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Article

Comparative Study of the Catalytic Activity of the Complexes $Cp^*RuCl(PAr_3)_2$ [Ar = $-C_6H_5$ and 4-$CF_3-C_6H_4$] in the ATRP of Styrene

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A polimerização do estireno por ATRP foi conduzida usando os complexos $Cp^*RuCl(PPh_3)_2$, e $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$ como catalisadores, a fim de avaliar a influência das propriedades eletrônicas dos ligantes fosfinas na velocidade e controle da polimerização. Os dados cinéticos para polimerizações realizadas com $Cp^*RuCl(PPh_3)_2$, mostram que os pesos moleculares aumentam linearmente com a conversão, com uma eficiência média de iniciação, de 0,77. Os pesos moleculares obtidos no estudo cinético com $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$ também aumentam com a conversão, mas mostram um marcado desvio abaixo dos pesos moleculares teóricos. Este comportamento foi explicado pela oxidação gradual, irreversível do catalisador $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$, como confirmado pela espectroscopia de RMN de ^{31}P. O catalisador $Cp^*RuCl(PPh_3)_2$ promove a polimerização com uma velocidade maior do que usando $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$, o que é consistente com as melhores propriedades de doação de elétrons de PPh_3 *versus* $P(4\text{-}CF_3-C_6H_4)_3$. Estudos preliminares da polimerização do estireno com ATRP em CO_2 supercrítico mostram que somente o catalisador $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$, com ligantes fluorados, é ativo.

Styrene polymerization by ATRP was conducted independently using the complexes $Cp^*RuCl(PPh_3)_2$, and $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$ as catalysts, in order to evaluate the influence of the electronic properties of the phosphine ligands on the rate and control of the polymerization. The kinetic data for polymerizations carried out with $Cp^*RuCl(PPh_3)_2$, show that molecular weights increase linearly with conversion with an average initiation efficiency of 0.77. The molecular weights obtained in the kinetic study with $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$ also increase with conversion but show a marked deviation below the theoretical molecular weights. This behavior was explained by the gradual, irreversible, oxidation of catalyst $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$ as confirmed by ^{31}P-NMR spectroscopy. Catalyst $Cp^*RuCl(PPh_3)_2$ promotes the polymerization with a rate of polymerization higher than that obtained using $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$; this is consistent with the better electron donating properties of PPh_3 *versus* $P(4\text{-}CF_3-C_6H_4)_3$. Preliminary studies of styrene polymerization by ATRP in supercritical CO_2, shows that only catalyst $Cp^*RuCl[P(4\text{-}CF_3-C_6H_4)_3]_2$, with fluorinated ligands, was active.

Keywords: atom transfer radical polymerization (ATRP), half sandwich ruthenium catalysts, styrene polymerization, supercritical carbon dioxide

Introduction

Half sandwich organometallic complexes containing transition metal from group 8 (Fe[1,2] and Ru[3-10]) are an important group of catalysts in the polymerization of vinyl monomers by ATRP. The reversible, one electron oxidation-reduction that these complexes experience during controlled radical polymerization, promotes the establishment of a dynamic equilibrium between active and dormant species, with equilibrium constant K_{ATRP} (= k_{act}/k_{deact}) that principally depends on the catalyst structure.[11] The ancillary ligands frequently used in this kind of complexes are η^5-cyclopentadienyl (Cp), η^5-pentamethylcyclopentadienyl (Cp*), η^5-indenyl (ind) or η^6-arene. The other ligands that complete the coordination sphere in half sandwich complexes applied in ATRP are alkyl or aryl phosphines, some arsines, or a few π-donor ligands like ethylene and acrylonitrile,[3,12] and halogen atoms (typically Cl or Br). The catalytic properties of the complexes can be modulated by varying the basicity

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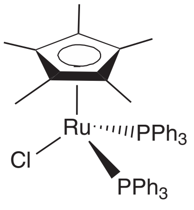
and steric volume of the phosphine ligands.[13] In this sense, in the present study we report the comparative catalytic activity of complexes **1** and **2** in the styrene polymerization by ATRP.



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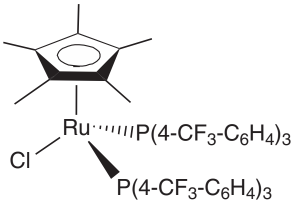


(**2**)

Experimental

Chemicals

Toluene was dried overnight over calcium chloride, filtered and distilled from sodium benzophenone ketyl and degassed by three evacuation/refill cycles under Ar before use. All reagents were purchased from Aldrich Co. Styrene was vacuum-distilled from calcium hydride before polymerization and used within three days of storage under N_2 at –15 °C. Ethyl 2-bromopropionate was used as received. The complexes $(Cp^*RuCl_2)_n$,[14] $[Cp^*RuCl]_4$[15] and $Cp^*RuCl(PPh_3)_2$ (**1**),[16] were synthesized according to literature procedures. The synthesis of $Cp^*RuCl[P(4\text{-}CF_3–C_6H_4)_3]_2$ (**2**) was previously reported starting from Cp*RuCl(COD).[17] Here, it was synthesized starting from $[Cp^*RuCl]_4$ as follows.

