Living radical polymerization of hydrophobic monomers catalyzed by cyclometalated ruthenium(II) complexes: Improved control and formation of block co-polymers

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ABSTRACT

Living radical polymerizations of three representative monomers, styrene (St), methyl methacrylate (MMA) and n-butyl acrylate (BA) catalyzed by cyclometalated ruthenium(II) complex, cis-[Ru(o-C$_6$H$_4$-2-py)(phen)(MeCN)$_2$]PF$_6$, has been investigated. It has been shown, that the control over all three homo-polymerizations may be significantly improved in the presence of small amounts of another ruthenium(II) complex, Ru(o-C$_6$H$_4$-2-py)(phen)$_2$]PF$_6$, bearing strongly bound bidentate ligands. Although the mechanism of the phenomenon is rather different in the case of St and in the case of MMA and BA polymerizations. The best control was achieved in polymerization of St, while BA polymerization remained the worst controlled. The possibility of formation of sequential di- and tri-block copolymers from these monomers has been demonstrated.

1. Introduction

The discovery of the concept of reversible deactivation radical polymerization (RDRP) gave a second wind for the polymer synthesis via radical mechanism and resulted in the preparation of functional polymeric materials with desirable molar mass and architecture, which was not possible to obtain using the free radical methodology [1–4].

Among the existing methods of RDRP, transition-metal-catalyzed living radical polymerization or atom-transfer radical polymerization (ATRP) is known as a versatile and robust approach allowing the synthesis of a broad spectrum of well-defined polymers and new materials such as block- and gradient copolymers, dendrimeric or brush macromolecules [3–7].

The method is based on the reversible activation of carbon-halogen polymer terminals by transition metal catalysts though a one-electron redox cycle. If the reversibility is fast enough and the equilibrium shifted to the dormant species, it allows minimizing a proportion of undesirable side reactions leading to the "dead" polymer chains. This is a catalytic process that can be mediated by many redox-active metal complexes, including Cu [3,5,7], Ru [4,6], Fe [8,9], Ni [10], Re [11] and Pd [12] complexes. Copper derivatives are the most often used since they have been found to be very effective catalysts in ATRP of different monomers in various media and, additionally, their synthesis

is usually straightforward [3,5].

The mechanism of the Cu-catalysis has been deeply investigated and the corresponding rules, such as the influence of ligand structure, initiating system and common monomer activities in ATRP have been established [5,7,13]. Although the Ru-based catalysts were among the first applied [14] and many Ru-complexes have been shown to be effective catalysts for living radical polymerization (LRP) of different vinylic and metha/acrylic monomers, they generally need some additives, such as aluminum isopropoxide or alkylamines, in order to promote the polymerization at a reasonable rate [4,6]. The large capacity of the coordination sphere of ruthenium (usually in an octahedral geometry), together with its high tolerance to functional groups, allow the coordination of a wide variety of ligands to the ruthenium center [15,16]. Since the catalytic performance is determined to a grand extend by ligand surroundings, ruthenium complexes remain very attractive candidates for searching new active catalysts. Among the available Ru-catalysts half-metallocene Cp* (pentamethylcyclopentadienyl) complexes are particularly promising since they are capable to promote LRP of three representative hydrophobic monomers; methyl methacrylate (MMA), methyl acrylate (MA) and styrene (St) under quite similar conditions [4,17,18].

Recently, a new cationic Cp*-ruthenium(II) complex bearing coordinating labile MeCN ligand has been reported by Sawamoto's group
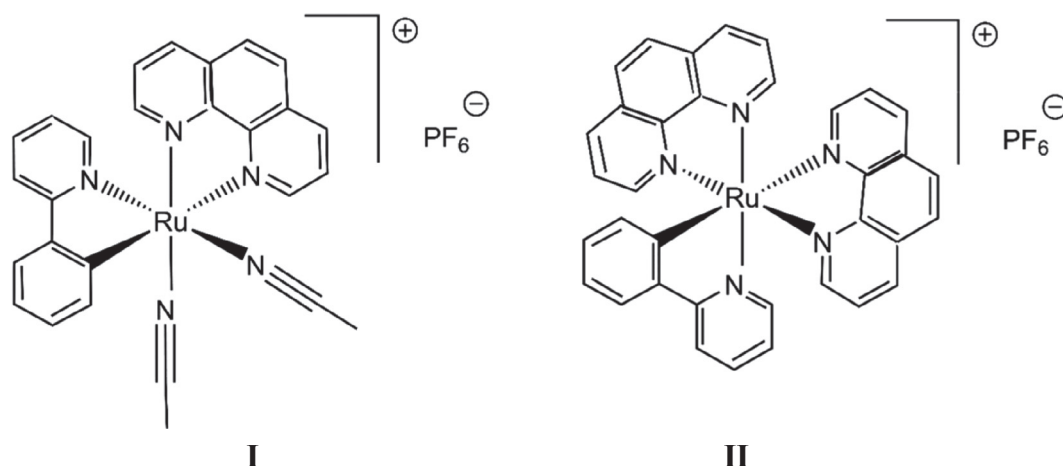
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Scheme 1. Structures of the *cis*-[Ru(*o*-C₆H₄-2-py)(phen)(MeCN)₂]PF₆ (**I**) and [Ru(*o*-C₆H₄-2-py)(phen)₂]PF₆ (**II**).

[19]. This compound turned out to be much more effective catalyst in the LRP of MMA and acrylates than its neutral precursors, acting without any additives and its activity could be tuned by the counterion.

Our research group has been working for some time on the use of cyclometalated Ru(II) compounds for LRP of hydrophilic and hydrophobic monomers [20–26]. It has been found that the complexes bearing labile ligands may be useful in LRP of monomers providing active radicals, such as vinyl acetate [20], but their application for polymerizations of conjugated monomers resulted in poorly controlled processes [21]. Additionally, they were not stable under the polymerization conditions, affecting their catalytic efficiency. On the other hand, much more stable complexes composed by strongly bound bidentate ligands as 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy) have been shown to be effective catalysis for LRP of St [22], but they did not promote LRP of metha/acrylic monomers [23].

Cationic cyclometalated *cis*-[Ru(*o*-C₆H₄-2-py)(phen)(MeCN)₂]PF₆ (**I**) complex (*cis* means that both acetonitrile ligands are in *cis* position relatively to the Ru-C bond [24], see Scheme 1) including strongly bound (*o*-C₆H₄-2-py, phen) and relatively labile MeCN ligands showed the best catalytic behavior so far [25–27]. Complex **I** was able to catalyze LRP of different monomers being light- and heat-activated. However, the level of control was not always satisfactory, particularly for the heat-activated polymerizations of MMA and *n*-butyl acrylate (BA).

In this paper we wish to report on the improvement of the control in the polymerizations mediated by **I** in the presence of small amount of another Ru complex bearing only bidentate ligands, [Ru(*o*-C₆H₄-2-py)(phen)₂]PF₆ (**II**) (see Scheme 1), and the synthesis of different sequential block copolymers formed by the three representative monomers St, MMA and BA using the same initiating system.

2. Experimental

2.1. Materials

All reagents were acquired from Aldrich Chem. Co. The monomers styrene, methyl methacrylate, and butyl acrylate, were washed with 5% sodium hydroxide solution and dried over magnesium sulfate overnight. They were passed through a column filled with neutral alumina and vacuum distilled under reduced pressure. Toluene (99.9%), 2-butanone (MEK, HPLC, ≥ 99.7%), MeOH (99%), THF (HPLC grade) and ethyl 2-bromoisobutyrate (EB*i*B) (98%) were used as received.

2.2. Measurements and characterization

The conversions were determined by gas chromatography (GC) using Shimadzu GC-2010 gas chromatograph from the residual monomer relative to the internal standard (*n*-decane). The molecular weights and the molecular weight distributions (MWD) of the polymers were determined by GPC chromatographyon a Waters 2695 ALLIANCE Separation Module apparatus equipped with two HSP gel columns (HR 4E molecular weight range from 50 to 1×10^5 and HR 5E from 2×10^3 to 4×10^6) in series and a RI Waters 2414 detector. THF was used as an eluent at 35 °C with a flow rate of 1.0 mL/min. Linear PSt and PMMA standards were utilized for the GPC calibrations.

