"Living" Radical Polymerization of Styrene Catalyzed by Cyclometalated Ruthenium(II) Complexes Bearing Nonlabile Ligands

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ABSTRACT: Cationic substitutionally inert cyclometalated ruthenium (II) and osmium (II) complexes, ([Mt(o-C$_6$H$_4$-2-py)(LL)$_2$]PF$_6$), where LL-1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy), were used for radical polymerization of styrene. Gradual modification of the complexes within the series allowed comparison of the catalytic activity and the redox properties. There was no correlation between the reducing powers of the complexes and their catalytic activities. The osmium compound of the lowest reduction potential was not active. All the ruthenium complexes catalyzed the polymerization of styrene in a controlled manner; but the level of control and the catalytic activity were different under the same polymerization conditions. [Ru(o-C$_6$H$_4$-2-py)(phen)$_2$]PF$_6$ demonstrated the best catalytic performance though its redox potential was the highest. It catalyzed the "living" polymerization with a reasonable rate at a catalyst-to-initiator ratio of 0.1. 1 equiv. of Al(OiPr)$_3$ accelerated the polymerization and improved the control, but higher amount of Al(OiPr)$_3$ did not speed up the polymerization and moved the process into the uncontrollable regime. Under the most optimal conditions, the controlled polymerization occurs fast without any additive and the catalyst degradation. Added free ligands inhibited the polymerization suggesting that the catalytically active ruthenium intermediates are generated via the reversible dechelation of bidentate phen or bipy ligands. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 3814–3828, 2009

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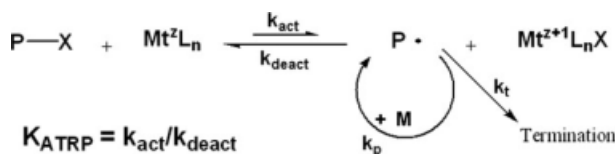
INTRODUCTION

The transition metal-calatyzed radical addition or Karasch reaction (ATRA) has attracted much attention as a powerful tool for a carbon–carbon bond formation.[1–3] Interest in transition metal

$$K_{ATRP} = k_{act}/k_{deact}$$

Scheme 1. Generally accepted mechanism of ATRP.

complexes, which are able to catalyze this kind of addition, has recently been renewed because of the development of atom transfer radical polymerization (ATRP) by Sawamoto and Matyjaszewski using ruthenium and copper complexes, respectively.[4,5] ATRA and ATRP have much in common, and ATRP can be considered as an extension of the ATRA reaction at high ratios of olefin (monomer) to halide (initiator). However, not all catalysts that are efficient in ATRA display the same activity/control in ATRP.[2,3,6,7] Many efficient catalytic systems based on different transition metals have been developed for ATRP, but copper compounds remain the most active and versatile catalysts, which are able to conduct polymerization of various vinyl monomers with a good control.[6,8–33] Ruthenium[II] plays a prominent role in the Kharasch chemistry, particularly $RuCl_2(PPh)_3$ has been known as one of the most efficient catalyst for ATRA.[2] Nevertheless, Ru-systems are still not so well developed for ATRP, in spite of the fact that these complexes were among the first reported for the purpose. The key element of ATRP is a transition metal complex Mt^zL_n, which interacts with dormant halide-capped chains P-X to give the active radicals $P^\bullet$ and the metal derivative $Mt^{z+1}L_nX$ oxidized by one electron (Scheme 1). Through this reversible redox process, populations of propagating radicals and dormant species are appropriately balanced to achieve a good controllability of molecular weight characteristics and end groups.

The equilibrium constant K_{ATRP} normally lies between 10^{-4} and 10^{-10} for satisfactorily controlled polymerizations,[34] which means that the great majority of the polymer chains exists as dormant species, and the catalyst predominantly remains in its original low oxidation state. Metal complexes active in ATRP should meet at least two criteria: (1) they should be able to receive a halogen from the dormant end and (2) they should readily but reversibly be oxidized.[35] The Scheme 1 represents ATRP mechanism in a general way and doesn't show, for example, ligand dissociation for coordinatively saturated complexes. The latter should have at least one labile ligand that should

dissociate to open a site for binding the halogen.[2,10,36] According to the scheme, electrochemical properties of the catalyst determine its activity: the low reduction potential facilitates the 1e oxidation and therefore low-potential complexes could be more active. Indeed, the kinetic work of the Matyjaszewski's group[25,26,37–39] has revealed a linear correlation between the catalytic activities and the redox potentials for different Cu complexes. Similar dependence was observed for a series of five-coordinated Fe^{II} catalysts,[40] but there was no correlation when the five- and four-coordinated complexes were compared. The four-coordinated complexes were more active ATRP catalysts despite their significantly higher redox potentials that were attributed to their less sterically crowded coordination sphere favorable for halide binding. The structure–ATRP activity relationship for Ru^{II} catalysts has a highly sophisticated character, even though there is quite direct correlation between the redox potential and the activity in ATRA reactions.[41] Sawamoto and coworkers[35] reported rough redox potential-activity correlation for the structurally analogous half-metallocene-type Ru^{II} complexes, but no relationship was observed when electronically equivalent but structurally somewhat dissimilar complexes were evaluated. Demonceau and coworkers[13,42] showed that the relationship for the half-sandwich p-cymene Ru^{II} based complexes, which were very active in ATRP of several vinyl monomers, is even more complex. Coarse correlation was found for a $[RuCl_2(p\text{-cymene})(PR_3)]$ series, but even within these structurally analogous complexes, the reliance was not completely reproducible and also depended on the monomer. In addition, no correlation was noticed for the related $[RuCl_2(p\text{-cymene})(NHC)]$ complexes (NHC = N-heterocyclic carbine) and no relationship was noticed when even slightly structurally different complexes were compared. Thus, electrochemical parameters could not be a clear-cut predictive tool of the catalyst's efficiency in ATRP, particularly for the Ru-compounds, and the electrochemistry-structure-ATRP activity relationship is far not clear yet. A recent analysis of Cu-, Ru- and Os-complexes of comparable ATRP activity referred the last two as very promising candidates for development of new highly active ATRP catalysts required for challenging systems.[39] They have higher reduction potentials than the Cu catalysts, but larger affinity to halide (halidophilicity).[39,43] Some Ru^{II} systems have higher aqua stability[44,45] and therefore may be more effective in water-

based polymerizations when compared with Cu catalysts, which are hydrolyzed to a significant extent.[8,46] The use of Os compounds is limited in polymer chemistry, and the ability of coordinatively unsaturated complexes OsBr(Cp*)PiPr$_3$ and Os(PPh$_3$)$_3$Hal$_2$ (Hal = Br, Cl) to mediate living radical polymerization has been recently discovered.[24,39] Osmium is more expensive and less environmentally friendly than Ru, but the Os-complexes have about 0.2–0.3 V lower reduction potentials compared with their Ru-analogues[47] and thus might surpass them in terms of activity.

The survey of Ru^{II} complexes used in controlled polymerization of alkenes indicates that most of them contain potentially labile ligands that may dissociate and open a coordinative site for the subsequent incorporation of halide atom of the initiator (Scheme 1).[8,9,48] The complex lability is both advantageous and disadvantageous. Without it, the activation step driven by k_{act} is problematic but too labile complexes are usually unstable under harsh catalytic conditions, decompose and polymerization may lose control.[49]

Therefore, it is a challenge to introduce a substitutionally inert transition metal catalyst, which shows significant stability under the catalytic conditions alongside with a substantial catalytic activity. Examples of such Ru^{II} species are reported in this work.