In a 100 mL round bottomed flask equipped with a Teflon stopcock, $[Cp^*RuCl]_4$ (202 mg, 0.186 mmol) and $P(4\text{-}CF_3–C_6H_4)_3$ (687 mg, 1.47 mmol, 8 equiv.) were suspended in dry THF (10 mL). The reaction was stirred at room temperature for 15 min, then the powder was filtered through a frit, and the solid washed with THF/pentane (3 × 5 mL). Drying under vacuum yielded the product as a yellow light powder (675 mg, 75% yield). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 7.2-7.8 (b, 24 H, Ar), 1.02 (s, 15H, Cp*), ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C) δ 142.6 (s broad, C*ipso*), 136.8 (s broad, C*ortho*), 133 (q, $^2J_{C\text{-}F}$ 33 Hz, C*para*), 126.1 (s broad, C*meta*), 125.7 (q, $^1J_{C\text{-}F}$ 272 Hz, CF_3), 92.9 (s, Cp*), 11.0 (s, Cp*); assignments of resonances to the $P(4\text{-}CF_3–C_6H_4)_3$ carbons were made with reference to published work.[18] ^{31}P NMR (121.6 MHz, CD_2Cl_2, 25 °C) δ 42.6 (s).

Preparation of active zinc dust. Zinc dust[19] (mesh = 325) was activated by washing with 1 mol L^{-1} sulfuric acid solution for 3-5 min, then successively with distilled water, ethyl alcohol and dry ether. The powder thus obtained was dried under vacuum line at room temperature for 5 h, and stored in a Schlenk tube under nitrogen atmosphere, in the freezer at –10 °C.

Characterization

Average molecular weights (M_n and M_w) and molecular weight distribution (MWD) of the polymers were measured using a Hewlett Packard 1100 size exclusion chromatograph (SEC) equipped with an in-line, vacuum degasser, an auto-sampler and with a differential refractive index as detector. The SEC equipment had three PLgel 5-10 µm columns (pore size 10^6, 10^5, 10^3; 300 × 7.5 mm) and one PLgel 10 µm guard column (50 × 7.5 mm) supplied by Polymer Laboratories. Tetrahydrofuran was used as eluent at 1.0 mL min^{-1} at 40 °C. Molecular weights were determined relative to polystyrene standards (1 × 10^6 - 400 Daltons). NMR spectra were recorded on a Jeol Eclipse 300^+ instrument operating at 7.05 T in $CDCl_3$ solvent at 25 °C, for ^1H at 300 MHz and referenced to internal $CHCl_3$; for ^{13}C at 75.4 MHz and referenced to internal $CDCl_3$; for ^{31}P at 121.4 MHz and referenced to external 85% H_3PO_4. For the analysis of end groups, 30 mg of sample were employed to collect the ^1H NMR spectra using about 64 scans.

Polymerizations

Styrene homo-polymerizations with **1** and **2** as catalysts: a 50 mL Schlenk tube was charged with 4.63 mL (40.2 mmol) of styrene and 1.35 mL of toluene, the tube was fitted with a rubber septum and degassed by three evacuation/refill cycles under argon. Next, 25.7 µL (0.198 mmol) of ethyl 2-bromopropionate (EtBrP) was added via syringe. Then, 1 mL samples of this solution were transferred via syringe into individual Schlenk tubes equipped with a Teflon stopcock, that were previously charged with 13.5 mg (17 µmol) of complex **1** or 20.5 mg (17 µmol) of complex **2**, and with 2 mg (30.6 µmol) of Zn dust, in the case of polymerizations conducted in presence of Zn. While maintained under an inert atmosphere, each tube was attached to the vacuum line, "freeze-pump-thaw" degassed once, and sealed under vacuum. The tubes were placed in an oil bath at 90 °C. At specific time intervals, the tubes were removed from the oil bath and cooled in ice water. Afterwards, the individual tubes were opened and about 1 mL of chloroform was added to dissolve the polymer. At this point, the corresponding conversion was determined by ^1H NMR spectroscopy. Afterwards, each polymer solution was precipitated into methanol (100 to 150 mL). The white product was filtered through a frit, washed with methanol and subsequently vacuum-dried overnight. The polymers were analyzed by ^{1}H NMR spectroscopy and SEC.

Polymerizations in carbon dioxide under supercritical conditions (scCO$_2$)

The polymerizations were conducted in a cylindrical steel cell of 25 mL volume at 22063.22 KPa as follows: the cylindrical cell was charged with 53 mg (42.5 µmol) of complex **2** or 34 mg (42.5 µmol) of complex **1** and a magnetic spinning bar under a flow of CO$_2$ gas. Separately, a solution of 4 mL (34.6 mmol) of styrene and 22 µL (0.169 mmol) of EtBrP were prepared in air, and 3 mL of this solution was injected via syringe into the cylindrical cell. Afterwards, 20684.3 KPa of pressure was applied through a mechanical/manual pump. Later, the cylindrical cell was heated to 90 °C using an external, electrically heated mantle, and a pressure of 22063.22 KPa was observed. At the end of reaction time, the reactor was cooled to room temperature and slowly depressurized until at atmospheric pressure, and the crude reaction mixture was dissolved in chloroform and the polymer precipitated in methanol. The yield was determined gravimetrically.