Theoretical molecular weights were calculated according to the following equation: $M_{n,th}$ = ([Monomer]₀/ [Initiator]₀) x conversion x $MW_{monomer}$ were 0 ≤ conversion ≤ 1.

^{1}H NMR spectra were obtained in solutions at room temperature on a Bruker Avance 300 MHz spectrometer.

2.3. Synthesis of Ru complexes

The complexes, *cis*-[Ru(o-C₆H₄-2-py)(phen)(MeCN)₂]PF₆ (**I**) and [Ru(o-C₆H₄-2-py)(phen)₂]PF₆ (**II**), were prepared according to the reported procedures [28,29].

2.4. Polymerization procedure

The polymerizations were carried out under argon atmosphere in 15 mL Schlenk glass tubes equipped with a stir bar.

2.4.1. Homopolymerizations

Styrene polymerizations were performed in bulk, all others polymerizations were carried out in solutions (monomer/solvent 50% v/v) with ethyl 2-bromoisobutyrate EB*i*B as initiator and *n*-decane (0.3 mL) as internal standard. The initial molar ratios in most polymerizations were [Monomer]₀/[EB*i*B]₀/[Ru^{II}]₀ = 200/1/1 or 400/2/1. The typical procedure was performed as follows: **I** (62 mg, 0.090 mmol) was added to a Schlenk tube under constant flow of argon, MMA (2.0 mL, 18.77 mmol) and toluene (2.0 mL) were introduced by a syringe and the mixture was degassed by freeze-pump-thaw cycles (3 times). After stirring about 15 min to generate homogeneous solutions, EB*i*B (0.014 mL, 0.093 mmol) was added via syringe and the tube was immersed into an oil bath previously preheated at 80 °C. Samples were taken periodically by N₂ purged syringe. Finally, the resulting polymeric products were precipitated in cold MeOH and analyzed by GPC. The samples for ^{1}H NMR analysis were passed through a layer of Florisil to remove the catalyst residues. The polymerizations of BA and St were performed similarly, but small amount of DMF (5% v/v) was added in the reaction mixtures of BA in order to improve the solubility of the Ru (II) complexes.

Table 1
Polymerizations mediated by **I**.

Monomer	t °C	Time (h)	Conv. (%)	$M_{n,GPC} \times 10^{-3}$	$M_{n,th} \times 10^{-3}$	DI
St	100	6	64	16.6	13.0	1.25
MMA	80	6	65	14.3	13.1	1.37
BA	80	6	81	16.0	20.7	1.77

Conditions: $[\text{Monomer}]_0/[\mathbf{I}]_0/[\text{EB}i\text{B}]_0 = 200/1/1$; St/bulk; MMA(BA)/toluene = 50/50 v/v.

2.4.2. Synthesis of AB block copolymers

AB block copolymers were prepared by two methods: (1) employing isolated macroinitiator in the subsequent polymerization of another monomer and (2) without isolation of macroinitiator.

The syntheses of the macroinitiators of PSt, PMMA and PBA were carried out under the same conditions as described for the homopolymerizations using a mixture of catalysts **I** and **II** in proportions of 80:20 for PSt-Br and 90:10 for PMMA-Br and PBA-Br correspondingly.

The macroinitiators were purified from the catalyst residues by filtration over Florisil. To obtain block copolymer of PSt-*b*-PMMA the procedure was as follows: PSt-Br (323 mg, 0.040 mmol), MMA (0.85 mL, 8.01 mmol) and **I** (26 mg, 0.040 mmol) were added to the flask and dissolved in toluene (0.9 mL). After stirring to generate homogeneous solutions, the reaction mixture was degassed and placed in an oil bath at 80 °C. After certain period of time the resulting product was precipitated into cold MeOH, filtered off and analyzed by GPC and ^{1}H NMR. The other block copolymers were obtained similarly using toluene as solvent at 80 °C, except for the extension reactions with St; these were performed in bulk at 100 °C. For the synthesis of PSt-*b*-PBA di-block, the following initial concentrations were used: PSt-Br (272 mg, 0.034 mmol), **I** (23 mg, 0.034 mmol) and BA (1.0 mL, 6.97 mmol). For PMMA-*b*-PBA di-block, the initial concentrations were: PMMA-Br (163 mg, 0.034 mmol), **I** (23 mg, 0.034 mmol) and BA (1 mL, 6.97 mmol). For PBA-*b*-PMMA di-block, the initial concentrations were: PBA-Br (120 mg, 0.046 mmol), **I** (30 mg, 0.046 mmol) and MMA (1 mL, 9.38 mmol). For PBA-*b*-PSt, the initial concentrations were: PBA-Br (237 mg, 0.043 mmol), **I** (28 mg 0.043 mmol) and St (1 mL, 8.72 mmol).

The synthesis of PMMA-*b*-PSt was performed without purification of the first PMMA block as described below: first, MMA was polymerized at 80 °C for 8.5 h (approx. 70% conversion), then the reaction was cooled to room temperature and evaporated to dryness under reduced pressure at 40 °C. The polymer sample was taken under argon flow for the GPC probe and then a fresh solution of St in toluene (50/50 v/v) was added via syringe. The mixture was stirred at room temperature to form an homogeneous solution and then immersed into an oil bath preheated at 100 °C. After certain period of time the solution was precipitated into cold MeOH and the resulting polymer was analyzed by GPC and ^{1}H NMR.

2.4.3. Synthesis of ABC triblock copolymer

Purified by filtration over a layer of Florisil PSt-*b*-PMMA (106 mg, 0.007 mmol) was employed as macroinitiator in the polymerization of BA (0.20 mL, 1.40 mmol) in MEK (0.5 mL, -) and **I** (8 mg, 0.012 mmol). All the reagents were added to the flask, degassed through the triple vacuum-argon cycle and dissolved at room temperature during 20 min affording an homogeneous solution, then the reaction mixture was heated in an oil bath at 70 °C for 20 h reaching a conversion of BA ~ 25%.

3. Results and discussion

3.1. Homopolymerizations

Cationic cyclometalated *cis*-[Ru(*o*-C$_6$H$_4$-2-py)(phen)(MeCN)$_2$]PF$_6$ (**I**), which has been used as the principal catalyst in the polymerizations of three representative monomers St, MMA, and BA, reported here is a 18-electron complex composed by two strongly bound (*o*-C$_6$H$_4$-2-py and phen) and two more labile MeCN ligands (see Scheme 1 for the structure). The compound is very stable and can be handled without any special precautions in air, additionally, its synthesis is fairly simple and effective [28,29]. LRPs of these monomers catalyzed by this complex under visible light irradiation and conventional heating have previously been reported [25–27].

Since the complex is coordinatively saturated it should be activated through the loss of one of the ligands [30,31] and, indeed, selective dissociation of one of the MeCN ligands under visible light was established as the reason of its activity in a number of photo-polymerizations [25,29]. Though the complex is resistant to thermo-substitution, it was also found to be active in radical polymerizations under thermally trigging conditions at 70–100 °C [27]. The main data on the polymerizations of three representative monomers, St, MMA and BA, catalyzed by **I** are given in Table 1.

