

Application and Modification of Cyclometalated Ruthenium(II) Complex $[\text{Ru}(\text{o-C}_6\text{H}_4\text{-2-C}_5\text{H}_4\text{N})\text{-(MeCN)}_4]\text{PF}_6$ for Atom Transfer Radical Polymerization

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Summary: Polymerizations of n-butyl acrylate (BA), methyl methacrylate (MMA) and styrene (St) were promoted by the Ru(II) cyclometalated complex with labile MeCN ligand in the presence of $\text{Al}(\text{O}i\text{Pr})_3$. The polymerization proceeds via radical mechanism and requires the loss of MeCN ligand. The poor control over the polymerizations can be explained in terms of the traditional ATRP scheme. However, the controllability may be significantly improved by addition of reducing SnCl_2 . Mechanism of the process is proposed.

Keywords: ATRP; cyclometalated Ru-complexes; metal-catalyzed polymerization; reducing agent in ATRP; Ru-catalyzed polymerization

Introduction

Polymerization of methyl methacrylate mediated by the Ru(II) complex was the first example of metal catalyzed living radical polymerization, named also atom transfer radical polymerization (ATRP), reported by M. Sawamoto in 1995.^[1] Since then different complexes of other transition metals have been successfully applied as catalysts for ATRP, including complexes of Cu, Fe, Ni, Co and Pd, with Ru(II) compounds as the second most frequently used catalysts after copper complexes.^[2] Methyl methacrylate, n-butyl acrylate, styrene and several other monomers have been polymerized and copolymerized in a controlled manner with narrow polydispersities (PDIs) using Ru catalysts.^[2–4]

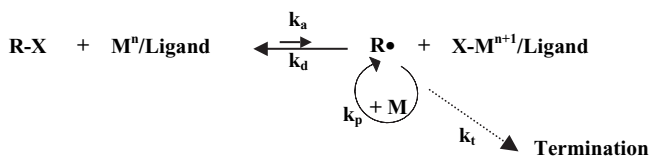
Low price of Cu, together with the relatively simple synthesis of its complexes and their high activity and good controllability of the polymerization of various monomers, make the Cu complexes leading compounds for this technique. Their catalysis mechanism has been extensively investigated and the general rules for the optimization of ligand systems, the initiator options and even the use of deactivators to improve the catalyst performance have been elaborated thanks to a number of works of K. Matyjaszewski's group and others.^[5] In the proposed mechanism the catalyst activity is strongly correlated not only with the redox potential, but also with the halogenophilicity of the metal center.

Ru is more expensive than Cu, however, it possesses one of the richest chemistries among all of the transition metals.^[6] The variety of options of the complexes' structures and ligands for Ru is enormous and much richer than for Cu. Since the reactivity of the catalysts is tuned by the ligands, the Ru compounds are some of the most interesting materials. Unfortunately, relatively few of the existing Ru complexes have been actually tested for

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**Scheme 1.**

ATRP reactions.

ATRP. Thus these complexes are worthy of study in order to find new catalysts of higher activity or that are capable of providing controlled polymerizations of monomers which are still problematic using existing approaches.

The mechanism of catalysis by Ru compounds is not so well established as for Cu. One of the reasons is related to the different structures and geometries of the complexes used for ATRP.^[7] Another reason is that many of the known Ru complexes require the use of Lewis acids, such as Al(OiPr)₃ or Ti(OiPr)₄, for their activation. This results in a reacting system much more complicated, especially for mechanistic studies. However, in general, as in the case of Cu catalysts, the catalytic activity correlates with the redox potential: the lower the redox potential of the complexes – the higher the catalytic activity. The difference in redox chemistry between Cu and Ru complexes is also responsible for difference in the initiation systems: some initiators that are effective for Cu catalysts are not successful in case of Ru-mediated polymerizations and vice versa.^[2,5c] Since the redox potential is determined not only by the nature of the metal center, but also by the ligands, the choice of the optimal initiator may be very individual for each of the complexes. In spite of all these details it is normally considered that organic halides mimicking the growing polymer radical are effective as initiators for most metal catalysts.^[2]

