

Cyclometalated 2-Phenylpyridine Complex [Ru^{II}(*o*-C₆H₄-py)(MeCN)₄]PF₆ as a Tunable Catalyst for Living Radical Polymerization

F. DIAZ CAMACHO,¹ R. LE LAGADEC,² ALEXANDER D. RYABOV,³ L. ALEXANDROVA¹

¹Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, México D.F., 04510

²Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, México D.F., 04510

³Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA, 15213

Received 3 September 2007; accepted 22 March 2008

DOI: 10.1002/pola.22774

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The cyclometalated complex [Ru^{II}(*o*-C₆H₄-py)(MeCN)₄]PF₆ (**1**) with a σ -Ru–C bond and four substitutionally labile acetonitrile ligands mediates radical polymerization of different vinyl monomers, viz. *n*-butyl acrylate, methyl methacrylate, and styrene, initiated by three alkyl bromides: ethyl 2-bromoisobutyrate, methyl 2-bromopropionate, and 1-phenylethyl bromide. The polymerization requires the presence of Al(O*i*Pr)₃ and occurs uncontrollably as a conventional radical process. The variation of the molar ratio of the components of the reaction mixture, such as initiator, Al(O*i*Pr)₃ and catalyst, affected the polymerization rates and the molecular weights but did not improve the control. A certain level of control has been achieved by adding 0.5 eq of SnCl₂ as a reducing agent. Tin(II) chloride decreased the rate of polymerization and simultaneously the molecular weights became conversion-dependent and the polydispersities were also narrowed. Remarkably, the level of control was radically improved in the presence of excess of the poorly soluble catalyst (**1**), when the added amount of (**1**) was not soluble any more, i.e., under heterogeneous conditions, the system became adjustable and the living polymerization of all three monomers was finally achieved. Possible mechanisms of the (**1**)-catalyzed polymerization are discussed.

© 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 4193–4204, 2008

Keywords: atom transfer radical polymerization (ATRP); living polymerization; metal-organic catalysts/organometallic catalysts

INTRODUCTION

Polymerization of methyl methacrylate (MMA) mediated by RuCl₂(PPh₃)₃ complex, the first example of metal-catalyzed living radical polymerization also called atom transfer radical poly-

merization (ATRP), was reported by the group of Sawamoto in 1995.¹ Since then highly efficient catalytic systems were developed to polymerize numerous monomers in a controllable fashion.^{2–11} The continual advance in ATRP over the last decade allows in nowadays the synthesis of new polymeric materials with complex and precisely defined architecture by the appropriate choice of the catalytic systems and the polymerization conditions.^{5,11–19} Variety of complexes of different transition metals has been successfully

Correspondence to: L. Alexandrova (E-mail: laz@servidor.unam.mx)

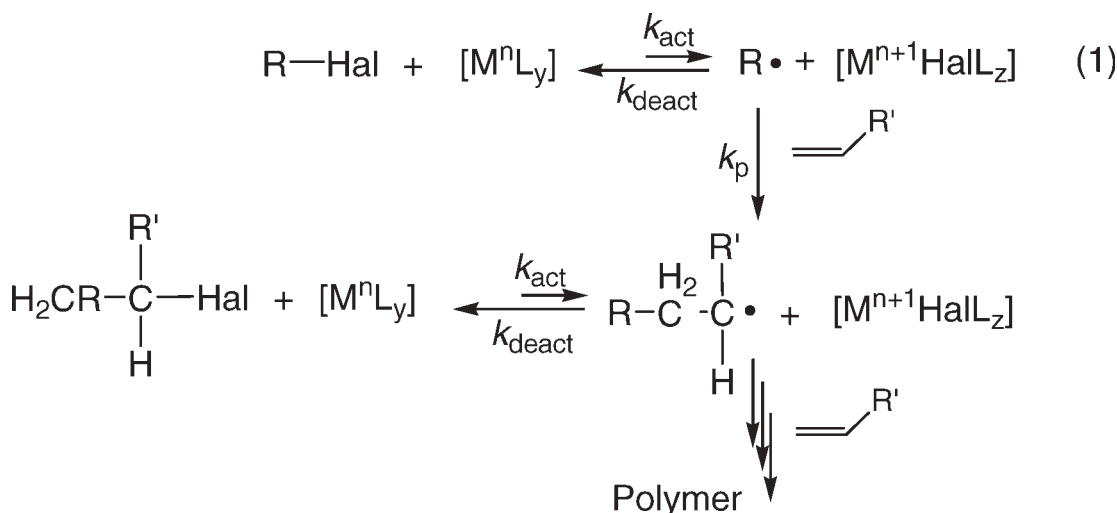
Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 46, 4193–4204 (2008)
© 2008 Wiley Periodicals, Inc.

applied as catalysts for ATRP,^{2–7,9,10,20–31} but copper complexes have found the widest application. According to the SciFinder Scholar, ~90% of all publications devoted to ATRP are the Cu-catalyzed polymerizations. This is because of relatively low cost of copper, easy synthesis of copper catalysts, and the fact that some copper complexes demonstrated high activity, actually the highest among all known catalysts.^{6,7} In addition, polymerization of various vinyl monomers is well controllable in the presence of the copper catalysts. Nevertheless some problems of ATRP are not yet resolved and a search for more active and universal catalysts for co- and polymerization is still very important—particularly for those monomers, which are still difficult to polymerize in a controllable manner and/or in aqueous media. The Ru(II) systems are less frequently employed as compared with those of Cu(I) and their potential is rudimentarily explored though the coordination chemistry of ruthenium(II) is exceptionally rich³² and vast variety of Ru(II)-based catalytic systems can be designed by a proper choice of the ligand environment.

There is no straightforward approach for designing metal catalysts for ATRP. A general consensus has been reached that the catalytic activity is related to the reduction potential of a complex.^{2,5,33,34} Complexes with lower reduction potentials are commonly more active due to easier one-electron interaction with an R–Hal initiator to form the R• radical together with a halide-bound metal species, which is by one oxidation equivalent above the initial state (Scheme 1).