Importantly, all the processes were conducted under similar conditions, using the same initiator and without any additives. The polymerizations were rather fast and proceeded to high conversions. However, the level of control was not very good, particularly at the early stages of the polymerizations. The polymerization kinetics plotted in semi-logarithmic coordinate and evolutions of the molecular weights
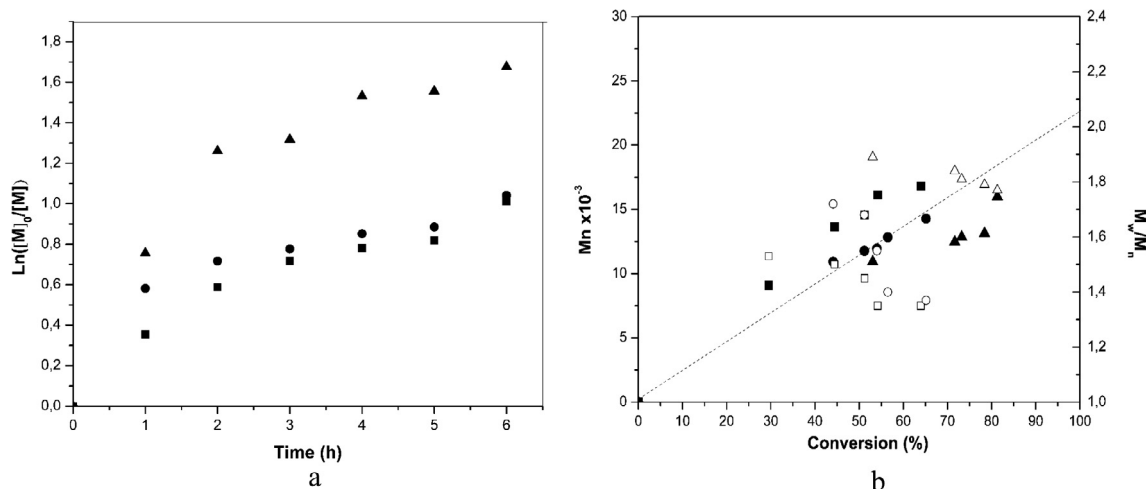

Fig. 1. (a) Kinetic plots and (b) Evolution of the molecular weights (closed symbols) and Mw/Mn (open symbols) with conversion for polymerizations of St (■□), MMA (○●) and BA (▲△) mediated by **I**. Conditions: St bulk, 100 °C; MMA/toluene (50/50 v/v) 80 °C; BA/toluene (50/50 v/v) 80 °C. [Monomer]$_0$/[EBiB]$_0$/[**I**]$_0$ = 200/1/1.

with conversion are depicted in Fig. 1.

As can be seen from the figure, the kinetic plots of the polymerizations did not pass through the origin of the coordinates (Fig. 1a). Some kind of "jump" in the conversion was observed at the beginning of the reactions, which was more pronounced in the polymerizations of MMA and BA than in the case of St polymerization. The growth in the molecular weights with conversion was observed in all cases, but the molecular weight distribution (MWD) was narrow enough only for PSt (Mw/Mn = 1.25). For the other two polymerizations, the dispersity indexes were not satisfactorily low, particularly for the BA process. Thus, the polymerization of St was a better controlled process among all others studied.

The abrupt growth in the rate observed at the early stage of the polymerizations may be consequence of the fast generation of radicals by **I**. The possible loss of one of MeCN ligands can result in a formation of a 16 electron complex with a vacant site in the coordination sphere capable to interact with an alkyl halide initiator (EB*i*B in our system) affording 17-electron Ru(III)-Br complex and initiating radical. The investigation of the behavior of **I** in different reaction media and using model reactions made us suspect that the unsaturated complex derived from **I** could be more stable in St than in MMA or BA. For example, the structural isomer of **I**, *trans*-[Ru(o-C$_6$H$_4$-2-py)(phen)(MeCN)$_2$]PF$_6$ with one MeCN ligand in *trans*-position of the Ru-C bond, was also tested in LRP of these monomers. It is known that, due to a strong *trans* influence, the *trans* isomer is much more active towards ligand substitution than its *cis*-analogue [24], and as such was expected to be more active catalyst.

However, it was able to mediate the polymerization of St with fairly the same level of control and rate as **I** (*cis*-isomer), but the polymerizations of MMA and BA did not proceed with this complex because of its very fast decomposition under the reaction conditions. This result may be considered as an indirect evidence that St was somehow able to stabilize the complex. We have now been able to obtain direct evidence of the stabilization of the unsaturated species derived from **I** by coordination of the styrene vinyl double bond that will be described in a forthcoming article.

On one hand, such stabilization allows the prolongation of the life of the 17-electron species, but, on the other hand, can decrease its activity or ability to interact with EB*i*B, that makes **I** to be more active in MMA and BA polymerizations. It may generate high radical concentration at the beginning of the reaction, resulting in the observed rate increase in both polymerizations.

A few years ago, we reported LRP of St catalyzed by another cyclometalated complex of [Ru(o-C$_6$H$_4$-2-py)(phen)$_2$]PF$_6$ (**II**) bearing only strongly bound bidentate ligands [22]. In spite of the strong bonds between the Ru center and the ligands, the complex was surprisingly active in the polymerization of St, but it was not able to mediate polymerizations of acrylate and methacrylate monomers [23].

In an attempt to improve the control and get smoother polymerizations several approaches were tested, including different temperature regimes, different solvents and variations of the Ru(II) catalysts. The best results were obtained when the complexes **I** and **II** were combined. The polymerization of St was almost perfectly controlled using a mixture of both catalysts. Semilogarithmic plots of conversion *vs* time together with evolution of the molecular weights with conversion for polymerization of St mediated by mixture of **I** and **II** in different ratios are presented in Fig. 2(a and b). The reaction proceeded very smoothly, the kinetic plots passed through the origin and no deviation from linearity even at the start was observed. The kinetic plots were linear independently on the composition of the combination of the catalysts. The reaction rate decreased when increasing the content of complex **II** in the mixture, which could be expected taking into account that the polymerization was slower when mediated by pure **II** than when mediated by pure **I**. The polymerization was fast and proceeded to high conversion in 6 – 8 h in the presence of 20%–50% of **II** in the catalytic mixture (Fig. 2a). The coincidence between experimental and

calculated molecular weights was better and the dispersity indexes were also much narrower than in the case of polymerizations mediated by pure catalysts **I** or **II**. The GPC traces of PSt synthesized in the process mediated by combination of **I**:**II** = 0.8:0.20 are depicted in Fig. 2c. Besides, though the polymerization was getting slower with decreasing the total catalyst concentration, it still proceeded with acceptable rate (conversion of 50% in 12 h) and good control (Mw/Mn ~ 1.2) even at initial molar ratio of [St]$_0$:[Ru^{II}]$_0$ = 2000:1.

The polymerizations of MMA and BA monomers were also tested using mixtures of **I** and **II**. The data on polymerizations of MMA and BA conducted by mixed catalyst (0.9 **I** + 0.1 **II**) are shown in Figs. 3 and 4, correspondingly. Interestingly, both polymerizations slowed down significantly even in the presence of only 10% of **II** in the mixture. For example, it took 12 h to reach conversions of 45% (Mn = 10.9 × 10^3 and DI = 1.29) and 61% (Mn = 27.0 × 10^3 and DI = 1.60) for MMA and BA, respectively, while almost quantitative conversions were obtained for both monomers in 6–7 h under the same conditions but using catalyst **I** only. After 20 h of reaction, conversions of 60% were obtained for MMA (Mn = 12.8 × 10^3 and DI = 1.31) and 88% for BA (Mn = 42.3 × 10^3 and DI = 1.61). Such effect could not be the consequence of a decrease in the content of **I** because variation within 10% of catalyst concentration had very little influence on the character of the polymerization. The changes in the kinetics of the polymerizations were very significant. Importantly, both reactions proceeded in a much smoother way, without the dramatic rise observed at the beginning, than those catalyzed by pure **I**. In order to demonstrate this effect more clearly the high conversion points are not depicted in the Figs. 3 and 4. As it can be seen from the Figures, lower values of dispersity indexes and better coincidence between the calculated and experimental molecular weights of both polymers, PMMA and PBA, were obtained using the mixed catalyst at low, up to 30–40%, conversions. While this tendency is maintained for high conversions in the case of MMA monomer, the BA monomer started to demonstrate a deviation from linearity at higher conversion, and the deviations increased with increase of the conversion. This effect is probably due to the instability of BA-Br terminals during such a long period of heating and, as a consequence, the growth of termination reactions. Therefore, it may be concluded that the control was also improved in these polymerizations, particularly for MMA and BA to limited conversions. Further increase in the content of **II** in the catalytic mixture to 20% resulted in very slow polymerizations.

3.2. Mechanistic considerations

Although the presence of small amounts of **II** in the main catalyst **I** resulted in better controlled polymerizations of all three monomers, St, MMA and BA, the mechanism may be complex and quite different in the case of St and in the case of MMA and BA polymerizations. First, such deceleration of the polymerization rate in the presence of only 10% of **II** noticed for MMA and BA was not observed for St. Second, as we already mentioned, complex **II** efficiently catalyzed the LRP of St, but was not active in the MMA and BA polymerizations. Activation of **II** in the polymerization of St was explained by the possible generation of one vacant site *via* the decoordination of the nitrogen atom of one phenanthroline ligand lying in *trans*-position of the Ru−C bond [22]. The better stabilizing capacity of St may facilitate such dissociation in contrast to MMA and BA.