We have reported the application of cationic cyclometalated Ru complex, namely [Ru^{II}(o-C$_6$H$_4$-py)(MeCN)$_4$]PF$_6$, for radical polymerization of various vinyl monomers.[50,51] However, the polymerizations proceeded uncontrollably. An acceptable level of control was reached in the presence of SnCl$_2$ as a reducing agent and the insoluble Ru^{II} catalyst. The system was complex, unstable, and impractical for applications. Moreover, the complexity of the system makes difficult mechanistic investigation of the process. Studied here, the series of easy-to-make cyclometalated Ru^{II} and Os^{II} complexes[52,53] incorporating 2-phenylpyridine (phpy), 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) ligands [M(o-C$_6$H$_4$-2-py)(LL)$_2$]PF$_6$ (LL = bipy or phen, Fig. 1) is characterized by enhanced resistance to ligand substitution. At the first sight, these complexes should not show catalytic activity in the controlled radical polymerization of styrene. However, as we demonstrate here, the Ru^{II} complexes, **1–4**, reveal both anticipated stability together with unexpectedly high catalytic activity. Apart from our studies, a cyclometalated Ni compound has been reported as a catalyst for ATRP.[54,55] Meanwhile, cyclometalated
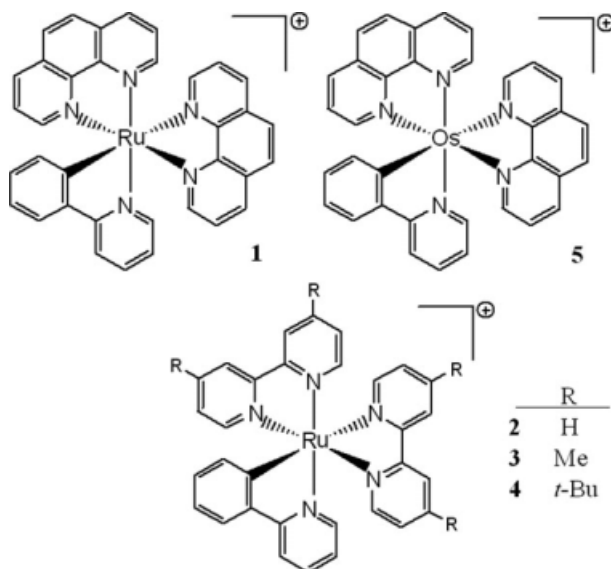

Figure 1. Structures of the complexes.

complexes have certain advantages as catalysts. Stabilized by chelation, the metal-carbon σ-bond makes these complexes robust and, most importantly, reduces notably their reduction potential.[52,56,57] The cationic nature of the complexes may also improve their catalytic properties as has been observed for other ruthenium compounds.[44,58,59]

EXPERIMENTAL

Materials

All reagents were purchased from Aldrich Chem. Co. Styrene (St) (99%) was washed three times with 1 wt % NaOH solution and passed through a column filled with neutral alumina. All other chemicals were used as received: anisole 99%, aluminum isopropoxide 99.99+%, ethyl-2-bromoisobutyrate (EBiB) 98%, and 1-phenylethyl bromide (PEB) 97%.

Synthesis of Ru and Os Complexes

The complexes, [Ru(o-C$_6$H$_4$-2-py)(phen)$_2$]PF$_6$ (**1**), [Ru(o-C$_6$H$_4$-2-py)(bipy)$_2$]PF$_6$ (**2**), [Ru(o-C$_6$H$_4$-2-py)(Me$_2$-bipy)$_2$]PF$_6$ (**3**) and [Os(o-C$_6$H$_4$-2-py)(phen)$_2$]PF$_6$ (**5**) were prepared according to the literature.[52,53,56] New [Ru(o-C$_6$H$_4$-2-py)(t-Bu$_2$-bipy)$_2$]PF$_6$ (**4**) was synthesized analogously to the other Ru complexes. The detailed experimental procedure and characterization of the complex are given as Supporting Information.

Polymerization Procedures

Polymerizations were carried out in bulk and solution (anisole 50/50 v/v) under nitrogen atmosphere at 100 °C. In a typical polymerization, the ruthenium complexes and the aluminum isopropoxide, Al(OiPr)$_3$, were added to a round-bottom flask with a constant flow of nitrogen, then the monomer and solvent were introduced via a syringe into the flask. The resulting solution was immersed in an oil bath previously heated to 100 °C and stirred for ~10 min until its complete homogenization. Next, the initiator was added to the heated homogeneous mixture. Most of the experiments were conducted under conditions where the molar ratio of [Monomer]$_0$/[Initiator]$_0$/[Complex]$_0$/[Al(OiPr)$_3$]$_0$ was held at 200/1/1/1 (8.7 M/43.5 mM/43.5 mM/43.5 mM) or without the Al additive at [Monomer]$_0$/[Initiator]$_0$/[Complex]$_0$ = 200/1/1 (8.7 M/43.5 mM/43.5 mM). EBiB and PEB were used as initiators. The samples were removed from the flask after certain time intervals using a degassed syringe. Samples for the GPC measurements were dissolved in THF, and the solution was passed through Florisil 60–100 Mesh column to remove the catalyst.

Analyses

Conversion was determined from the concentration of residual monomer measured by gas chromatography (GC) using a Shimadzu GC-2010 gas chromatograph equipped with one capillary column RESTEK stabilwax (30 m, 0.53 mm ID, and 0.5 μmdf). n-Decane (13.0 mM) as an internal standard was added in every polymerization. Analysis conditions: injector temperature, 220 °C; temperature program, 4 min 40 °C, 15 °C/min until 220 °C, 2 min 220 °C.

The molecular weights and molecular weight distributions of the polymers were analyzed by GPC (Waters 2695 ALLIANCE Separation Module) equipped with two HSP gel columns (HR MB-L molecular weight range from 5×10^2 to 7×10^5 and MB-B from 10^3 to 4×10^6) in series and a RI Waters 2414 detector. THF was used as an eluent at 35 °C with a flow rate of 0.5 mL/min. Linear polystyrene standards were utilized for the GPC calibrations. Theoretical molecular weights were calculated without taking into account the end groups according to the following equation: $M_{n,th}$ = ([Monomer]$_0$/[Initiator]$_0$) × Conversion × MW$_{monomer}$, where $0 \leq$ conversion ≤ 1.

Electrochemical measurements were performed on a PC-interfaced potentiostat-galvanostat AUTOLAB PGSTAT 12. A three-electrode setup was used with a BAS working glassy carbon electrode, Ag/AgCl reference electrode, and auxiliary Pt electrode. Before each measurement, the working electrode was polished with a diamond paste and rinsed with acetone and distilled water. The measurements were performed in 0.1 M n-Bu$_4$PF$_6$ solution of acetonitrile. The concentration of the complexes was kept at 10^{-3} M in all runs. The voltammograms of the complexes are shown in Supporting Information.

^{1}H NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer using CDCl$_3$ and d$_7$-DMF as solvents.

UV–vis measurements were performed on a Cary 400 UV–vis spectrophotometer (Varian). Anisole solutions of the complexes of 0.20–0.22 mM concentrations were used for these measurements. To get similar level of the absorption (the complex concentration), 10 μL aliquots were taken from the reaction mixture of the basic composition of [St]$_0$/[Initiator]$_0$/[Ru^{II}]$_0$ = 200/1/1 in bulk and diluted to 2 mL with anisole.