There are severe limitations on the rate constants of activation (k_{act}) and deactivation (k_{deact}). Polymerization will occur in a controllable fashion, i.e., the molecular weight is a linear function of conversion and the polydispersity (PDI) is narrow, when the equilibrium is significantly shifted to the left, i.e., $k_{deact} \gg k_{act}$ with $K = k_{act}/k_{deact}$ in the range 10^{-4} to 10^{-9} as estimated for Cu-complexes.³⁵ If the deactivation is not fast enough and the equilibrium constant is larger, a catalyst is active but the control is poor and the process proceeds as a conventional radical polymerization. If the equilibrium constant is too low, the polymer chains grow controllably but the polymerization is very slow. Thus, a good ATRP catalyst should meet severe requirements; though its performance could additionally be improved by adding metal alkoxides (particularly for the Ru-catalyzed processes),^{2,36–38} amines,³⁹ amino alcohols,⁴⁰ zero-valent metals.^{2,41} The additives increase the rate and in some cases even improve the control. Matyjaszewski et al., suggested to enhance the control by adding deactivator,⁴² a complex of copper(II) with relatively high K , such as Me₆TREN/CuBr₂, that readily reacts with a growing radical chain and deactivates it to form a Cu(I) species, which reduces $[M^n + ^1HalL_y]$ and by that increases the overall effective rate constant k_{deact} (Scheme 1).

The basic principles described above for designing a catalyst for living radical polymerization of vinyl monomers are applied here for the cationic cyclometalated complex $[Ru^{II}(o-C_6H_4-py)(MeCN)_4]PF_6$ (**1**). Most of the ruthenium



Scheme 1. Generally accepted mechanism of ATRP; charges of complexes and the termination step are not shown for clarity.

complexes used so far for ATRP are either neutral or phosphine containing compounds.^{1–5,9–11,26,30} We have described in a series of studies, the highly effective synthesis of cationic ruthenacycles as well as preliminary results on the use of such complexes as catalysts for living radical polymerization.^{43–46} Cyclometalated complexes have not practically been used for ATRP, though cyclometalated compounds have certain advantages as catalysts for this kind of polymerization. We have found only one example of the catalysis by a cyclometalated nickel(II) complex of controlled polymerization of methacrylic monomers.⁴⁷ Stabilized by chelation, the metal-carbon bond makes complexes such as **(1)** robust, and, most importantly, reduces dramatically its reduction potential.^{43–45} In particular, a cyclometalated 2-phenylpyridine (phpy) ligand of charge -1 is structurally similar to neutral 2,2'-bipyridine (bpy) but a replacement of bpy by phpy in the coordination sphere of ruthenium reduces the reduction potential by ~ 0.7 to 0.8 V per single substitution.^{44,45} The cationic nature of **(1)** could also significantly improve the catalytic properties of the complex as it has been observed for other ruthenium compounds,^{48–50} which catalytic activity increased in atom transfer radical addition reactions as well as in ATRP when the cationic form of the same complex was used instead of the neutral species. The cationic complexes have also demonstrated better behavior in aqueous system than their neutral analogues.^{48,49} Another important advantage of cycloruthenated 2-phenylpyridine complexes with coordinated acetonitriles is an easy exchange of MeCN, photochemically or thermally, by various ligands. If the ligands are more electron donating than MeCN, the substitution results even in more reducing compounds.⁵¹ Third, the coordinative position *trans* to the ruthenium-carbon bond is strongly activated due to the ground state *trans* influence of the phenyl carbon donor. Therefore, this site seems to be perfectly designed for the activation step driven by k_{act} (Scheme 1). Compound **(1)**, which was described and extensively characterized previously,⁵² has four MeCN ligands. Thus, the range, within which the reduction potential can be varied by substitution, is essentially unlimited. This creates a whole spectrum of options for designing and improving the catalyst performance. Herein we investigated the influence of additives such as aluminum isopropoxide, Al(O*i*Pr)₃, and reducing tin(II) chloride on catalytic performance of **(1)**. It will be shown how by a proper adjustment of the

reaction mixture the **(1)**-mediated polymerizations switch from a typically radical to the living radical polymerizations of MMA, *n*-butyl acrylate (BA) and styrene (St).

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich Chem. Co. except RuCl₃·*n*H₂O, which was a Strem reagent. The monomers, MMA, BA, and St, were dried over magnesium sulfate, distilled under reduced pressure and kept under argon. Other reagents and solvents were used as received. Synthesis, characterizations, and X-ray structural characterization of **(1)** was described elsewhere.⁵² The freshly prepared complex has a lemon-yellow color, it is not very stable in the air and gradually turns yellowish green and then dark green. To minimize undesirable side effects the complex was synthesized prior to every polymerization procedure.

Polymerization Procedures

All operations were carried out under a nitrogen atmosphere. In a typical polymerization **(1)** and Al(O*i*Pr)₃ were added to a round bottom flask and degassed by vacuum/nitrogen cycles (three times). Then the monomer was introduced via a syringe into the flask and degassed by three freeze-pump-thaw cycles. The resulting solution was stirred for a half an hour at 40 °C until a yellow homogeneous solution was obtained. Finally, the initiator was added to the mixture and the flask was immediately immersed in an oil bath previously heated to the desired temperature. The polymerizations were conducted at 80 °C for MMA and BA and 100 °C for St. The samples were removed from the flask after certain time intervals using degassed syringes. The polymerization was stopped when the reaction mixture became very viscous. Samples for GPC measurements were dissolved in THF, the solution was passed through Florisil 60–100 Mesh column and concentrated by rotary evaporation.

Analysis

The conversions were determined gravimetrically and from the concentration of residual monomer by gas chromatography (GS) with *n*-decane as an internal standard, using a

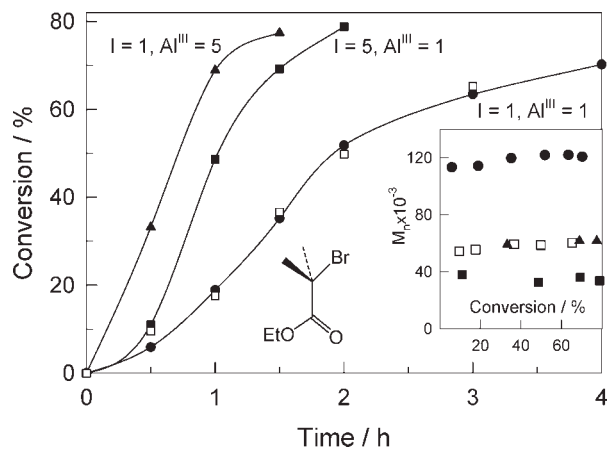


Figure 1. Effect of concentration of each component on kinetic and molecular weights in the EBiB initiated polymerization of MMA at 80 °C; (●)—the basic composition ratio of $[M]_0/[I]_0/[1]_0/[Al]_0 = 200/1/1/1$ or 9.35 M/47 mM/47 mM/47 mM (■)—5-fold increase in the initiator concentration, $[M]_0/[I]_0/[1]_0/[Al]_0 = 200/5/1/1$ or 9.35 M/234 mM/47 mM/47 mM; (▲)—4-fold increase in the $Al(OiPr)_3$ concentration, $[M]_0/[I]_0/[1]_0/[Al]_0 = 200/1/1/4$ or 9.35 M/47 mM/47 mM/188 mM; (□)—2.5-fold increase in the Ru(II) concentration, $[M]_0/[I]_0/[1]_0/[Al]_0 = 200/1/2.5/1$ or 9.35 M/47 mM/117 mM/47 mM.

