Homogeneous Radical Polymerization of 2-Hydroxyethyl Methacrylate Mediated by Cyclometalated Cationic Ruthenium(II) Complexes with PF_6^- and Cl^- in Protic Media

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ABSTRACT: Cationic coordinatively saturated complexes of ruthenium(II), $[Ru(o\text{-}C_6H_4\text{-}2\text{-}py)(phen)(MeCN)_2]^+$, bearing different counterions of PF_6^- and Cl^- have been used in the radical polymerization of 2-hydroxyethyl methacrylate in protic media and acetone under homogeneous conditions. Exchange of PF_6^- by Cl^- increases the solubility of the complex in water. Both complexes led to the fast polymerization under mild conditions, but control was achieved only in methanol and acetone and was better for the complex with Cl^-. The polymerization accelerated in aqueous media and proceeded to a high conversion even with a monomer/catalyst = 2000/1, but without control. Polymerization mediated by complex bearing Cl^- was slower in protic solvents but faster in acetone and always resulted in lower molecular weight polymers. Thus, the nature of the anion strongly affected the catalytic activity of the complexes and may serve as way of fine-tuning the catalytic properties. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4562–4577, 2011

KEYWORDS: atom transfer radical polymerization (ATRP); cationic ruthenium complexes; 2-hydroxyethyl methacrylate; living polymerization; organometallic catalysts

INTRODUCTION 2-Hydroxyethyl methacrylate (HEMA) is an important industrial monomer; HEMA-based polymers have wide commercial applications mostly in the biomedical area, as hydrogels and drug delivery scaffolds, or in the manufacture of soft contact lenses.[1–4] As is, HEMA can be polymerized only via a radical mechanism, and the polymer is industrially produced by conventional free radical process in aqueous media.[5] Using free radical process, control over the molecular weights and terminal groups of the polymer is nearly impossible. Polymerization by the anionic technique requires protection of the alcohol group of the HEMA, and effective living anionic polymerization of the protected forms of HEMA has been developed.[6–8] However, the obvious drawback of this approach is that it is a multistep procedure, involving the synthesis of protected HEMA, its polymerization, and the subsequent polymer deprotection. Additionally, living anionic polymerization requires low temperatures, and the use of protic solvents must be avoided.

Rapid and intensive development of living radical polymerization techniques during the last decade now allows polymerization of a vast range of monomers, including different functional monomers, with precise control and architecture.[9–11] Initially, HEMA was polymerized in a living/controlled manner via the RAFT technique.[12,13] Metal-catalyzed or atom transfer radical polymerization (ATRP) is another versatile method that has been successfully applied for controlled polymerization of different monomers.[9–11,14–16] However, the control is sometimes difficult for functional monomers, particularly, when protic media are required for the polymerization, as is the case for HEMA because a transition metal catalyst, key element of ATRP, may be poisoned by the functional group, suffer undesirable side reactions, or a lack of solubility. Nevertheless, preparation of well-controlled homo- and co-polymers of non-protected HEMA by ATRP in different solvents has been reported using both copper- and ruthenium-based catalysts.[15,16] Thus, well-defined PHEMA and its copolymer with MMA have been synthesized in methylethylketone/alcohol (*n*-propanol or methanol) mixtures within the temperature range of 50–70 °C by direct ATRP and AGET ATRP methods using hydrophobic bromide initiators with CuCl/2,2′-bipyridine (bpy) and $CuCl_2$/bpy in conjunction with a tin(II) reducing agent correspondingly.[17,18] Recently, controlled synthesis of low-molecular-weight PHEMA in MeOH at room temperature, with $CuBr_2$/tris(2-pyridylmethyl)amine by a new ARGET

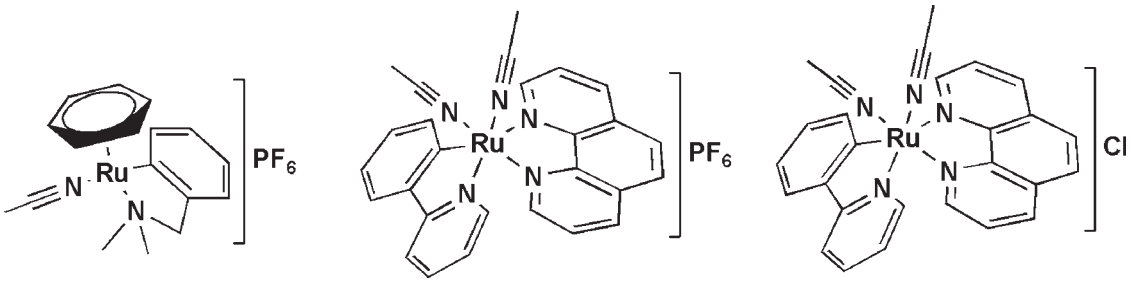

FIGURE 1 Structures of the cyclometalated ruthenium(II) complexes (**I**) [(η^6-C_6H_6)Ru(C_6H_5-*o*-CH_2NMe_2)(MeCN)]PF_6, (**IIa**) [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6, and (**IIb**) [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]Cl.

ATRP approach, has been published, but the polymerization was slow.[19] Additionally, to achieve the controllable conditions, a large excess of the reducing agent was used, and the polymerization proceeded at high $CuBr_2$ concentration.[19,20] Statistical copolymers of HEMA with another hydrophilic monomer, (dimethylamino)ethylmethacrylate (DMAEMA), has been obtained via ATRP in different aprotic polar solvents, at 45 °C, using similar halide initiator Cu-based catalyst systems.[21,22] Better results were obtained in DMF and DMSO. On the other hand, high-yield synthesis of near-monodisperse homopolymer and block copolymer of HEMA has also been reported at ambient temperature in MeOH and MeOH–water mixtures with CuBr/bpy catalyst and a hydrophilic bromide initiator, but very high catalyst concentrations were necessary.[23,24] Some other hydroxyl-functionalized methacrylates have also been polymerized controllably with copper catalysts in MeOH–water mixtures.[25] In all cases, the polymerizations in aqueous media were faster, but less controlled, than those in pure alcohol.[25,26] Fuji et al. reported living radical polymerization of HEMA catalyzed by three neutral (two hydrophobic and one hydrophilic) ruthenium(II) complexes containing chloride and phosphine ligands.[27] The polymerizations were carried out in MeOH at 80 °C with different alkylhalide initiators. Higher activity and controllability were observed in the polymerizations mediated by the hydrophilic complex because of its better solubility in the medium. The hydrophobic complexes were poorly soluble, and the polymerization induced by them proceeded under heterogeneous conditions. Recently, more effective homogeneous fine-controlled polymerization of HEMA mediated by another neutral tritolylphosphine ruthenium(II) complex, Cp*RuCl $[P(m\text{-Tol})_3]_2$, has been reported. The polymerization proceeded in ethanol at 40 °C at high rate in the presence of an aminoalcohol additive, which also permitted a notable reduction of the catalyst concentration.[15,28,29] Syntheses of stereospecific and yet stereogradient well-controlled PHEMA using a Cp*RuCl$[P(Ph)_3]_2$ catalyst in conjunction with an excess of *n*-Bu_3N additive have also been described.[30,31] The stereospecificity was induced by the appropriate choice of the solvent, such as, aprotic amide solvents, DMF or DMA, and fluoroalcohol, similarly to the effects seen in free radical polymerizations.

However, despite the obvious success of living radical polymerization of hydrophilic monomers by the ATRP approach, the number of catalytic systems that permit the controlled polymerization in protic, especially aqueous media, is still very limited. The copper-based catalysts suffered undesirable side reactions, such as disproportionation of Cu(I) activator and halide ligand substitution by solvent from Cu(II) deactivator,[26] that requires high content of the catalyst.

