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Polymerization of ε-caprolactone using ruthenium(II) mixed metallocene catalysts and isopropyl alcohol: Living character and mechanistic study

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ABSTRACT

A series of ruthenium(II) complexes with the general formula $[Ru(\eta^5\text{-}C_5H_5)\ (\eta^6\text{-substituted arene})]^+[PF_6]^-$ (substituted arene = 2-phenylpyridine (**1**), dibenzosuberone (**2**) and toluene (**3**)), in combination with isopropyl alcohol were used for the polymerization of ε-caprolactone. The polymerization was found to be quantitative and controlled, with PDI in the range 1.1–1.3. By means of MALDI-ToF analyses, functionalization studies with D,L-lactide and NMR monitoring techniques, it has been found that the polymerization proceeds via a *living* Activated Monomer mechanism (AM) involving an η^6–η^4 change of the coordination mode of the arene. These experimental results were corroborated by DFT studies. The growth of several polymer chains per ruthenium atom highlights interesting potentialities for molecular weight control and catalyst economy. The stability of the ruthenium complexes allows their recovery at the end of the polymerization, which can be viewed as a further advance in a green chemistry frame.
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1. Introduction

Ring-opening polymerization (ROP) of polar monomers has an important impact in modern polymer chemistry due to the widespread medical applications, biocompatibility and biodegradability of the final polymers [1]. The catalysts used more often in this type of polymerization are mainly based on oxophilic metal derivatives, containing tin [2], aluminum [3,4], lithium [5], titanium [6] and rare earths [4,7]. Their activity relies on their ability to form active species, which depends on the involved mechanism. While in classical living ROP one initiator leads to the growth of one polymer chain, via Coordination Insertion (CI) [4,8] and Activated Monomer (AM) [1a,9–17] based ROP several macromolecular chains can be generated per initiator. In this case the initiator becomes a true "catalyst". This is achieved via introduction of protic compounds in addition to the catalyst, mostly alcohols. Transfer reactions are then occurring, as reported in the pioneering work of Inoue et al. [18]. Chain-end functionalization and catalyst economy can thus be achieved via these pathways. Although ruthenium based catalysts are nowadays very well established [19], their use in ring-opening polymerization of lactones is still an emerging field [20]. It is known that ruthenium complexes display a great variety of properties, such as high electron transfer ability, high Lewis acid properties and stability of reactive metallic species which make this metal a good candidate to this chemistry. The ability for transfer reactions to alcohols in ε-caprolactone polymerization was observed using the $RuCl_2(PPh_3)_3$/1,3-propanediol system (T = 150 °C; 30 h) via a Coordination-Insertion mechanism [20a]. The same authors also studied the ligand influence in the ruthenium sphere of coordination using TpRuCl(L)(L′) complexes (Tp = HB(pz)$_3$ = hydrotris(pyrazolyl)borate, L = L′ = PPh_3, L = PPh_3 and L′ = $PHPh_2$, L = L′ = PMe_2Ph, L = PPh_3 and L′ = PMe_2Ph) [20b]. Better catalytic activities were obtained using these catalysts instead of $RuCl_2(PPh_3)_3$, together with the occurrence of transfer reactions to alcohols. Finally, another research group studied a more simple catalytic system based on ruthenium(III) chloride in bulk, which suggested an Activated Monomer mechanism [20c].

In this paper we have performed the ring-opening polymerization of ε-caprolactone using three Ru(II) cationic complexes of the general formula $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-substituted arene})]^+[PF_6]^-$ (substituted arene = 2-phenylpyridine (**1**), dibenzosuberone (**2**), and

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toluene (**3**)), in combination with isopropyl alcohol. Two of these ruthenium complexes were already synthesized (**1** and **2**) [21] for anti-tumoral studies purposes, and we prepared the new toluene adduct 3, in order to assess the impact of the molecular structure towards the performance of these complexes as catalysts for the polymerization of ε-caprolactone. Since the polymerizations were found to be slow enough to allow the study of the involved mechanism, thorough investigations could be carried out by means of NMR monitoring techniques (^{1}H, ^{13}C, 2D) and MALDI-ToF analyses, aiming to study the ligand influence in the process.