Even if detailed mechanistic studies are beyond the scope of the present report, some experiments were performed in order to explain the unusual catalytic behavior of the mixture of two ruthenium(II) complexes. When a 1:1 mixture of complexes **I** and **II** was stirred for up to 48 h at room temperature in various solvents (CD$_3$CN, CDCl$_3$, acetone-d_6), no changes could be detected by ^{1}H NMR. When the same mixture in acetone-d_6 was heated at 60 °C for 24 h, complex **II** remained intact, while complex **I** was isomerized into its *trans* isomer, consistent with our previous reports [24]. Thus, under those conditions, the
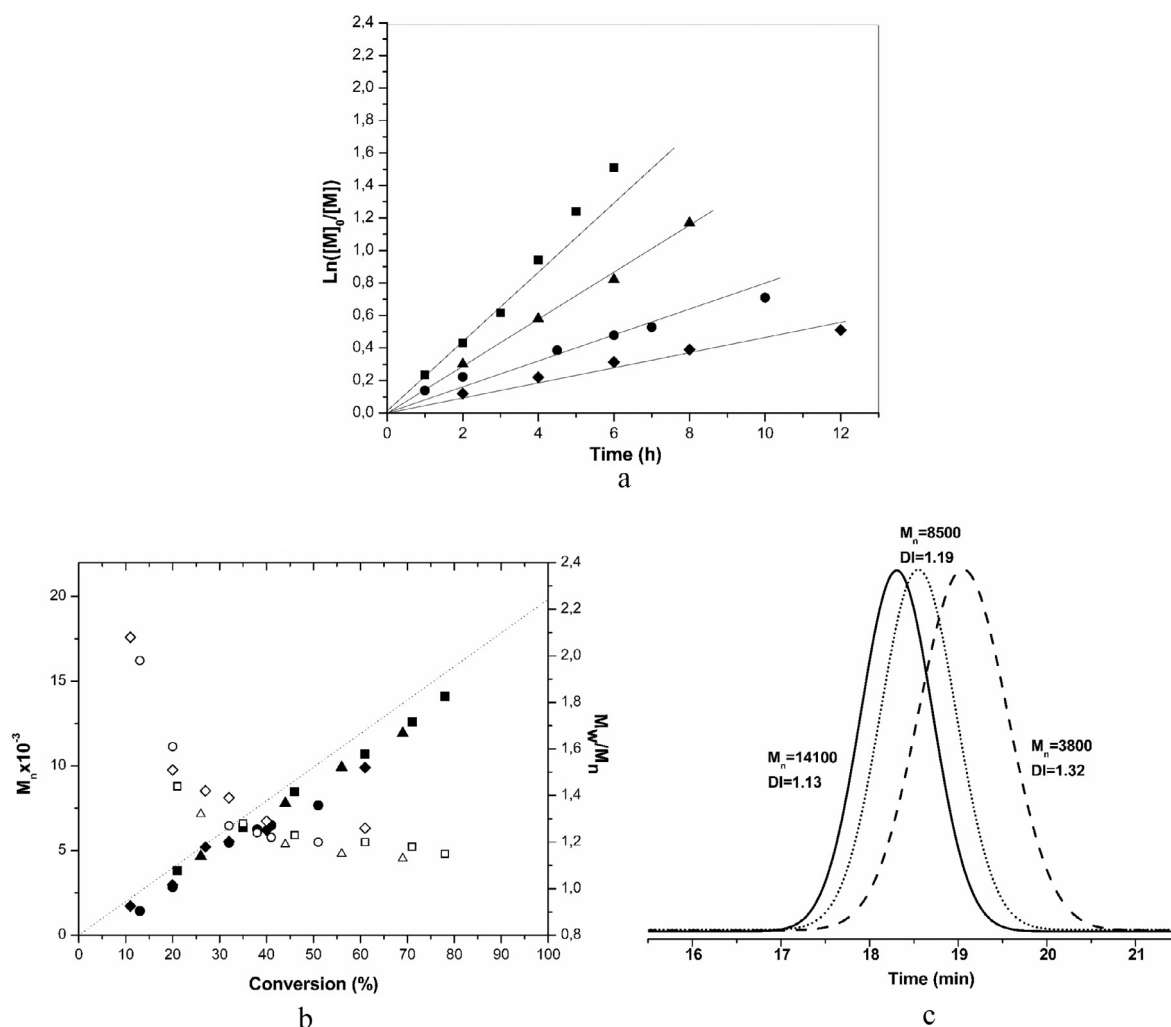
Fig. 2. (a) Kinetic plots, (b) Evolution of molecular weights (closed symbols) and Mw/Mn (open symbols) with conversion for polymerizations of St mediated by mixed (**I + II**) catalyst at 100 °C in bulk. (■□) $[St]_0/[EBiB]_0/[0.8\ I + 0.2\ II]_0 = 400/2/1$; (▲△) $[St]_0/[EBiB]_0/[0.5\ I + 0.5\ II]_0 = 400/2/1$; (●○) $[St]_0/[EBiB]_0/[0.2\ I + 0.8\ II]_0 = 400/2/1$; (◆◇) $[St]_0/[EBiB]_0/[0.5\ I + 0.5\ II]_0 = 2000/20/1$. (c) GPC curves for PSt obtained with $[St]_0/[EBiB]_0/[0.8\ I + 0.2\ II]_0 = 400/2/1$.

generation of a new species coming from the reaction between the **I** and **II** metalacycles could be discarded. Nevertheless, in order to have such important effect on the kinetics of the polymerizations, complex **II** should be involved in the redox equilibrium of between Ru(II) and Ru (III) species. Composed by strongly bound ligands, complex **II** should be much less reactive towards ligand substitution than **I** and, thus, may be able to generate Ru(III) deactivators such as $[Ru(o\text{-}C_6H_4\text{-}2\text{-}py)$ $(phen)_2]^{2+}(X^-)_2$ $(X^- = PF_6^-$ and/or $Br^-)$ via a one electron outer sphere mechanism by trapping counterion from decomposed residues of **I** or reacting with initiator. The formation of such deactivator should affect the ATRP equilibrium, shifting to dormant species and, therefore, achieving slower and better controlled process. When a 1:2 mixture of **II** and EBiB in acetone-d_6 was heated at 60 °C for one hour, the ^{1}H NMR signals corresponding to **II** disappear, along with the generation of a series of new broad signals, which could be indicative of the formation of a Ru(III) species. Unfortunately, we were not able to isolate and fully characterize the new compound.

However, more experiments should be performed in order to confirm the mechanism. The major problem is that the model reactions should be carried out under conditions similar to those of the polymerizations, but the complexes have limited solubility in non-polar organic media that did not allow to run NMR experiments of good quality.