The ruthenium catalysts generally are more tolerant to both hydroxyl-functional group and the presence of water as a result of the low oxophilic nature of the ruthenium center.

During the past 10 years, easy and efficient synthesis of cyclometalated ruthenium(II) complexes has been developed by our group.[32,33] Some of the complexes have been successfully applied to controlled/living radical polymerizations of traditional hydrophobic monomers, such as styrene and acrylates.[34,35] The complexes are cationic and do not contain chloride or phosphine ligands as the grand majority of the ruthenium catalysts so far used in ATRP. Most of our complexes are extremely stable in air, especially in the solid state, and may be stored and used in a reaction without any precaution. The ionic nature of the complexes may be advantageous in many aspects. First, as has been shown by a comparison of neutral and cationic Ru(II) complexes of similar structures, the ionic complexes are much more active catalysts in ATRP of hydrophobic monomers.[36,37] Second, because of their ionic character these complexes are reasonably soluble in protic solvents, and this represents a considerable advantage for the polymerization of hydrophilic monomers such as HEMA. Moreover, the effect of the counterion and its role on the polymerization processes has attracted very little attention, particularly for the ruthenium-based catalysts. Although a simple anion exchange may significantly modify some of the complex's properties, such as its solubility. This study deals with the direct homopolymerization of HEMA mediated by two cationic cyclometalated ruthenium complexes differing only by anions, [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6 and [Ru(*o*-C_6H_4-2-py)(phen) $(MeCN)_2$]Cl (see Fig. 1 for the structure), under mild conditions. Kinetic features of the polymerization and the catalytic behavior of the complexes in different solvents, acetone, methanol, methanol–water mixtures, and pure water, have been investigated. It has been shown that counterion has very strong effect on activity of the catalyst and controllability of the polymerizations in both protic and aprotic media. The effect depends on solvent.

To the best of our knowledge, this is the first example of homogeneous radical polymerization mediated by ruthenium(II) catalysts carried out in water.

RESULTS AND DISCUSSION

Effect of the Catalyst Structure

Initially, we tried to polymerize HEMA using another ruthenium(II) compound incorporating σ-bound *N*,*N*-dimethylbenzylamino (dmba) ligand, [Ru(η^6-C_6H_6)(C_6H_5-*o*-CH_2NMe_2)(MeCN)]PF_6 (**I** in Fig. 1), which synthesis required one step less than the mentioned above [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6 catalyst (**IIa** in Fig. 1).[32,33] The complexes are 18 electron coordinatively saturated compounds, bearing both strongly bound (dmba, phpy, and phen) and more labile (benzene and MeCN) ligands. It was shown that both catalysts could mediate radical polymerizations of methyl methacrylate (MMA) with a moderate level of control, but **I** was more active and able to polymerize MMA at 50–60 °C, whereas the polymerizations catalyzed by **IIa** proceeded at 80 °C but were better controlled.[38,39] The higher activity of **I** could be explained by the fact that the benzene ring is very labile and as such can easily generate three active vacant sites in the coordination sphere, whereas in complex **IIa**, the two acetonitrile molecules are more strongly bound to the ruthenium making the ligand exchange reactions more difficult.[32] The **IIa** compound is more resistant to oxidation; it is very stable in air in the solid state and in organic solutions. Because of their ionic character, the complexes are well soluble in polar solvents such as ketones, alcohols, and HEMA, and homogeneous reaction conditions were reached at ambient temperature.

Preliminary experiments in the bulk at 50 °C with catalyst **I** showed that the polymerization of HEMA was very fast (~90% conversion in 6 h) but poorly controlled, and a high-molecular-weight ($M_{n,GPC} \approx 17{,}500$) polymer of broad polydispersity (PDI ≈ 2.3) was obtained even at low conversions. The molecular weights grew slightly with the reaction time reaching ~22,000 at 46% but did not change further and PDIs always remained above 2. The polymerization in MeOH mediated by the same catalyst **I** did not show any improvement in the control and was somewhat slower. Our attempts to improve the control by reducing the reaction temperature did not give positive results: no polymerization was detected at 40 °C.

The catalyst **IIa** did not demonstrate any activity at 40 °C either. Bulk polymerization at 50 °C with this catalyst was slower (~60% conversion in 6 h) compared to that with **I** and also resulted in a polydisperse product of about 22,000 molecular weight. However, the polymerizations with **IIa** carried out in MeOH and acetone solutions at the same temperature were much more successful. Both polymerizations were fast, proceeded to high conversions, and higher molecular weight polymers were obtained at the end ($M_{n,GPC}$ = 36,800 at 82% in MeOH and 43,800 at 87% in acetone). Semilogarithmic kinetic plots for these reactions depicted in Figure 2 show quite linear tendency in both solvents, but some acceleration was observed in the acetone polymerization after 4 h of reaction when a conversion of 60% was achieved. At lower conversion, the reaction rates were almost equal.

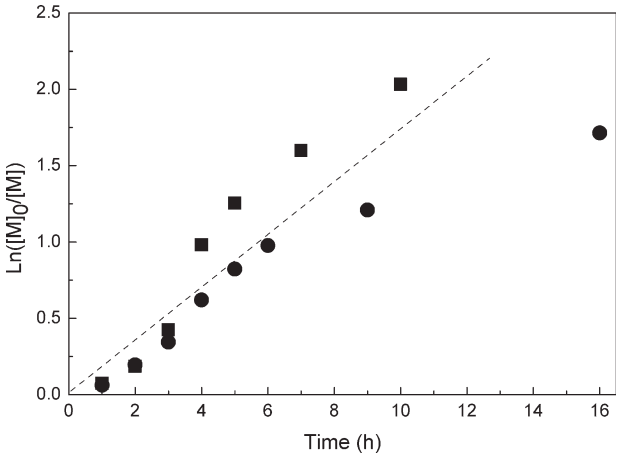

FIGURE 2 Kinetic plots of polymerizations of HEMA catalyzed by **IIa** at 50 °C in methanol (●) and acetone (■) with the initial molar ratio of $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/1$.

Acetone is a poor solvent for PHEMA, but at low conversions the polymer was completely soluble because of the high content of the monomer in the system. Additionally, as it will be shown below, the polymer obtained at low conversions had relatively low molecular weights that also favored its solubility. When the polymerization progressed and reached around 60% of conversion, the system converted into a jelly-like homogeneous mass, which was getting denser with further increase in the conversion. The acceleration detected in acetone is referred to so-called gel effect, which is observed in highly viscous media for free radical polymerizations because of the impediment of the termination process.[40] The high viscosity may be resulted from elevated concentration of a high-molecular-weight polymer or use of bad solvents.[41,42] The strength of this gel effect, and therefore the conditions under which it is observed, depends on the monomer. The polymerization of HEMA was characterized by a strong gel effect at monomer concentrations of above 1 M.[43–45] This kind of effects should not be observed for ideal "living" polymerization because all the polymer terminals should be capped and thus no termination should occur. On the other hand, even in the successful examples of living radical polymerizations, it is not possible to avoid completely the termination and about 5–10% termination reactions are normally present.[46] The acceleration observed in the acetone polymerization of HEMA mediated by **IIa** was very insignificant compared to the effects reported for the free radical processes.[43–45] The corresponding molecular weight data versus conversion for the methanol and acetone polymerizations are shown in Figure 3. As can be seen from the figure, development of the molecular weights with the conversion was very similar in both solvents, and the molecular weights increased linearly with conversion. The molecular weights obtained in acetone polymerization at high conversions were