RESULTS AND DISCUSSION

General Observations

All the five catalysts, **1–5**, used in the study have similar 18 e octahedral structures, where the only difference between the ruthenium complexes, **1–4**, lies in the diimine ligands (see Fig. 1). On going from phen (**1**) and bipy (**2**) to Me$_2$bipy (**3**) and then to t-Bu$_2$bipy (**4**), the complexes become bulkier and slightly different electronically. The Ru^{II}/Ru^{III} reduction potentials ($E_{1/2}$) in acetonitrile of **1** and **2** are almost identical (543 mV and 540 mV versus Ag/AgCl, respectively). The electron-donating groups of the t-Bu$_2$bipy and Me$_2$bipy ligands lower the potentials to 436 and 441 mV (MeCN versus Ag/AgCl) correspondingly. Although reducing power of the complexes **3** and **4** with substituted bipy ligands are practically equal, t-Bu substituent is significantly bulkier. The osmium complex **5** is a structural analogue of the ruthenium complex **1**, but because of the osmium metal center **5** is much more reducing—its reduction potential equals 310 mV versus Ag/AgCl. Thus, we are able to compare catalytic performance of the complexes of very similar structures depending on their reducing power and bulkiness. Bulkier substituents are supposed to make an access

Table 1. Polymerization of St in Bulk at 100 °C Mediated by **1** and **2**

Complex	Initiator		Time (h)	Conv. (%)	$M_{n,GPC} \times 10^{-3}$ (g/mol)	$M_{n,th} \times 10^{-3}$ (g/mol)	PDI
1	PEB	a	8	57	8.8	11.8	1.27
		b	6	57	7.4	11.8	1.22
1	EBiB	a	8	60	10.1	12.5	1.36
		b	5 (16)	66 (87)	14.4 (15.9)	13.7 (18.0)	1.23 (1.52)
2	PEB	a	10	35	11.1	7.3	1.48
		b	8	66	9.7	13.7	1.30
2	EBiB	a	6	34	8.7	7.1	1.47
		b	5	58	10.0	12.0	1.20

[a] $[St]_0/[Initiator]_0/[Ru^{II}]_0 = 200/1/1$ (without $Al(OiPr)_3$).
[b] $[St]_0/[Initiator]_0/[Ru^{II}]_0/[Al(OiPr)_3]_0 = 200/1/1/1$.

for halogen atom to the metal center more difficult. It should also be noted that the grand majority of the Ru complexes applied so far to ATRP had one or two coordinated halogens (chlorides), and most of them were phosphine containing neutral compounds.[8,9,11,12,15,16,48] The complexes used in the study are halogen-free ionic coordinatively saturated compounds. Complexes of this kind have never been applied for ATRP. Additionally, as mentioned in the introduction, these complexes are very stable and could be stored as solids in air at ambient temperature indefinitely and used in the reactions without special precautions.

All four Ru^{II} compounds were able to mediate the radical polymerization of St, but with different rates and levels of control, under the same polymerization conditions (see below). The radical mechanism of the process was verified by applying the radical scavenger (2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO) methodology. The polymerizations did not proceed when a 5-fold excess of TEMPO with respect to the alkyl bromide (initiator) was introduced in the reaction mixture from the very beginning. Addition of the same amount of TEMPO after 3 h of polymerization stopped the process; the conversion remained constant and did not change with time. No polymerization was observed either in the absence of the alkyl halide when the St-catalyst system was kept at 100 °C for 16 h, but the addition of the initiator into this previously heated system led to a notable degree of polymerization even after 2 h.

Kinetics of the Polymerizations and a Comparative Analysis of the Catalysts

Because the compounds **1** and **2** have the equal redox potentials and closely related but different

phen and bipy ligands, the comparative study of their catalytic behavior was performed. Data for the bulk polymerizations mediated by these two complexes for different reaction conditions: type of the initiator, and presence or absence of $Al(OiPr)_3$, are presented in Table 1; kinetic curves are shown in Figure 2. Both catalysts turned out to be very active in ATRP of St: high conversions were reached in 6–10 h depending on the catalyst and the reaction conditions. As seen from the Figure 2, the plots of $\ln([M]_0/[M])$ as a functions of the reaction time are linear in all cases, indicating a constant radical concentration throughout the polymerization process. The polymerizations were faster in the presence of $Al(OiPr)_3$. Pseudofirst-order rate constants (k_{obs}) of the polymerizations
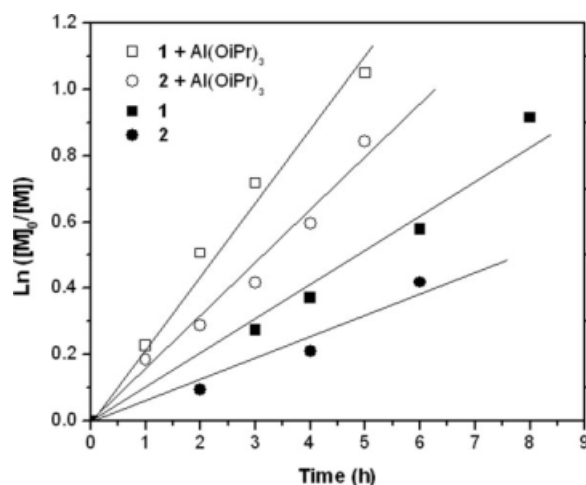
Figure 2. Semilogarithmic plots for bulk polymerization of St, mediated by **1** and **2** using EBiB as initiator in the presence and absence of $Al(OiPr)_3$ at 100 °C; ($\square$)-$[M]_0/[I]_0/[\mathbf{1}]_0/[Al]_0 = 200/1/1/1$; ($\bigcirc$)-$[M]_0/[I]_0/[\mathbf{2}]_0/[Al]_0 = 200/1/1/1$; ($\blacksquare$)-$[M]_0/[I]_0/[\mathbf{1}])_0 = 200/1/1$; and ($\bullet$)-$[M]_0/[I]_0/[\mathbf{2}]_0 = 200/1/1$.
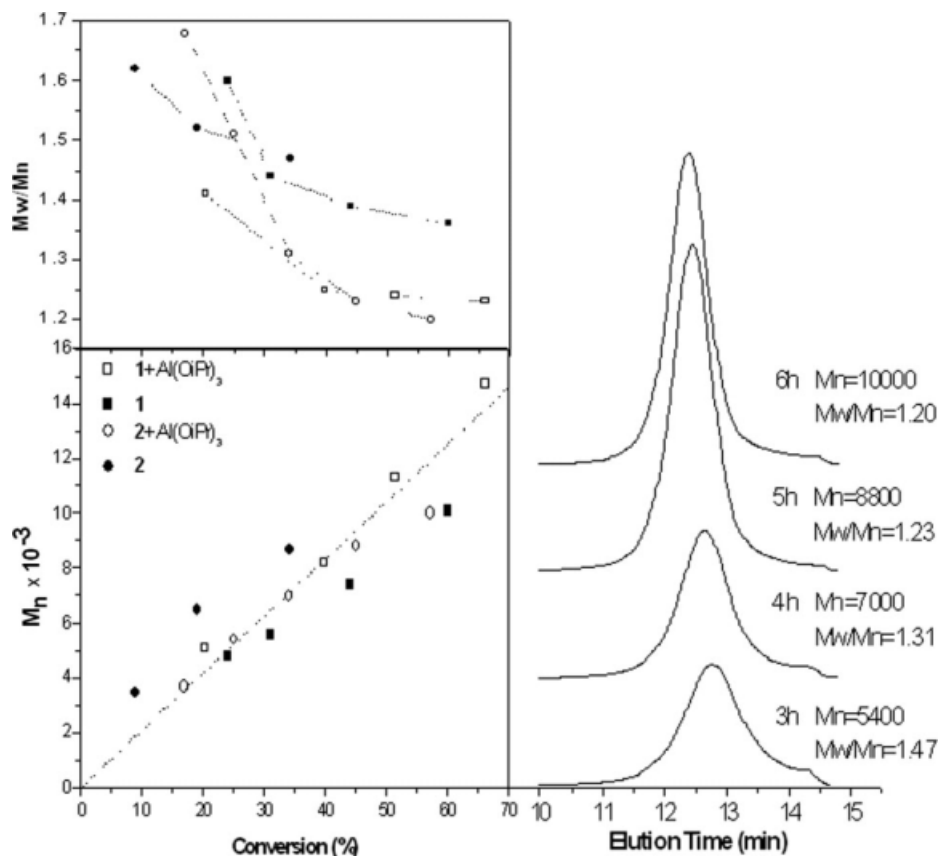
Figure 3. Evolution of M_n and PDIs with conversion for the bulk polymerization of St mediated by **1** and **2** with EBiB as initiator at 100 °C. ($\square$)-$[M]_0/[I]_0/[\mathbf{1}]_0/[Al]_0 = 200/1/1/1$; ($\bigcirc$)-$[M]_0/[I]_0/[\mathbf{2}]_0/[Al]_0 = 200/1/1/1$; ($\blacksquare$)-$[M]_0/[I]_0/[\mathbf{1}]_0 = 200/1/1$; and ($\bullet$)-$[M]_0/[I]_0/[\mathbf{2}]_0 = 200/1/1$. GPC chromatograms are shown for ($\bigcirc$) system.

