

Cyclometalated Ruthenium(II) Complex as a Versatile Catalyst for Living/Controlled Radical Polymerization of Hydrophobic and Hydrophilic Monomers

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Summary: Cyclometalated complex, *cis*-[Ru(phpy)(phen)(MeCN)₂]PF₆, bearing strongly bound ligands (phpy = 2-phenylpyridine, phen = 1, 10-phenanthroline) and relatively labile (MeCN) ligands, in conjunction with ethyl 2-bromoisobutyrate (EBiB), was used for radical polymerization of three hydrophobic, styrene (St), methyl methacrylate (MMA), *n*-butyl acrylate (BA), and one hydrophilic, 2-hydroxyethyl methacrylate (HEMA), monomers. The polymerizations were fast and reasonably controlled; the molecular weights increased with conversion and were close to the calculated values. The best control was achieved in polymerization of St. The complex was able to mediate this polymerization with acceptable rate and level of control even at a monomer/catalyst ratio of 2000. The living character of the polymerizations was confirmed by chain extension experiments; the degree of polymer “livingness” was less for PMMA than for PSt. Because of ionic nature, the complex was well soluble in MeOH and thus catalyzed polymerization of HEMA under homogeneous conditions at 50 °C.

Keywords: atom transfer radical polymerization (ATRP); cationic ruthenium complexes; living polymerization

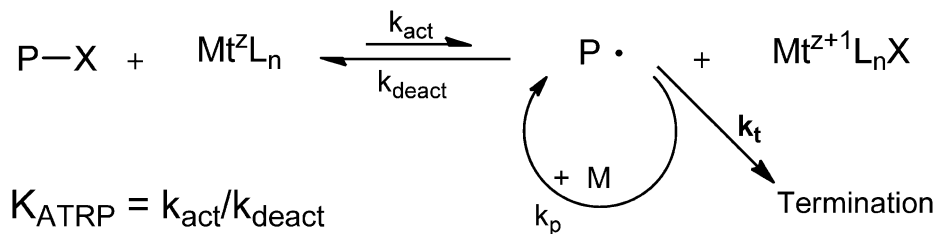
Introduction

Atom transfer radical polymerization (ATRP) is one of the most adaptable controlled/“living” radical polymerization methods. Since its discovery in 1995,^[1,2] the continuous progress of ATRP has resulted in the development of highly efficient catalytic systems which were able to polymerize numerous monomers with unprecedented control over the molecular weight characteristic and end groups. This allowed the synthesis of new polymeric materials such as block- and gradient-copolymers, dendritic or brush macromolecules.^[3–8] ATRP is a catalytic process based on the reversible

reaction of a low-oxidation state transition metal complex $M^{z+}L_n$ with dormant halide-capped chains P-X to give the active radicals (P•) and the corresponding higher-oxidation state metal complex with a coordinated halide ligand $XM^{z+1}L_n$ (Scheme 1).^[5,6] For a successful process the equilibrium should be strongly shifted toward the dormant species maintaining the populations of propagating radicals low. The “livingness” of this polymerization process can be ascertained from the first-order kinetics of consumption of the monomer, accompanied by a linear increase in polymer molecular weights with conversion. A variety of complexes of different transition metals has been successfully applied as catalysts for ATRP, including complexes of Cu,^[2–4,6,7] Ru,^[1,5,8–10] Fe,^[11–15] Ni,^[16–17] Re,^[18] Pd.^[19] However, the development of new active, robust and versatile catalysts is still an important subject of research. Catalytic systems of high activity which, at

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**Scheme 1.**

General mechanism of ATRP.

the same time, are able to control the polymerization of different monomers is now required for further progress in ATRP. Ruthenium complexes are considered as one of the most promising candidates for development of such systems. Ruthenium catalysts are characterized by a wide range of design parameters arising from their high tolerance to functional group and enormous variety of ligands^[8–10,20–27] that allows their application for polymerization in highly polar and/or protic media. Moreover, their catalytic activity and controllability may be tuned by appropriate choice of ligand combination. These advantages may overcome the relatively high cost of the ruthenium.^[9]

Despite the obvious success of living radical polymerization of hydrophobic monomers by ATRP, the number of catalytic systems which permit the controlled polymerization of hydrophilic monomers in protic, particularly in aqueous media, is still very limited. The copper-based catalysts suffered undesirable side reactions, such as disproportionation of Cu(I) activator and halide ligand substitution by solvent from Cu(II) deactivator,^[28] that requires high content of the catalyst. Therefore, the design of new and versatile catalytic systems, useful for the polymerization of both hydrophobic and hydrophilic monomers, represents a major challenge in ATRP.