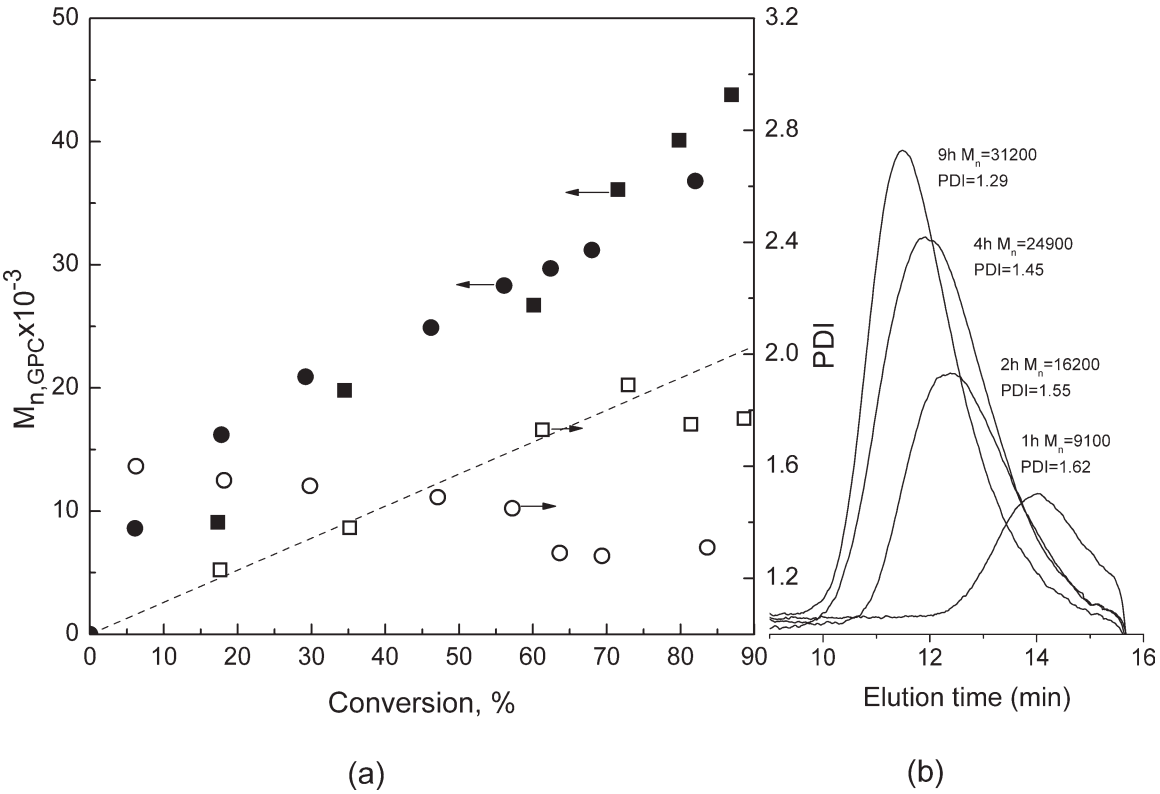

FIGURE 3 (a) Experimental and theoretical (---) molecular weight data for polymerizations of HEMA catalyzed by **IIa** at 50 °C with the initial molar ratio of $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/1$ in methanol (●—$M_{n,GPC}$ and ○—PDI) and in acetone (■—$M_{n,GPC}$ and □—PDI). (b) GPC traces of the PHEMA synthesized in methanol.

higher, but the difference was negligible. Thus, we believe that the polymerization, to a great extent, proceeded in the living fashion and the polymer terminals were appropriately capped according to the established mechanism.[9,10,14] The NMR analysis of the synthesized polymer and the extension chain experiments confirmed the hypothesis (see below).

Polydispersities behaved differently in acetone and MeOH polymerizations. In acetone, PDIs were low initially and increased gradually with the conversion, whereas in MeOH, PDIs progressed as normally observed in ATRP, that is, narrowed with the conversion, and PHEMA of fairly narrow PDI (1.27 at 62% conversion) was obtained. Further experiments for more detailed investigation of the process were then carried out in MeOH. Radical mechanism of the polymerizations was confirmed using TEMPO as radical scavenger in MeOH and water reactions. It is worth noting that the polymerization did not proceed in the presence of the catalyst without addition of the initiator.

Effect of the Catalyst and Initiator Concentrations

PHEMA of different molecular weights were obtained by varying the concentrations of the catalyst and initiator. As expected, the polymerization was faster with increase of the initiator concentration (Fig. 4), and a twofold multiplication in the initiator concentration resulted in ~90% conversion in only 4 h.

The molecular weights grew with the conversion at this concentration of initiator in a similar way as observed for the lower initiator concentration, whereas the PDIs were slightly broader at moderate conversions and achieved the highest value of 1.76 at a conversion of 90% (Fig. 5). Twofold decrease in the catalyst concentration to monomer/catalyst

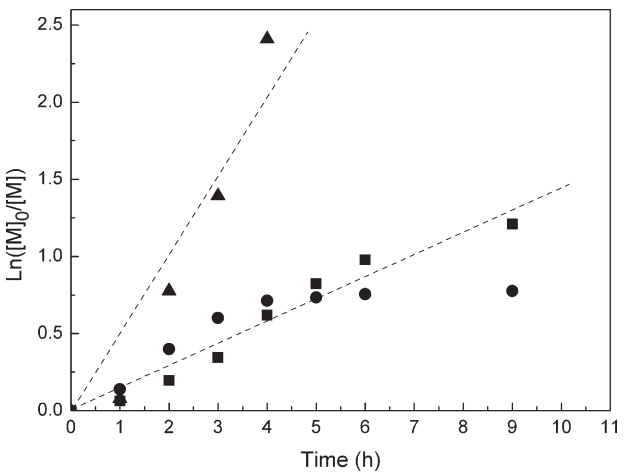

FIGURE 4 Kinetic plots of polymerizations of HEMA catalyzed by **IIa** at 50 °C in methanol with various concentrations of the catalyst and initiator: (■) polymerization using the initial molar ratio of $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/1$; (●) polymerizations with $([HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.5/1)$; and (▲) $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/2$.

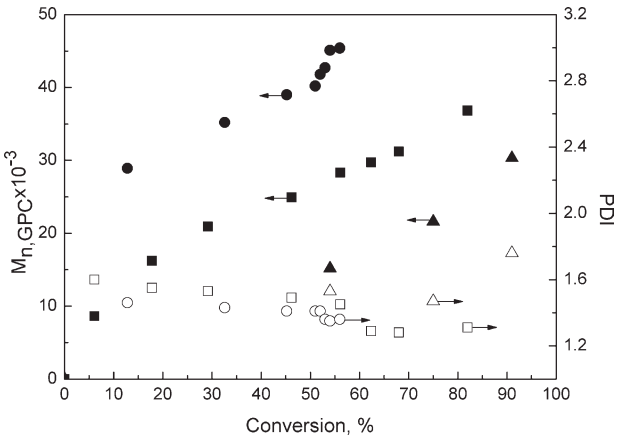

FIGURE 5 Evolution of the molecular weights and PDIs with conversion at various concentrations of the catalyst and initiator. Initial molar ratio of $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/1$ (■—$M_{n,GPC}$ and □—PDI); $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.5/1$ (●—$M_{n,GPC}$ and ○—PDI); and $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/2$ (▲—$M_{n,GPC}$ and △—PDI).

ratio of 200/0.5 almost did not affect the polymerization rate at the beginning, but after 4 h the polymerization slowed down drastically and stopped at about 50% conversion (Fig. 4). Control was also worse in this case, even though the molecular weights still grew with conversion, the values were much higher than those obtained at 200/1 monomer/catalyst ratio, and the dependence was not linear. The PDIs demonstrated tendency of narrowing with the conversion but were also broader (see Fig. 5) than those obtained with the higher catalyst content.