Recently, new cyclometalated Ru (II) compounds whose synthetic route is relatively simple and highly effective, have been reported.^[8] Introduction of the metal-carbon σ -bond makes the complexes more robust and at the same time allows a

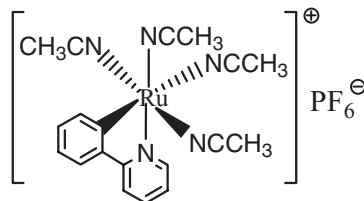
reduction of their redox potential. Additionally, some of the complexes demonstrate high lability of acetonitrile ligands under certain conditions and thus species with much lower redox potentials have been generated. The ability to release ligands is also very important for the coordinatively saturated complexes since, to be active in ATRP, the complexes should be able to receive a halogen from the dormant species (see Scheme 1). Thus it is interesting to examine these ruthenacycles with labile ligands as catalysts for ATRP.

Here we report the application of one such complex, cycloruthenated compound of 2-phenylpyridine, namely [Ru(o-C₆H₄-2-C₅H₄N)(MeCN)₄]PF₆, further referred as [Ru(Phpy)(MeCN)₄]PF₆ (for the structure see Fig. 1), as a catalyst for ATRP of various vinyl monomers, such as St, MMA and BA. Other Ru complexes of the series are under investigation and the results will be reported soon.

Experimental

Materials

All the monomers BA, MMA, St were dried over magnesium sulfate, distilled

**Figure 1.**Structure of the [Ru(Phpy)(MeCN)₄]PF₆ complex.

under reduced pressure and kept under argon. The other reagents and solvents were used as received from Aldrich Chem. Co. Synthesis, characterizations and X-ray analysis of the structure of $[\text{Ru}(\text{C}_6\text{H}_4\text{-2-C}_5\text{H}_4\text{N})(\text{MeCN})_4]\text{PF}_6$ were detailed in the reference.^[8a] The complex is not stable in air and was synthesized prior to every polymerization procedure.

Polymerization Procedures

The polymerizations were conducted in bulk using the Schlenk technique at 80 °C for MMA and BA and 100 °C for St. The Ru(II) complexes and $\text{Al}(\text{OiPr})_3$ were degassed under vacuum and purged with N_2 (three cycles). Then the monomer was added via a syringe and the mixture was stirred for 15–20 min until a homogeneous solution of yellow color was obtained. Finally the initiator was added to the mixture. After this the flask was submerged in an oil bath previously heated to the desired temperature. The samples were removed from the flask at 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. 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. The theoretical molecular weights were calculated without taking into

account the end groups according to the follow equation:

$$M_{n,\text{th}} = ([\text{Monomer}]_0 / [\text{Initiator}]_0) \times \text{Conversion} \times \text{MW}_{\text{monomer}},$$

where $0 \leq \text{Conversion} \leq 1$.

Results and Discussion

Firstly, the $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]\text{PF}_6$ was tried in the polymerization of all the monomers without any Lewis acid additives under the conditions described in the Experimental. No polymerization or only traces of the polymers were obtained in some cases. Addition of $\text{Ti}(\text{OiPr})_4$ did not improve the performance of the complex. Polymerizations were observed only when $\text{Al}(\text{OiPr})_3$ was added to the reaction. For comparison of the results the ratio of $[\text{M}]_0 / [\text{I}]_0 / [\text{Ru}(\text{II})]_0 / [\text{Al}(\text{OiPr})_3]_0$ was held at 200/1/1/1 for all experiments. The initiators were chosen in every case for better modeling of the corresponding dormant terminals, therefore ethyl 2-bromoisobutyrate (EBriB) was used for MMA, methyl-2-bromopropionate (MBrP) for BA and 1-phenylethyl bromide (PEBr) for St polymerizations, as is commonly accepted.^[2] Under these conditions the complex did promote polymerizations of all the monomers. As can be seen from the data shown in the Table 1 and Figures 2–4 the polymerizations were fast and proceeded in uncontrolled manner. The molecular weights did not depend on the conversion and from the beginning were much higher than the values expected for quantitative initiation. In particular, a low efficiency of the initiation was observed for the system Ru(II)-EBriB, applied for the MMA polymerization. The molecular weight distributions were also broad confirming poor control in all the systems. The radical mechanism of the polymerization was verified using the stable radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) trapping methodology. The polymerizations