conducted in the presence of Al(OiPr)$_3$ equal 0.22 and 0.16 h^{-1} for the catalysts **1** and **2**, respectively. However, both complexes were sufficiently active to mediate radical polymerization of St even without any additives with somewhat lower k_{obs} values of 0.11 h^{-1} for **1** and 0.06 h^{-1} for **2**. In general, their activities were higher than those reported for the majority of Ru-based catalysts.[6,10–13,16,45,60,61] The molecular weights of thus obtained PSt were very close to the calculated values and evaluated linearly with conversion. The polydispersities (PDIs) were also fairly narrow (Table 1 and Fig. 3). Al(OiPr)$_3$ is known as an additive that accelerates ATRP mediated by various metal complexes, but it is particularly effective for the Ru-compounds.[9,11,62–67] Usually, it not only increases the polymerization rate but also improves the control over the process. In fact, as we observed for **1** and **2**, the molecular weights were closer to their theoretical values and PDIs were narrower when the Al additive was used

(Table 1 and Fig. 3). Nevertheless, the polymerizations catalyzed by **1** were faster, less affected by the Al additive and the initiator nature than the polymerizations mediated by **2.** Both the polymerization rate and the molecular weight characteristics were not very significantly changed in the presence of Al(OiPr)$_3$, and no difference was observed between the polymerization rates initiated by PEB and EBiB for the catalyst **1**, only the PDIs were somewhat narrower in the case of the PEB initiator. On the other hand, the polymerizations mediated by **2** were much more sensitive to both factors: the presence of the Al additive and the type of initiator. The polymerization accelerated drastically, and the level of control was notably improved by addition of Al(OiPr)$_3$ and EBiB also turned out to be a more efficient initiator than PEB. It is not the first time we have dealt with different behaviors of the complexes with phen and bipy ligands; the different activity of these two ligands in substitution reactions was
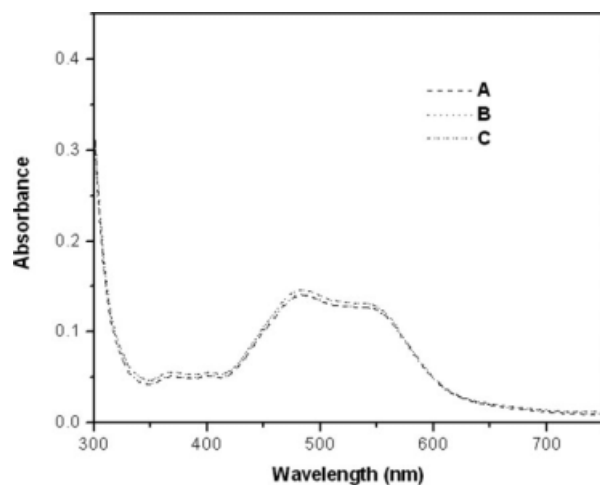
Figure 4. UV–vis spectra of anisole solutions of **2** and the reaction system in bulk at $[St]_0/[2]_0/[EBiB]_0 = 200/1/1$ composition ratio. (A) 0.22 mM solution of **2**; (B) solution of the original reaction mixture before the polymerization; and (C) 6 h after polymerization.

discovered and described by our group.[56,68] These two ligands are closely related and this is reflected in the similarity of the complex's structures; the Ru—C and Ru—N bond lengths as well as the bond angles in these two complexes are very similar.[52,56] Detailed comparison of the X-ray data does not show any important difference between these two structures that could allow us to explain the difference in the chemical behavior between the bipy and phen ligands. The only noticeable different feature is the angles between the ligand planes. In the complex **2**, all the angles are distributed uniformly, close to 90°; meanwhile in the complex **1**, the angle between phpy and phen next to Ru—C σ-bond is notably bigger (~96°) than all of the others (~90°). This may mean that the phen ligands are a bit more "compact" in space than the bipy ligands.

The catalysts remain predominantly in the oxidation state +2 during the polymerizations, and no color changes of the reaction mixtures were noticed in the presence or absence of Al(OiPr)$_3$. UV–vis monitoring of the solution (anisole) reaction performed with **2** demonstrated the only one band in the visible region with maximum at 480 nm which corresponds to the absorption of the complex in its original +2 oxidation state (Fig. 4). Moreover, the absorption intensity did not change during the reaction indicating the same catalyst concentration in the system. Thus, the complexes are stable and do not degrade under the polymerization conditions.

The difference between PDIs of the polymers obtained with and without Al(OiPr)$_3$ may be explained by different rate of the initiator consumption during the polymerizations. GC measurements showed that EBiB was completely consumed in the first 5 min of the bulk polymerization mediated by **1** in the presence of Al(OiPr)$_3$; meanwhile, in the absence of the additive, about 15% of the initiator was still found in the reaction mixture after 15 min of the reaction. A complete consumption of EBiB in the bulk polymerization without Al(OiPr)$_3$ was observed after 30–35 min from the start of the reaction. Another initiator applied, PEB, was completely consumed after 10 min of the polymerization mediated by **1** in the absence of Al(OiPr)$_3$. This was also reflected in more narrow PDIs obtained in the PEB-initiated polymerization (see data in the Table 1).