Determination of Molecular Weight of PHEMA by ^{1}H NMR

The discrepancy between the molecular weight of PHEMA determined by GPC and the real values has been highlighted in various articles.[17,18,23,27] Significantly higher molecular weights given by GPC were attributed to difference in hydrodynamic volumes between PHEMA and hydrophobic PMMA or PSt calibration standards. In a similar way, the GPC molecular weights presented in this article are higher than the calculated values (see, e.g., Figs. 3 and 5), and thus the plots did not pass through the origin. To evaluate the real molecular weight of PHEMA synthesized here, two different approaches were used: analyses of the end group and composition of a block copolymer of PHEMA and PMMA.

To obtain well-separated α-end signals from the initiator, HEMA was polymerized in MeOH using 1-phenylethyl bromide (PEB) as an initiator. The polymerization was carried out under the same basic conditions reported for EB*i*B, that is, 50 °C, 50/50 v/v HEMA/MeOH, and $[HEMA]_0/[\mathbf{IIa}]_0/[PEB]_0 = 200/1/1$. The reaction was stopped after 2 h. Conversion achieved was 19%, similar to the conversion obtained with EB*i*B after the same reaction time (18%). The polymer containing catalyst and probably traces of the monomer was then dissolved in MeOH and passed twice through a silica column for better purification from the catalyst residue. The purified polymer was analyzed by GPC and ^{1}H NMR techniques. $M_{n,GPC} = 19{,}600$ and PDI = 1.61 were obtained, and ^{1}H NMR spectrum of this PHEMA is presented in Figure 6(a).

The spectrum revealed two broad peaks at about 7.2 and 7.8 ppm. Signals at those chemical shifts have been reported by different groups as α-end signals originating from the phenyl ring of PEB initiator.[47,48] These peaks were not detected in the spectrum of PHEMA synthesized with EB*i*B [Fig. 6(b)]. There are no signals in the aromatic region of the latter, indicating that practically all residual catalyst trapped in the polymer was absorbed by silica. The main signals of the catalyst lie between 8.0 and 8.3 ppm [see Fig. 6(c)], and this interval is clean in the spectrum of the PEB-initiated PHEMA. Taking into account all the above, we believe that the aromatic resonances observed in the PEB-initiated PHEMA belong to the initiator incorporated at the α-end. Rough estimation based on the integration of these two signals (five protons) and monomer units of the polymer gave a molar ratio of HEMA to PEB as (85–88)/1, which corresponds to molecular weights in the range of 11,100–11,400. Thus, the molecular weight obtained by end-group analysis was about 70% lower than the molecular weight obtained from the GPC data. The result coincides with the deviations given in the literature.[18,27]

Synthesis of the PMMA-*b*-PHEMA Copolymer

An effort to estimate the real molecular weight of the PHEMA was also performed analyzing a block copolymer of MMA and HEMA. As mentioned above, the catalyst **IIa** was able to mediate "living" radical polymerization of MMA.[38] The polymerization proceeded at 80 °C in toluene solution using EB*i*B initiator with satisfactory level of control. The molecular weights were close to the calculated values and grew linearly with conversion but were slightly higher than the calculated values, and PDIs were also not as narrow as those in the processes described earlier.[48–52] Some data of this polymerization are summarized in Table 1.

A PMMA of $M_n = 6500$ and PDI = 1.30 (GPC, DMF eluent) prepared according to this protocol was used as a macroinitiator in the subsequent polymerization of HEMA carried out at 50 °C in acetone solution as PMMA is not soluble in MeOH. A viscous solution was already obtained after 2 h, and the polymerization was stopped after 6 h when the system converted into a gel. At this point, the conversion of HEMA was determined to be equal to 68%, and the resulting copolymer was characterized by GPC and ^{1}H NMR. The characteristic signals for both blocks of PMMA and PHEMA are clearly seen in the ^{1}H NMR spectrum of the copolymer (Fig. 7).

The GPC traces presented in Figure 8 demonstrate important increase in the molecular weight to ~32,800, indicating efficient formation of the copolymer. The values of the molecular weights achieved are close to the molecular weights of the HEMA homopolymer obtained at a similar conversion in acetone (Fig. 3). However, the GPC curve of the copolymer is much broader because the macroinitiator applied is not

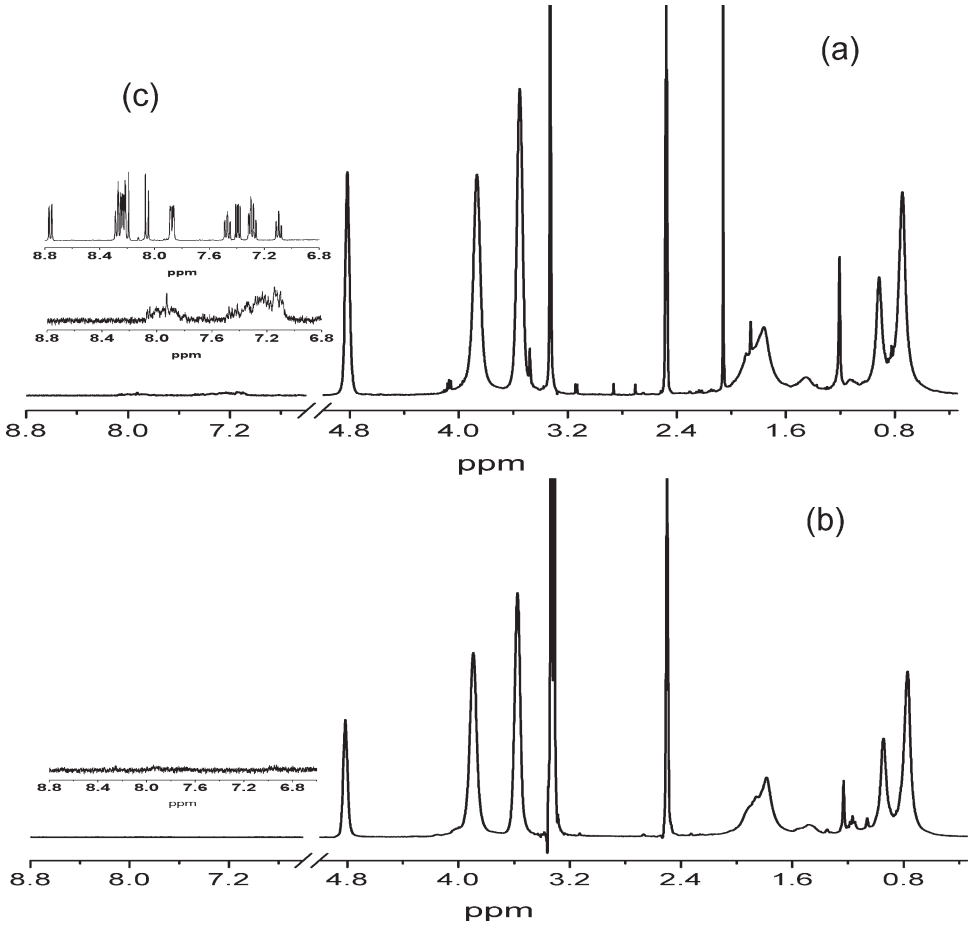

FIGURE 6 (a) ^{1}H NMR spectrum of PHEMA in d_6-DMSO obtained in the system $[HEMA]_0/[\mathbf{IIa}]_0/[PEB]_0 = 200/1/1$ in methanol at 50 °C (The peak at 2.09 ppm in (a) corresponds to acetone residual peak). (b) ^{1}H NMR spectrum of PHEMA in d_6-DMSO obtained in the system $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/1/1$ in methanol at 50 °C. (c) ^{1}H NMR spectrum of **IIa**.

monodisperse and not symmetrical because of the percentage of dead chains in the PMMA initiator.