Results and Discussion

The kinetics of the polymerizations of styrene (St) with **1** or **2** as catalysts were conducted under the same conditions of concentration and temperature in order to compare the catalytic activity between two iso-structural and iso-electronic complexes. In Figure 1a, we compare the rate of polymerization (R$_p$) inferred from the values of k_p^{app}. The R$_p$ obtained with **1** was higher than that obtained with complex **2**. This result is in agreement with the better electron-donating properties of PPh$_3$ *versus* P(4-CF$_3$–C$_6$H$_4$)$_3$,[20,21] causing catalyst **1** to have higher electron density and to be more active than **2**. Also, from Figure1a, it is observed that the lines obtained by linear regression do not pass through the origin, suggesting the presence of a period of high rate promoted by a high concentration of activator (*i.e.*, catalysts in their lower oxidation state). After the first several hours, R$_p$ decreases and remains constant indicating a roughly constant radical concentration.

With regard to the controlled growth of the molecular weights, Figure 1b shows that M$_n$ values of the polymer produced using complex **1** grow linearly with monomer conversion and are close to the theoretical molecular weights ($M_{n(th)}$), with an average initiation efficiency of 0.77 ($f = M_{n(th)} / M_{n(SEC)}$). The initiation efficiency values are in agreement with a period of enhanced polymerization rates at the beginning of the polymerization (due to a high radical concentration) and the presence of radical termination to some extent. In ATRP, in the first hours of reaction, the deactivator concentration is too low (in our system an unknown Ru(III) species) in order to efficiently deactivate the initial propagating radicals,[22] so the resulting initiation efficiency is somewhat less than one.

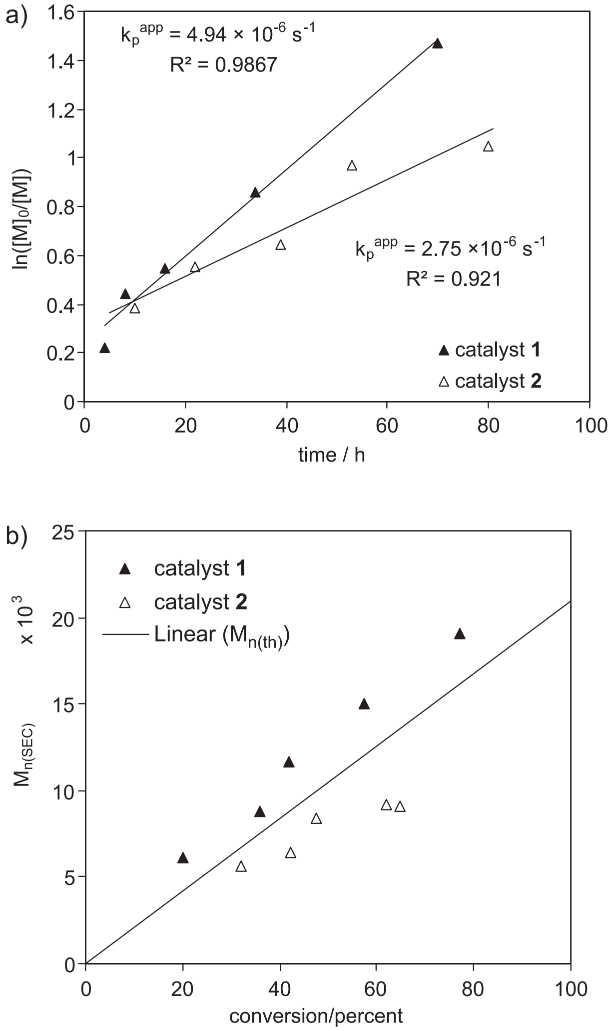


Figure 1. a) Semilogarithmic kinetic plot, and b) dependence of M$_n$ upon monomer conversion for ATRP of St at 90 °C in toluene with complexes **1** and **2** as catalysts. [St]$_0$ = 6.7 mol L^{-1}, [EtBrP]$_0$ = 33 mmol L^{-1}, [**1**]$_0$ = [**2**]$_0$ = 17 mmol L^{-1}.

The M$_n$ values obtained in the reaction with catalyst **2** (Figure 1b) also grew with conversion but only up to around 60% conversion and with some deviation below the $M_{n(th)}$ values.

This tendency can be explained by proposing that catalyst **2** undergoes a gradual and irreversible oxidation to the corresponding Ru(III) complex. In a separate polymerization conducted in an NMR tube, the styrene polymerization with **2** as catalyst was monitored by ^{31}P NMR spectroscopy in order to observe the catalyst evolution during the reaction. Figure 2 shows a series of NMR spectra arranged as a function of time of heating. The signal corresponding to complex **2** (at 42.4 ppm) gradually disappears generating as the only detectable products free phosphine (−5.6 ppm) and phosphine oxide (signal at 22.6 ppm), the latter present as contaminant from the beginning of the reaction.

Expansion of the region around 42 ppm in Figure 2 shows the presence of two very close signals. One of them corresponds to complex **2** (42.4 ppm), and the other one (42.2 ppm) was assigned to the complex Cp*RuBr[P(4-CF_3–C_6H_4)$_3$]$_2$ (**3**), formed by the halogen atom interchange between catalysts **2** and initiator (Et 2–BrP). As can be seen from the relative intensities, this interchange reaction occurs as soon as the mixture of reactants was prepared and is completed after 1 h of heating.