Cyclometalated Ru(II) compounds whose effective synthesis was developed in our group^[29,30] may be quite interesting for ATRP because of several reasons. First, stabilized by chelation, the metal carbon σ -bond makes

these complexes robust and increases electron density on the metal center (lower reduction potential). Particularly, the use of cyclometalated 2-phenylpyridine (phpy) ligand, which is structurally similar to neutral 2,2'-bipyridine, reduces the reduction potential by approx. 0.7 V per single substitution.^[29] This may result in increase of the catalytic activity because of facilitation of the one electron transfer process. Second, the cationic nature of these complexes may also be advantageous for reactions in aqueous systems and, additionally, higher catalytic activity has been observed for the ionic Ru(II) compounds versus their neutral analogs.^[31–34] Several of these cyclometalated complexes have already been reported for ATRP of various monomers.^[35–37]

Here, we would like to report the application of one these complexes, namely *cis*-[Ru(phpy)(phen)(MeCN)₂]⁺PF₆⁻ (**1**), (see Figure 1 for the structure), for ATRP of

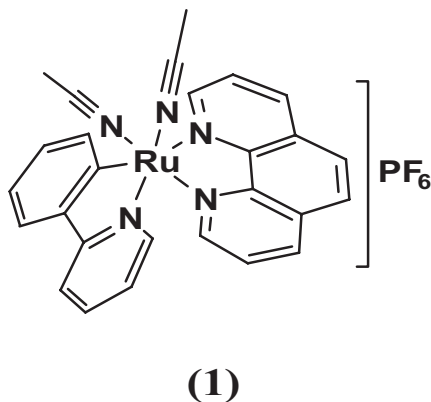


Figure 1. Structure of the complex.

different hydrophobic and hydrophilic monomers, such as St, MMA, BA and HEMA. The complex is coordinatively saturated and composed by combination of strongly bound ligands (p_hpy, phen) and relatively labile (MeCN) ligands. Such combination makes the complex stable on one hand, but permits its easy activation on the other hand.

Experimental Part

Materials

All reagents were purchased from Aldrich Chem. Co. The monomers MMA, St, BA and HEMA were passed through a column filled with neutral alumina, and then were vacuum distilled under reduced pressure. Methyl ethyl ketone (MEK) (99.9 + %) was distilled prior to use, all other reagents: toluene (99.9%), MeOH (HPLC grade), EBiB (98%), and aluminum isopropoxide (Al(O*i*Pr)₃) were used as received.

Synthesis of Ru Complexes

The complex **1** was prepared according to the literature.^[30]

Polymerization Procedure

The polymerizations were carried out in solutions (monomer/solvent = 50% v/v) under nitrogen atmosphere using Schlenk technique. The system of catalyst **1** in conjunction with EBiB was applied in all experiments. Initial molar composition of [Monomer]₀/[**1**]₀/[EBiB]₀ = 200/1/1 was used in most of the polymerizations. Several polymerizations were carried out in the presence of 1 eq. of Al(O*i*Pr)₃ relatively to **1** ([**1**]₀/[Al]₀ = 1/1). A typical example for polymerization of St is given subsequently. Complex **1** (57.9 mg, 21.7 mM) was placed in a 25 mL Schlenk tube equipped with magnetic stir bar and then St (2 mL, 4.35 M) and toluene (2 mL, 4.7 M) were added at room temperature. The mixture was degassed by freeze-pump-thaw cycle (3 times). The tube was immersed in oil bath thermostated at 100 °C and in approx. 5 min when the mixture was

completely homogeneous EBiB (13.2 μL, 21.7 mM) was introduced by syringe. Polymerizations of all other monomers were conducted by similar way under appropriate conditions. Polymerization of MMA was conducted at 80 °C in toluene and at 70 °C in MEK. Polymerization of BA was conducted in MEK at 70 °C, and polymerization of HEMA at 50 °C in MeOH. The samples were removed at certain time intervals using degassed syringes. All the samples were purified by filtration on a Florisil column (Ø = 13 mm and h = 25 mm) to remove the catalyst and were characterized by GPC.