Shimadzu GC-2010 gas chromatograph equipped with a Restek 30 m stabilwax column. Analysis conditions: injector temperature, 220 °C; detector temperature, 220 °C; temperature program, 4 min 40 °C, 15 °C/min until 220 °C, 2 min 220 °C. Additionally consumption of the initiator was verified by GS-MS using gas-chromatograph HP, Model 5890 series B connected with mass-spectrometer Joel JMS-AX505HA. 1H NMR spectra were recorded using a Bruker Avance 400 spectrometer. The molecular weights and molecular weight distribution of the polymers were analyzed by GPC (Waters 2695 ALLIANCE Separation Module) equipped with two HSP gel HR MB-L (molecular weight range from 5×10^2 to 7×10^5 and MB-B from 10^3 to 4×10^6) columns in series and a RI Waters 2414 detector. THF was used as the eluent at 35 °C with a flow rate of 0.5 mL/min. Linear polystyrene and poly(methyl methacrylate) standards were utilized for the GPC calibrations. Theoretical molecular weights were calculated without taking into account the end groups according to the following equation: $M_{n,th} = ([Monomer]_0/[Initiator]_0) \times Conversion \times MW_{monomer}$, where $0 \leq Conversion \leq 1$.

RESULTS AND DISCUSSION

General Observations

The (1) catalyst did promote polymerizations of three different monomers, MMA, BA, and St in the presence of $Al(OiPr)_3$. Not even a trace of polymer was detected without the aluminum additive after heating for 24 h. A radical mechanism of the process was verified applying the radical scavenger (2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO) methodology. Details of the reactions have been reported elsewhere.⁴⁶ The standard molar composition of the reaction mixture $[M]_0/[I]_0/[1]_0/[Al]_0$ used in this study equals 200/1/1/1. Here M, I, (1), and Al stand for monomer, initiator, catalyst, and $Al(OiPr)_3$, respectively. Under these conditions the polymerization occurs fast and uncontrollably as a conventional free radical process. The molecular weights were high from the beginning, much higher than the calculated values, and did not depend on conversion. The PDIs were also broad, viz. 1.6–1.8 for MMA and St, and ~ 2.2 for BA (Figs. 1 and 2, Tables 1–3). Such a behavior is likely due to the fact that rapidly established equilibrium 1 in Scheme 1 is not

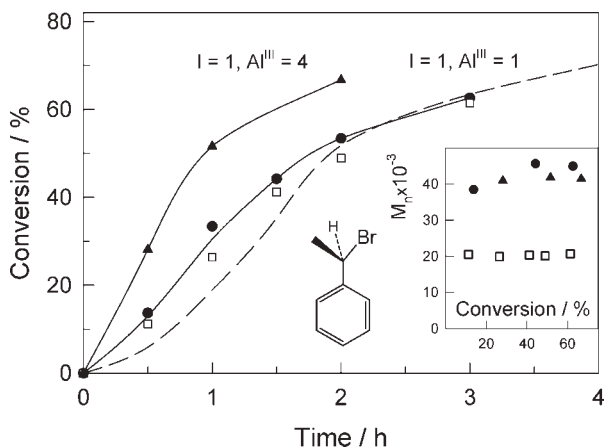


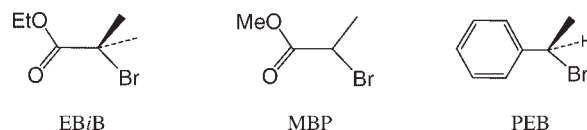
Figure 2. Effect of the concentration of the catalysts and $Al(OiPr)_3$ on the conversion and molecular weights in the PEB initiated polymerization of MMA at 80 °C. (●)—the basic composition ratio $[M]_0/[I]_0/[1]_0/[Al]_0 = 200/1/1/1$ or 9.35 M/47 mM/47 mM/47 mM; (▲)—4-fold increase in the $Al(OiPr)_3$ concentration, $[M]_0/[I]_0/[1]_0/[Al]_0 = 200/1/1/4$ or 9.35 M/47 mM/47 mM/188 mM; (□)—2.5-fold increase in the Ru(II) concentration ($[M]_0/[I]_0/[1]_0/[Al]_0 = 200/1/2.5/1$ or 9.35 M/47 mM/117 mM/47 mM). Kinetic of the EBiB initiated polymerization at the 200/1/1/1 basic component ratio is shown by dash line for comparison.

Table 1. Polymerization of Methyl Methacrylate Promoted by **1** at 80 °C and Various Compositions of the Reaction Mixture

| Initial Compositions and Molar Ratios | Time (h) | Conv. (%) | $M_{n,th} \times 10^{-3}$ (g mol ⁻¹) | $M_{n,ex} \times 10^{-3}$ (g mol ⁻¹) | PDI |
|--|----------|-----------|--|--|------|
| MMA/PEB/(1)/Al/Sn 200/1/1/0 | 0.5 | 10.5 | 2.1 | 38.4 | 1.62 |
| | 1.5 | 44.2 | 8.9 | 45.6 | 1.53 |
| 200/1/2.5/1/0 | 0.5 | 11.2 | 2.3 | 20.5 | 1.52 |
| | 1.5 | 41.3 | 8.3 | 20.3 | 1.54 |
| 200/1/1/4/0 | 0.5 | 28.1 | 5.6 | 40.9 | 1.68 |
| | 1.0 | 51.6 | 10.3 | 41.4 | 1.60 |
| 200/1/1/1/0.5 | 1.0 | 4.2 | 0.8 | 16.8 | 1.30 |
| | 4.5 | 21.6 | 4.3 | 28.9 | 1.19 |
| 200/1/1/4/0.5 | 1.0 | 16.7 | 3.3 | 38.1 | 1.62 |
| | 3.0 | 64.4 | 12.9 | 37.6 | 1.64 |
| 200/1/2/1/0.5 | 1.0 | 3.5 | 0.7 | 1.4 | 1.28 |
| | 4.0 | 22.0 | 4.4 | 5.0 | 1.20 |

sufficiently shifted to the left, i.e., the crucial condition $k_{deact} \gg k_{act}$ does not hold. Significant amount of Ru(III) species was formed within first 5 min suggested by an observation of a color change from yellow due to (**1**) to dark green typical of less stable oxidized ruthenium species which slowly turn into a black precipitate.⁴³ It is worth noting that (**1**) behaves similar in chlorinated solvents such as chloroform and dichloroethane at 25 °C. The yellow homogeneous solution becomes dark green and a black powder starts to precipitate after several hours. A mechanism of the both processes is presumably similar, i.e. (**1**) reacts with a C-Hal bond via eq 1 to afford a labile oxidized Ru(III) intermediate, which is particularly unstable under the polymerization conditions.

