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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.

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

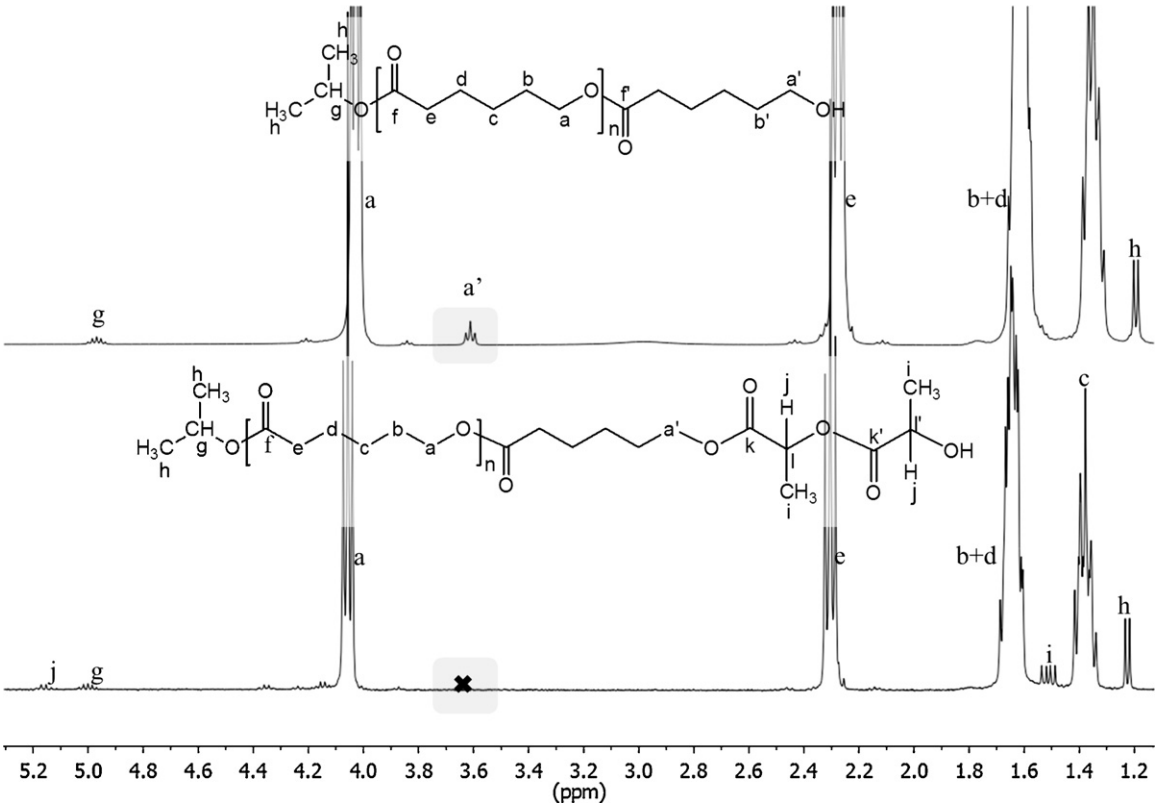


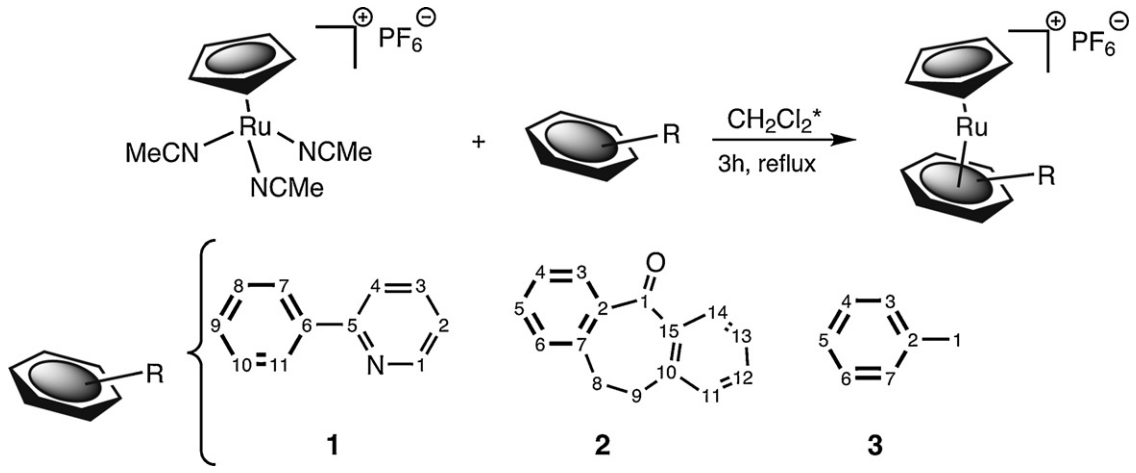
Fig. 1. ^{1}H NMR Spectra of a non-functionalized PCL (top) and end-functionalized PCL (bottom) in $CDCl_3$.

in good yield from the same precursor similarly but in toluene, leading straightforwardly to the toluene adduct, and was recrystallized from dichloromethane/diethyl ether. The purity of the compound was confirmed by elemental analysis. The ^{1}H NMR chemical shift of the cyclopentadienyl ring is displayed as a typical singlet at 5.47 ppm at higher fields than the usual monocationic complexes with sigma bonded co-ligands, whereas the η^6 coordination of the toluene molecule was established by a significant shielding of the signals of the related protons. ^{13}C NMR data were in agreement with the values of the ^{1}H NMR spectra. For an unambiguous identification of the NMR signals the use of ^{1}H and ^{13}C bi-dimensional techniques were necessary. The ^{31}P NMR spectrum showed the expected septuplet ($[PF_6]^-$) at approximately −144 ppm. The UV–visible spectra of the complex obtained in 10^{-3} to 10^{-5} M dichloromethane solutions showed the characteristic of π–π^* transitions bands expected from the presence of the aromatic ring.