In a separate experiment conducted in an NMR tube with 10 equiv. of styrene, 1 equiv. of Et 2–BrP and 1 equiv. of complex **2**, we also confirmed the aforementioned halogen interchange reaction by ^{1}H NMR spectroscopy as we observed a mixture of the initiators Et 2–BrP and Et 2–ClP in 1/1.72 proportion, as indicated by integral values, at room temperature. After 1 h of heating at 90 ºC, the signals of both initiators disappear, giving rise to oligomeric chains.

The gradually decreasing intensity of the signal at 42.4 ppm assigned to complex **3** in Figure 2 is presumably due its conversion to give complex Cp*RuClBrP(4-CF_3–C_6H_4)$_3$ (**4**), (Scheme 1), or a related complex which is paramagnetic, and does not show a ^{31}P NMR signal in the spectral width −300 to 300 ppm. This side reaction, which involves loss of phosphine from the oxidized deactivator complex, perturbs the redox equilibrium needed for the ATRP process.

We were not able to isolate the Ru(III) complex **4**, nor detect it by ^{1}H NMR spectroscopy after the end of polymerization, due to the small amount of precursor catalyst **2** introduced in the NMR tube (5.9 mg, 4.95 μmol). However, the easy oxidation of **2** to give Cp*RuCl_2P(4-CF_3–C_6H_4)$_3$ (**5**) occurs when it is dissolved in CD_2Cl_2 for its NMR spectroscopic characterization. After 1 h at room temperature, the ^{1}H NMR spectrum shows a mixture of complexes **2** and **5**. The signals corresponding to complex **5** are broad and located over a large spectral width. For example, the ^{1}H NMR spectrum in CD_2Cl_2 at room temperature shows signals at δ 24.3 (br,15H), 14.4 (br, 2H), 9.6 (br, 3H) and 7.2 (br, 7H).

Recently, the use of Zn dust as a reducing agent in the ATRA (atom transfer radical addition) reaction of chloroform to styrene, to prevent the accumulation of the oxidized form of a ruthenium catalyst was reported.[23] The mechanism of the ATRA has many similarities with ATRP,[24] so in order to prevent the gradual, irreversible, oxidation of complex **2** during its action as catalyst we decided to investigate the polymerization of styrene in the presence of two equivalents of zinc with respect to catalyst **2**.

As shown in Figure 3, the kinetics of the polymerization of St with activated Zn and **2** as catalyst goes with practically the same rate of polymerization, inferred from

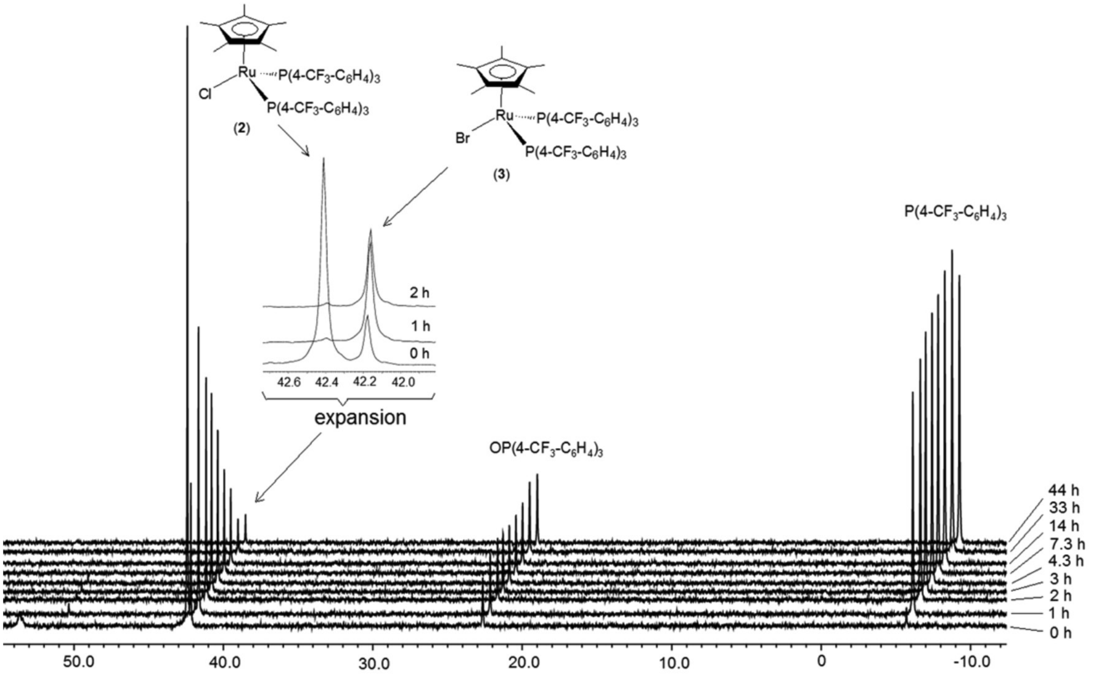
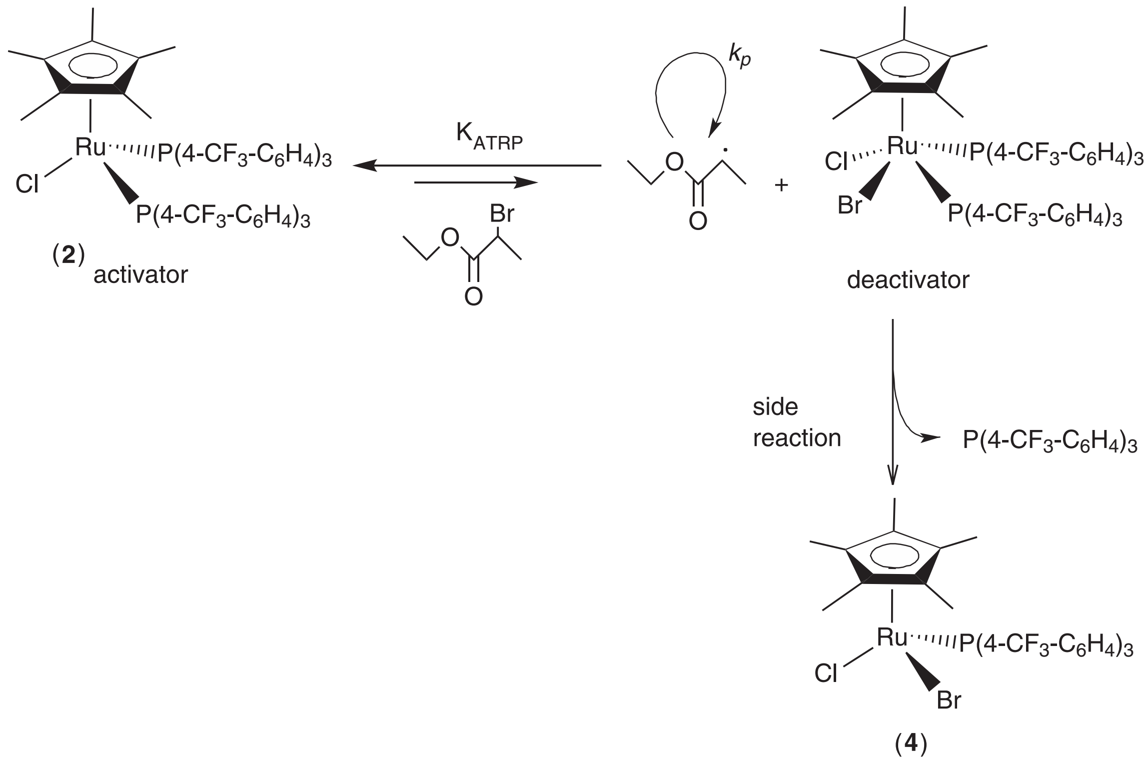