The involvement of an atom transfer pathway in this Ru-catalyzed polymerization was supported by end group analysis of the polystyrene synthesized. Figure 5 presents the ^{1}H NMR spectrum of PSt with $M_{n,GPC} \approx 7400$ produced by the PEB-initiated process. The spectrum closely reminds those reported in the literature.[12,69,70] A broad triplet at about 4.4 ppm is assigned to the proton located in the α-position of the bromine (ω-end); meanwhile, the methyl protons from PEB moiety are seen at 0.8–1.1 ppm. The molecular weight estimated from the ratio of integrals of the signals from the aromatic protons and the end group proton at 4.4 ppm was equal to 7100 (68 monomer units per chain), and this is in a good agreement with the M_n from GPC data.

An additional method for verifying the functionality of the polymers obtained is a chain-extension experiment. Such experiment was conducted at 100 °C in anisole solution (50/50 v/v) using as a macroinitiator PSt of 7900 molecular weight (synthesized previously in EBiB-initiated polymerization catalyzed by **1**). The macroinitiator was purified by column chromatography and stored as a solid for a few days before use in the extension experiment. Its SEC curve was not altered after the storage. The molar ratio of $[St]_0/[macroinitiator]_0/[1]_0 = 200/1/1$ was held in this experiment. The monomer conversion of 28% was reached in 8 h under these conditions. The SEC traces of the PSt macroinitiator and the chain-extended polymer are shown in Figure 6. As can be seen from the figure, both SEC curves are unimodal and the M_n increased in about two times and thus was very close to the calculated one for this level of conversion. The PDI of the
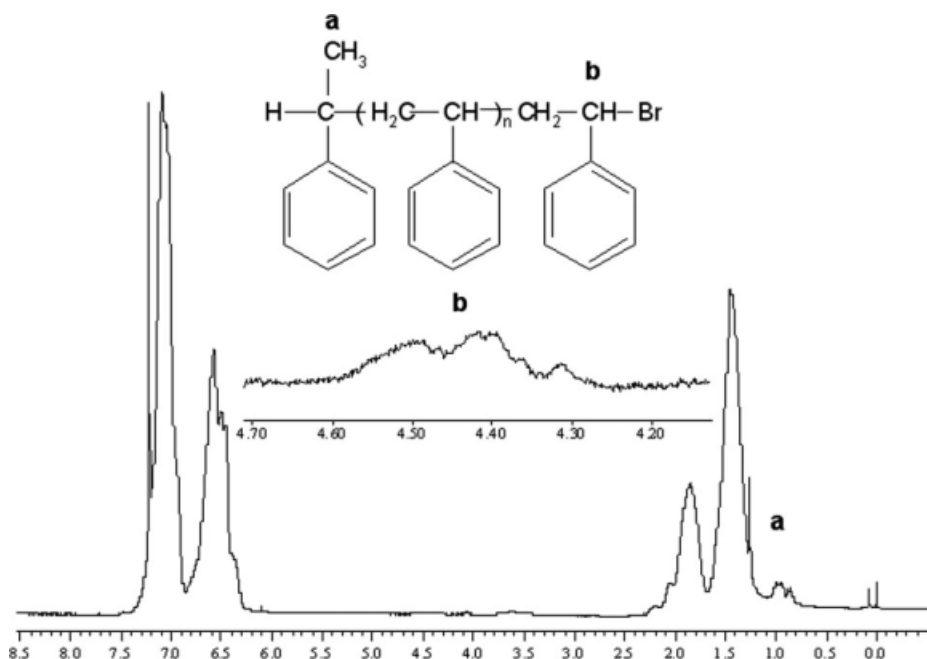
Figure 5. ^{1}H NMR spectra of PSt (solvent CDCl$_3$) obtained in the system of $[M]_0/[PEB]_0/[1]_0/[Al(OiPr)3]_0 = 200/1/1/1$, bulk at 100 °C.

chain-extended PSt was broader than those of the polymer obtained with the low-molecular weight initiators because of some tailing from low-molecular weight products as usually observed in chain-extension and block copolymer synthesis.[71–73] The absence of significant shoulder on the low-molecular-weight side of the SEC curve of the chain-extended polymer indicated that the chain end functionality of the macroinitiator was relatively high. Therefore, ATRP mechanism of the process and "living" nature of the system was confirmed by these two experiments.

To verify the influence of the reducing power of the catalysts, a comparative study of the solution EBiB-initiated polymerizations mediated by all four Ru complexes was performed without any additive. The corresponding kinetic data, evolution of the molecular weights, and PDIs with conversions are given in Figures 7 and 8. As can been seen from the figures, all complexes mediated polymerization of St with relatively high rates and also demonstrated fairly good catalytic performance; the molecular weights grew linearly with conversions and were very close to the calculated values. The PDIs became narrower with conversion as usual. However, the PDIs were notably broader for the polymers obtained with the complexes **3** and **4**, with the substituted bipy ligands, than those for the PSt synthesized with **1** and **2**. It is worthy noting that, again, as in the

case of the bulk polymerizations, no correlation between the activities and reducing powers of the catalysts was found. Thus, the rates of polymerizations catalyzed by **2** and **3** were very similar (k_{obs} were of 0.035 and 0.040 h^{-1}, respectively) though the potential of **3** is by more than 100 mV lower. The polymerization catalyzed by **4** with the bulkiest ligands was notably faster, k_{obs} of 0.060 h^{-1}, than those mediated by **2** and **3**, even
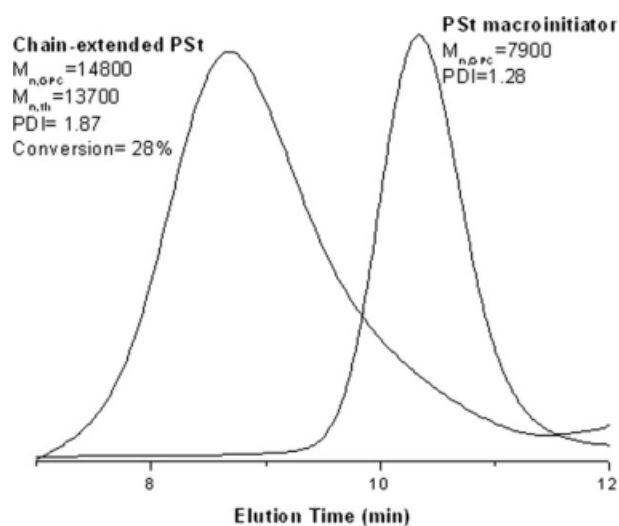

Figure 6. GPC curves of PSt-Br macroinitiator and its chain-extended polymer obtained at 100 °C in anisole (50/50 v/v); $[St]_0/[macroinitiator]_0/[1]_0 = 200/1/1$.
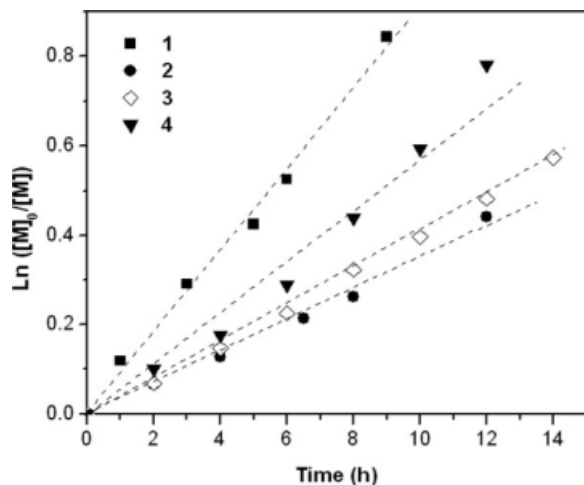
Figure 7. Semilogarithmic plots for EB*i*B initiated polymerization of St mediated by complexes **1**–**4**; anisole solution (50/50 v/v), 100 °C, no Al(O*i*Pr)$_3$ added; (■)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/1/1; (●)-[M]$_0$/[I]$_0$/[**2**]$_0$ = 200/1/1; (◇)-[M]$_0$/[I]$_0$/[**3**]$_0$ = 200/1/1; and (▼)-[M]$_0$/[I]$_0$/[**4**]$_0$ = 200/1/1.

though the redox potentials of **3** and **4** are almost equal. Interestingly, the highest rate (k_{obs} = 0.091 h^{-1}) was again observed for the polymerization conducted by **1** despite its high redox potential. This polymerization was also better controlled as can be estimated from the molecular weight data; the experimental molecular weights were very close to the theoretical values, and the PDIs were also the narrowest. Hence, the complex **1** showed the best catalytic performance, and its behavior could not be accounted for just in terms of the electrochemical properties.