The molar composition of the copolymer was estimated from the ^{1}H NMR spectrum by the integration ratio of the signal at 3.65 ppm from —CH_3 of PMMA and the signal at 4.04 ppm from —CH_2— of PHEMA (c and e in Fig. 7) to be 33% PMMA and 67% PHEMA. Supposing that the molecular weight of the PMMA block obtained by GPC is absolute, as GPC was calibrated by PMMA standards, the molecular weight of the PHEMA block was evaluated as 17,100 and the sum gives 23,600 for the PMMA-*b*-PHEMA. Thus, once again the molecular weight evaluated by ^{1}H NMR was lower than the one from GPC, and the difference coincided satisfactorily with that obtained from the terminal group analysis. However, even with this correction, the molecular weights obtained with **IIa** were still higher than the calculated values assuming a 100% efficiency of the initiator. In fact, the efficiency of the initiator turned out to be lower, about 60%, as will be discussed below (see section Effect of the Counterion), and this last adjustment gave a satisfactory coincidence between the real molecular weights and the values obtained from the GPC.

Effect of Water on the Polymerization Catalyzed by IIa

Catalyst **IIa** is not soluble in water but demonstrated reasonable solubility in water/MeOH and water/HEMA mixtures that permitted to carry out the polymerization in aqueous media under homogeneous conditions. The polymerization in water/HEMA at 50 °C using the usual 200/1/1 initial

TABLE 1 Polymerizations of MMA in Toluene at 80 °C

Time (h)	Conv. (%)	$M_{n,GPC} \times 10^{-3}$ (g/mol)	$M_{n,th} \times 10^{-3}$ (g/mol)	PDI
1.5	25	6.5	5.0	1.30
3	52	10.6	8.3	1.22

$[MMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200:1:1$.

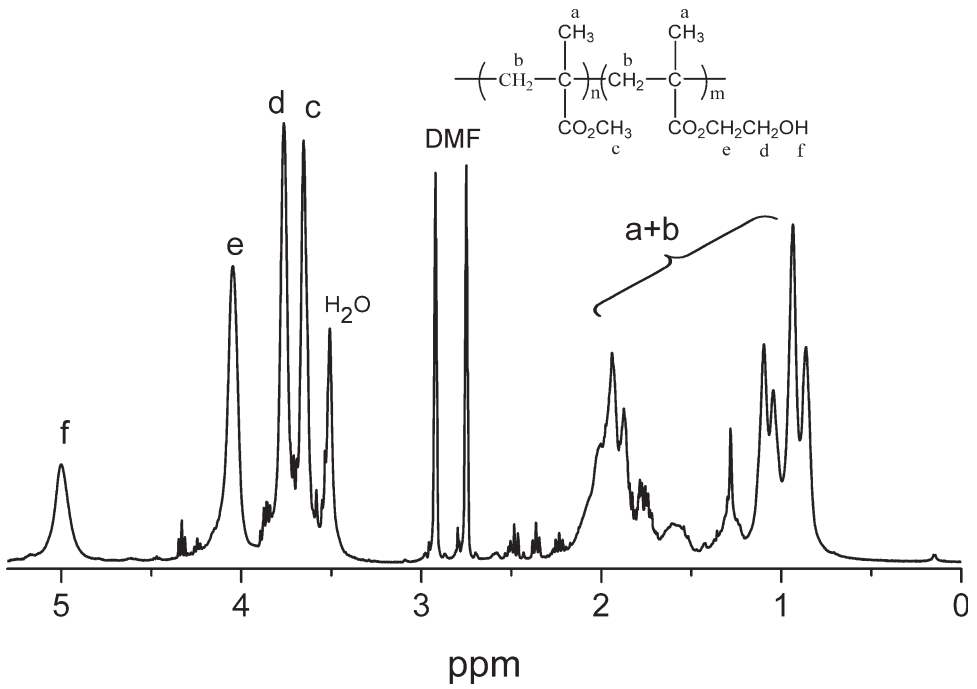

FIGURE 7 ^{1}H NMR spectrum of PMMA-*b*-PHEMA in d_7-DMF.

reagent ratio was very fast: the system was completely polymerized within 30–40 min. Decrease of the temperature to 40 °C slowed down the polymerization, and a conversion of 94% was obtained in 2 h. The polymer was characterized by high molecular weights and broad PDI (see Table 2), but was completely soluble in DMF at room temperature in contrast to PHEMA obtained in pure aqueous media with a copper catalyst,[23] showing that the polymer synthesized was essentially lineal with minimum crosslinking. Further decrease of the temperature to 30 and 35 °C did not result in the polymerization. Thus, 40 °C was the minimum temperature to polymerize HEMA in aqueous media. The results of the polymerizations in MeOH/water mixtures of various compositions at 40 °C are shown in Table 2. It is worth to stress again that the polymerization did not proceed in pure MeOH at 40 °C. The polymerization was faster but worse controlled with increased amount of water in the reaction medium.

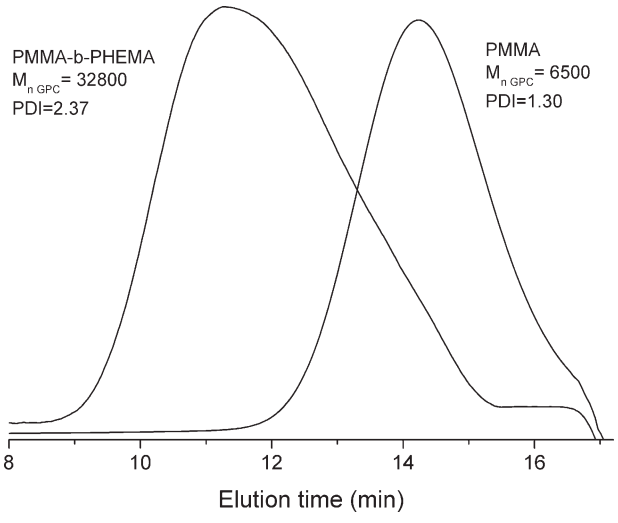

FIGURE 8 GPC traces of the PMMA-Br macroinitiator and PMMA-*b*-PHEMA.

The same tendency with respect to the water content was found for the ATRP of hydrophilic methacrylates catalyzed by copper-based complexes.[23,26,53] We did not find any reports on the application of ruthenium catalysts in water under homogeneous conditions, but influence of water on the ruthenium-catalyzed polymerization of hydrophobic monomers is rather controversial. Acceleration in the presence of water has been observed for the polymerization catalyzed by neutral ruthenium compounds,[54] but for polymerizations mediated by Schiff base cationic complexes the acceleration has not been always detected.[36,37] Depending on the ligands attached to the ruthenium center, the polymerization may be slower in the presence of water, but control was generally not affected or in some cases improved.

The high activity of **IIa** in water suggested a reduction of the catalyst content in the reactions. As the catalyst concentration was decreased twofold, the polymerization rate also decreased, and the plot of $\ln([M]_0/[M])$ versus time for this polymerization (Fig. 9) is linear.