3.3. Synthesis of block-copolymers

One of the principal advantages of RDRP is the possibility to obtain new polymeric materials based on traditional monomers, such as sequential block copolymers, for example. Such copolymers because of the covalent bonding of two or more different monomers exhibit quite unusual morphology that give rise to their unique properties [32–35]. Block copolymers formed by three or more distinct types of blocks (ABC) are of particular interest [36,37]. The syntheses of sequential block copolymers *via* ionic living polymerization frequently require rigorous conditions and, besides, may only be applied to a limited range of monomers [34,38]. RDRP methodologies allowed the preparation of a broad suite of new block copolymers under significantly less stringent reaction conditions [1–7,39]. Recent development in ATRP has successfully enlarged monomer combination for block-copolymers [3,6,7]. High-end functionality in the 1st block is an indispensable condition for the formation of well-defined block-copolymers. However, this may not be sufficient when a combination of monomers with different reactivities is implied. The order of the monomer addition is also very important for the efficient preparation of block-copolymers. Such order is well established for the Cu-catalyzed ATRP as methacrylates > styrene ~ acrylates, meaning that PMMA should be chain-extended by St and not *vice versa,* if the method of halogen exchange is not used for improving cross-propagation [7,40]. Such detailed studies have not been reported for other transition metal catalysts. Therefore, we have
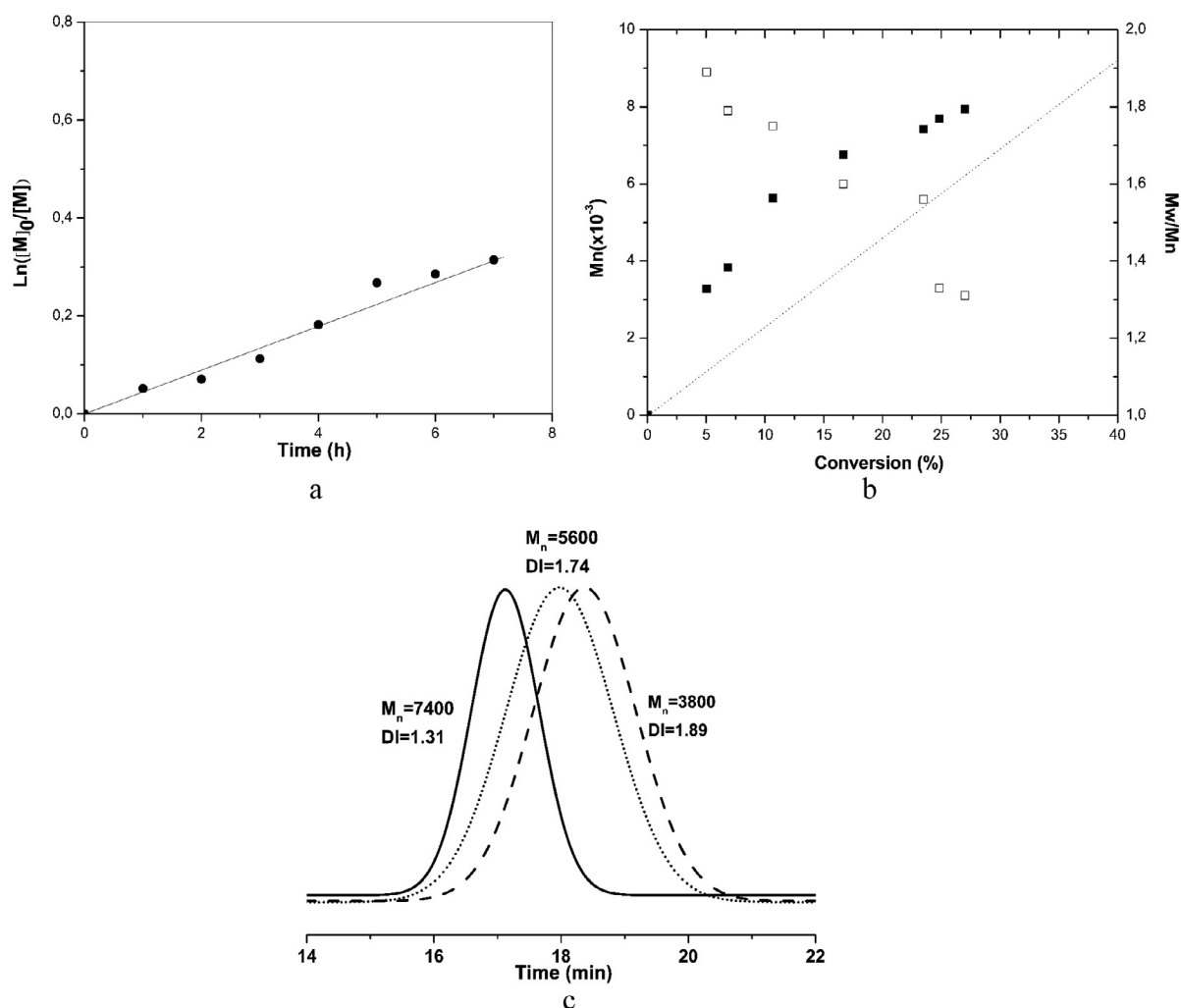
Fig. 3. (a) Kinetic plot of polymerization of MMA mediated by mixed catalyst (0.9 **I** + 0.1 **II**) at 80 °C in toluene (50/50 = v/v) with the ratio of $[MMA]_0/[EBiB]_0/[Ru]_0 = 200/1/1$. (b) Evolution of Mn (closed symbols) and Mw/Mn (open symbols) with conversion; (c) Examples of GPCs of PMMA obtained under these conditions.

examined the possibility of generating AB di-block copolymers employing the most representative monomers, St, MMA and BA, varying sequence of addition.

3.3.1. Block copolymers from PSt

Since the polymerization of St was the best controlled process using our Ru(II) catalysts, we decided to start with PSt-Br macroinitiator, that was employed in subsequent polymerization of MMA and BA. The conditions of the second polymerizations were very similar to those of the homopolymerizations. Indeed, the chain extension with MMA was quite successful; the conversion reached 40% after 6 h of the second polymerization and a two-fold increase in the molecular weights from 8,000 to 16,000 was obtained in this reaction time according to the GPC analysis, as can be seen from data presented in Table 2 and Fig. 5. Furthermore, the GPC curve after the second polymerization (Fig. 5a) was quite symmetrical meaning that the grand majority of the PSt-chains were successfully extended.

Analysis of the block co-polymer by ^1H NMR spectroscopy exhibited the presence of the characteristic signals from both PSt and PMMA structures (see Fig. 5b) according to the data reported in the literature [41–45]. The group of signals around δ 1.5–2.2 ppm was attributed to the protons α-CH and β-CH$_2$ from both monomer units. Another group of signals observed between δ 6.3 and 7.2 ppm was assigned to the aromatic protons of the styrene units and, finally, the characteristic singlet from the methoxy group of PMMA was detected at δ 3.7 ppm.

The ratio of the integrals of the aromatic signals from PSt (5 protons) and the singlet from PMMA at δ 3.7 ppm (3 protons) resulted in values of molecular fractions of $F_{PSt} = 0.48$ and $F_{PMMA} = 0.52$, that coincides well with 2-fold increase in the molecular weights obtained by GPC.

However, when the PSt-Br was employed as a macroinitiator in the polymerization of BA, the second polymerization was very slow and resulted in the copolymer with bimodal MWD (see Fig. 6); thus, GPC analysis reveal very slow initiation of BA polymerization by PSt-Br as most of the PSt chains remained unreacted with BA.