Most data shown in Table 1 are given for moderate (under 70%) conversions. Only a few polymerizations investigated here were permitted to reach high conversions. One example is presented in the Table 1 (line 4, data in parenthesis). For bulk process in the presence of accelerating Al(O*i*Pr)$_3$, it required 16 h to reach about 90% of conversion. The reaction systems were very viscous even at 60–66% of conversion, but at 87%, the system was completely solidified, and stirring was stopped. The molecular weights went on to grow with conversion even when they are high, as one can observe from the data in Table 1, but the gap between estimated and experimental molecular weights was bigger than those observed for the polymers obtained at low and moderate conversions. The PDIs were also broader when compared with PDIs at moderate conversions. The semilogarithmic plot of ln([M]$_0$/[M]) versus the

reaction time started to deviate from the linear dependence at conversions higher than 70%. This may be explained by strong influence of diffusion in very viscous systems, but the polymerization under the diffusion controlled conditions was not the objective of this research.

Influence of the Al(O*i*Pr)$_3$ Content and the Catalyst Concentration

In attempt to clarify the catalytic mechanism, the additional experiments were performed varying the initial molar ratios between monomer, catalysts, and Al(O*i*Pr)$_3$ in the reaction mixture. The polymerizations were carried out in bulk with EB*i*B initiator and **1** as the best catalyst using compositions with the following ratios of [St]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/4; 200/1/1; 200/1/0; 200/0.5/0; and 200/0.1/0 (no Al(O*i*Pr)$_3$ in the last three
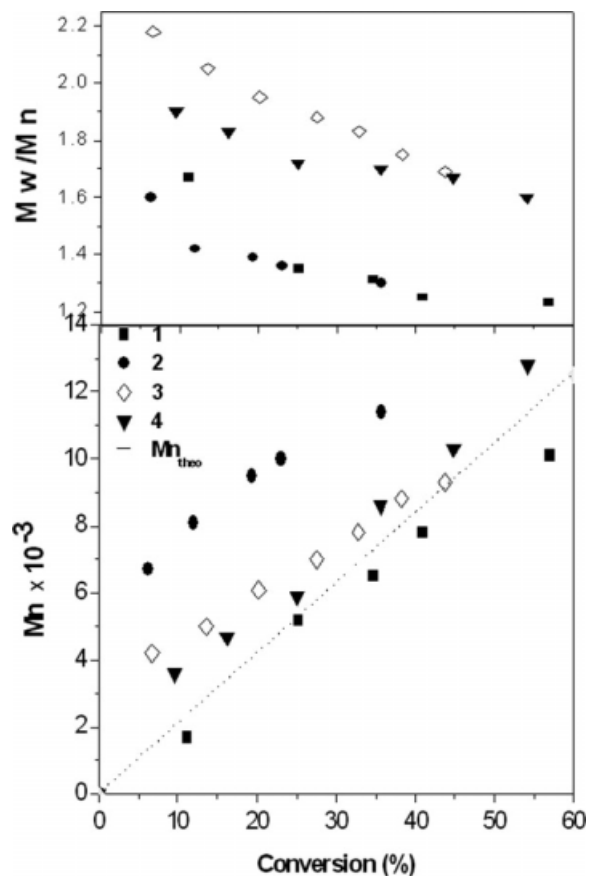

Figure 8. Evolution of M_n and PDIs with conversion for the EB*i*B initiated polymerization of St mediated by **1**–**4**; 100 °C, anisole solution (50/50 v/v), no Al(O*i*Pr)$_3$ added; (■)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/1/1; (●)-[M]$_0$/[I]$_0$/[**2**]$_0$ = 200/1/1; (◇)-[M]$_0$/[I]$_0$/[**3**]$_0$ = 200/1/1; and (▼)-[M]$_0$/[I]$_0$/[**4**]$_0$ = 200/1/1.
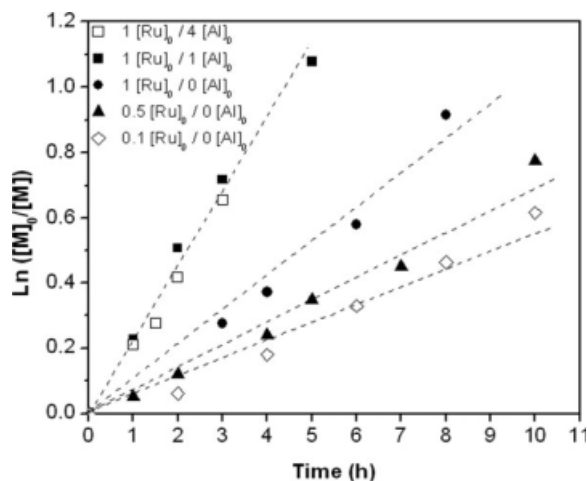
Figure 9. Effect of concentration of **1** and Al(OiPr)$_3$ on kinetic of the EBiB initiated polymerization of St; 100 °C, bulk; (□)-[M]$_0$/[I]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/1/4; (■)-[M]$_0$/[I]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/1/1; (●)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/1; (▲)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/0.5; and (◇)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/0.1.

compositions). The monomer to initiator ratio was held at 200/1 in all experiments. The results are presented in Figures 9 and 10. As was already shown above, the complex **1** controlled well the polymerizations at our standard composition of [St]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/1 or without the additive at [St]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/0. The presence of the Al additive led to a faster polymerization and also improved the control, but improvement was not very significant. However, a 4-fold increase in the aluminum concentration in the reaction mixture ([St]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/4) did not cause a further acceleration of the polymerization, the k_{obs} remained the same (0.22 h^{-1}), but this did result in a loss of the control, particularly at the beginning of the reaction, as can be seen from Figures 8 and 9. The polymer obtained had much higher than expected molecular weights and broad (around 2) PDIs. Similar effect of the Al(OiPr)$_3$ content on the polymerizations mediated by other cyclometalated compound, [Ru(o-C$_6$H$_4$-py)(MeCN)$_4$]PF$_6$, has been reported,[50,51] but this complex did not mediate polymerizations without the Al additive. To our knowledge, this kind of phenomenon has not been reported for any other complexes. On the contrary, most of the data reported have been obtained with a large excess of Al(OiPr)$_3$ to catalyst and the excess did not lead to a loss of the control, as in our case. The exact role of Al(OiPr)$_3$ is not clear although several attempts to elucidate the mechanism have