Figure 2. ^{31}P NMR spectra during ATRP of St at 90 °C in C_6D_6. The polymerization was conducted in an NMR tube sealed under vacuum. $[St]_0 = 3.3$ mol L^{-1}, $[EtBrP]_0 = 22.7$ mmol L^{-1}, $[\mathbf{2}]_0 = 8.97$ mmol L^{-1}. The first spectrum (0 h) was collected before heating.



Scheme 1. Proposed ruthenium species formed during the ATRP polymerization of styrene with complex **2** as catalyst.

the k_p^{app} values, suggesting that the reducing agent does not affect the radical concentration.

The effect of Zn on the control of M_n values is more effective, as can be seen in Figure 3b, M_n increases linearly with conversion and without the apparent chain transfer reaction that was present in the polymerization without zinc. Now, the initiation efficiency is around 0.77 and similar to that obtained with catalyst **1**, suggesting that catalyst oxidation in the presence of Zn occurs to a lesser extent.

The MWD obtained in polymerization reactions with **1** (Figure 4a) were narrow (PDI = 1.10 to 1.13) suggesting a fast interchange between active and dormant species. The PDI values (1.14 to 1.20) obtained in the kinetic studies with complex **2** were a little broader compared with those obtained using complex **1**, a likely consequence of the oxidation of catalyst **2** during polymerization (Figure 4b). The MWD obtained in the presence of zinc (Figure 4c) showed PDI values (1.16 to 1.20) similar to those obtained using complex **2** without zinc, suggesting that zinc has only a modest, if any, effect on the rate of interchange between Ru(II) and Ru(III) species.

Styrene polymerization in $scCO_2$ with complexes 1 and 2 as catalysts

Preliminary experiments of styrene polymerization in carbon dioxide under supercritical conditions ($scCO_2$) were conducted in order to evaluate the solubility and catalytic activity of complex **2** under these conditions. $scCO_2$ offers many advantages as a solvent for radical polymerization due to its effective function as inert medium (low dielectric constant and small transfer constant to solvent), low viscosity, and the possibility of controlling its solvent power.[25,26] However, conventional organic polymers (hydrophilic or hydrophobic) of medium to high molecular weight are insoluble in $scCO_2$,[27] with the exception of fluoropolymers, polysilicones and some poly(ether carbonates).[28] Under these circumstances it is desirable that reagents and products involved in reactions conducted under $scCO_2$, possess fluorine or silicon atoms in their structures in order to be soluble in the reaction medium. DeSimone and co-workers[25] reported the first work of ATRP polymerization under $scCO_2$ of fluorinated acrylate and methacrylate monomers, using a catalyst system based on Cu(I). They studied the effect of the perfluoroalkyl chain of the ligands and the alkoxide group of monomers on the conversion. Other studies of polymerization in $scCO_2$ have been reported using RAFT and SFRP methodologies.[26,29] In Table 1, we summarize the results obtained in three preliminary polymerizations in $scCO_2$.