The reduction in the reaction rate was accompanied by a diminution in the molecular weights, and the highest value of $M_{n,GPC} = 59{,}200$ was obtained at 80% conversion after 5 h of the polymerization. The evolution of the molecular weights and PDIs with conversion under these conditions is shown in Figure 10. Molecular weights were higher than

TABLE 2 Polymerizations of HEMA in Methanol, Water/Methanol Mixtures Containing Varying Amounts of Water at 40 °C

MeOH/H_2O (v/v)	Time (h)	Conv. (%)	$M_{n,GPC} \times 10^{-3}$ (g/mol)	$M_{n,th} \times 10^{-3}$ (g/mol)	PDI
100/0	24	–	–	–	–
85/15	6	24	17.5	6.2	1.88
50/50	6	69	44.9	18.0	1.93
15/85	3	83	71.6	21.6	2.09
0/100	2	94	110.0	25.7	2.00

$[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200:1:1$.

those obtained in MeOH, but noticeably demonstrated a tendency to grow with conversion, even if PDI values remained high. Thus, in water polymerization at 40 °C and the initial ratio of monomer/catalyst = 400/1, high conversion and certain level of control were achieved. Further reduction of the catalyst content to levels of $[HEMA]_0/[\mathbf{IIa}]_0$ of 1000/1 and 2000/1 led to limited conversions as the reaction stopped at ~50 and 30% yields, respectively (Fig. 9).

Effect of the Counterion

Complex **IIa** is soluble in organic protic solvents but is insoluble in water even at elevated temperatures. To investigate how the hydrophilic nature of the catalyst may affect the polymerization, several polymerizations mediated by complex **IIb** were carried out. This complex is structurally identical to the complex **IIa**, and the only difference between them is the counterion (see Fig. 1). Exchange of PF_6^- by Cl^- allowed to improve dramatically the solubility in water and at the same time did not affect other important properties such as the reduction potential and extinction coefficients. The important role of counterion for both copper and ruthenium catalysts in ATRP has been discussed in several publications, and it has been shown that counterion has a strong influence on the catalytic activity and on the control in the polymerization.[36,37,55,56] The effect depends on various factors, such as the polarity of the reaction medium or the nature of the ligands bound to the metal center. However, the information available on the nature of this phenomenon remains limited, particularly for ruthenium, as the grand majority of the complexes studied so far are neutral. Further studies are required to fully explain the effect observed.

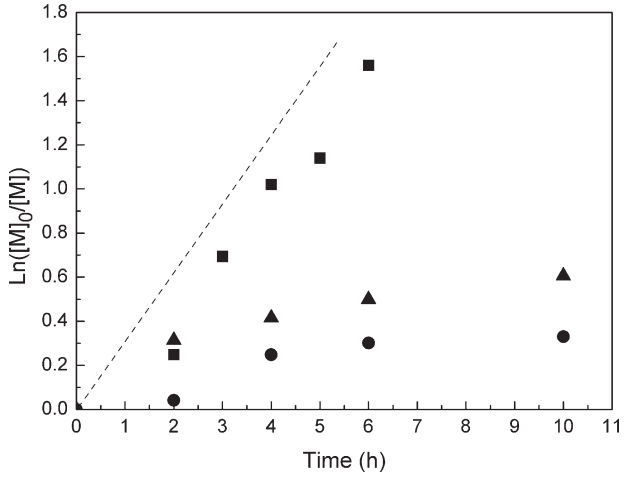

FIGURE 9 Kinetic plots of polymerizations of HEMA catalyzed by **IIa** at 40 °C in water with different concentrations of the catalyst: (■) polymerization with the initial molar ratio of $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.5/1$; (▲) polymerizations with $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.2/1$; and (●) $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0$=200/0.1/1.

Data of the HEMA polymerization in MeOH mediated by **IIb** are presented in Figures 11 and 12. The polymerization was carried out at 50 °C using initial ratio of HEMA/**IIb**/EB*i*B = 200/1/1, that is, under the same conditions as with **IIa**. The kinetic plot in Figure 11 shows that the polymerization is slower than when mediated by **IIa** (48% conversion in 6 h for **IIb** vs. 64% for **IIa**), and the polymer of about 35–40% lower molecular weights was obtained with the catalyst **IIb** if the same conversions were compared. Evolution of the molecular weights and PDIs with conversion is shown in Figure 12.

The dependence of the molecular weights on conversion was quite linear for this polymerization, and PDIs abruptly narrowed and were quite narrow at high conversions (below 1.3). Taking into account the difference between the real molecular weight and the molecular weight obtained by GPC, we may conclude that for **IIb**, the molecular weights of PHEMA coincided well with the estimated values, meaning there was a better controlled polymerization.

Surprisingly, the polymerization catalyzed by **IIb** was very fast in acetone; its semilogarithmic plot is also given in Figure 11. The polymerization rate in acetone with **IIb** was even faster than that mediated by **IIa** under similar conditions (72 vs. 60% in 4 h, respectively), but again PHEMA of lower molecular weight was obtained (see Fig. 12). Thus, although the difference in the polymerization rates was opposite in MeOH and acetone for the catalysts **IIa** and **IIb**, the tendency with respect to the molecular weights was maintained: lower molecular weight PHEMA was obtained with catalyst **IIb**.

Analysis of the initiator consumption during acetone polymerizations demonstrated that more than 90% of EB*i*B was consumed during first 30 min in the reaction mediated by **IIb** and only 60% in that mediated by **IIa**. Therefore, the