Table 1.

Polymerizations of Styrene, n-Butyl Acrylate and Methyl Methacrylate Promoted by $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]\text{PF}_6$ Complex in the Presence of Various Amount of SnCl_2 .

Molar ratios	Time, min	Conv, %	$M_n \times 10^{-3}, \text{g} \cdot \text{mol}^{-1}$	PDI
St /PEBr /Ru(II) /Al(OiPr)₃ /SnCl₂				
200 / 1 / 1 / 1 / 0	60	36	28.3	1.69
	240	68	30.8	1.66
200 / 1 / 1 / 1 / 0.1	60	16	18.7	1.72
	240	42	31.2	1.68
200 / 1 / 1 / 1 / 0.3	60	8	10.9	1.66
	240	35	28.4	1.60
200 / 1 / 1 / 1 / 0.5	60	6	4.8	1.31
	240	12	15.4	1.18
200 / 1 / 1 / 1 / 0.7	60	5	4.5	1.38
	240	13	14.8	1.22
BA /MBrP /Ru(II) /Al(OiPr)₃ /SnCl₂				
200 / 1 / 1 / 1 / 0	30	14	66.6	2.27
	120	73	67.9	2.12
200 / 1 / 1 / 1 / 0.1	60	16	55.4	2.11
	240	75	65.8	1.95
200 / 1 / 1 / 1 / 0.3	120	15	39.1	1.61
	240	69	59.2	1.56
200 / 1 / 1 / 1 / 0.5	120	10	23.2	1.31
	240	48	52.3	1.22
200 / 1 / 1 / 1 / 0.7	120	8	33.8	1.38
	240	45	58.6	1.34
MMA /EBriB /Ru(II) /Al(OiPr)₃ /SnCl₂				
200 / 1 / 1 / 1 / 0	30	6	112.8	1.79
	120	54	121.9	1.74
200 / 1 / 1 / 1 / 0.1	30	7	72.3	1.81
	120	36	92.2	1.75
200 / 1 / 1 / 1 / 0.3	60	7	54.6	1.46
	270	32	67.8	1.37
200 / 1 / 1 / 1 / 0.5	60	5	37.8	1.28
	270	23	58.8	1.16
200 / 1 / 1 / 1 / 0.7	60	5	33.8	1.38
	270	26	58.6	1.27
MMA /PEBr /Ru(II) /Al(OiPr)₃ /SnCl₂				
200 / 1 / 1 / 1 / 0	30	11	38.4	1.62
	120	57	46.1	1.48
200 / 1 / 1 / 1 / 0.5	60	4	16.8	1.33
	270	19	28.7	1.19

did not proceed when the five fold excess of TEMPO with respect to alkyl bromide was introduced in the reaction mixture from the very beginning. The addition of the same amount of TEMPO after the first hour of polymerization stopped the process: conversions remained constant and did not grow further with time. Thus the radical character of the polymerization was confirmed and we can apply the traditional ATRP Scheme for the detailed discussion.