3.2. Ring-opening polymerization of ε-caprolactone

3.2.1. ROP in the presence of ruthenium catalysts without alcohol

The polymerizations were performed in toluene with the initiator complex alone. The results are summarized in Table 1. All the catalytic systems lead to the polymerization of ε-caprolactone at 120 °C with fair yields in 24 h and PDI in the range 1.3–1.6. MALDI-ToF analyses (see SI) show the presence of two distributions. The main one is in accordance with $(n \times 114) + 18$ Da, in agreement with a polymer containing a hydroxy-terminated chain-end and an acid



Scheme 1. Reaction scheme for the synthesis of the Ru(II) derived complexes [Ru(η^5-C_5H_5)(η^6-arene)][PF_6] and structures of the η^6-arene ligands (**1**–**3**) numbered for NMR and DFT purposes (the Ru-coordinated ring is represented in bold); *synthesis of **3** in toluene.

Table 1
Polymerizations of ε-caprolactone using ruthenium initiators (**1**–**3**).

Run[a]	Initiator	Yield (%)	$\overline{M_n}$ SEC[b] (g mol^{-1})	PDI	$\overline{M_n}$ calc.[c] (g mol^{-1})
1	**1**	56	4900	1.3	6400
2	**2**	62	6000	1.6	7000
3	**3**	60	5900	1.4	6800

[a] Reactions performed during 24 h at 120 °C, monomer/initiator = 100.
[b] Number-average molecular weight determined by SEC using PS standards corrected for polycaprolactone.
[c] Calculated polycaprolactone number average molecular weight considering the yield and one growing polymer chain per ruthenium atom.

end-group. A minor distribution of $(n \times 114)$ Da species was also observed, corresponding to a cyclic structure. As discussed hereafter, the polymerizations performed with an alcohol co-initiator do not lead to cyclic structure and do furthermore lead to narrower distributions. We have thus decided to focus our study with the polymerizations in the presence of isopropyl alcohol.

3.2.2. ROP in the presence of the ruthenium catalysts and alcohol initiator

In the presence of the protic species, all the catalytic systems lead to the controlled polymerization of ε-caprolactone at 120 °C with PDI values in the range 1.2–1.3 (runs 4, 6 and 7, Table 2). A good agreement is observed between the molecular weight values obtained by SEC and NMR analyses, highlighting the absence of cyclic structures. This is confirmed by MALDI-ToF analyses (see SI). Initiation efficiencies between 38% (catalyst 1) and 74% (catalyst 2), with respect to isopropyl alcohol, are observed. These data correspond to a number of polymer chains per ruthenium of 1.9 and 3.7, respectively, while total efficiency should lead to five polymer chains per Ru considering the alcohol/catalyst ratio. Concerning the influence of the temperature, no reactions occurred during 24 h at 50 or at 70 °C. However, using a pre-heating period of 30 min at 120 °C followed by the same overall reaction time at 50 or 70 °C resulted in an even more controlled polymerization, with PDI values around 1.1 (entries 5, 8 and 9, Table 2). Furthermore, the initiation efficiencies are improved (*i.e.* from 44% to 72% for catalyst 1, runs 4 and 5, respectively). A ligand effect may thus be advanced. The bulky arene ligand in **2** leads to the highest initiation efficiency *vs.* **1** and **3**, suggesting that the small isopropyl alcohol molecule is more competitive in this case for the nucleophilic attack on the activated monomer than the longer and bulkier growing polymeric chain (see further, mechanism Scheme 4).

As mentioned previously, the use of ruthenium catalysts for ROP of ε-CL is still rare. The three systems already studied used $RuCl_2(PPh_3)_3$ [20a], TpRuCl(L)(L′) [20b] (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) and $RuCl_3.xH_2O$ [20c] as initiators. Using $RuCl_2(PPh_3)_3$ and TpRuCl(L)(L′) in combination with alcohols, transfer reactions were observed (eff. = 86–95%, calculated from NMR analysis) via a Coordination-Insertion mechanism. The polymerizations proceed during approximately 30 h for a monomer/catalyst ratio of 1000 at 150 °C. Our system affords lower initiation efficiencies (*cf.* Table 2, determined by means of GPC analysis) but is working under smoother conditions.

3.3. Mechanistic study

Since this family of $(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})$ complexes was efficient towards the controlled polymerization of ε-CL, it was of all interest to investigate the mechanism involved in such reactions. It is worth to mention that, up to now, an extensive mechanistic study involving ruthenium-based catalysts cannot be found in the literature, as far as we know.