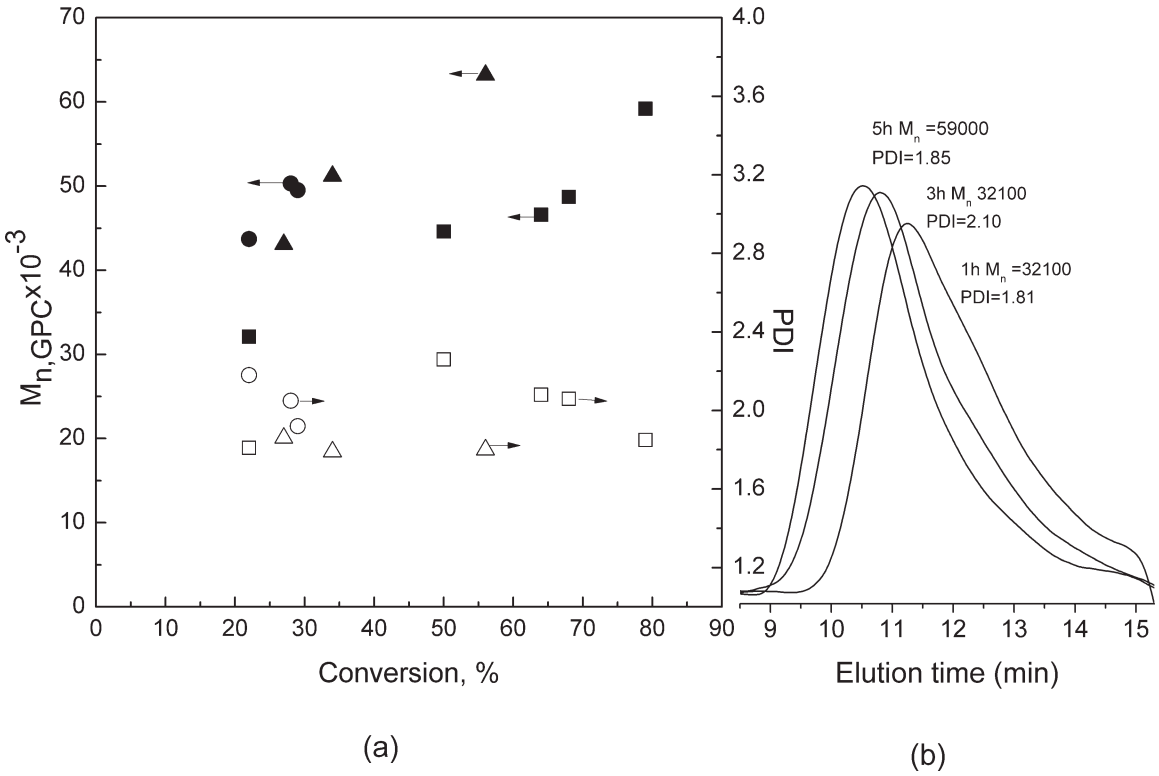

FIGURE 10 (a) Dependence of the M_n and PDI of PHEMA synthesized in water at 40 °C on conversion at different **IIa** concentrations. Polymers obtained in the mixtures with the initial molar ratio of $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.5/1$ (■—$M_{n,GPC}$ and □—PDI); $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.2/1$ (▲—$M_{n,GPC}$ and △—PDI); and $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.1/1$ (●—$M_{n,GPC}$ and ○—PDI). (b) GPC traces of the PHEMA obtained in $[HEMA]_0/[\mathbf{IIa}]_0/[EBiB]_0 = 200/0.5/1$.

higher molecular weight PHEMA synthesized with **IIa** may be explained by relatively low efficiency of the initiator in these polymerizations.

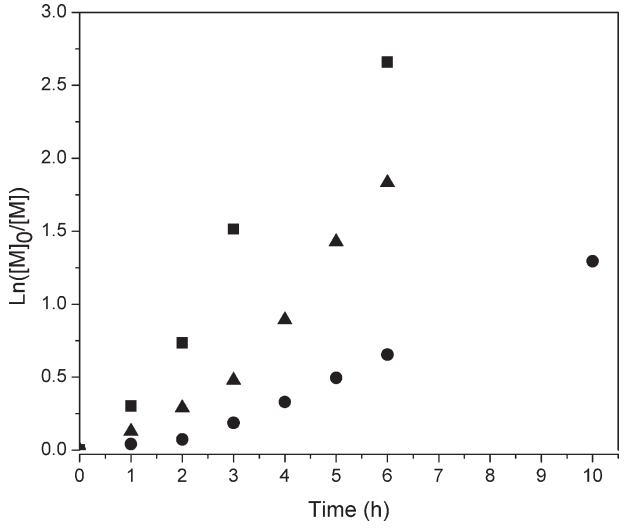

FIGURE 11 Kinetic plots of polymerizations of HEMA catalyzed by **IIb** at 50 °C in methanol (●) and acetone (■) with the initial molar ratio of $[HEMA]_0/[\mathbf{IIb}]_0/[EBiB]_0 = 200/1/1$ and water at 40 °C with the initial molar ratio of $[HEMA]_0/[\mathbf{IIb}]_0/[EBiB]_0 = 200/0.1/1$ (▲).

Chain Extension

The living nature of the polymerization was verified by the chain extension methodology. As evolution of the molecular weight characteristic against conversion is better for the polymerization catalyzed by **IIb** in methanol, this catalyst was chosen for synthesis of the macroinitiator. The chain extension experiments were performed by two different protocols: (1) with separation and purification of the PHEMA macroinitiator obtained in the first polymerization and (2) without the separation of the macroinitiator. In the first case, the macroinitiator as white powder-like substance was added to the next polymerization of HEMA in MeOH at $[HEMA]_0/[\text{macroinitiator}]_0/[\mathbf{IIa}]_0 = 200/1/1$ initial ratio. In the second case, the liquid volatile part from first synthesis (solvent and unreacted monomer) of the macroinitiator was evaporated in vacuum without heating, and new portion of HEMA and MeOH/water were added (for details, see Experimental part). Both second polymerizations proceeded successfully, but were much slower than those with EB*i*B; the yields were 39% at 12 h and 31% at 6 h in the MeOH and MeOH/water systems, respectively. The GPC traces of the PHEMA macroinitiators and the chain-extended polymers obtained by both ways are shown in Figure 13. As can be seen from the figure, the molecular weights increased very significantly in both experiments, and distributions were broader than those of macroinitiator as usually observed in chain extension and block copolymer synthesis.[57,58] The absence of significant

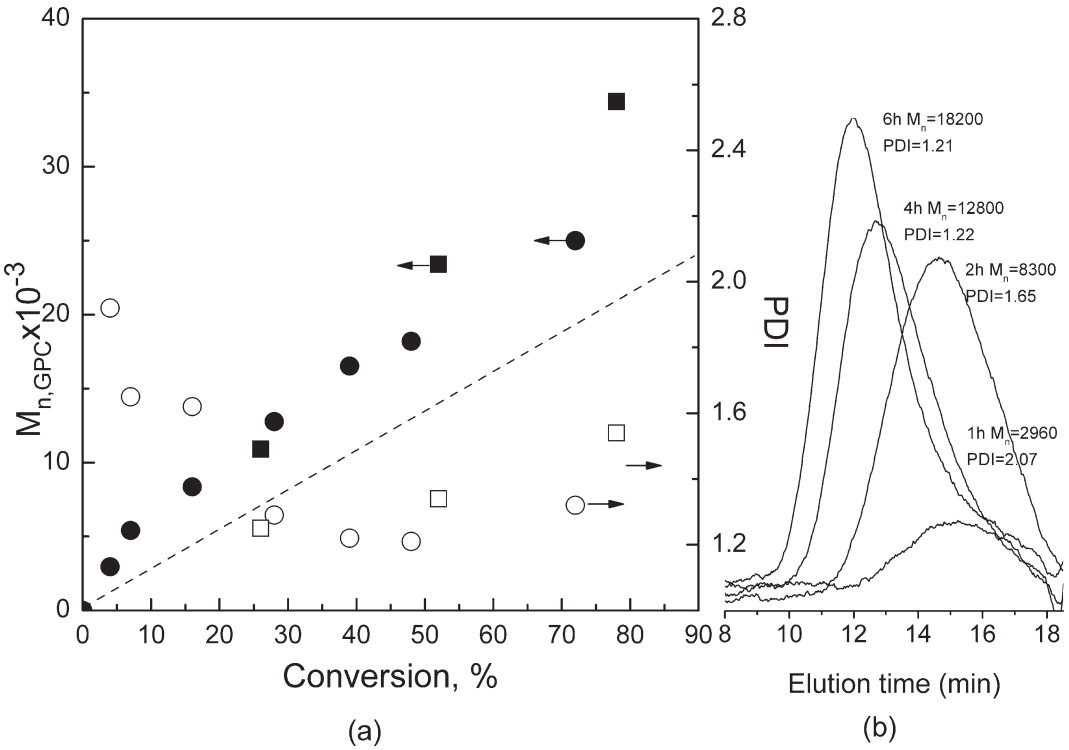

FIGURE 12 (a) Experimental and theoretical (---) molecular weight data for polymerizations of HEMA catalyzed by **IIb** at 50 °C with the initial molar ratio of $[HEMA]_0/[\mathbf{IIb}]_0/[EBiB]_0 = 200/1/1$ in methanol (●—$M_{n,GPC}$ and ○—PDI) and acetone (■—$M_{n,GPC}$ and □—PDI) (50/50 v/v). (b) GPC traces of PHEMA obtained in methanol.