Chain-Extensions

Chain extensions were performed using macroinitiator methodology under the conditions described for the corresponding homopolymerizations using the [monomer]₀/[macroinitiator]₀/[**1**]₀ = 200/1/1 ratio. For example, the chain-extension experiment for PSt was conducted in toluene solution (50% v/v) at 100 °C using a PSt macroinitiator ($\overline{M}_{n, GPC}$ = 5700), previously obtained with **1** and EBiB as described above for the St homopolymerization. Meanwhile, the chain extension for PMMA was conducted at 70 °C in MEK (50% v/v) with a PMMA macroinitiator ($\overline{M}_{n, GPC}$ = 5500) obtained under the conditions used for the MMA homopolymerization. The procedure was as follow: **1** (57.9 mg, 21.8 mM) and PSt macroinitiator (0.498 g, 21.8 mM) were placed in a 25 mL Schlenk tube equipped with magnetic stir bar and then St (2 mL, 4.35 M) and toluene (2 mL, 4.7 M) were added at room temperature. The mixture was degassed by freeze-pump-thaw cycle (3 times), and then immersed in an oil bath at 100 °C for 12 h.

Measurements

Monomer conversions in St, MMA and BA polymerizations were determined from the concentration of residual monomer 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 lmdf). An internal

standard, *n*-Decane (13.0 mM), was added in every polymerization. Conversions in polymerization of HEMA were determined gravimetrically.

The molecular weight and the molecular weight distributions of the polymers were determined by GPC. For the characterization of hydrophobic polymers, a Waters 2695 ALLIANCE Separation Module equipped with a RI Waters 2414 detector and 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) was used with THF eluent at 35 °C. PHEMA was analyzed by a Waters 717 plus Autosampler equipped with two Styrogel HR4E and HR5E columns (MW range 50 to 1×10^5 and 2×10^3 to 4×10^6 respectively) connected to a Waters 410 RI detector and a 10 mM solution of LiBr in DMF at 45 °C was used as eluent.

Results and Discussion

The catalytic activity of **1** was tested for radical polymerizations of three commercially important hydrophobic (St, MMA

and BA) and one hydrophilic (HEMA) monomers. All polymerizations were conducted in solution (monomer/solvent 50% v/v) with EBiB as initiator using different solvents, concentrations of ingredients and temperature conditions. In some cases $\text{Al}(\text{O}i\text{Pr})_3$, which is frequently used with Ru^{II} based catalysts,^[38,39] was added. The main data are presented in Table 1. As one can see from Table, **1** turned out to be very active in all polymerizations and high conversions were achieved in 6 hours for all monomers when the initial molar ratio of $[\text{Monomer}]_0/[\mathbf{1}]_0/[\text{EBiB}]_0 = 200/1/1$ was used. The radical mechanism of the process was verified applying the radical scavenger (2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO) methodology for hydrophobic and hydrophilic monomers.^[35–37] No polymerizations were observed when **1** and EBiB were added separately.

Levels of control were different for each monomer and depended on the polymerization conditions. Thus, St was polymerized fast and with good control at 100 °C in toluene. Kinetics for the St polymerizations using different initial compositions of the reaction mixture are shown

Table 1.

Polymerizations of St, MMA, BA and HEMA mediated by **1** with EBiB as initiator.