3.3.1. End-group analysis

An end-group analysis was done by NMR spectroscopy. The ^{1}H NMR spectra of the polymers established the presence of an isopropoxy end-group as shown by the signals in the spectrum at 4.97 ppm as a septuplet ($(CH_3)_2CHOCO$) and at 1.20 ppm as a doublet ($(CH_3)_2CHOCO$) (Fig. 1, top). At δ = 3.61 ppm one can observe the characteristic triplet of a $-(CH_2)_4-CH_2-OH$ end group. The ^{13}C NMR spectra confirmed these observations.

Concerning the MALDI-ToF analyses, the main distribution found for a typical run (run 6) was $(n \times 114) + 60$ Da (given in supporting information), which is in accordance with a polycaprolactone terminated by one alcohol end-group and bearing at the other side an isopropoxy end-group. However, some minor species terminated by an acidic end-group ($(n \times 114) + 18$ Da) were also detected, probably resulting from the presence of some residual water molecules in the reaction mixture. Importantly, no cyclic structures were found in the spectrum.

3.3.2. Living character of the polymerization

In order to establish the livingness of the polymerization we considered to functionalize polycaprolactone with D,L-lactide. If the polymerization process is *living*, subsequent addition of lactide after the consumption of ε-caprolactone should lead to an end-functionalized polymer where the end-group would be different from that resulting from the homopolymerization of ε-caprolactone. Thus, a polycaprolactone block was first synthesized at 120 °C for a monomer/catalyst ratio of 100 with catalysts **1** and **3** (monomer/isopropyl alcohol = 20). When quantitative yield was reached, D,L-lactide was added. The mixture was left to react for another 24 h and the polymerization was subsequently quenched with methanol, and then the polymer recovered. NMR analysis of the end-functionalized polymers revealed that functionalizations with D,L-lactide had efficiently occurred, since the spectrum of the

Table 2
Polymerizations of ε-caprolactone using ruthenium initiators (**1**–**3**) and isopropyl alcohol.

Run[a]	Initiator	Temperature (°C)	Yield (%)	$\overline{M_n}$ SEC[b] (g mol^{-1})	PDI	$\overline{M_n}$ NMR[c] (g mol^{-1})	$\overline{M_n}$ calc.[d] (g mol^{-1})	Initiation efficiency[e] (%)	Chains per Ru
4	**1**	120	96	5000	1.2	5600	2200	44	2.2
5	**1**	50[f]	72	2300	1.1	1750	1650	72	3.6
6	**2**	120	60	1900	1.3	1800	1400	74	3.7
7	**3**	120	77	4800	1.3	5400	1800	38	1.9
8	**3**	50[f]	43	1750	1.1	1600	1000	57	2.9
9	**3**	7[g]	86	2700	1.1	2850	1950	72	3.6

[a] Reactions performed during 24 h, monomer/initiator = 100, monomer/isopropyl alcohol = 20.
[b] Number-average molecular weight determined by SEC using PS standards corrected for polycaprolactone.
[c] Number-average molecular weight determined by ^{1}H NMR.
[d] Calculated polycaprolactone number average molecular weight considering the yield and one growing polymer chain per isopropyl alcohol molecule.
[e] Initiation efficiency = $(\overline{M_n}$ calc.$/\overline{M_n}$ SEC$) \times 100$.
[f] Temperature of reaction = 30 min at 120 °C + 23 h 30 min at 50 °C.
[g] Temperature of reaction = 30 min at 120 °C + 23 h 30 min at 70 °C.