Three commonly accepted initiators were used in the study: ethyl 2-bromoisobutyrate (EBiB), methyl 2-bromopropionate (MBP), or 1-phenylethyl bromide (PEB).



The polymerizations proceeded similarly with all of them in an uncontrollable regime. However the molecular weights of polyMMA obtained using EBiB was about 3 times higher than those using PEB as an initiator (cf. Insets to Figs. 1 and 2). Since the reaction conditions were the same, such a big difference in the molecular weights should be due to a lower efficiency of the EBiB initiator compared with the PEB. This was confirmed by the GC-MS analysis. Less than 20% of EBiB was consumed within first 15 min of the reaction and its amount did not change during next 3 h. In contrast, PEB was consumed completely in a matter of 15 min. The corresponding kinetic curves

Table 2. Polymerization of Styrene Promoted by **1** at 100 °C and Various Compositions of the Reaction Mixture

| Initial Compositions and Molar Ratios | Time (h) | Conv. (%) | $M_{n,th} \times 10^{-3}$ (g mol ⁻¹) | $M_{n,ex} \times 10^{-3}$ (g mol ⁻¹) | PDI |
|--|----------|-----------|--|--|------|
| St/PEB/(1)/Al/Sn 200/1/1/1/0 | 0.5 | 13.6 | 2.8 | 27.7 | 1.71 |
| | 3.0 | 60.4 | 12.6 | 29.3 | 1.67 |
| 200/1/1/1/0.5 | 1.0 | 6.3 | 1.4 | 4.8 | 1.31 |
| | 4.0 | 12.2 | 2.5 | 15.4 | 1.18 |
| 200/1/2/1/0.5 | 1.0 | 4.6 | 0.9 | – | – |
| | 4.0 | 11.0 | 2.3 | 2.8 | 1.25 |

Table 3. Polymerization of *n*-Butyl Acrylate Promoted by **1** at 80 °C and Various Compositions of the Reaction Mixture

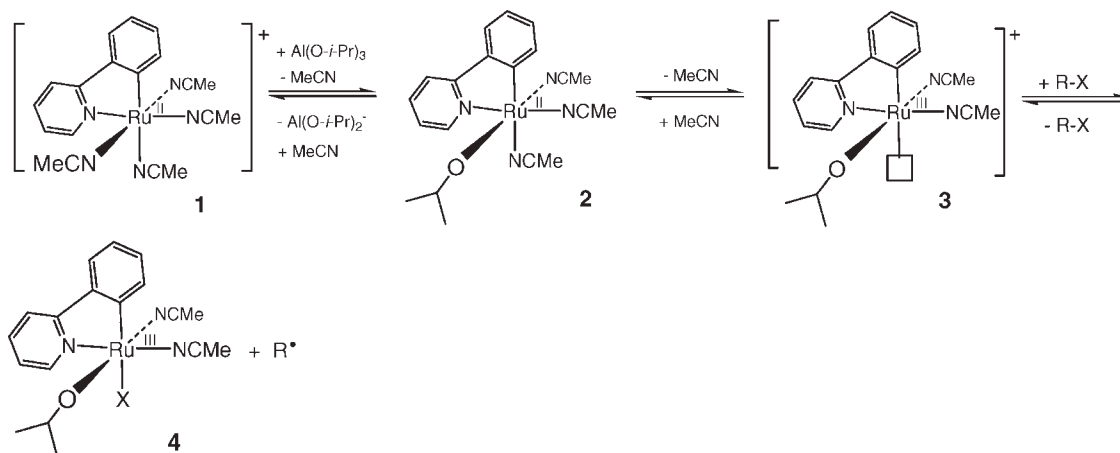
| Initial Compositions and Molar Ratios | Time (h) | Conv. (%) | $M_{n,th} \times 10^{-3}$ (g mol ⁻¹) | $M_{n,ex} \times 10^{-3}$ (g mol ⁻¹) | PDI |
|--|----------|-----------|--|--|------|
| BA/MBP/(1)/Al/Sn 200/1/1/0 | 0.5 | 13.7 | 3.5 | 66.6 | 2.37 |
| | 2.0 | 75.8 | 19.6 | 67.9 | 2.19 |
| 200/1/1/0.5 | 1.0 | 9.6 | 2.5 | 23.2 | 1.31 |
| | 4.0 | 48.3 | 12.5 | 52.4 | 1.22 |
| BA/PEB/(1)/Al/Sn 200/1/2/1/0.5 | 1.0 | 9.8 | 2.6 | 3.7 | 1.38 |
| | 3.0 | 45.6 | 11.8 | 12.8 | 1.31 |

of the polymerizations are also different particularly at early stages of the polymerizations (solid and dash lines in Fig. 2). The curve for EB*i*B is *S*-shaped presumably due to a slow initiation. The PEB-initiated polymerization is faster at the beginning and the curve is not *S*-shaped. In spite of the structural resemblance of the dormant species, the main rule in the choice of the initiator in ATRP, EB*i*B was referred by several authors as poor initiator for MMA polymerization mediated by RuCl₂(PPh)₃ as well as by highly active Cu-catalysts.^{53–55} The lack of efficiency was explained by slow initiation due to back strain effect. However, in the both cases the polymerizations occurred rather controllably. Meanwhile in our systems, where the polymerization proceeds rather by a conventional radical mechanism, the difference in the molecular weights initiated by EB*i*B and PEB is too big to be explained by steric effects. Therefore, we assume that for the complex (**1**) used here the efficiency of the initiation is determined by the interaction between the alkyl halide and the complex and thus the much lower efficiency of EB*i*B could be due to the poor efficiency of the bromine abstraction. It may be because of better precoordination of the Ru(II) complex with PEB since both phenyl and ester substituents contribute equally to stabilize the generated secondary radicals.³⁵