The data obtained can be explained in terms of fast activation and slow deactivation processes. In order to achieve a good control of polymerization, the reversibility

should be very fast and the equilibrium should be significantly shifted to the left ($k_d \gg k_a$) allowing the dormant species to dominate in the system. The Ru(II) complexes in the presence of $\text{Al}(\text{OiPr})_3$ abstracts halogen from the initiators and thus converts into the Ru(III) species. The change of color from yellow, characteristic for the original complexes in its +2 oxidation state, to dark green-brown was observed during polymerizations of all of the monomers, and this change occurred in the first 5 min of the reactions. The most likely complex turns out to be very stable in its oxidative form and does not revert back

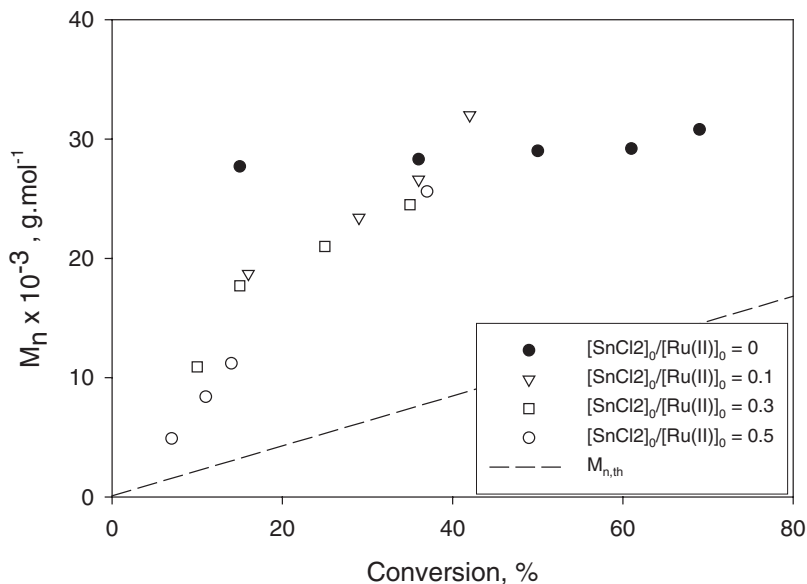


Figure 2.

Evolution of M_n with conversion for the polymerization of St with various amounts of SnCl_2 . $[\text{St}]_0 = 8.73 \text{ M}$; $[\text{PEBr}]_0 = 0.0436 \text{ M}$; $[\text{[Ru(Phpy)(MeCN)}_4\text{]PF}_6]_0 = 0.0436 \text{ M}$; $[\text{Al(OiPr)}_3]_0 = 0.0436 \text{ M}$; $[\text{SnCl}_2]_0 = 0.0044\text{--}0.0218 \text{ M}$.

to the original reduction state or its reduction is not efficient. Thus the polymerization of the monomers proceeds as a conventional free radical process.

However, even the molecular weights of all the polymers were much higher than the calculated values (see data in the Table 1 and Figures 2–4), the difference was less for

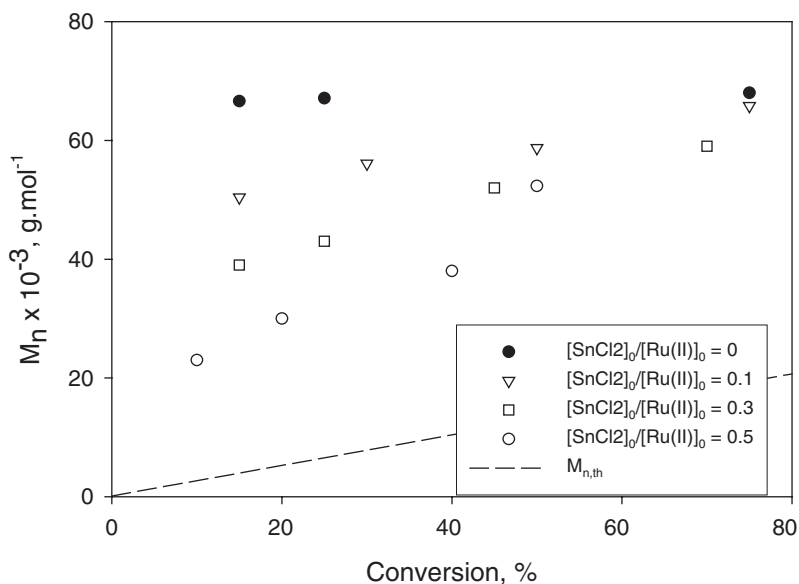


Figure 3.