been made including experimental and theoretical studies.[67,74] There are two possibilities: it may activate the C—Hal bond or interact with a catalyst and thus activate it. We performed ^{1}H NMR studies of the complex **2**, the behavior of which was more affected by the aluminum additive presence. The spectra of the model mixtures of **2** and EBiB at [2]$_0$/[EBiB]$_0$ = 1/5 M ratio were monitored for 10 h under the polymerization conditions (100 °C) in d$_7$-DMF solution without and with Al(OiPr)$_3$ (1 equiv. to the catalyst). We failed to observe any new signals which might be assigned to the interaction products between the complex and Al(OiPr)$_3$ even after extended heating. On the other hand, because the complexes **1** and **2** have limited solubility in the monomer and to obtain homogeneous solutions, the mixtures were kept at 100 °C for ~10–15 min before the initiator addition, and we observed that the solubility of **2**,
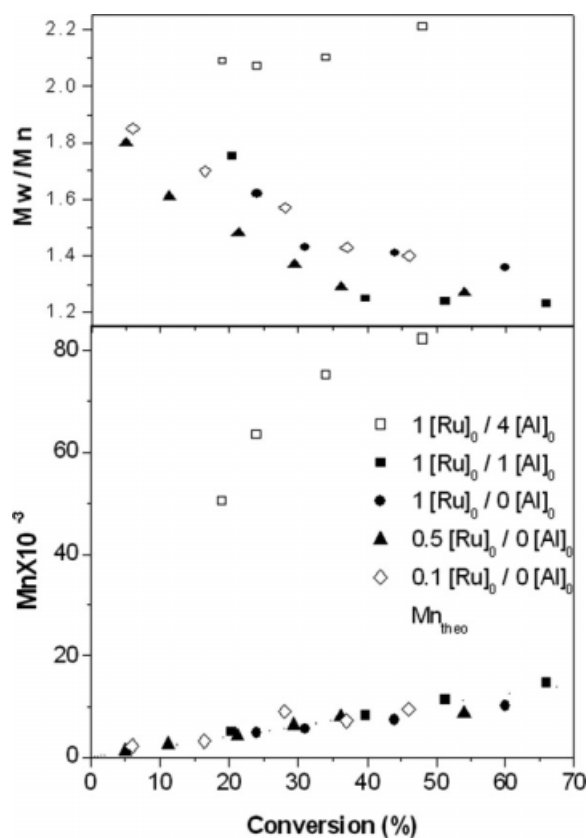

Figure 10. Effect of concentration of **1** and Al(OiPr)$_3$ on molecular weights and PDIs for the EBiB initiated polymerization of St, 100 °C, bulk; (□)-[M]$_0$/[I]$_0$/[(**1**)]$_0$/[Al]$_0$ = 200/1/1/4; (■)-[M]$_0$/[I]$_0$/[**1**]$_0$/[Al]$_0$ = 200/1/1/1; (●)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/1; (▲)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/0.5; and (◇)-[M]$_0$/[I]$_0$/[**1**]$_0$ = 200/1/0.1.

in particular, was improved in the presence of the additive. However, we failed to obtain any other evidence of the interaction between Al(OiPr)$_3$ and the complexes. At the same time, it was shown by GC data that the initiator was consumed much faster in the presence of the Al additive. So, that is why we speculate in favor of the C—Hal activation. The ease of the C—Hal bond cleavage results in a huge rise of the radical concentration at the beginning of the reaction and hence the control becomes worse. The reaction did not accelerate because of high portions of the termination reactions, but moderate activation of the C—Hal bond, which probably takes place at low Al(OiPr)$_3$ concentration, provides faster consumption of the initiator and thus the control is improved.

Taking into account the high stability and good catalytic performance so far seen for the complex **1**, the polymerizations at lower concentrations of **1** (catalyst/initiator molar ratios of 0.5 and 0.1) were performed in the absence of Al(OiPr)$_3$. The results are shown in Figures 9 and 10. As can be seen from the kinetic curves, a two times decrease in the catalyst concentration resulted in a slower polymerization, but the affect was very moderate: k_{obs} decreased from 0.11 to 0.071 h^{-1}. Thus, the polymerization was still proceeding at reasonable rate, and the molecular weight characteristics were well controlled. The further decrease in a catalyst/initiator ratio to 0.1 only slightly affected the polymerization; the rate almost did not change (k_{obs} = 0.059 h^{-1}) compared with the rate at 0.5 catalyst/initiator ratio. The molecular weights grew linearly with conversion and remained very close to the calculated value. The PDIs were broader than those observed for the higher catalyst concentrations but still remained reasonably narrow.

Minimization of the catalyst concentration without a significant decrease in the polymerization rate and worsening the "living" character of the process is one of the principal objectives of ATRP. For the grand majority of the catalysts applied, a catalysts/initiator molar ratio of 1/1 was used. However, several highly active Cu- and Ru-based catalyst systems which are able to mediate "living" polymerization of various vinyl monomers at much lower catalyst/initiator ratio have been reported.[6,7,10,11,16,25,26] The lowest catalyst/initiator ratio of 0.01–0.005 in "living" polymerizations has been reached for Cu-catalysts.[26] Ruthenium complexes have been reported so far to catalyze polymerizations of methyl acrylate (MA), methyl methacrylate (MMA), and St with good control with reasonable rates at a catalyst/initiator ratio of 0.1,[11]

but the data were obtained in the presence of amino-additive. The complex **1** therefore may be considered as one of the most active Ru-catalysts for ATRP of St.

Surprisingly, the cyclometalated Os complex **5**, a very stable compound possessing the lowest redox potential, more than 200 mV lower than that of **1**, was not able to mediate polymerization of St. Only traces of the polymer were detected after 30 h of the reaction in bulk under the standard conditions without Al(OiPr)$_3$. The amount of the polymer obtained was not enough even for the characterization. It was obvious that **5**, in spite of its highest reducing power, demonstrated the worst catalytic behavior among all cyclometalated complexes studied here.

Influence of Free Ligands and the Proposed Mechanism

The complexes used in this research are coordinatively saturated compounds. This means that there is no space within their coordination spheres where the halogen might enter. They neither have halogen ligands, which can participate in exchange with the halogen at the terminals or from the initiator. Thus, the complexes to be able to accept the halogen atom should release one of the ligands. Monitoring the reaction by ^{1}H NMR technique did not show the existence of any free ligand. However, if the ligand release is a key step of this catalytic mechanism, the process may be suppressed by presence of free strongly coordinating ligands in the reaction solution, and that should lead to a shift of the equilibrium in the Scheme 1. That is why the kinetics of the bulk polymerizations under the standard conditions mediated by **1** was also studied in the presence of four strongly coordinating compounds: phen, bipy, phpyH, and PPh$_3$. The former three N-donor ligands were added in a 2-fold excess over the catalyst and only a 1.4-fold excess of PPh$_3$ was applied due to its low solubility in St. The monomer conversions and molecular weight characteristics of PSt obtained under the ligand excess conditions are shown in Table 2.

As one can see, the polymerization was strongly retarded in the presence of all the free added ligands, but the retardation effect caused by phen was the lowest. The presence of PPh$_3$, even if it was added in the smallest quantities, affected drastically the polymerization kinetics. The polymers obtained under these conditions were characterized by very broad PDIs, and their weights did not show any dependence on conversion.