Monomer	$[\text{M}]_0:[\mathbf{1}]_0:[\text{EBiB}]_0$	Solvent (50% v/v)	Temperature (°C)	Time (hr)	Conv. (%)	$\bar{M}_{\text{theor}} \times 10^{-3}$	$\bar{M}_{\text{exp}} \times 10^{-3}$	PDI
St	200:1:1	Toluene	100	6	66	13.2	15.8	1.20
St	200:1:1*	Toluene	100	6	75	15.0	16.1	1.18
St	200:1:0.5	Toluene	100	6	38	15.0	14.9	1.29
St	200:0.5:1	Toluene	100	6	54	10.8	13.3	1.35
St	200:0.1:1	Toluene	100	6	42	8.4	8.7	1.38
St	200:1:1	Toluene	80	12	<5	–	–	–
St	200:1:1	MEK	70	8	<3	–	–	–
MMA	200:1:1	Toluene	100	6	81	16.2	12.8	1.83
MMA	200:1:1	Toluene	80	3	52	10.4	10.6	1.22
				6	68	13.6	14.8	1.21
MMA	200:1:0.5	Toluene	80	3	28	11.5	9.9	1.53
				6	36	14.4	13.2	1.30
MMA	200:0.1:1	Toluene	80	6	16	2.9	3.3	1.64
MMA	200:1:1	MEK	70	6	71	14.2	11.8	1.40
MMA	200:1:1	MEK	50	12	12	2.4	3.2	1.36
BA	200:1:1	Toluene	100	1	38	9.7	27.1	1.72
				2	81	24.0	31.7	1.61
BA	200:1:1	MEK	70	6	70	17.9	15.9	1.63
HEMA	200:1:1	MeOH	50	6	62	16.1	29.7	1.29
HEMA	200:0.5:1	MeOH	50	6	53	13.8	42.6	1.40
HEMA	200:1:2	MeOH	50	4	90	31.3	23.4	1.73

*With $\text{Al}(\text{O}i\text{Pr})_3$ in 1 eq. ratio to EBiB.

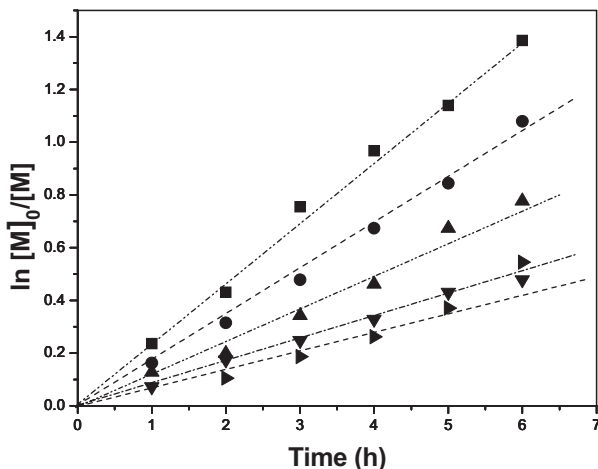


Figure 2.

Semilogarithmic plots for the EBiB initiated polymerization of St, mediated by **1** in the presence and absence of $\text{Al}(\text{O}i\text{Pr})_3$ and with different catalyst concentrations at 100°C in toluene (50% v/v); (■) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/1/1$; (●) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/1/0$; (▲) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/0.5/0$; (▼) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/0.1/0$; (►) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/0.5/1/0$.

in Figure 2. The plots of $\ln([\text{M}]_0/[\text{M}])$ as a function of the reaction time were linear for all compositions, indicating a constant radical concentration throughout the polymerization process. The polymerization proceeded with and without $\text{Al}(\text{O}i\text{Pr})_3$ almost with similar rate although it was slightly faster in the presence of the Al additive. Evolution of the molecular

weights with conversion together with an example of GPC traces are given in Figure 3. The GPC profiles were monomodal and shifted to higher values with conversion. The molecular weights of the PSt were very close to the calculated values and grew up linearly with conversion. Presence of the Al additive also slightly improved the control since the molecular

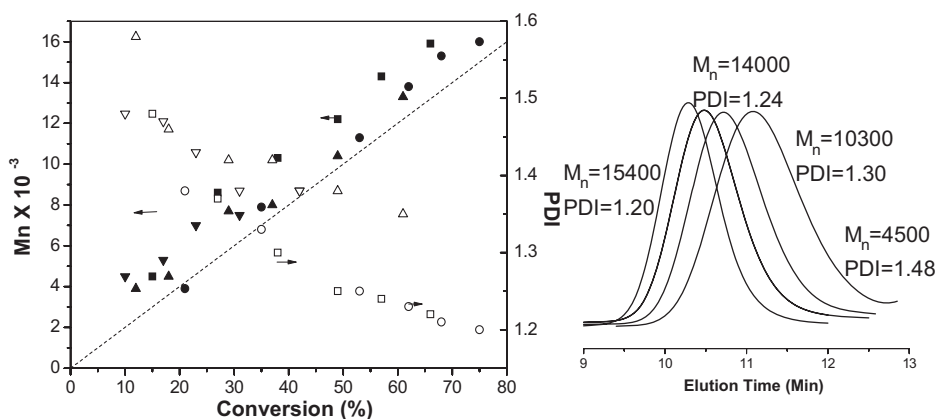


Figure 3.