2. Experimental

2.1. Materials and methods

All the experiments were carried out under nitrogen atmosphere using standard *Schlenk* techniques. Solvents were dried using standard methods [22]. ε-Caprolactone was dried over calcium hydride and distilled under reduced pressure before use. Isopropyl alcohol was dried with sodium metal for 48 h at room temperature, further refluxed over magnesium and distilled before use. The starting material[Ru(η^5-C_5H_5)(NCMe)$_3$][PF_6] was prepared by irradiation of [Ru(η^5-C_5H_5)(η^6-C_6H_6)][PF_6] according to a published method [23]. All ligands were purchased and used without further purification. The complexes [Ru(η^5-C_5H_5)(η^6-substituted arene)]$^+$[PF_6]$^-$ (substituted arene = 2-phenylpyridine (**1**), dibenzosuberone (**2**)) were synthesized according to the literature [21].

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at probe temperature. The ^{1}H $(CD_3)_2CO$ and ^{13}C $(CD_3)_2CO$ chemical shifts are reported in parts per million (ppm) downfield from internal Me_4Si and the ^{31}P $(CD_3)_2CO$NMR spectra are reported in ppm downfield from external standard, 85% H_3PO_4. Phase sensitive NOESY with gradients was performed with a mixing time of 4 s. The spin-lattice (T_1) relaxation time constant of the various ^{1}H nuclei were determined by an inversion recovery pulse sequence with a recycle delay (D1) between 10 ms and 15 s.

Electronic spectra were recorded at room temperature on a *Jasco V-560* spectrometer in the range 200–900 nm.

Elemental analyses were obtained at Ecole Nationale Supérieure de Chimie de Lille, using a Vario Micro (Elementar Method). Data acquisition, integration and handling were performed using the software package EAS Vario Micro (CHN).

Size exclusion chromatography (SEC) was performed in THF as eluent at 40 °C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters Styragel columns (HR2, HR3, HR4, HR5E). The calibration was done using polystyrene standards. A correction factor of 0.56 was applied for the determination of true number-average molecular weight of polycaprolactone [24].

MALDI-ToF spectra were recorded in the linear mode using a Bruker Daltonics Ultraflex II MALDI TOF/TOF mass spectrometer.

The DFT calculations were made using Gaussian09 package and the Becke's three parameter exchange-correlation functional with Lee, Yang and Parr correlations (B3LYP). All geometries optimizations were made without symmetry constrains, using LanL2DZ basis sets for the transition metal and a 6-31G(d,p) basis set for the remaining elements. Frequency calculations were also performed at the B3LYP level to confirm the nature of the stationary points. One imaginary frequency was obtained for the transition state and no imaginary frequency was obtained for the minima. The transition state was further confirmed by following its vibrational mode downward on both sides using Intrinsic Reaction Coordinate (IRC) method as implemented in Gaussian, where the same minima were obtained. All thermochemistry analyses were performed using the same basis sets, at 278.15 K and 1 atm, as implemented in Gaussian. For the studied complex, the accuracy of this functional was tested comparing the minima of energy of the ruthenium complex with its crystallographic structure. A good agreement was observed.

2.2. Synthesis of [Ru(η^5-C_5H_5)(η^6-toluene)]$^+$[PF_6]$^-$ (**3**)

Complex **3** was synthesized by reflux of a suspension of [Ru(η^5-C_5H_5)(NCMe)$_3$][PF_6] in toluene for 3 h. A white toluene insoluble product was obtained. The remaining solution was cannula-filtrated and the product was treated with *n*-hexane, dried under vacuum and further recrystallized in dichloromethane/diethyl ether to afford a pure compound in 90% yield. ^{1}H NMR [$(CD_3)_2CO$, Me_4Si, δ/ppm]: 6.33 [*d*, 2, H_3+H_7]; 6.25 [*t*, 2, H_4+H_6]; 6.20 [*t*, 1, H_5]; 5.47 [*s*, 5,η^5-C_5H_5]; 2.04 [*s*, 3, H_1]; ^{31}P NMR[$(CD_3)_2CO$, δ/ppm]: −144.07 [*sept*, PF_6^-]; ^{13}C NMR [$(CD_3)_2CO$, δ/ppm]: 103.4 [C_2]; 88.1 [C_3+C_7]; 86.3 [C_4+C_6]; 85.5 [C_5]; 81.4 [η^5-C_5H_5]; 20.5 [C_1]. UV–vis in CH_2Cl_2, λ_{max}/nm (ε/M^{-1} cm^{-1}): 330 (167). Anal. calcd. for $C_{12}H_{13}PF_6Ru$: C, 35.74; H, 3.25. Found: C, 35.45; H, 3.23.