Dependence of M_n on conversion for the polymerization of BA with variable amounts of SnCl_2 . $[\text{BA}]_0 = 6.95 \text{ M}$; $[\text{MBrP}]_0 = 0.0347 \text{ M}$; $[\text{[Ru(Phpy)(MeCN)}_4\text{]PF}_6]_0 = 0.0347 \text{ M}$; $[\text{Al(OiPr)}_3]_0 = 0.0347 \text{ M}$; $[\text{SnCl}_2]_0 = 0.0035\text{--}0.0173 \text{ M}$.

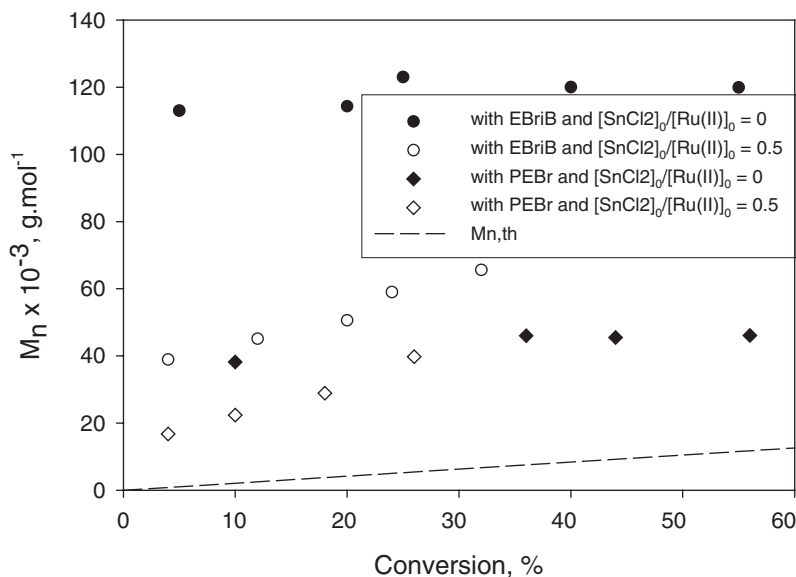


Figure 4.

Dependence of M_n vs conversion for the polymerization of MMA with various initiators in the presence of 50% of SnCl_2 relative to the catalyst at 80 °C. $[\text{MMA}]_0 = 9.35 \text{ M}$; $[\text{In}]_0 = 0.0467$; $[\text{Ru}(\text{phpy})(\text{MeCN})_4]\text{PF}_6]_0 = 0.0467 \text{ M}$; $[\text{Al}(\text{OiPr})_3]_0 = 0.0467 \text{ M}$; $[\text{SnCl}_2]_0 = 0.0217 \text{ M}$.

PSt initiated by PEBr and the highest molecular weights were obtained in the MMA - EBriB system. In general, the molecular weights of the PMMA exceeded those of PSt by about 4 times. Taking into account that the ratio monomer/catalyst/initiator was the same for all the polymerizations, such a large difference may be most logically explained by a lower efficiency of the EBriB initiator compared to the PEBr in these Ru-catalyzed systems or a faster propagating rate of MMA comparing to the St at the similar but slow initiation rate in both systems. To clarify this the polymerization of MMA was repeated using the PEBr initiator. The molecular weights thus obtained were almost 3 times lower: they dropped from $\sim 120,000$ to $\sim 40,000$ (see the Table 1) and thus were close to the molecular weights of the PSt. The molecular weights distributions were also narrowed from 1.8–1.7 to 1.6–1.5, but in general the control over the molecular weights was still very poor. The low efficiency of the EBriB was noted before in $\text{RuCl}_2(\text{PPh})_3$ mediated polymerization