Evolution of \bar{M}_n and PDIs with conversion for the EBiB initiated polymerization of St mediated by **1** in the presence and absence of $\text{Al}(\text{O}i\text{Pr})_3$ and with different catalyst concentrations at 100°C in toluene (50% v/v); (■) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/1/1$; (●) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/1/0$; (▲) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/0.5/0$; (▼) $[\text{M}]_0/[\text{EBiB}]_0/[\text{1}]_0/[\text{Al}]_0 = 200/1/0.1/0$; GPC chromatograms are shown for the (●) system.

weights were closer to their theoretical values and PDIs were narrower. Nevertheless, in general the catalytic activity of **1** was less affected by the additive than that of other Ru^{II} catalysts.^[38,39] As expected, the polymerization was much slower and the polymer of almost 2 times higher molecular weight was obtained at two-fold decrease in the concentration of EB*i*B (Figure 2 and 3). Considering the good catalytic performance for the complex **1** in the polymerization of St, we tried the reactions at lower concentrations of **1** (complex/initiator molar ratios of 0.5 and 0.1) in the absence of Al(O*i*Pr)₃. As it can be seen from the kinetic curves (Figure 2), a two-fold decrease in the catalyst concentration resulted in a slower polymerization, but the effect was modest, the polymerization conducted at reasonable rate, and the molecular weight characteristics were well controlled (Figure 3). Molecular weights were close to the calculated values and PDIs decrease with the conversion, but were broader than those obtained using a 1:1 complex/initiator ratio. The further decrease of the complex/initiator ratio to 0.1 reduce even more the rate, but 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 complex concentrations but still under 1.5. One of the main objectives in ATRP is the reduction of the catalyst concentration without a significant decrease in the polymerization rate and control. The lowest catalyst/initiator ratio of 0.01–0.005 in “living” polymerizations has been reached for Cu-catalysts.^[7] Ruthenium complexes have been reported so far to catalyze polymerizations with good control at reasonable rate at the lowest catalyst/initiator ratio = 0.1, but in the presence of amino-additive.^[40] The complex **1** therefore may be considered as one of the most active Ru-catalysts for ATRP of St. Decrease of the temperature to 80 °C resulted in very slow polymerization (Table 1).

Polymerizations of MMA and BA in toluene at 100 °C were very fast but poorly

controlled (see Table 1). The control in the MMA polymerization was significantly improved reducing the temperature to 80 °C, the molecular weights were close to the theoretical values and grew with conversion. PDIs were also relatively narrow. When a two-fold lower concentration of EB*i*B was used, the rate of the polymerization decreased as expected but the molecular weights remained similar to the calculated ones. The MMA polymerization proceeded at this temperature even at ten-fold decrease in the catalyst concentration to the **1**/initiator molar ratios of 0.1 but was very slow. Since complex **1** is ionic, its solubility in toluene was very limited and the completely homogeneous solutions in MMA or St/toluene mixtures were obtained starting from 80 °C. Further decrease of the temperature to 70 °C resulted in heterogeneous systems because of insoluble catalysts. Moreover, **1** was not completely soluble even at 80 °C in the BA/toluene mixture and therefore it was not possible to investigate influence of the temperature in the toluene polymerization of BA.

In order to improve the solubility, MEK was used and the polymerizations of MMA and BA were investigated in this solvent at 70 and 50 °C. St did not polymerize under these conditions. As can be seen from the Table 1, MMA polymerized practically with the same rate in MEK at 70 °C as in toluene at 80 °C, but resulted in more polydisperse PMMA. Kinetic plots of the polymerization of MMA and BA in semi-logarithmic coordinates in MEK at 70 °C using initial molar composition of $[MMA]_0/[I]_0/[EBiB]_0 = 200/1/1$ and evolution of the molecular weight characteristics with conversion are shown in Figure 4 and 5 correspondingly. Kinetic curve for the MMA polymerization in toluene at 80 °C was very similar to that in MEK at 70 °C, and for this reason it is not given here. The semilogarithmic plot of MMA concentration vs. time was not lineal, presenting some curvature which suggests that the radical concentration did not remain constant during the