Influence of the Composition Components

The polymerization of MMA was investigated under different concentrations of (**1**), initiator (EB*i*B and PEB), and Al(O*i*Pr)₃ (Figs. 1 and 2; Table 1). As expected, a 5-fold increase in the EB*i*B concentration accelerated the polymerization and lowered the molecular weight (Fig. 1)

but the *S*-shaped kinetic curve and the lack of control were still observed. The molecular weights dropped from ~120,000 to < 40,000, but the difference between the calculated and measured molecular weights stays about the same. Similarly, an increase in Al(O*i*Pr)₃ concentration in the EB*i*B initiated system increased the rate even more (Fig. 1), practically eliminated the *S*-character and caused an decrease in the molecular weights by a factor of two. These facts indicate a faster and more efficient initiation. The chromatographic data showed that the consumption of EB*i*B was drastically improved by the presence of 4-fold excess Al(O*i*Pr)₃, the initiator was completely consumed within 15 min. The rate of PEB-initiated polymerization also increased when the concentration of Al(O*i*Pr)₃ was raised (Fig. 2) but it had little effect on the molecular weights as they remained of the same order as those obtained under the standard 200/1/1/1 molar ratio (Inset to Fig. 2). Such a difference between the two initiating systems may be explained in terms of the initiators consumption. However, an increase in Al(O*i*Pr)₃ content did not improve the control in any of the cases. The color change during the polymerization was exactly the same as observed for the 200/1/1/1 systems. The Al(O*i*Pr)₃ additive accelerated the polymerizations catalyzed by Ru, Ni, Fe, Os, Re, and Cu complexes^{2,56,57} through either activating the C-Hal bond of the initiator or by interacting with the catalyst. In some cases the acceleration was even accompanied by an improvement of the controllability of the polymerizations.³⁶ Recent studies suggest the interaction of Al(O*i*Pr)₃ with the oxidized metal complex somehow stabilizes the complex in its high oxidation state and thus shifts the equilibrium to the active radical side.^{56,58} However this does



Scheme 2. Postulated plausible transformations of complex (1) related to step 1 in Scheme 1.

not explain the fact that polymerization does not proceed in the absence of the aluminum additive as in our systems. Meanwhile interaction mechanism between Al(O*i*Pr)₃ and the original Ru(II) complex, which we propose below, provides a better explanation. Since the polymerization does not occur without Al(O*i*Pr)₃, complex (1) does not react with any of the initiators. The reduction potential of (1) in MeOH equals 0.50 V (0.1 M KPF₆, versus Ag/AgCl) and such might be too high for reaction 1 in Scheme 1. Replacement of MeCN in the coordination sphere of (1) to form, for example, a complex such as (2) (Scheme 2) should decrease the reduction potential and thus increase the driving force for reaction 1. As a result, the activation of the C-Hal bond becomes feasible accounting for a faster consumption of EB*i*B at higher concentrations of Al(O*i*Pr)₃. The fact that the control was not improved suggested that equilibrium 1 is still insufficiently shifted to the left. The concentration of plausible intermediate (4) was still too high and needs to be minimized.

Changes in the concentration of (1) revealed remarkable effects. It should be mentioned first that it could not be decreased much because the polymerization became too slow. Its increase is also limited by the solubility in all the monomers used. At a monomer-to-catalyst ratio of 200/1 the complex is completely soluble only at 80 °C and above. The solubility is incomplete at [M]₀/[(1)]₀ = 200/1.5 and the system is heterogeneous even at elevated temperatures. Therefore, it was surprising to see that a 2.5-fold increase in the catalyst concentration resulted in a drop of the molecular weight in the both EB*i*B and

PEB systems, the polymerization rate being practically unchanged (Figs. 1 and 2). The level of control was again poor. The molecular weights decreased by 2-fold (Insets to Figs. 1 and 2) but they did not depend on the conversion. The color of the heterogeneous reaction mixtures does not convert into dark green as in the case of homogeneous systems. Instead they maintain the light brown color during all the process and the intact (1) remained in a solid phase after running the polymerization for 3 h. These observations are difficult to rationalize keeping in mind that the system is heterogeneous, the catalyst concentration remains constant, and the degradation of (1) is substantially less. The concentration of (1) diminishes with time in the homogeneous system because of the fast degradation of the oxidized complex but is approximately constant under heterogeneous conditions. This leads to a more efficient interaction between (1) and the halogenated terminals during all the polymerization and that in its turn is responsible for decrease in the molecular weights. It is difficult to explain why it does not accelerate the polymerization. We speculate that the ruthenium oxidized species are also stabilized in some way and the equilibrium in Scheme 1 is being shifted more to the dormant species compared with the homogeneous system. All of the above can result in a decrease in molecular weights without the rate acceleration, but the control over the molecular weights is still very poor. To this end, variation of the molar ratio of the components of the reaction mixture affects the polymerization rate and the molecular weights but suitable controllable conditions have not been found.

Effect of Reducing Agent SnCl₂

The results described above indicate that the molecular weights are affected by changing the composition of the reaction mixture. Nevertheless the polymerizations have features typical of the uncontrolled free radical process suggesting that a high concentration of radicals R[•] is generated in reaction 1 (Scheme 1). Adding of reducing agents is an efficient approach to shift pseudo-equilibrium 1 to the left as it was demonstrated for the Cu-catalyzed polymerizations.⁵⁹ We also reported the notable improvement of the control for the Ru-mediated polymerization by adding tin(II) chloride.⁴⁶ Thus, 0.5 eq of SnCl₂ was introduced to the standard reaction mixture ([M]₀/[I]₀/[(1)]₀/[Al]₀ = 200/1/1/1) and this affected the polymerizations of all three monomers. The polymerization rate dropped significantly in the presence of SnCl₂ (conversion after 24 h was ~30, 25, and 50% for MMA, St, and BA, respectively), the molecular weights decreased as well, being now dependent on conversion, and PDIs became narrower (Fig. 3, and data in the Tables 1–3). The reaction mixture maintained its original yellow color indicating the dominance of Ru(II) species in the system. However, though the molecular weights were a function of conversion, the dependences were not linear and had a noticeable jump at early stages followed by linear portions. Exemplified by EBiB- and PEB-initiated polymerizations of MMA, the data are shown as inset to Figure 3. It seemed that the system produced too many radicals R[•] at the very beginning, the concentration of which was then reduced with the help of SnCl₂. Therefore, a delicate tuning of the system required for minimizing the initial burst of R[•]. Since addition of extra Al(O*i*Pr)₃ ([M]₀/[I]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/1/4/0.5) resulted in loss of any control (Table 1) though the polymerization speeded up, we have used an excess of no more soluble catalyst (1) for setting up the conditions for the thoroughly controlled living polymerization.