2.3. Ring-opening polymerization of ε-caprolactone

Polymerizations have been performed in dried reactors purged with dry nitrogen. In a typical run, the solvent (0.5 mL), the ruthenium complex (45.1 μmol), the monomer (4.5 mmol) and the isopropyl alcohol (0.23 mmol) were added, following this order, under a nitrogen atmosphere. Reactors were sealed with a rubber septum and placed in a sand bath at a given temperature for a given time. The final polymers were quenched with methanol, recovered from chloroform/methanol mixture and dried under vacuum until constant weight. ^{1}H NMR [$CDCl_3$, Me_4Si, δ/ppm]: 5.00 [*sept*, 1, H_g]; 4.05 [*t*, 2, H_a]; 3.65 [*t*, 2, $H_{a'}$]; 2.30 [*t*, 2, H_e]; 1.60 [*m*, 4, H_b+H_d]; 1.38 [*m*, 2, H_c]; 1.22 [*d*, 6, H_h]. ^{13}C NMR [$CDCl_3$, δ/ppm]: 173.6 [C_f]; 173.1 [$C_{f'}$]; 67.6 [C_g]; 62.6 [C_a]; 34.2 [C_e]; 32.4 [$C_{b'}$]; 28.4 [C_b]; 25.6 [C_d]; 24.6 [C_c]; 21.9 [C_h]. The numeration is from Fig. 1.

2.4. Living character of the polymerization

A polycaprolactone block was first synthesized as described in the previous section and after complete conversion, D,L-lactide (2.25 mmol) was added. The mixture was left to react for 24 h at 120 °C and then the polymerization was quenched with methanol and the polymer recovered and dried under vacuum. ^{1}H NMR [$CDCl_3$, Me_4Si, δ/ppm]: 5.16 [*m*, 2, H_j]; 5.00 [*sept*, 1, H_g]; 4.06 [*t*, 2, H_a]; 2.30 [*t*, 2, H_e]; 1.65 [*m*, 4, H_b+H_d]; 1.53 [*dd*, 6, H]; 1.38 [*m*, 2, H_c]; 1.22 [*d*, 6, H_h]. ^{13}C NMR [$CDCl_3$, δ/ppm]: 175.0 [$C_{k'}$]; 173.6 [C_f]; 173.1 [$C_{f'}$]; 69.4 [C_l]; 67.5 [C_g]; 66.7 [$C_{j'}$]; 65.3 [$C_{a'}$]; 64.2 [C_a]; 34.1 [C_e]; 28.4 [C_b]; 25.5 [C_d]; 24.6 [C_c]; 21.9 [C_h]; 20.5 [$C_{i'}$]; 16.9 [C_i]. The numeration is from Fig. 1.

2.5. NMR monitoring study

NMR monitoring was performed at different times during the polymerization of ε-CL in an NMR tube during 24 h at 100 °C in C_6D_6 using initiators **1**–**3** in combination with isopropyl alcohol. After 24 h reaction the oligomerization was quenched with an excess of methanol directly in the NMR tube.

3. Results and discussion

3.1. Synthesis of [Ru(η^5-C_5H_5)(η^6-substituted arene)]$^+$[PF_6]$^-$ (substituted arene = 2-phenylpyridine (**1**), dibenzosuberone (**2**), toluene (**3**))

The three catalysts used for this study are presented in Scheme 1. Catalysts **1** and **2** were synthesized from a solution of [Ru(η^5-C_5H_5)(NCMe)$_3$][PF_6] in CH_2Cl_2 with a slight excess of the molar equivalent of the adequate ligand [21]. Complex **3** was prepared

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