As can be seen, only polymerizations carried out with catalyst **2** generate polystyrene, showing the important role of the fluorine atoms present in the $P(4-CF_3-C_6H_4)_3$ ligand of complex **2**. The PS was obtained in low yield and was

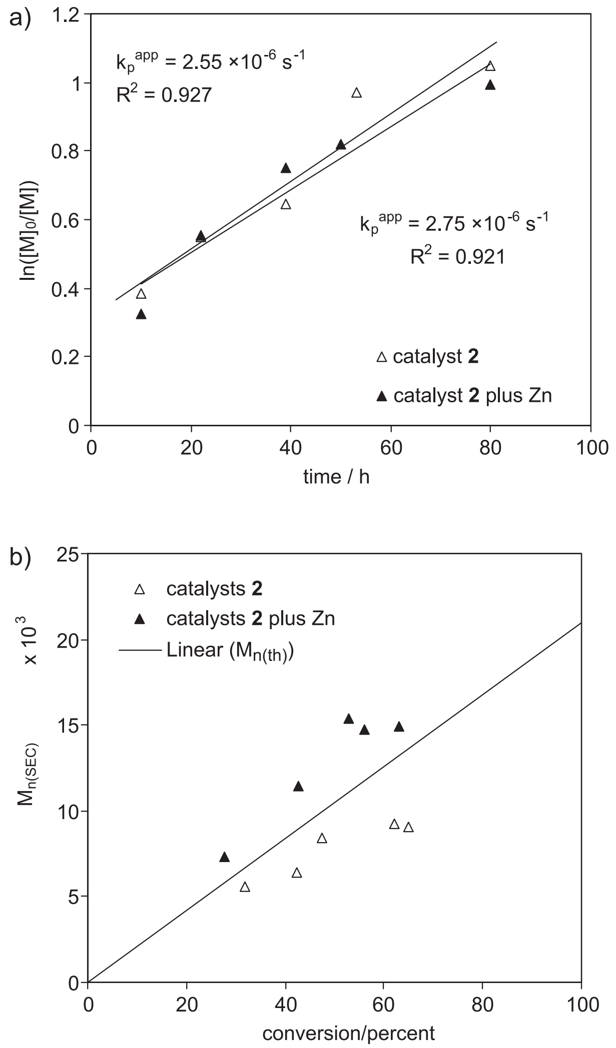


Figure 3. a) Semilogarithmic kinetic plot and b) dependence of M_n upon monomer conversion for ATRP of St at 90 °C in toluene, with complex **2** as catalyst, with and without Zn. $[St]_0 = 6.7$ (mol L^{-1}), $[EtBrP]_0 = 33$ (mmol L^{-1}), $[\mathbf{2}]_0 = 17$ (mmol L^{-1}), $[Zn]_0 = 170$ (mmol L^{-1}). (Since Zn is insoluble, properly the indicated concentration corresponds to the amount of Zn added to Schlenk).

of low molecular weight, basically due to the precipitation of PS in $scCO_2$ after which the polymeric chains cannot be activated for additional chain extension. Extending the reaction time to 48 h does not help to increase the conversion and or molecular weight.

The SEC trace of the PS obtained after 48 h of reaction is shown in Figure 5. The curve is bimodal with $M_n = 1500$ for the main peak (89% of total area), $M_n = 11600$ for the minor peak (11% area) and $M_n = 1650$ for overall curve, as shown in Table 1. The peak with $M_n = 11600$ represent dead polymeric chains that are presumably formed by bimolecular termination. Typically, premature termination reactions present in an ATRP process in organic solution, is around 8 to 10%[22] and our result is in accord with these findings. Moreover, an increase in termination in radical polymerizations when CO_2 is used as solvent has also been reported.[29]

The ^{1}H NMR spectroscopic analysis of PS obtained after 48 h of reaction showed signals characteristic of end groups: a broad signal centered at 4.4 ppm assigned to a proton alpha to Br in the –CH(Br) Ph end group, and another broad signal at 3.95 ppm, assigned to the methylene protons of the ethoxy group of the –CH(Me) CO_2Et end group. The degree of polymerization (DP_n) was calculated from the ratio of the integrals of the aromatic protons divided by five and the integrals of α-proton in the halogenated fragment. The DP_n is around 25 which gives an $M_{n(NMR)} = 2760$ which matches more or less with the M_n obtained by SEC. The percent of functionalization found by ^{1}H NMR spectroscopy was 83%, and was computed from the integral ratio of the proton α- to bromine and the methylene protons of the ethoxy group divided by 2. The percent of functionalization indicated that termination occurred to the extent of about 17%, a value which is little higher than that found by SEC but is