3.3.2. Block copolymers from PMMA

In order to synthesize PMMA-*b*-PSt copolymer we used an unpurified PMMA sample obtained at ~70% of conversion as described in the Experimental Section. After evaporation to dryness in vacuum at 40–45 °C (no polymerization was observed at this temperature), the residual PMMA was dissolved in toluene at room temperature and a fresh portion of St was added via syringe. Then the Schlenk flask with the reaction mixture was placed at 100 °C for another 9 h in order to obtain a reasonably high conversion of ~65%. The GPC traces of both polymers, initiating PMMA and obtained after the second St polymerization, are shown in Fig. 7a. As can be seen, both curves were monomodal and a significant increase of the molecular weights from 16,100 to 30,300 was detected after the second polymerization. The ^1H NMR analysis clearly showed the presence of PMMA and PSt in the copolymer. Amount of the St units in the copolymer determined from
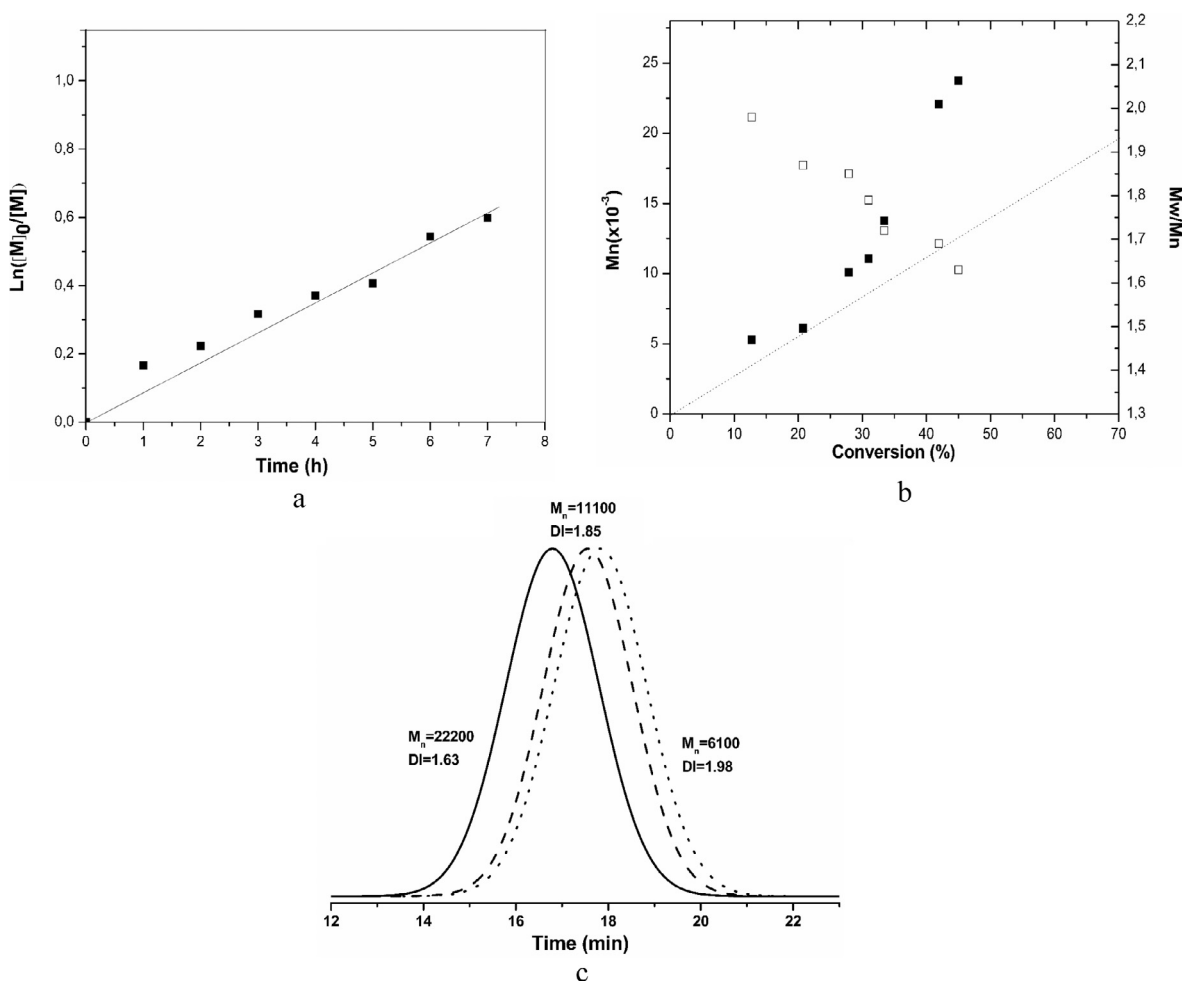
Fig. 4. (a) Kinetic plots for polymerization of BA mediated by mixed (0.9 **I** + 0.1 **II**) catalyst at 80 °C in toluene (50/50 = v/v) with the ratio of $[BA]_0/[EBiB]_0/[Ru^{II}]_0 = 200/1/1$. (b) Evolution of Mn (closed symbols) and Mw/Mn (open symbols) with conversion; (c) GPC traces of PBA obtained under these conditions.

the spectrum was almost equal to the amount of MMA units ($F_{PSt} = 0.50$ and $F_{PMMA} = 0.50$) that coincides quite well with the increase in the molecular weights detected by GPC calibrated with the PSt standards. The small difference between the molecular weights determined by GPC and the ^{1}H NMR methods could be explained by the difference in hydrodynamic volumes between PMMA and PSt. However, the MWD of the resulting PMMA-*b*-PSt co-polymer was broader than the MWD of the initiating PMMA. It may indicate the initiation of St by PMMA-Br macroinitiator was not complete, although no visible low molecular weight shoulder was observed in GPC curve of the copolymer.

The PMMA macroinitiator with Mn = 4800 and Mw/Mn = 1.66 was used to initiate polymerization of BA. The MWDs of the macroinitiator and resulting diblock copolymer together with its ^{1}H NMR spectrum are shown in Fig. 8. The GPC curve of the copolymer was monomodal and indicated an increase in the molecular weights to 7400. Additionally, MWD of the copolymer was narrower than that of the macroinitiator, meaning the effective initiation of the subsequent polymerization of BA. The signals from both monomer units of MMA and BA were detected in the ^{1}H NMR spectrum [46] and the ratio between the integrals of singlets at δ 3.7 ppm assigned to the methyl ester protons (3H, MMA) and at δ 4.10 ppm from methylene of BA units (2H) allows to estimate the content of fraction of PMMA and PBA in the copolymer as $F_{PMMA} = 0.85$ and $F_{PAB} = 0.15$ that is in good agreement with the GPC result.

3.3.3. Block copolymers from PBA

The polymerization of BA was the most complex to control using both pure **I** and mixed **I** + **II** Ru catalysts. MWDs of the resulting PBA were always broader than those of PSt and PMMA. Therefore, we did

Table 2
Synthesis of block copolymers.

Macroiniciator	Monomer added	T (°C)	time (h)	% Conv	$M_{n(GPC)init.}$	$M_{n(GPC)ext.}$	DI
PSt-Br	MMA	80	6	40	8000	16,200	1.49
PSt-Br	BA	80	6	44	7400	bimodal	3.71
PMMA-Br	St	100	9	65	16,100	30,300	1.80
PMMA-Br	BA	80	20	18	4800	7400	1.49
PBA-Br	MMA	80	6	29	2600	4900	3.31
PBA-Br	St	100	6	35	5500	8900	2.62

Extension conditions: $[Macroinitiator]_0/[I]_0/[Monomer]_0 = 1/1/200$; 80 °C for extensions with MMA and BA; 100 °C for extensions with St.
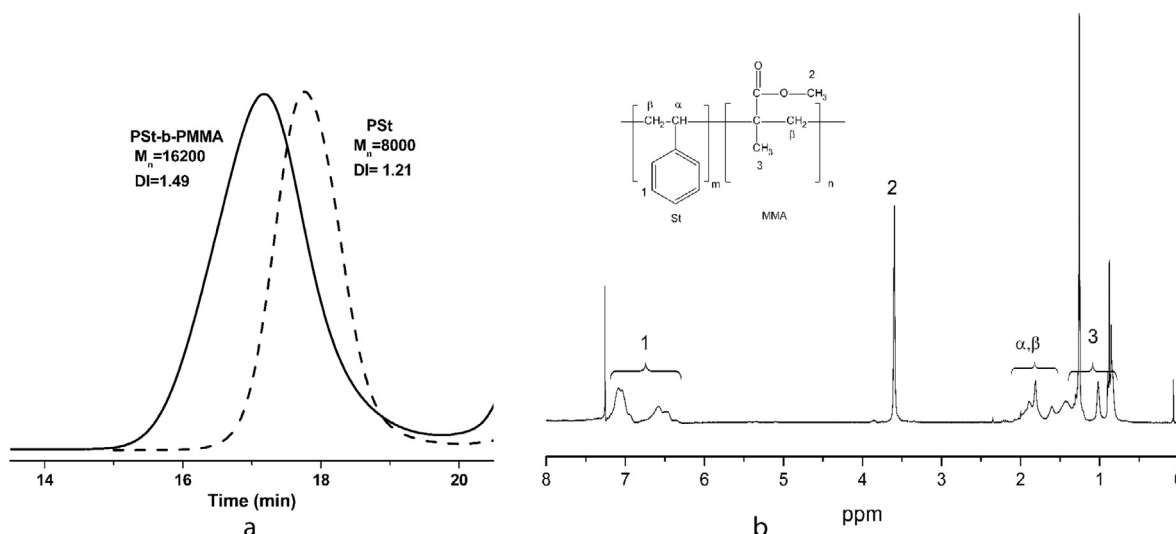
Fig. 5. (a) GPC traces of PSt macroinitiator and PSt-*b*-PMMA; (b) ^{1}H NMR spectrum (CDCl₃) of PSt-*b*-PMMA co-polymer.
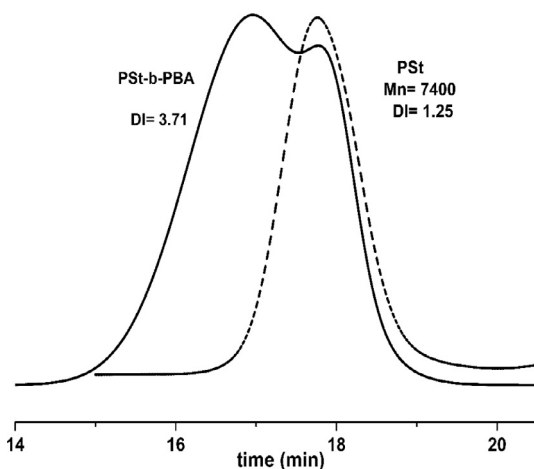

Fig. 6. GPC traces of PSt macroinitiator and co-polymer obtained after the chain extension with BA.

not expect high efficiency from the second polymerizations initiated by PBA. Indeed, the extension of PBA with MMA produced a co-polymer of very broad MWD (Mw/Mn = 3.31) as shown in Fig. 9. Even if an increase in the molecular weights was observed after the extension, it was difficult to evaluate the extension efficiency because of the broad MWD. The signals from PMMA were also detected in the ^{1}H NMR spectrum of the copolymer, confirming the formation of PBA-*b*-PMMA.