Table 2. Polymerization of St in Bulk at 100 °C Mediated by **1** in the Presence of Excess of Different Free Ligands

Ligand in Excess	$[Ligand]_0/[1]_0$	Time (h)	Conv. (%)	$M_{n,GPC} \times 10^{-3}$	$M_{n,th} \times 10^{-3}$	PDI
–	No ligand added	3	24.0	4.8	5.0	1.60
		6	44.0	7.6	9.2	1.39
phen	2:1	2	4.5	3.5	0.9	2.9
		6	32.1	4.3	6.7	3.1
phpyH	2:1	2	4.3	6.0	0.9	3.0
		6	17.3	5.9	3.6	3.3
bipy	2:1	2	4.2	1.13	0.9	3.9
		6	9.6	0.94	2.0	4.3
PPh$_3$	1.4:1	3	5.0	7.4	1.0	2.8
		6	15.1	10.3	3.1	2.7

Therefore, the polymerization process was strongly affected by presence of the free ligands in the reaction mixture, and this suggests a formation of a vacant site at the metal center of the complex by the release of one or half of the ligand, because they are bidentate, as a key step of the mechanism. The fact that the dissociation was not confirmed by ^{1}H NMR implies that only one of the Ru—N bonds is cleaved, thus one vacant site is formed at the metal center and one of the ligands remains bound by means of one Ru—N or Ru—C (in case of phpy) bond. Additionally, the fact that the excess of free phen had less influence on the polymerization rate than the three others confirms indirectly the aforementioned hypothesis. The phen ligand is a fluxionally rigid molecule. Its decreased conformational mobility may make the access and coordination to the vacant site more difficult. Therefore, the inhibition by phen is the weakest in the series.

Cleavage of any of the Ru—N bonds is possible, but we speculate in favor of the Ru—N bond which is *trans-* to the metal-carbon bond. This bond is the longest in all the complexes due to the *trans*-influence of σ-bond phenyl ring as supported by the X-ray structural data.[52,56,68] Moreover, this distance in **1** (2.13 Å) is bigger than in **2** (2.08 Å), also it is longer in the substituted bipy complex **3** (2.12 Å) in comparison to **2**. The variation is not important but it is a possible explanation of the difference in activity of the catalysts. Thus, the following mechanism shown in the Scheme 2 is proposed for these catalysts.
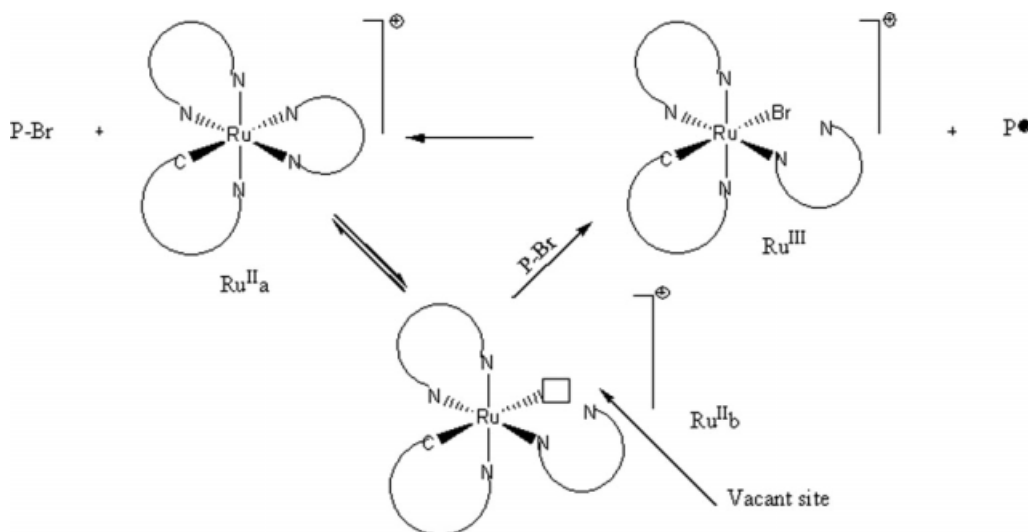
Scheme 2. Proposed mechanism.

The catalysts do not lose completely any of the ligands and therefore remain very stable during the polymerization process. Ligands are more strongly bound to Os^{II} in the complex **5** and dissociate less readily.[53] The vacant site is more difficult to create for Os^{II} than for Ru^{II} and therefore **5** is inactive in ATRP though its reduction potential is the lowest. Understanding of the inactivity of **5** is an extra evidence for the reaction mechanism shown in Scheme 2.

The catalysts **1** and **2** were also tried for the polymerization of MMA. Under the normal conditions reported in this article (100 °C, bulk, 200/1/1 M ratio), the polymerization was poorly controlled. When the reaction temperature was decreased to 80 °C, the catalysts were poorly soluble in pure MMA as well as in its mixture with anisole. To improve the solubility of catalysts, DMF was used as a solvent instead of anisole at 80 °C. The control was notably improved, but PDIs were still broad. Such broad PDIs in the presence of DMF were noted before in the literature.[75] Now, we are concentrating on the catalysts **3** and **4** for the polymerization of MMA. These catalysts are much better soluble, and the "living" polymerization conditions of MMA are currently under investigation in our group.

CONCLUSIONS

A series of novel highly stable cyclometalated Ru^{II}- and Os^{II}- based catalysts has been applied for "living" radical polymerization of St. The complexes are structurally very similar: 18 e octahedral compounds with two bidentate closely related bipy or phen ligands. Switching from bipy to phen allowed the modification of the complexes without affecting their reducing power, whereas the incorporation of Me or *t*-Bu groups in the diimine ligand decreased the reduction potential and increased the steric factor. The Os^{II} complex, **5**, was the most reducing compound. Thus, within the series, the complexes were gradually modified and the comparative study of their performance as catalysts in ATRP of St was carried out. No correlation was found between the reducing power of the complexes and their catalytic activity. In contrary, the complex **5** had the lowest redox potential but was not able to mediate the polymerization. All the Ru^{II} compounds demonstrated high catalytic activity and were able to catalyze the "living" polymerization without any accelerator additive. The best catalytic performance: high ac-

tivity together with good controllability, was observed for **1**, the complex with phen ligands and possessing one of the lowest reducing powers. The complex catalyzed the fast ATRP of St with a fairly good control even at a catalyst-to-initiator molar ratio of 0.1. No dependence of the catalytic activities on the redox potentials was observed even within the Ru^{II} complexes with bipy ligands (**2–4**). The complexes **3** and **4** with substituted bipy ligands mediated the polymerization with higher rate than the less reducing **2**. However **3** and **4** had an equal redox potentials, but **4** was more active than **3**.

The complexes with different phen and bipy ligands but of equal reducing power, **1** and **2**, showed not only different catalytic activity, but were also differently affected by addition of $Al(OiPr)_3$, a typical activating additive widely used with Ru-catalysts. Presence of the aluminum additive at a catalyst/$Al(OiPr)_3$ molar ratio = 1/1 accelerated the polymerization and improved the control in the processes mediated by both catalysts; however, the polymerization catalyzed by **1** was affected to a lesser extent. Higher concentration of the Al additive did not accelerate the polymerization further and led to a loss of the control. Addition of free ligands, phpyH, phen, bipy, and PPh_3, into the reaction mixture inhibited the polymerization suggesting that the catalytically active ruthenium intermediates are generated via the reversible dechelation or "half-dissociation" of the bidentate ligands.

Thus, for this series of coordinatively saturated compounds, electrochemical parameters are useless for the prediction of their catalytic behavior in ATRP. The ability to release the ligand is presumably a much more crucial factor than the reducing power.

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