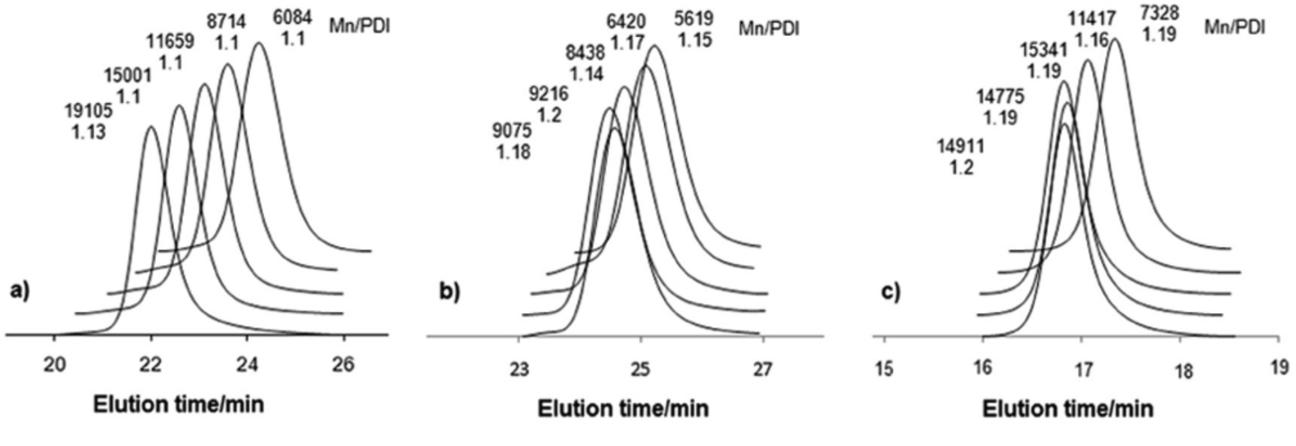


Figure 4. Evolution of the SEC traces for ATRP of styrene at 90 °C in toluene with; a) complex **1** as catalyst, b) complex **2** as catalyst and c) complex **2** as catalyst and Zn as reducing agent. $[St]_0 = 6.7$ (mol L^{-1}), $[EtBrP]_0 = 33$ (mmol L^{-1}), $[\mathbf{2}]_0 = 17$ (mmol L^{-1}), $[Zn]_0 = 170$ (mmol L^{-1}). The traces are normalized.

Table 1. Experimental conditions and characterization data for polymerization of Styrene by ATRP under $scCO_2$

Catalyst	Molar relation M/I/C[a]	time / h	Conv.[b] / (%)	$M_{n(NMR)}$[c]	$M_{n(SEC)}$[d]	PDI[d]
none	200/1/0	24	0	---	---	---
(**1**)	200/1/0.25	24	traces	---	---	---
(**2**)	200/1/0.25	24	3	2864	2298[e]	1.99
(**2**)	200/1/0.25	48	4	2760	1648[e]	1.96

Polymerizations were conducted in a cylindrical steel cell of 25 mL volume at 22063.22 KPa and 90 °C. [a]Molar ratio where M is styrene as monomer, I is ethyl-2-bromopropionate as initiator and C is catalyst. [b]Conversion, determined by gravimetry. [c]M_n determined by ^{1}H-NMR spectroscopy according to the equation $M_{n(NMR)} = [(I_{Ar}/5)/I_{H\alpha Br})]\times(104.15) + 181$, where I_{Ar} is the integral value of the aromatic peaks and $I_{H\alpha Br}$ is the integral value of the end group hydrogen, alpha to bromine, located as a broad signal at 4.5 ppm, and 104.15 and 181 are the molecular weights of styrene and ethyl-2-bromopropionate, respectively. [d]M_n determined by SEC using THF as eluent on the basis of a polystyrene calibration curve. [e]Observed as a bimodal curve.

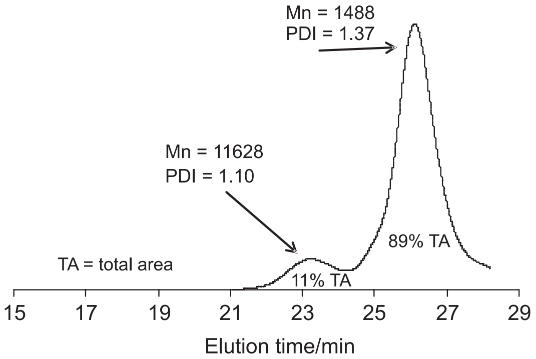


Figure 5. SEC trace of the polystyrene obtained in $scCO_2$ by ATRP after 48 h of reaction at 90 °C with complex **2** as catalyst.

in accord with reported data about enhanced termination reactions in $scCO_2$.[29]

The analysis of PS by IR spectroscopy obtained after 48 h of reaction also gives evidence of the end-functionalization of the chains by the initiator fragment; signals with medium intensity at 1731 and 1179 cm^{-1} were assigned to ν(C=O) and ν_{as}(O=C–OEt) of the ester group of the initiator. For comparison, the stretching signals of the pure ethyl 2-bromopropionate were observed at 1740 and 1168 cm^{-1}.

This analysis shows that PS obtained in $scCO_2$ follows the initiation and propagation mechanism by ATRP since the initiator fragments are present at the end of the polymeric chains.