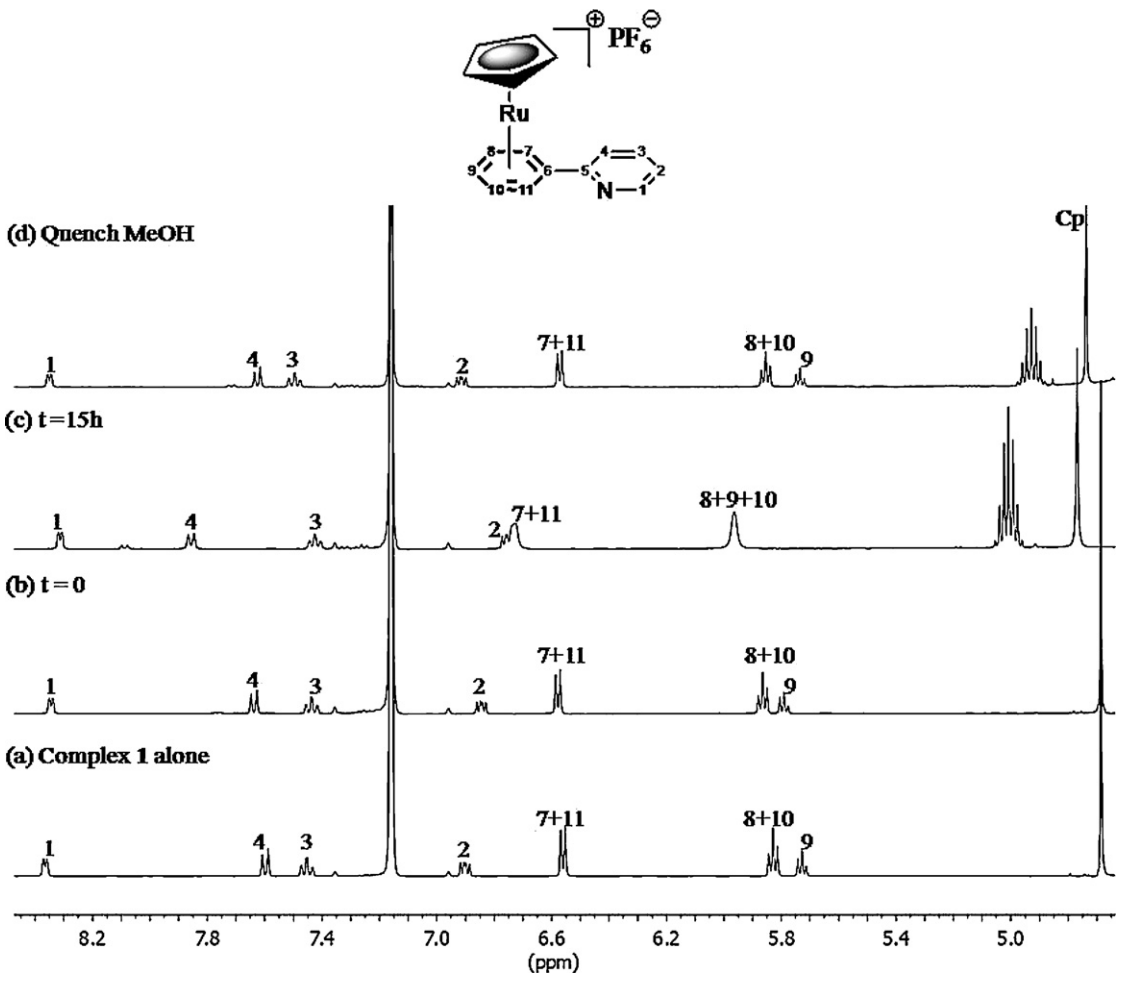


Fig. 2. ^{1}H NMR spectra in C_6D_6 for (a) complex **1** alone; (b) complex **1** with ε-caprolactone and isopropyl alcohol at $t = 0$; (c) complex **1** with ε-caprolactone and isopropyl alcohol at $t = 15$ h; (d) complex **1** ε-caprolactone and isopropyl alcohol after quench.

polymer did not contain the triplet at *ca.* 3.6 ppm characteristic of the $-(CH_2)_4$-CH_2OH chain-end (e.g. Fig. 1, bottom for catalyst **1**). Its absence clearly indicates that lactide was added at this side of the growing polymer chain. Integrating the ^{1}H NMR spectrum gave the information that only one lactide molecule was inserted per polylactone chain. The ^{13}C NMR confirmed this result.

3.3.3. NMR monitoring study and catalyst recovery

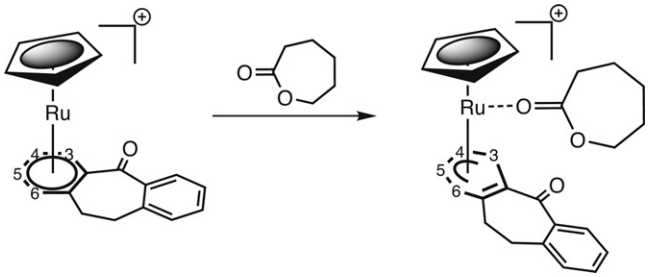
An extensive NMR study was performed for the polymerization of ε-CL by Ru(II) initiators **1**–**3**. The studies were done in C_6D_6 in a sealed NMR tube equipped with a teflon valve, in the presence of isopropyl alcohol at 100 °C, for 24 h under nitrogen. The NMR spectra were recorded at the beginning, in the course and at the end of the polymerization (Fig. 2, arene ligand peaks range). The addition order was the same as adopted for a standard polymerization, *i.e.*, catalyst, solvent (C_6D_6), ε-caprolactone and isopropyl alcohol. For all complexes an immediate interaction of the Ru complex with the monomer was observed, the most important modifications always occurring on the η^6-coordinated ring. For example, in complex **1** we observed the shielding and gathering of H_8, H_9 and H_{10} into a unique singlet peak (Fig. 2(c)). H_7 and H_{11} were also shielded and turned into a singlet peak. These shifts, together with the fact that H_2 was shielded, suggested that the 2-phenylpyridine ligand was somehow affected during the polymerization (Fig. 2). We can thus postulate a change in the hapticity of the η^6-coordinated ring. This would consequently allow a more facile interaction between the metallic center and the incoming subsequent lactone monomer. After quenching the reaction at 24 h with methanol, the ^{1}H NMR spectrum was almost identical to that of the original complex (Fig. 2(d)). This fact expresses the integrity of Ru complexes at the end of polymerization, which allows considering them as true catalysts. Indeed, after recrystallization of the remaining solution from the NMR tube, we were able to obtain back pure crystals for the complexes **1** and **2**.