Setting Up Controlled/Living Polymerization

Bearing in mind that an increase in the concentration of (1) decreased the molecular weights and at the same time did not affect the rate, we applied this strategy in the presence of SnCl₂. The PEB-initiated polymerization of MMA with [M]₀/[I]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/2/1/0.5, i.e.,

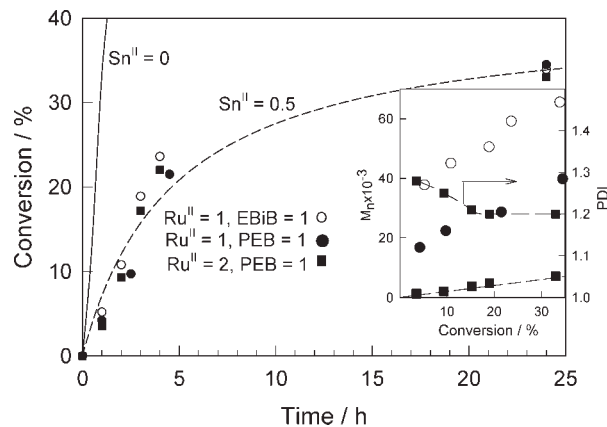


Figure 3. Polymerization of MMA in the presence of SnCl₂ at 80 °C: dependence of the conversion and the molecular weights on the type of initiator and concentration of the catalyst. The EBiB and PEB initiated polymerizations at [M]₀/[I]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/1/1/0.5 or 9.35 M/47 mM/47 mM/47 mM/23 mM are shown by ○ and ● symbols correspondingly; ■ symbol corresponds to PEB initiated polymerization with 2-fold excess of the Ru(II), [M]₀/[I]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/2/1/0.5 or 9.35 M/47 mM/94 mM/47 mM/23 mM. The PEB initiated polymerization of MMA without SnCl₂ and at the basic component ratio is shown by solid line for comparison.

using 2 eq of (1), proceeded with the same rate as in the presence of 1 eq of (1), identical conversions being reached for the same time intervals (Fig. 3). Importantly, a much better control was achieved under these conditions (Fig. 3, Table 1). There were no jumps in molecular weights at low conversions observed in the 200/1/1/1/0.5 systems. The molecular weights grew linearly with conversion and the difference between the experimental and calculated molecular weights was negligible. PDIs were also narrow and demonstrated a tendency to get lower with conversion. The PMMA sample of $M_{n, GPC} \approx 3700$ and PDI = 1.25 obtained under these conditions was purified and analyzed by the ¹H NMR spectroscopy (Fig. 4). In general the spectrum is very similar to a spectrum of PMMA prepared by a free radical method.⁶⁰ There are signals from the methyl (δ 0.8–1.4), methylene (a broad signal at δ 1.8–2) and methoxy group (ca. δ 3.5) protons of the PMMA main chain. The NMR spectroscopy is a powerful tool for the identification and quantification of the end groups.^{27,53,61–64} Thus, the signal at ca. δ 3.7 is attributable to the methoxy group protons next to the halogen chain end (a in Fig. 4). A small

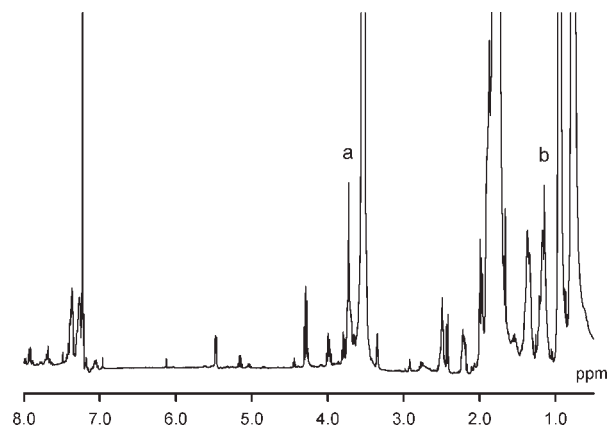


Figure 4. ¹H NMR spectrum of polyMMA (solvent CDCl₃) obtained in the system [M]₀/[PEB]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/2/1/0.5 at 80 °C.

signal at ca δ 2.5 presumably comes from the methylene protons of MMA unit adjacent to the ω -end C-Br bond. The characteristic α -end signals from the initiator are seen at ca. δ 7.2 and 7.7. A sharp peak at δ 1.15 (b in Fig. 4) can also be assigned to the methyl end group. The integration is complicated due to the signal overlap and possible resonances from the residual catalyst. Integration of the main chain methoxy group signal at $\delta \sim 3.5$ and the methoxy end group signal at $\delta \sim 3.7$ allows estimating the $M_{n,NMR}$ of ~ 3000 , which is consistent with that found by GPC (~ 3700).

Similar features were observed for the polymerization of St and BA at [M]₀/[I]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/2/1/0.5 (Fig. 5, Tables 2 and 3).

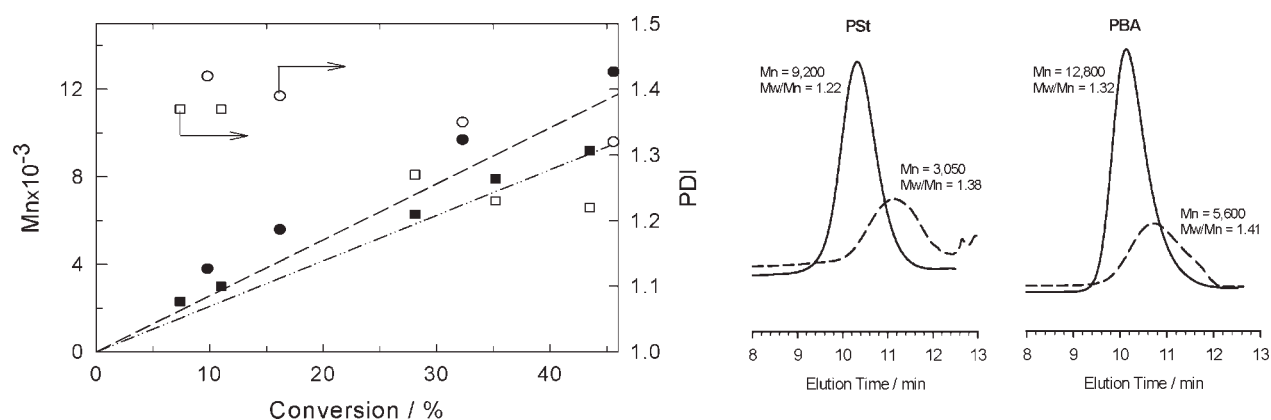


Figure 5. Evolution of Mn, PDI and GPC chromatograms with conversion for PEB-initiated polymerization of St (■ Mn and □ PDI) and BA (● Mn and ○ PDI) in the presence of SnCl₂ at the composition ratio [M]₀/[I]₀/[(1)]₀/[Al]₀/[Sn]₀ = 200/1/2/1/0.5 or 8.72 M/44 mM/88 mM/44 mM/22 mM for St and 6.95 M/35 mM/70 mM/35 mM/17 mM for BA. Dash line—calculated Mn for poly(butyl acrylate). Dash-dot-dot—calculated Mn for poly(styrene).