Conclusions

We found that catalyst **1** was more active than catalyst **2** in the ATRP of styrene under the same polymerization conditions, as a consequence of the better electron-donating properties of PPh_3 compared to P(4-CF_3–C_6H_4)$_3$. In the case of polymerization conducted with complex **2**; this complex gradually suffers irreversible oxidation that results in a reduction in the control of the polymerization. Addition of Zn dust as reducing agent increases control over molecular weight however, it does not influence the rate of polymerization. The monitoring of the polymerization of styrene using catalyst **2** by ^{31}P NMR spectroscopy shows fast halogen interchange between initiator and complex **2**. After the polymerization is initiated, the gradual disappearance of catalyst **2** suggests an irreversible oxidation of the catalyst. The preliminary study of the styrene polymerization by ATRP with complexes **1** and **2** as catalysts in $scCO_2$ shows that this process is feasible but only with catalysts that have ligands with perfluoroalkyl groups. The flocculation of PS in the $scCO_2$ medium occurs when the polymeric chains have a DP_n around 30 and, in order to avoid it, additional experiments in the presence of an emulsifier should be conducted.

Supplementary Information

Figures S1-S5 is available free of charge at http://jbcs.sbq.org.br as a PDF file.

Acknowledgments

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References

1. Kamigaito, M.; Onishi, I.; Kimura, S.; Kotani, Y.; Sawamoto, M.; *Chem. Commun.* **2002**, 2694.
2. Kotani, Y.; Kamigaito, M.; Sawamoto, M.; *Macromolecules* **2000**, *33*, 3543.
3. Kamigaito, M.; Ando, T.; Sawamoto, M.; *Polym. Prepr.* **2002**, *43,* 3.
4. Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M.; *J. Am. Chem. Soc.* **2002**, *124*, 9994.
5. Delfosse, S.; Richel, A.; Simal, F.; Demonceau, A.; Noels Alfred, F.; Tutusaus, O.; Núñez, R.; Viñas, C.; Teixidor, F. In *Advances in Controlled/Living Radical Polymerization*, American Chemical Society: Columbus Ohio 2003, Vol. 854, pp. 116-129.

6. Simal, F.; Demonceau, A.; Noels, A. F.; *Angew. Chem., Int. Ed.* **1999**, *38*, 538.
7. Simal, F.; Sebille, S.; Hallet, L.; Demonceau, A.; Noels, A. F.; *Macromol. Symp.* **2000**, *161*, 73.
8. Delfosse, S.; Guillaume, B.; Richel, A.; Demonceau, A.; Noels, A. F.; Tutusaus, O.; Núñez, R.; Viñas, C.; Teixidor, F.; Baran, J.; *Polym. Prepr.* **2002**, *43,* 5.
9. Tutusaus, O.; Delfosse, S.; Simal, F.; Demonceau, A.; Noels, A. F.; Núñez, R.; Viñas, C.; Teixidor, F.; *Inorg. Chem. Commun.* **2002**, *5*, 941.
10. De Clercq, B.; Verpoort, F.; *Tetrahedron Lett.* **2002**, *43*, 4687.
11. Tang, H.; Arulsamy, N.; Radosz, M.; Shen, Y.; Tsarevsky, N. V.; Braunecker, W. A.; Tang, W.; Matyjaszewski, K.; *J. Am. Chem. Soc.* **2006**, *128*, 16277.
12. Saenz-Galindo, A.; Textle, H. M.; Jasso, A. R.; Torres-Lubián, J. R.; *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 676.
13. Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F.; *Tetrahedron Lett.* **2000**, *41*, 6071.
14. Oshima, N.; Suzuki, H.; Moro-Oka, Y.; *Chem. Lett.* **1984**, *13*, 1161.
15. Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D.; *Organometallics* **1990**, *9*, 1843.
16. Chinn, M. S.; Heinekey, D. M.; *J. Am. Chem. Soc.* **1990**, *112*, 5166.
17. Serron, S. A.; Luo, L.; Li, C.; Cucullu, M. E.; Stevens, E. D.; Nolan, S. P.; *Organometallics* **1995**, *14*, 5290.
18. Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; *Organometallics* **1986**, *5*, 956.
19. Yamamura, S.; Hirata, Y.; *J. Chem. Soc. C* **1968**, 2887.
20. Rahman, M. M.; Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P.; *Organometallics* **1989**, *8*, 1.
21. Fernandez, A. L.; Reyes, C.; Prock, A.; Giering, W. P.; *J. Chem. Soc., Perkin Trans. 2* **2000**, 1033.
22. Kwiatkowski, P.; Jurczak, J.; Pietrasik, J.; Jakubowski, W.; Mueller, L.; Matyjaszewski, K.; *Macromolecules* **2008**, *41*, 1067.
23. Thommes, K.; Içli, B.; Scopelliti, R.; Severin, K.; *Chem.--Eur. J.* **2007**, *13*, 6899.
24. Matyjaszewski, K.; Xia, J.; *Chem. Rev.* **2001**, *101*, 2921.
25. Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J.; *Macromolecules* **1999**, *32*, 4802.
26. Odell, P. G.; Hamer, G. K.; *Polym. Mater. Sci. Eng.* **1996**, *74*, 404.
27. Guan, Z.; DeSimone, J. M.; *Macromolecules* **1994**, *27*, 5527.
28. Sarbu, T.; Styranec, T.; Beckman, E. J.; *Nature* **2000**, *405*, 165.
29. Arita, T.; Beuermann, S.; Buback, M.; Vana, P.; *e-Polymers*, *3*, **2004**, 1; http://www.e-polymers.org accessed in November 2004.

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