NOESY and T_1 NMR experiments were performed in order to detect any spatial interactions between the Ru complex and the ε-caprolactone monomer. These experiments were done using complex **2** alone and under polymerization conditions. The best results were obtained for a mixing time D8 = 4 s. We only observed interactions of the protons of **2** between themselves, and the same for the lactone protons. T_1 values were calculated in both cases, *i.e.* for the complex alone and under the polymerization conditions (Table 3). The data indicated a decrease of T_1 values especially for protons H_5, H_6 and H_4 belonging to the η^6-coordinated ring, thus confirming the previous ^{1}H NMR observations. This definitely

Table 3
T_1 data (s) at 298 K.

Conditions	H_{14}	H_{11}	H_3	H_5+H_6	H_4	Cp
Complex **2** alone	3.917	2.578	3.591	2.421	2.557	5.401
Complex **2** polymerization conditions[a]	4.362	2.210	3.463	1.788	1.946	4.951

[a] In the presence of the ε-CL and isopropyl alcohol.



Scheme 2. Change in the coordination mode of the arene ligand of **2** upon ε-caprolactone interaction.

shows that the coordination mode of the arene is changed during the polymerization, in accordance with the hypothesis advanced above (Scheme 2). However, since modifications in T_1 values were not too pronounced, we should consider an interaction displaying a labile character rather than the existence of a strong interaction between the lactone and the ruthenium complex.

3.3.4. Plausible mechanism

The above experiments related to the identification of the end groups, associated with the *in situ* NMR studies results, allow us to postulate a mechanism for these Ru-mediated polymerizations. Four different possible mechanisms for the ring-opening polymerization of ε-caprolactone are generally accepted: anionic, Coordination-Insertion, Active Chain End (ACE) and Activated Monomer (AM) mechanism [1a,15b]. Two of them could be readily eliminated, namely, anionic and Coordination-Insertion mechanisms. Indeed, the only anionic moiety present in our system is the hexafluorophosphate counteranion of the Ru cationic complexes and it was assumed that it would only contribute to the stability of the ionic pair. On the other hand, if the reaction would proceed via a Coordination-Insertion mechanism, the formation of a Ru–O–R alkoxide [25] active species would have been observed by NMR analysis, which was not the case. Therefore, we should consider a cationic type mechanism, ACE or AM. The propagation step, the ring opening mode as well as the polymer chain-ends are different for these two mechanisms, which allows distinguishing between them. An alkyl-oxygen bond cleavage (Scheme 3b) was only observed in the literature when the ACE mechanism was operating [14b], while an acyl-oxygen bond cleavage (Scheme 3a) occurs for the AM mechanism. In addition, in an AM mechanism the presence of protonated species such as alcohols is required. If the reaction proceeded via an acyl-oxygen bond cleavage, the end-group of the polymer should display a carboxylate –OC(O)R group, while an alkoxy RO– termination should result from an alkyl-oxygen bond cleavage. Using isopropyl alcohol as initiator, the polymer was found to contain an isopropoxy end group (found at δ = 5.0 ppm and 1.2 ppm; ^{1}H NMR), consistent with an acyl-oxygen bond cleavage (Scheme 3a), as previously reported [26].

To finally prove that the AM mechanism was operating in these ruthenium-mediated ring-opening polymerizations of ε-caprolactone, an ultimate end-group analysis was made by ^{1}H NMR monitoring of the polymerization. As seen in Scheme 3, in AM mechanisms during any stage of the reaction every macromolecule contains two end-groups, –CH_2OH and –COOR, contrarily to ACE mechanism. Having this in mind, an oligomer of ε-CL was prepared *in situ* in a sealed NMR tube. The oligomerization was left to proceed during 24 h at 100 °C in C_6D_6 using initiators **1**–**3** in the presence of isopropyl alcohol. NMR monitoring was then performed to see which kind of end-group(s) were appearing during the polymerization. As observed on Fig. 3, both expected end-groups are present along the polymerization, thus allowing to demonstrate that an AM mechanism was involved. In addition, the end-functionalization

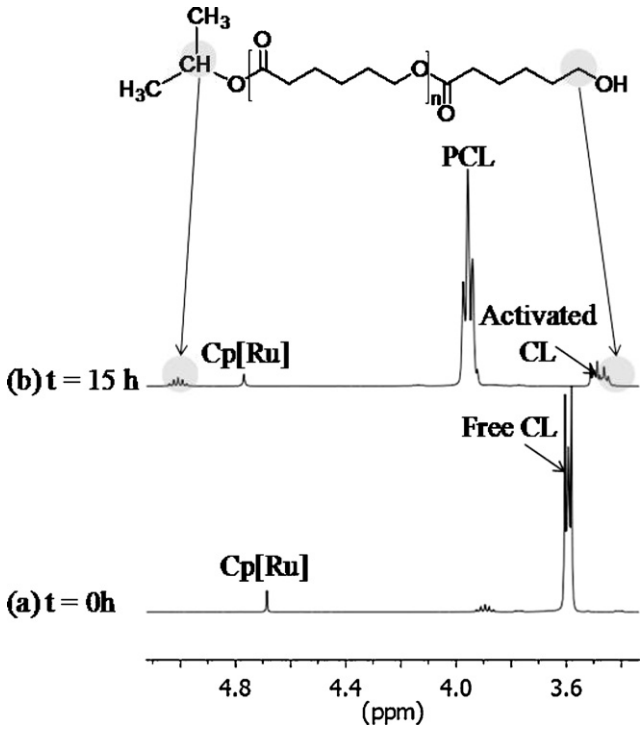


Fig. 3. ^{1}H NMR spectra in C_6D_6 for complex **1** in polymerization conditions at (a) t = 0 and (b) t = 15 h.