The better result was obtained when PBA macroinitiator was applied for St polymerization. In spite of high Mw/Mn value the GPC curve of the copolymer was symmetrical and monomodal as can be seen from Fig. 10. Additionally, MWD of the PBA-*b*-PSt copolymer was not as broad as MWD of PBA-*b*-PMMA copolymer, and an increase of the molecular weights as a result of the second polymerization was clearly noted in the chromatogram. Analysis of the copolymer structure by ^{1}H NMR spectroscopy confirmed the presence of PBA and PSt in the co-polymer (Fig. 10b). The copolymer composition of $F_{PBA} = 0.41$ and $F_{PSt} = 0.59$ was determined from the integration of the signals in the aromatic region at δ 7.2–6.3 ppm (5H, PSt) and the singlet at δ 4.1 ppm assigned to O-CH₂- (2H, PBA). The coincidence between GPC and NMR data was satisfactory.

Thus, summarizing the data on the chain extensions discussed above, it may be concluded that in the radical polymerization mediated
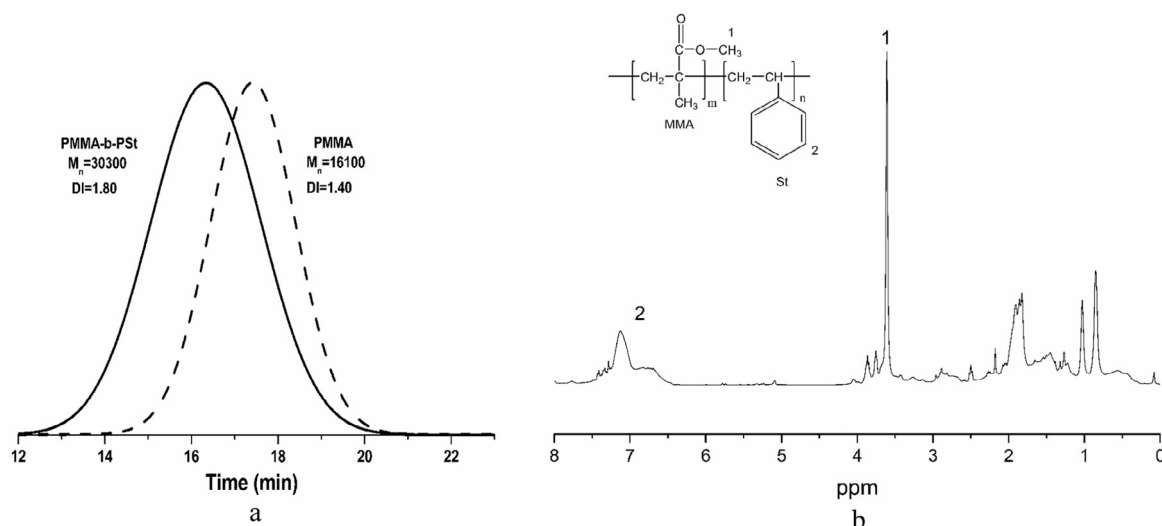

Fig. 7. (a) GPC traces of PMMA macroinitiator and PMMA-*b*-PSt; (b) ^{1}H NMR spectrum (CDCl₃) of PMMA-*b*-PSt co-polymer.
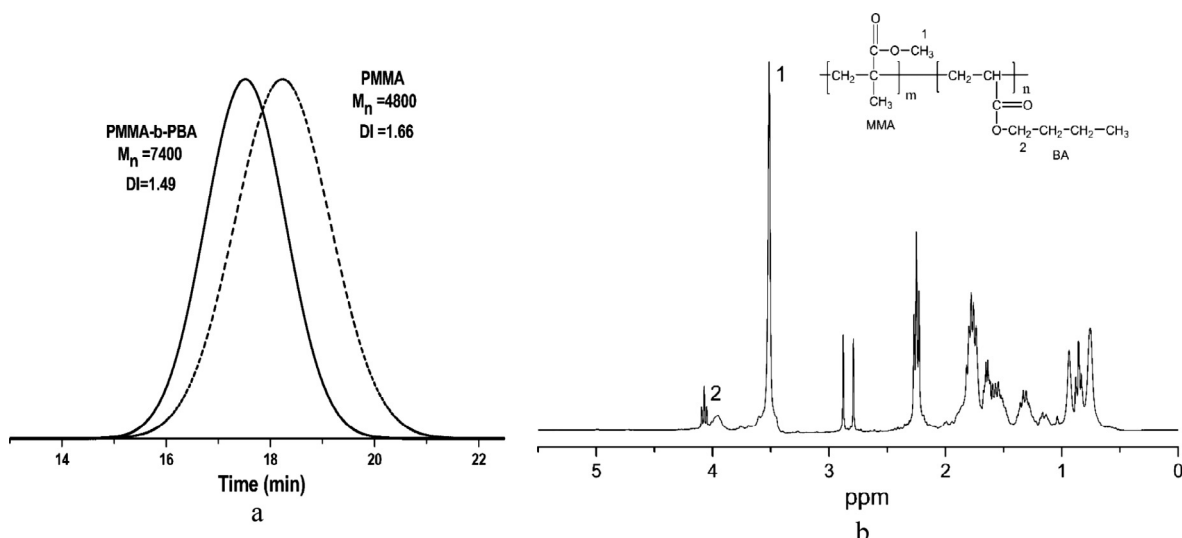
Fig. 8. (a) GPC traces of PMMA macroinitiator and PMMA-*b*-PBA; (b) ^{1}H NMR spectrum (CDCl$_3$) of PMMA-*b*-PBA co-polymer.
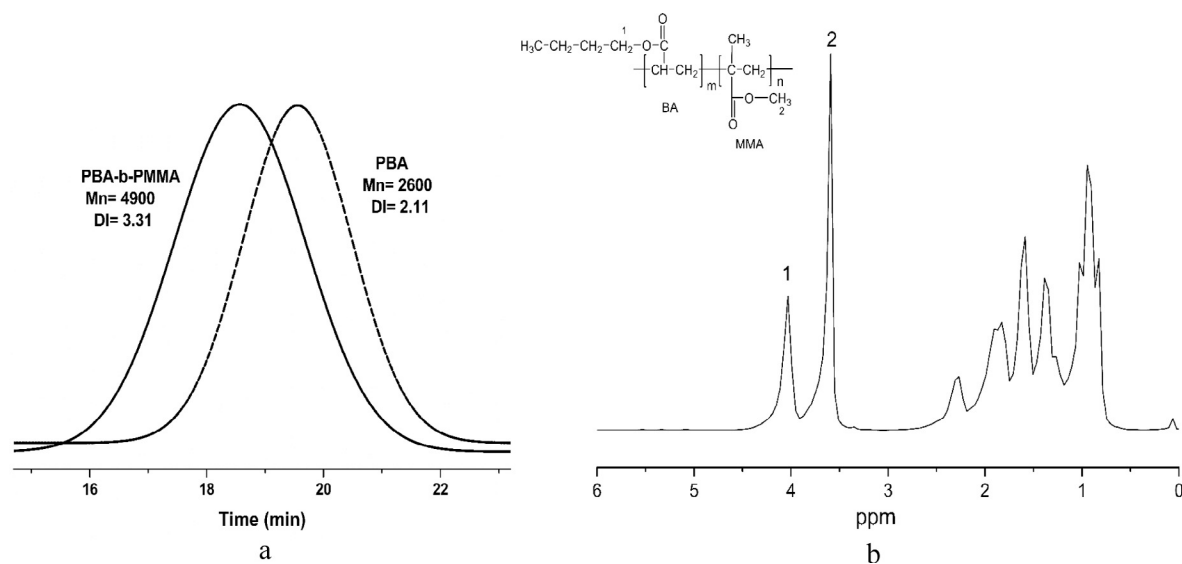