There were no jumps. Low molecular weights obtained at the beginning grew linearly with conversion in a good agreement with the calculated values. The PDI were also satisfactorily narrow in the range of 1.2–1.5 depending on the monomer. The fastest polymerization rate and the broadest PDIs were recorded for BA because of its highest polymerization constant k_p that makes it difficult to polymerize this monomer controllably. Nevertheless, the acceptable controllability was achieved for BA as well, the PDIs were less than 1.5 from the very beginning and the molecular weights were close to the calculated values.

Mechanistic interpretations of the results reported in this work could only be tentative at a moment. The initiating systems are rather complex (an initiator, the Ru(II) catalyst, a reducing agent, and an Al additive), but the control was achieved only in the presence of all the components. As it was shown and described above no polymerization proceeds without Al(O*i*Pr)₃, but only the presence of SnCl₂ improves the level of control. Increase of the catalyst concentration without addition of the SnCl₂ did not make important difference in character of the polymerizations, they still proceeded by free radical mechanism. The polymerization proceeded in “living” fashion only when all these components were added at certain proportions. All our attempts to clarify the mechanism and the role of every component in the system did not lead to direct conclusions and therefore the mechanism of this heterogeneous

process and exact roles of SnCl_2 and $\text{Al}(\text{O}i\text{Pr})_3$ could be too speculative at the moment. The most valuable fact is achieving the controllable polymerizations by adding a slight excess of (1) which is only partially soluble in the reaction mixtures. Thus the system becomes heterogeneous, but we do not consider any special superficial reactions that lead to the better control over the polymerizations. We rather believe that the insoluble part of the complex serves as a “stock” of fresh catalyst which might slowly dissolve while the dissolved catalyst being decomposed or releases small quantity of acetonitrile as proposed later. This does not affect the polymerization rate, as it could be anticipated because the concentration of (1) in solution does not increase, but set ups the control when combined with the reducing agent SnCl_2 . The action of the octahedral 18e complex (1) in the polymerization should be accompanied by dissociation of one, two, or even more acetonitrile ligands as tentatively shown in Scheme 2.⁶⁵ Otherwise step 1 is not possible or should involve a seven-coordinated 19e ruthenium(III) intermediate formed as a result of addition of halide to (1). This case is also problematic. If steps such as shown in Scheme 2 do hold, acetonitrile should disfavor reaction 1, shift it to the left, and thus decrease the concentration of radicals generated. It was verified that even a small excess of free MeCN added to the system, inhibits the polymerization completely (0.11 mL of acetonitrile was added to 2 mL of the reaction mixture). Therefore, it can be postulated that the role of insoluble extra (1) with four dissociable acetonitrile ligands is in releasing of small amount of MeCN in the bulk. This extra free acetonitrile is involved in slowing down the apparent rate constant k_{act} through the mass-law retardation and shifting equilibrium 1 to the left thus setting up the conditions for controllable polymerization.

CONCLUSIONS

Radical polymerization of vinyl monomers MMA, BA and St promoted by the cyclometalated cationic complex (1) occurs in the presence of $\text{Al}(\text{O}i\text{Pr})_3$. At the standard ratio of the components of the reaction mixture $[\text{M}]_0/[\text{I}]_0/[(1)]_0/[\text{Al}]_0$ of 200/1/1/1 no control over molecular weights was achieved for neither of the monomers. Variation in the $[\text{M}]_0/[\text{I}]_0/[(1)]_0/[\text{Al}]_0$ ratio did affect the polymerization rate and molecular weights but

did not improve the control. The molecular weights did not depend on conversion and remained practically unchanged during the polymerization; PDIs were also broad. Some level of control was achieved when SnCl_2 , as a reducing agent, was added to the formulation. Tin(II) chloride strongly decreased the polymerization rate, made the molecular weights dependent on conversion, and narrowed PDIs. The control was though unsatisfactory due to the jump in molecular weights at the beginning of the process. The universal formulation for the “living” polymerization of all three monomers has been achieved by using a 2-fold “excess” of complex (1) in the reaction mixture. Under these reaction conditions (1) was not completely soluble any more and the insoluble part of the complex probably serves as a “stock” of fresh catalyst. This is the first example of successful application of a cyclometalated ruthenium(II) compound for the living radical polymerization in a tunable system. Though these polymerization systems are complex and involve many ingredients they seem to be promising for the controlled polymerization of vinyl acetate, which it is very difficult to achieve through the existing ATRP catalysts.^{66,67}

The financial support from CONACyT and PAPIIT is gratefully appreciated. The authors are also grateful to M.S. S. Lopez Morales for the chromatographic analysis and I.Q. G. Cedillo Valverde for the NMR measurements.

REFERENCES AND NOTES

1. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721–1723.
2. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689–3746.
3. Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M. *J. Am Chem Soc* 2002, 124, 9994–9995.
4. Simal, F.; Demmonceau, A.; Noels, A. F. *Angew Chem Int Ed* 1999, 38, 538–540.
5. Braunecker, W. A.; Matyjaszewski, K. *Prog Polym Sci* 2007, 32, 93–98.
6. Tsarevsky, N. V.; Braunecker, W. A.; Tang, W.; Brooks, S. J.; Matyjaszewski, K.; Weisman, G. R.; Wong, E. H. *J Mol Catal A: Chem* 2006, 257, 132–137.
7. Tang, H.; Aruslamy, N.; Radosz, M.; Shen, Y.; Tsarevsky, N.; Braunecker, W. A.; Tang, W.; Matyjaszewski, K. *J Am Chem Soc* 2006, 128, 16277–16285.
8. Xia, J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 2434–2437.