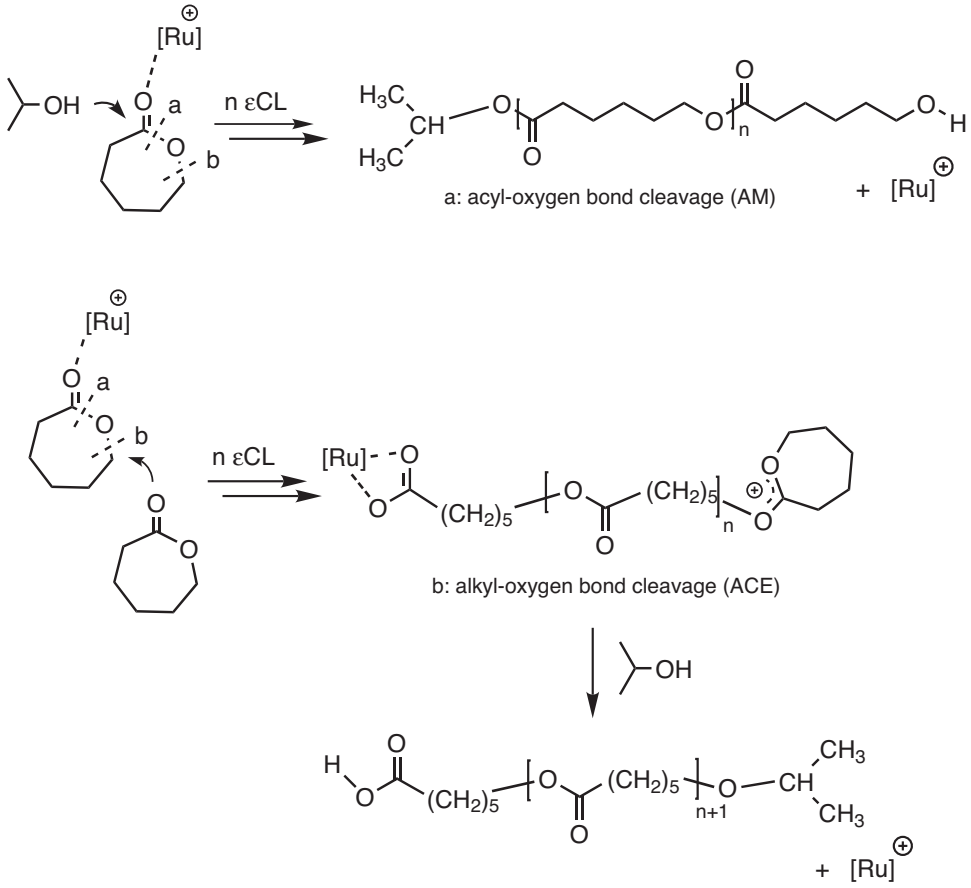
with D,L-lactide came also to support this hypothesis for two reasons: (i) the disappearance of the triplet located at *ca.* 3.6 ppm characteristic of the –$(CH_2)_4$–CH_2OH chain-end; and (ii) the fact that this is a *living* polymerization, which could only be possible in an AM type mechanism (in an ACE type mechanism, the transfer to alcohol is irreversible and the alcohols acts as a termination agent; Scheme 3).

As a summary, we are indubitably in the presence of a cationic Activated Monomer mechanism because: (i) the end-group analysis reveals that the lactone ring opens via acyl-oxygen bond cleavage; (ii) during the NMR monitoring of the polymerization the two chain-ends are present at any time during the reaction; and (iii) MALDI-ToF analyses have shown that no undesirable cyclic species are present. In addition, since the protons that suffer from more chemical shifts variations are those belonging to the η^6-coordinated arenes, the attack of the ruthenium initiator to the lactone should occur on that side. Based on these evidences, we propose the following AM mechanism (Scheme 4).