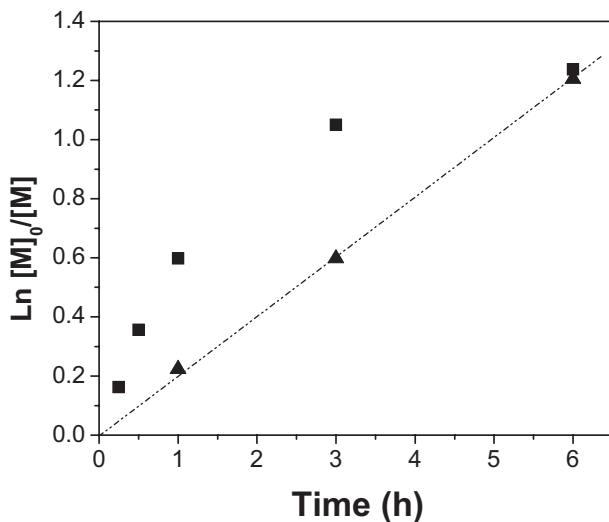


Figure 4.

Semilogarithmic kinetic plots for the polymerizations of MMA and BA, mediated by **1** using EBiB as initiator and at 70 °C in MEK (50% v/v); (■) $[MMA]_0/[EBiB]_0/[1]_0 = 200/1/1$; (▲) $[BA]_0/[EBiB]_0/[1]_0 = 200/1/1$.

polymerization probably because of a high percentage of the termination reactions. However, the polymer molecular weight increased with conversion and coincided reasonably well with the theoretical values. In contrast to the MMA polymerization, the kinetic dependence for the polymeriza-

tion of BA in MEK is well approximated by a straight line. The molecular weights of PBA also increased with conversion but PDIs remained broad although gradually narrowed in the course of the polymerization. Both monomers, MMA and BA, could be polymerized in MEK even at

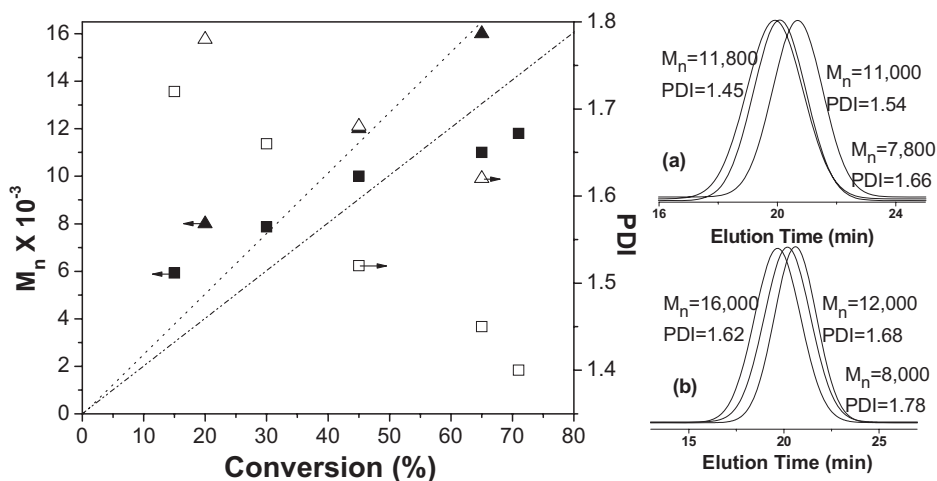


Figure 5.

Evolution of \bar{M}_n and PDIs with conversion for the polymerizations of MMA and BA mediated by **1** using EBiB as initiator at 70 °C in MEK (50% v/v); (■) $[MMA]_0/[EBiB]_0/[1]_0 = 200/1/1$; (▲) $[BA]_0/[EBiB]_0/[1]_0 = 200/1/1$; GPC chromatograms are shown for (a) $[MMA]_0/[EBiB]_0/[1]_0 = 200/1/1$ and (b) $[BA]_0/[EBiB]_0/[1]_0 = 200/1/1$.

50 °C but the reaction was very slow (see Table 1).