9. De Clercq, B.; Verpoort, F. *Macromolecules* 2002, 35, 8943–8947.
10. Quebatte, L.; Haas, M.; Solari, E.; Scopelliti, R.; Nguen, Q. T.; Severin, K. *Angew Chem Int Ed* 2005, 44, 1084–1088.
11. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rec* 2004, 4, 159–175.
12. Miura, Y.; Satoh, T.; Narumi, A.; Nizhizawa, O.; Okamoto, Y.; Kakuchi, T. *J Polym Sci Part A: Polym Chem* 2006, 44, 1436–1446.
13. Min, K.; Li, M.; Matyjaszewski, K. *J Polym Sci Part A: Polym Chem* 2005, 43, 3616–3622.
14. Shibata, T.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *J Polym Sci Part A: Polym Chem* 2006, 44, 3609–3615.
15. Munirasu, S.; Ruhe, J.; Dhamodharam, R. *J Polym Sci Part A: Polym Chem* 2006, 44, 2848–2861.
16. Terashima, T.; Ouchi, M.; Ando, T.; Kamigaito, M.; Sawamoto, M. *J Polym Sci Part A: Polym Chem* 2006, 44, 4966–4980.
17. Miura, Y.; Satoh, K.; Kamigaito, M.; Okamoto, Y.; Kaneko, T.; Jinnai, H.; Kobukata, S. *Macromolecules* 2007, 40, 465–473.
18. Lutz, J. F.; Hoth, A. *Macromolecules* 2006, 39, 893–896.
19. Yamamoto, S.; Pietraski, J.; Matyjaszewski, K. *Macromolecules* 2007, 40, 9348–9353.
20. Stoffelbach, F.; Haddlenton, D. M.; Poli, R. *Eur Polym J* 2003, 39, 2099–2105.
21. Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1999, 32, 2420–2424.
22. Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1997, 30, 4507–4510.
23. O'Reilly, R. K.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Polym Bull* 2004, 23, 2921–2928.
24. Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1998, 31, 6756–6761.
25. Braunecker, W. A.; Itami, Y.; Matyjaszewski, K. *Macromolecules* 2005, 38, 9402–9404.
26. Saenz-Galindo, A.; Maldonado Textle, H.; Rosales Jasso, A.; Torres-Lubian, J. *J Polym Sci Part A: Polym Chem* 2005, 44, 676–678.
27. Zhang, H.; Schubert, U. S. *J Polym Sci Part A: Polym Chem* 2004, 42, 4882–4894.
28. Matsubara, K.; Matsumoto, M. *J Polym Sci Part A: Polym Chem* 2006, 44, 4222–4228.
29. Teodorescu, M.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 2000, 33, 2335–2339.
30. Drozdak, R.; Allaert, B.; Ledoux, N.; Dragutan, I.; Dragutan, V.; Verpoort, F. *Coord Chem Rev* 2005, 249, 3055–3074.
31. Wang, G.; Zhu, X.; Zhu, J.; Cheng, Z. *J Polym Sci Part A: Polym Chem* 2006, 44, 483–489.
32. Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984.
33. Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 2000, 33, 5825–5829.
34. Richel, A.; Tutusaus, O.; Vinas, C.; Teixidor, F.; Demonceau, A.; Noels, A. F. *Polym Prep (Am Chem Soc, Div Polym Chem)* 2005, 46, 227–228.
35. Tang, W.; Matyjaszewski, K. *Macromolecules* 2007, 40, 1858–1863.
36. Ando, T.; Kato, M.; Kamagaito, M.; Sawamoto, M. *Macromolecules* 1996, 29, 1070–1072.
37. Katani, Y.; Kamagaito, M.; Sawamoto, M. *Macromolecules* 1999, 32, 2420–2424.
38. Katani, Y.; Kamagaito, M.; Sawamoto, M. *Macromolecules* 1999, 32, 6877–6880.
39. Hamasaki, S.; Sawaochi, C.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 2002, 35, 2934–2940.
40. Ando, T.; Sawauchi, C.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 3597–3605.
41. Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* 1997, 30, 7348–7350.
42. Inoue, Y.; Matyjaszewski, K. *Macromolecules* 2003, 36, 7432–7438.
43. Ryabov, A. D.; Sukharev, V. S.; Alexandrova, L.; Le Lagadec, R.; Pfeffer, M. *Inorg Chem* 2001, 40(25), 6529–6532.
44. Ryabov, A. D.; Le Lagadec, R.; Estevez, H.; Alexandrova, L.; Fisher, A.; Pfeffer, M. *Inorg Chem* 2005, 44, 1626–1634.
45. Le Lagadec, R.; Alexandrova, L.; Estevez, H.; Pfeffer, M.; Laurinavicius, V.; Razumiene, J.; Ryabov, A. D. *Eur J Inorg Chem* 2006, 14, 2735–2738.
46. Diaz Camacho, F.; Lopez Morales, S.; Le Lagadec, R.; Alexandrova, L. *Macromol Symp* 2006, 242, 25–33.
47. Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssie, Ph. *Macromolecules* 1996, 29, 8576–8582.
48. De Clercq, B.; Verpoort, F. *Polym Bull* 2003, 50, 153–160.
49. Opstal, T.; Verpoort, F. *Angew Chem Int Ed* 2003, 42, 2876–2879.
50. Quebatte, L.; Scopelliti, R.; Severin, K. *Eur J Inorg Chem* 2005, 16, 3353–3358.
51. Lever, A. B. V. *Inorg Chem* 1990, 29, 1271–1285.
52. Ryabov, A. D.; Estevez, H.; Alexandrova, L.; Pfeffer, M.; Le Lagadec, R. *Inorg Chim Acta* 2006, 359, 883–887.
53. Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* 1997, 53, 15445–15457.
54. Matyjaszewski, K.; Wang, J. L.; Grimaud, T.; Shipp, D. A. *Macromolecules* 1998, 31, 1527–1534.
55. Karanam, S.; Goossens, H.; Klumperman, B.; Lemstra, P. *Macromolecules* 2003, 36, 3051–3060.
56. Ando, T.; Kamagaito, M.; Sawamoto, M. *Macromolecules* 2000, 33, 6732–6737.
57. Braunecker, W. A.; Itami, Y.; Matyjaszewski, K. *Macromolecules* 2005, 38, 9402–9404.

58. Poli, R.; Stoffelbach, F.; Maria, S.; Mata, J. *Chem Eur J* 2005, 11, 2537–2548.
59. Jakubowski, W.; Min, K.; Matyjaszewski, K. *Macromolecules* 2006, 39, 39–45.
60. Kroschwitz, J. I. *Polymers: Characterization and Analysis, Encyclopedia Reprint Series*, J. Wiley & Sons; NY, 1990.
61. Qin, D. Q.; Qin, S. H.; Qiu, K. Y. *J Polym Sci Part A: Polym Chem* 2001, 39, 3464–3473.
62. Bon, S. A. F.; Steward, A. G.; Haddleton, D. M. *J Polym Sci Part A: Polym Chem* 2000, 38, 2678–2686.
63. Wang, G.; Zhu, X.; Cheng, Z.; Zhu, J. *J Polym Sci Part A: Polym Chem* 2006, 44, 2912–2921.
64. Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M. *J Am Chem Soc* 2006, 128, 11014–11015.
65. Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Weinheim: VCH, 1991.
66. Wakioka, M.; Baek, K. Y.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 2002, 35, 330–333.
67. Kaneyoshi, H.; Matyjaszewski, K. *J Polym Sci Part A: Polym Chem* 2007, 45, 447–459.