplex has been successfully used for the aerobic oxidation of alcohols. Research is in progress to further investigate the solid-state properties of this novel class of polymers.

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