Complex **1** demonstrated high activity in the polymerization of hydrophilic HEMA in MeOH (Table 1). Polymerization was fast at 50 °C and afforded high molecular PHEMA of relatively narrow PDI using composition

of $[\text{HEMA}]_0/[\mathbf{1}]_0/[\text{EBiB}]_0 = 200/1/1$. Semi-logarithmic kinetic plots for HEMA polymerizations with different catalyst and initiator concentrations are depicted in Figure 6. The plots exhibit a linear tendency at $[\text{HEMA}]_0/[\mathbf{1}]_0 = 200/1$. Figure 7 shows the evolution of molecular weights during

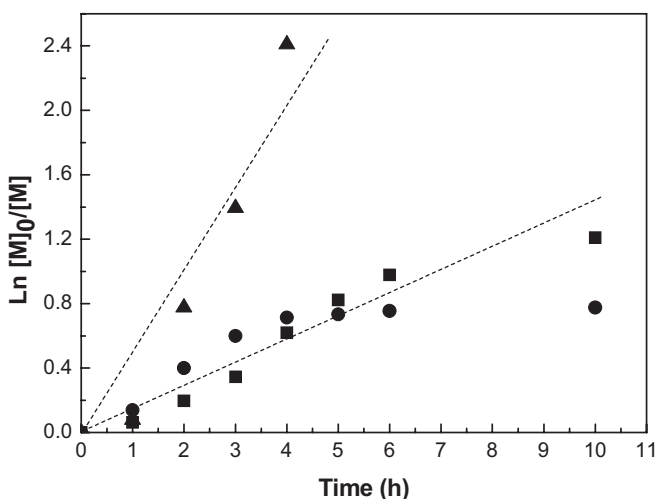


Figure 6.

Semilogarithmic plots for polymerization of HEMA, mediated by **1** using EBiB as initiator and with different catalyst/initiator ratios at 50 °C in MeOH (50% v/v); (■) $[\text{M}]_0/[\text{EBiB}]_0/[\mathbf{1}]_0 = 200/1/1$; (●) $[\text{M}]_0/[\text{EBiB}]_0/[\mathbf{1}]_0 = 200/1/0.5$; (▲) $[\text{M}]_0/[\text{EBiB}]_0/[\mathbf{1}]_0 = 200/2/1$.

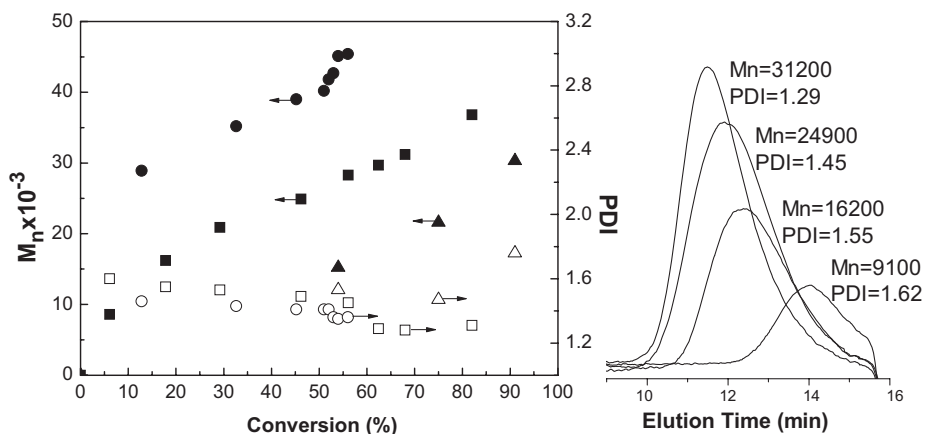


Figure 7.

Evolution of \bar{M}_n and PDIs with conversion for the polymerization of HEMA mediated by **1**, using EBiB as initiator and different catalyst/initiator ratios; at 50 °C in MeOH (50% v/v); (■) $[\text{M}]_0/[\text{EBiB}]_0/[\mathbf{1}]_0 = 200/1/1$; (▲) $[\text{M}]_0/[\text{EBiB}]_0/[\mathbf{1}]_0 = 200/1/0.5$; (●) $[\text{M}]_0/[\text{EBiB}]_0/[\mathbf{1}]_0 = 200/2/1$; GPC chromatograms are shown for the (■) system.

the polymerization. As can be seen from Figure 7, the molecular weights also grew with conversion at this concentration of the catalysts but were about 2 times higher than the calculated values principally because of difference in hydrodynamic volumes between PHEMA and PMMA standards used for GPC calibration. The polymerization accelerated significantly when a twofold increase in the initiator concentration was used resulting in 90% conversion in only 4 h. While a twofold decrease in the complex **1** concentration, barely affects the polymerization rate at the beginning, but after 4 h the polymerization slowed down drastically and stopped at about 50% conversion (Figure 6). Control was also worse in this case.