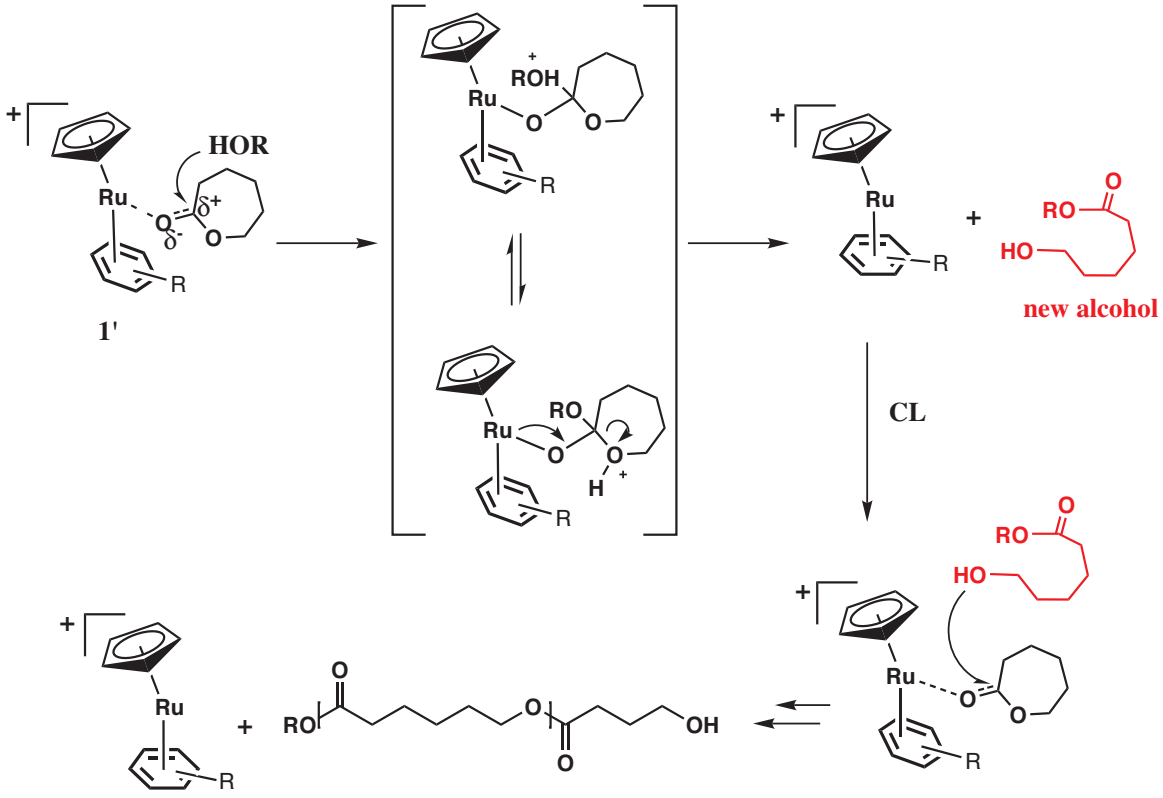
Firstly, the coordination of ε-CL to the ruthenium center takes place with the concomitant change in the coordination mode of the arene (η^6–η^4), affording the cationic complex **1′**. The latter can then be attacked by an isopropyl alcohol molecule (ROH) to produce the corresponding linear hydroxyl-ester (in red) via acyl-oxygen bond cleavage. When released, this free hydroxyl-ester can serve as a new alcohol to attack the activated monomer of a new species **1′**.

3.3.5. DFT study

In order to further confirm the proposed mechanism, DFT studies were performed using the B3LYP functional, which was also successfully used in recent mechanistic studies of polymerization of ε-caprolactone involving alcohols and sulfonic derivatives or even transition metal catalysts as activators [27–29]. Complex **2** and methanol were chosen for our DFT studies due to low computational effort. Crystallographic data were used to corroborate the optimized structure. Differences between the optimized and crystal structure of **2** did not differ more than 3.5% from the crys-



Scheme 3. Ring-opening modes of ε-caprolactone and their end-groups in the presence of isopropyl alcohol.



Scheme 4. Proposed mechanism for the polymerization of lactone by Ru(II) initiators **1**–**3**, in the presence of isopropyl alcohol (ROH; counter ion omitted).

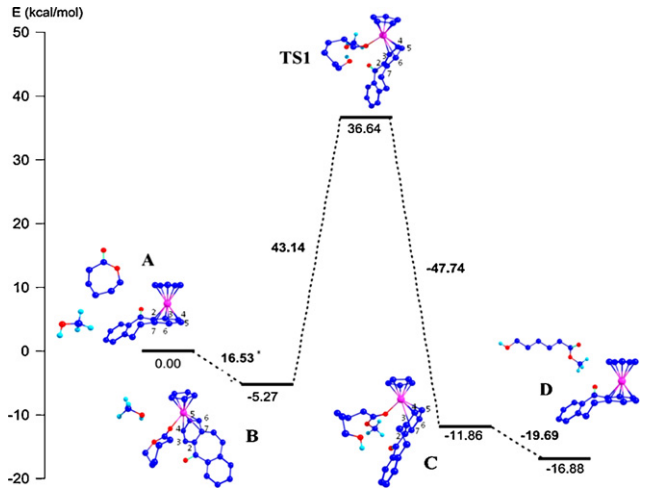


Fig. 4. Computed potential energy profile for the proposed initiation mechanism of ε-caprolactone polymerization with complex 2; in bold and nearby the dashed lines are free Gibbs energies for the corresponding reaction step; all hydrogens were omitted for clarity; *cf.* in text.

tal structure, showing the good accuracy of the chosen method to compute structural features of the studied complex.

The first obvious step in the mechanism should be the activation of the monomer by the ruthenium complex. In this case, a coordination site is needed for the lactone activation by Lewis acid/base interaction and hence an η^6–η^4 ring slippage was hypothesized, following our NMR observations. Optimization of such a structure resulted in form B in Fig. 4 (form **A** represents the three individual structures outside interaction distances and it is set to the zero potential of the scale), where an η^4-arene was obtained with the lactone occupying the vacant position, resulting in an 18-electron pseudo-octahedral ruthenium complex. Table 4 shows the selected computed relative bond distances in all the possible hapticities for the ligand. Concerning the Cp–Ru distances, it is clear that the cyclopentadienyl ligand (Cp) is not directly involved in the mechanism since the variation of Ru–Cp distances is minimal all along the computed steps and especially from A to B, which corresponds to the coordination of the monomer to the Ru center.