Fig. 9. (a) GPC traces of PBA macroinitiator and PBA-*b*-PMMA; (b) ^{1}H NMR spectrum in CDCl$_3$ of PBA-*b*-PMMA co-polymer.
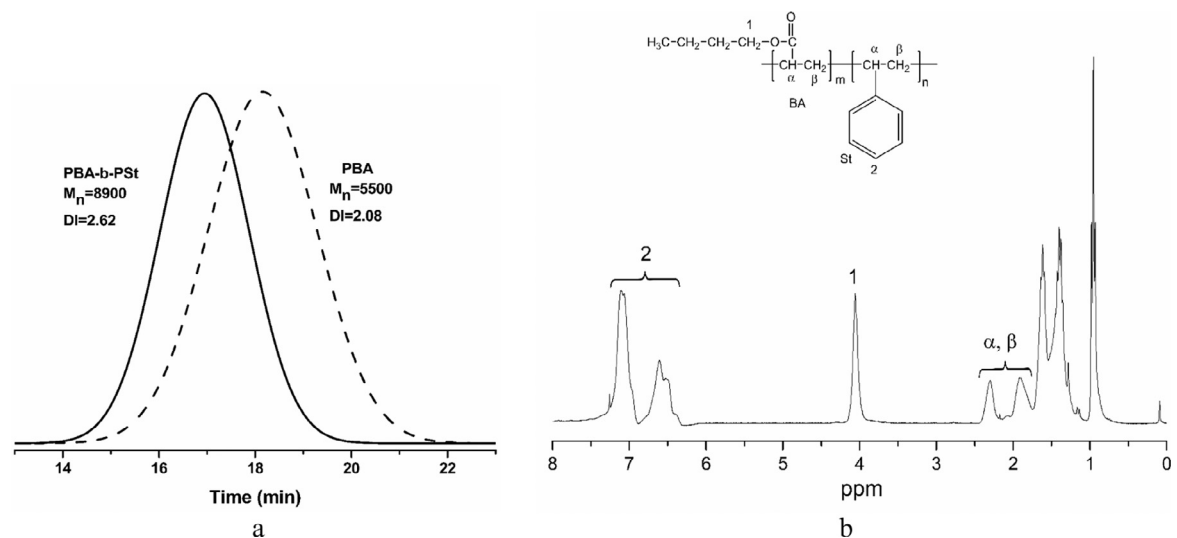

Fig. 10. (a) GPC traces of PBA macroinitiator and PBA-*b*-PSt; (b) ^{1}H NMR spectrum (CDCl$_3$) of PBA-*b*-PSt co-polymer.
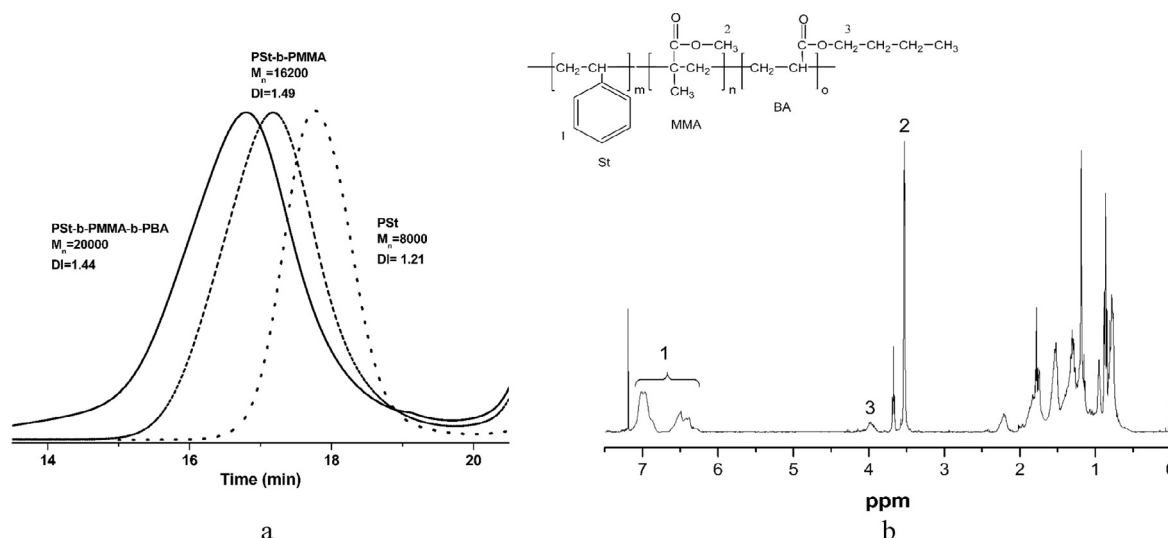
Fig. 11. (a) GPC traces of the PSt macroinitiator; PSt-*b*-PMMA and PSt-*b*-PMMA-*b*-PBA (b) ^{1}H NMR spectrum (CDCl$_3$) of PSt-*b*-PMMA-*b*-PBA terpolymer.

by the Ru(II) cyclometalated complexes, the PSt may be extended by MMA, but its extension by BA was not successful; while PMMA may be extended by both St and BA. The extension of PBAmacroinitiator was more problematic because of its high dispersity index. However, the GPC curve of PBA-*b*-PSt presented a more suitable shape than that of PBA-*b*-PMMA.

Besides, since Ru(II) complexes used in this study did not contain halogens, the rule of halogen exchange in order to improve cross-propagation could not be applied. Therefore, we decided to use the synthesized PSt-*b*-PMMA copolymer of approx. 0.5:0.5 composition and extended it by BA in order to obtained sequential ABC tri-block copolymer. The results are given in Fig. 11.

According to GC analysis ~25% of BA was consumed in 20 h of reaction. Again, as in the case of PMMA-b-PBA, the extension was very slow. The GPC traces (Fig. 11a) revealed an increase of the molecular weights from 16,200 to 20,000 after the extension, that coincided reasonably well with the calculated molecular weight of PBA after 25% of conversion. The resulting GPC curve was monomodal and MWD was not broadened after the extension. The ^{1}H NMR analysis of the extended PSt-*b*-PMMA showed the presence of BA units in the resulting co-polymer in amount of approx. 20% relatively to PSt (one BA unit per 5 St units), that is also in fairly good agreement with the GPC data.

Thus, it was possible to obtain an ABC block-copolymer, composed by three most representative monomers, St, MMA and BA, using Ru-cyclometalated catalysts.

4. Conclusions

The cyclometalated Ru (II) complex, *cis*-[Ru(*o*-C$_6$H$_4$-2-py)(phen)(MeCN)$_2$]PF$_6$, was capable to mediate the living radical polymerization of three representative monomer St, MMA and BA under very similar conditions. The polymerization of St was better controlled than the polymerizations of the other two monomers. The control was significantly improved in the presence of small amounts of another Ru cyclometalated compound bearing only strongly bound phpy and phen ligands. However, homo-polymerization of St remained the best controlled process with Mn/Mw = 1.15–1.12, while the polymerization of BA resulted in the polymer with the broadest MWD.

The possibility of the synthesis of the sequential block copolymers based on these catalytical system was also investigated. It was found that PSt may be successfully extended by MMA, but its extension by BA resulted in copolymer with bimodal MWD because of inefficient cross-propagation. On the other hand, the chain extension of PMMA was possible by both St and BA, although the resulting PMMA-*b*-PSt

copolymer displayed high dispersity index that may mask unreacted PMMA chains. It was also possible to obtain block copolymers started from PBA, and although both, PSt-*b*-PBA and PMMA-*b*-PBA, were characterized by broad MWD, the extension by St looked more effective that that by MMA.

Finally, triblock copolymer of PSt-*b*-PMMA-*b*-PBA was successfully synthesized using the order of the monomer addition described above.

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