The “living” character was verified by chain extension experiments for St and MMA polymerizations conducted in toluene using the macroinitiator methodology (for details see Experimental). The previously synthesized PSt or PMMA of low molecular weights were then applied as initiators, instead of EBiB, in the second polymerizations of St or MMA respectively. In both cases, the second polymerizations developed smoothly and afforded the higher molecular weight polymers but were slower than those with EBiB. The GPC traces of the PSt and PMMA macro-

initiators and the corresponding chain-extended polymers are given in Figure 8. As can be seen from the figure both profiles of chain-extended polymer are unimodal and about 2 times increase in \overline{M}_n was observed. PDIs of chain-extended polymers were broader than those of the polymers obtained with low molecular weight initiator but in the case of PSt, practically all chains were extended since its chain-extended profile is symmetrical without any low molecular weight shoulder. Meanwhile, the PMMA-extended profile clearly shows a shoulder arising from the dead chain of the macroinitiator, although the majority of the chains were successfully extended. Percentage of chains extended in the second St and MMA polymerizations evaluated from the corresponding GPC curves gave approx. 90 and 72% respectively. Thus, the chain-extension experiments coincide well with the kinetic data for both polymerizations, where lineal dependence in semilogarithmic coordinates were noticed for St polymerization, while the kinetic plot for MMA polymerization showed curvilinear tendency because of higher portion of terminations. Chain-extension of PHEMA in MeOH have previously been reported, using a cyclometalated ruthenium complex similar to **1** (Cl^- instead of PF_6^-) as the catalyst.^[36]

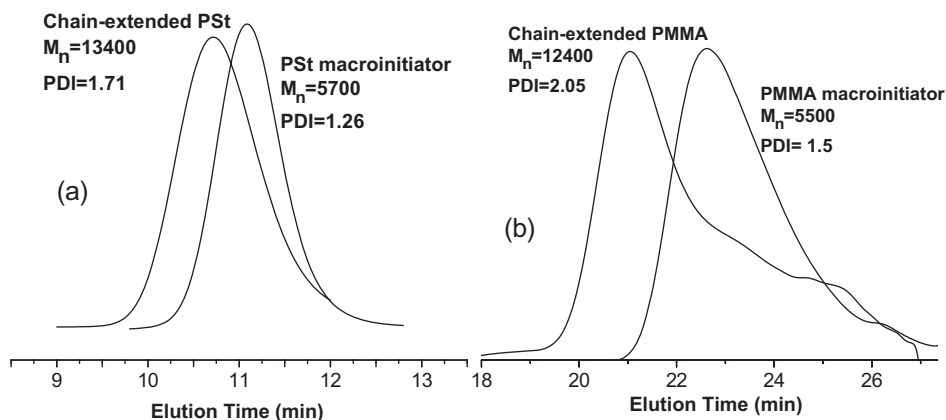


Figure 8.

GPC curves of macroinitiators and the corresponding chain-extended polymers for PSt (a) and for PMMA (b).

Conclusion

The same system based on Ru^{II} cyclo-metalated complex **1** and EBiB was used for ATRP of three typically hydrophobic and one hydrophilic monomer. In all cases, the polymerizations proceeded in a great extent by living fashion and were reasonably controlled. The best results were obtained for polymerization of St where the molecular weights increased in lineal proportion with conversion, and were very close to the calculated values, with narrow PDIs. The polymerization of MMA conducted at lower temperature was characterized by higher percentage of the dead chains in comparison with that of St. Kinetics for the polymerization of BA demonstrated lineal dependence in semilogarithmic coordinates and good coincidence of the experimental molecular weights with the calculated ones, but the polymer was quite polydisperse. Due to its ionic nature, **1** was soluble in protic media and therefore it was possible to apply the same system for ATRP of HEMA in MeOH. Such versatility of the reported catalytic system should be advantageous for the synthesis of different block-copolymers.

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