Nevertheless, the presence of the Cp ligand seems to be relevant for this reaction due to the electronic properties that make this ligand act as σ/π electron acceptor and π electron donor as well. As a consequence, there is a control of the ruthenium Lewis acidity/basicity and hence a stabilization of the Ru···O interaction.

As for the Ru–arene distances, the Ru–C2 and Ru–C3 ones were calculated above 3.00 Å, as soon as the monomer is coordinated to the metal (B), which indicates that typical η^6 hapticity is no longer maintained until the regeneration of the ruthenium catalyst (D).

In view of the Ru–(C5–C6) (2.38 and 2.34 Å) and Ru–(C4–C5–C6–C7) (2.48 and 2.47 Å) distances (*cf.* Table 4, structures B and C respectively), an η^4 coordination mode of the arene ligand may be postulated since an η^2 mode would lead to unstable 16-electron electronically unsaturated ruthenium species. In Fig. 4 it is also seen that the Ru···O distance is not affected throughout the mechanism, showing the strong interaction between the metal center and the monomer. Furthermore, the absence of a true Ru–alkoxide species is corroborated by the regularity of carbonyl bond length of the ester group in all the mechanistic steps, as shown in the last entry of the same table. From the energetic point of view, coordination of this monomer to the metal center represents *ca.* 5.3 kcal/mol exergonic stabilization of potential energy of the system, with an activation barrier of only *ca.* 16.5 kcal/mol (*vide infra** Fig. 4). All these data support that the ruthenium(II) metal center acts as a strong monomer activator for the initiation step.

The second step of the reaction mechanism involves a nucleophilic attack of the alcohol molecule to the activated carbonyl group leading to a transition state (TS1 in Fig. 4) containing a four-membered ring, where a hydrogen atom is positioned between the methanolic and the lactone oxygen atoms. This type of mechanism is comparable to a concerted reaction or also as a σ-bond metathesis where two new sigma bonds are formed simultaneously (lactone acyl C_{CL}–OMe and O_{CL}–H) with cleavage of the methanol O_{Me}–H and the lactone acyl C_{CL}–O_{CL} single bonds. The carbonyl group of the caprolactone has, at this stage, a pseudo-tetrahedral sp^3 carbon. From the energetic point of view this process has a relatively high barrier, comparable to other catalytic pathways, of *ca.* 43.1 kcal/mol leading to an energetic demanding process and hence justifying the dependence on temperature observed experimentally, where a preheating period at 120 °C is required. Finally, the desired step of ring opening of the lactone should occur, resulting in a hydroxy-ester (C in Fig. 4). In this case, a lowering of 47.7 kcal/mol in the Gibbs energy was estimated. At this point, the opened ring has a folded conformation and a rotational barrier of 2.1 kcal/mol was obtained for the unfolding of the linear ester (not shown in the figure). With such a small barrier, one might consider that the unfolding of the alkyl chain is simultaneously followed by de-coordination of the ring-opened monomer (D in Fig. 4). This de-coordination also leads to a drop of Gibbs energy of 19.7 kcal/mol, showing that once the hydroxy-ester is formed, it is easily released by the catalyst. Polymerization should then proceed with new monomer coordination to the metal center followed by the nucleophilic attack of the new hydroxy-ester, formed in the previous initiation step, allowing the chain growth of the polymer. To summarize, this DFT study is in good agreement with the first steps of an AM polymerization mechanism.

Table 4
Selected bond lengths for the optimized structures.

Structure	Bond distances (Å)			
	A	B	TS1	C
Cp	1.87	1.86	1.84	1.81
Ru-η^2-coordinated arene[a]	–	2.38	2.39	2.34
Ru-η^4-coordinated arene[b]	–	2.48	2.48	2.47
Ru-η^6-coordinated arene	1.79	2.71	2.73	2.67
Ru···O	–	2.15	2.16	2.17
Ester C=O	1.21	1.24	1.25	1.24

[a] (C5–C6) for structures B and C and (C4–C5) for structure TS1.
[b] (C4–C5–C6–C7) for structures B and C and (C3–C4–C5–C6) for structure TS1.

4. Conclusion

We have shown in this study that a family of ruthenium(II) complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-substituted arene})]^+[PF_6]^-$ act as efficient catalysts for the polymerization of ε-caprolactone via a *living* Activated Monomer mechanism with up to 74% chain transfer efficiency. The mechanism of the polymerization was established by means of a study involving NMR monitoring investigations and MALDI-ToF analyses. It was confirmed by DFT calculations that were undertaken for the first time for a Ring Opening Polymerization taking place by Activated Monomer mechanism. It is important to note that this type of mechanism allows the synthesis of end-functionalized polymers along with good control of the molecular weight. Another unprecedented interesting feature is the stability of these ruthenium catalytic complexes that allows their recovery at the end of the reaction. This fact, together with the growing of several polymer chains per metal atom can be considered as a further advanced in terms of catalyst economy in a green chemistry frame.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.06.015.

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