of MMA as well as for the highly active Cu-catalysed system and was explained by a decrease in the initiation rate due to back strain effect.^[5c,h,f,9] However, in both cases the polymerizations were under control and the deviations in molecular weights were not so significant. Meanwhile in our systems, when the polymerization proceeds rather by a conventional radical mechanism, the difference in the molecular weights initiated by EBriB and PEBr is too big to be explained by the steric effect. Therefore, we assume that for the $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]\text{PF}_6$ applied 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 EBriB could be due to the poor efficiency of the bromine abstraction. The abstraction of bromide from PEBr may be easier than from EBriB because of the formation of a more stable 1-ethylphenyl radical in the former case. As can be observed from Table 1, the MMA polymerization was significantly faster for the PEBr initiation: the monomer conversions in the first half an

hour were almost twice as high as the conversions monitored for the EBriB initiation. This can obviously be explained by a higher concentration of the radicals formed, and therefore indirectly corroborates the hypothesis of the difference in bromine abstraction between these two initiators.

The catalyst activity in each specific case can be tuned up by changing the ligands. Thus the electron-donating ligands reduce the redox potential of the complex or labile ligands can facilitate vacant-site generation for halogen incorporation upon radical formation.^[2] As was demonstrated in the reference^[8a] one of the specific features of the $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]\text{PF}_6$ is the ability quite easily to release one of its MeCN ligands and this is probably the reason for its activity in ATRP. In confirmation of this idea MMA polymerizations initiated by PEBr were conducted in two solvents, toluene and acetonitrile (1:1 monomer: solvent by volume) at the same 200/1/1/1 monomer/initiator/ $\text{Ru}(\text{II})/\text{Al}(\text{OiPr})_3$ ratio at 80 °C. The polymerization in toluene maintains the same characteristic as in the bulk, but was slower because of dilution. Conversion of about 45% was reached after 6 hours of reaction. The molecular weights of the polymer were within 40,000 – 45,000, very similar to the bulk polymerization, and did not show a dependence on conversion. PDI was also broad, between 1.60 – 1.71. Meanwhile not even traces of the polymer were obtained in acetonitrile after 6 h. Thus, one can conclude that the mobility of MeCN ligand is responsible for the catalytic activity of this $\text{Ru}(\text{II})$ compound, but obviously this was not sufficient to produce a controlled process because of the inefficient deactivation. To promote the complex reduction and therefore to improve its deactivation tin(II) chloride (SnCl_2), which is known as a good reducing agent^[10] and also easily available, was utilized in the polymerizations. The amount of SnCl_2 was varied from 10 to 70 mol. % relative to the catalyst. Introducing larger amounts caused problems of solubility both catalyst and SnCl_2 ; they aggregated together to form a

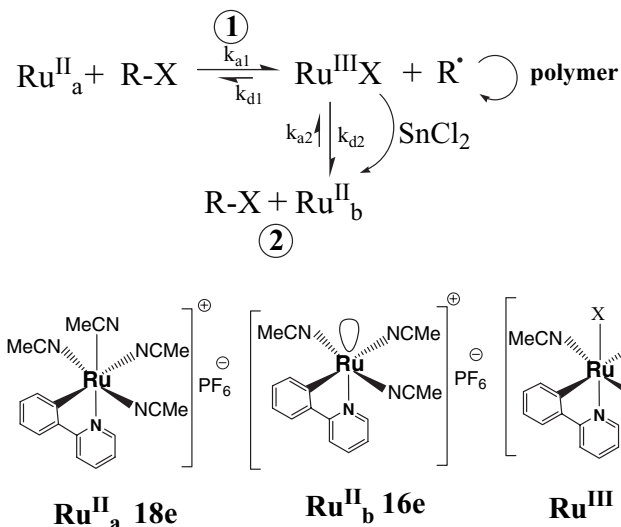
precipitate. The results of the polymerizations of St, BA and MMA using the various $[\text{SnCl}_2]_0/[\text{catalyst}]_0$ ratios are also summarized in Table 1. According to these results the polymerization rate was significantly decreased in the presence of the reducing SnCl_2 .

The application of reducing additives is known practice to remove the excess of catalysts in the oxidation state generated via irreversible radical termination.^[2,11] Such reduction generates a higher radical concentration and therefore leads to a rate enhancement and a worse control over the process. For example, zerovalent metals such as $\text{Cu}(0)$ and $\text{Fe}(0)$ reduce corresponding $\text{Cu}(\text{II})$ or $\text{Fe}(\text{III})$ into active $\text{Cu}(\text{I})$ and $\text{Fe}(\text{II})$ compounds and increase the polymerization rate by about 10 times.^[11] We observed the opposite result in that: the polymerization rate of all the monomers decreased with increase in the SnCl_2 content (see data in Table 1). Simultaneously the molecular weights decreased and, moreover, started to depend on the conversion and the PDIs were narrower.

The best performance was observed at a $\text{SnCl}_2/\text{Ru}(\text{II})$ ratio of 0.5. Here the lowest molecular weights and the narrowest PDIs were achieved. Further increases in the SnCl_2 concentration did not improve the values. In addition, the reaction mixture maintained its original yellow color, indicating of the reduction of $\text{Ru}(\text{III})$ to $\text{Ru}(\text{II})$.

Evolutions of the molecular weights with conversion without the reducing SnCl_2 and in its presence for all the monomer used are shown in Figures 2–4. As can be seen when SnCl_2 is added to the reaction mixture the molecular weights grew with conversion and PDIs as narrow as 1.2 – 1.18 have been reached at the $\text{SnCl}_2/\text{Ru}(\text{II})$ ratio of 0.5. However even at this ratio the molecular weights still exceeded the estimated values. Apparently the mechanism involved here is more complicated than a simple reduction of $\text{Ru}(\text{III})$ to the original $\text{Ru}(\text{II})$ complex. To explain all the facts the following mechanism is proposed (Scheme 2).

The original $\text{Ru}(\text{II})$ ($\text{Ru}(\text{II})_a$ in Scheme 2) abstracts a bromine from initiator and



Scheme 2.

Mechanism of the polymerization in the presence of reducing SnCl_4 .

converts into Ru(III) compound. In absence of SnCl₂ the equilibrium is slow and shifted to the Ru(III) side and thus the polymerization proceeds as a conventional radical process. When SnCl₂ introduces in the reaction it causes reduction of the Ru(III) formed, but to new Ru(II) complex (Ru(II)_b in Scheme 2), not to the original Ru(II)_a. Indeed, as it was shown above, polymerizations did not occur in acetonitrile and thus the lost of one of MeCN ligands is a necessary condition for the formation of Ru(III) with a halogen in its coordination sphere. However it is of low probability that the reduction of the Ru(III) in any of the monomer solution would result in formation of the same Ru(II) complex with four acetonitrile in the coordination sphere. Most probable the formation of unsaturated 16e Ru(II) complexes with one vacant site (Ru(II)_b in Scheme 2). Such obtained Ru(II)_b complex should be easier to undergo reversible reduction-oxidation cycle and thus may participate in equilibrium between dormant species and active radicals. So it means existence of two processes in the system: (1) the first is uncontrolled polymerization induced by the Ru(II)_a and (2) the second is a controlled process catalyzed by formed in situ new Ru(II)_b complex. The

scheme proposed explains satisfactory the results of the obtained results though more research has to be done to understand the mechanism of this very sophisticated system.

Acknowledgement: The financial support from CONACyT (D 40135 Q) is gratefully acknowledged.

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