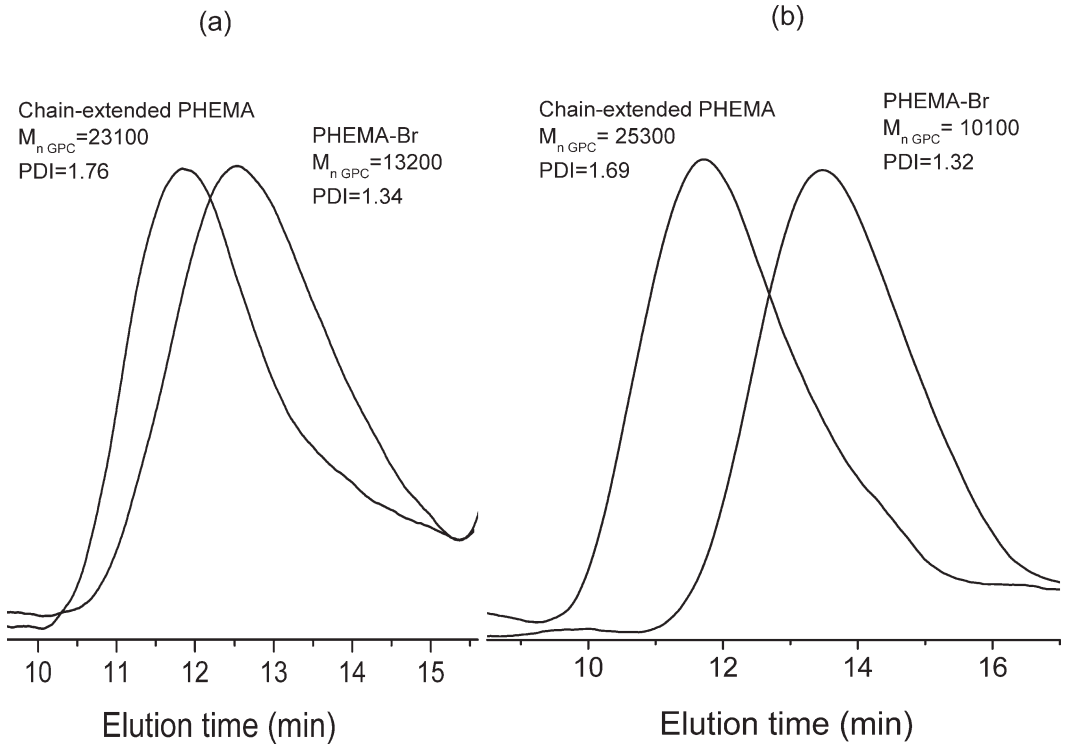

FIGURE 13 GPC curves of PHEMA-Br macroinitiator and its chain-extended polymer obtained with **IIb** complex at 50 °C (a) in methanol and (b) methanol/water mixture.

TABLE 3 Polymerizations of HEMA in Water at 40 °C at Different Initial Molar Ratios of $[HEMA]_0/[\mathbf{IIb}]_0/[EBiB]_0$

Initial Molar Ratio	Time (h)	Conv. (%)	$M_{n,GPC} \times 10^{-3}$ (g/mol)	$M_{n,th} \times 10^{-3}$ (g/mol)	PDI
200/1/1	3	87	56.4	22.6	1.86
200/0.5/1	1	36	70.1	9.6	2.06
	3	93	69.4	24.1	2.49
200/0.2/1	2	21	81.3	5.4	2.46
	6	95	82.9	24.7	2.10
200/0.1/1	2	25	107.6	6.5	2.66
	6	84	114.6	21.8	2.61

shoulder on the low-molecular-weight side of the GPC curves of the chain-extended polymers indicated that the chain-end functionality of the macroinitiator was relatively high.

Effect of Water on the Polymerization Catalyzed by IIb

Polymerization in water mediated by **IIb** carried out at 40 °C was also much faster than in methanol at 50 °C. The data for the polymerizations catalyzed by different amounts of **IIb** are shown in Table 3. As can be seen, the polymerization in water catalyzed by **IIb** at the 200/1/1 initial ratio was slower than the polymerization mediated by **IIa** under the same conditions but resulted in much lower molecular weight product. As the catalyst concentration was reduced, rate of the polymerization decreased and simultaneously the molecular weights increased. The polymerization with the lowest catalyst concentration ($[HEMA]_0/[\mathbf{IIb}]_0 = 2000/1$ in Table 3) afforded the polymer of the highest molecular weight (about 100,000).

However, in contrast to the polymerizations in water catalyzed by **IIa**, when the polymerizations did not proceed further than 50 and 30% at $[HEMA]_0/[\mathbf{IIa}]_0 = 1000/1$ and 2000/1 respectively, complex **IIb** was able to mediate the polymerization at very high conversions (compare Figs. 9 and 11). Semilogarithmic kinetic plot of the polymerization at the $[HEMA]_0/[\mathbf{IIb}]_0 = 2000/1$ remained linear until the highest conversion (Fig. 11), but the molecular weight characteristics were not controlled as no dependence of the molecular weights versus the conversion was observed.

Comparison of the Catalysts IIa and IIb

Thus, we can say that the nature of the counterion of the cyclometalated ruthenium(II) complex has a strong influence on the kinetics of the polymerization as complex **IIa** with PF_6^- mediated faster polymerization than **IIb** with Cl^- in both protic solvents, methanol and water, but the polymerization was slower in aprotic acetone. However, the control in methanol was better with **IIb** as the molecular weights were close to the calculated values and the PDIs were also narrower. A maximum activation rate constant, irrespectively of the polarity of solvents, has also been reported for ionic copper catalysts with PF_6^- anion comparing to the halide anions, but the effect diminished dramatically in water.[56] Our data for the ionic ruthenium complexes demonstrated on the contrary that the complex with PF_6^- was much more active in protic solvents and the effect maintained in water as well. However, the situation was vice versa in aprotic acetone where the complex **IIb** with Cl^- was more active. The polymerizations catalyzed by **IIa** also resulted in synthesis of higher molecular weight PHEMA in all solvents studied probably because of lower efficiency of initiation.

The polymerizations carried out in the presence of coordinating MeCN revealed strong inhibition of the process at 5 equiv of MeCN relatively to catalyst and complete suppression of the reaction at 10 equiv of MeCN in MeOH and water. The results were very similar for both **II** complexes indicating that a release of one ligand in order to create a vacant site in the coordination sphere is essential for the catalysis.

The catalyst behavior under the reaction conditions in different solvents was investigated by UV–vis analysis. Both catalysts **IIa** and **IIb** are very stable in solid state and may be stored in open air and in solutions at ambient temperature. However, under the polymerization conditions the catalysts are not as stable. The changes in UV–vis spectra of the reaction mixture in MeOH during the polymerization with the catalyst **IIa** are shown in Figure 14(a). It should be noted that the same changes were observed for the catalyst **IIb**.

Band of the original ruthenium(II) complex gradually decreased with time, and a new band with maximum at 390 nm, which could correspond to the absorption of a ruthenium(III) species, appeared.[33] Rough estimation showed that about 30% of the complex is converted into this species after 8 h, but the main band in the spectrum still belongs to the original complex. The data were confirmed by ^1H NMR in CD_3OD at 50 °C using *n*-decane as an internal standard. After 8 h, about 25% of the original complex has disappeared, but no new clear signals, except from free MeCN at 2.05 ppm and some undefined broad signals, are detected, indicating the possible formation of paramagnetic ruthenium(III) species. However, the spectral changes were not so substantial during polymerization in acetone. As can be seen from the Figure 14(b), the spectra in acetone before and after 8 h of polymerization are very similar. Thus, deviation from linearity of the kinetic plot for the polymerization in methanol at prolonged time of reaction may be caused by the loss of the catalyst.

Interestingly, both catalysts are quite stable under the water reaction conditions. The UV–vis spectra of the polymerization mixtures with catalysts **IIa** and **IIb** before and after 1.5 and

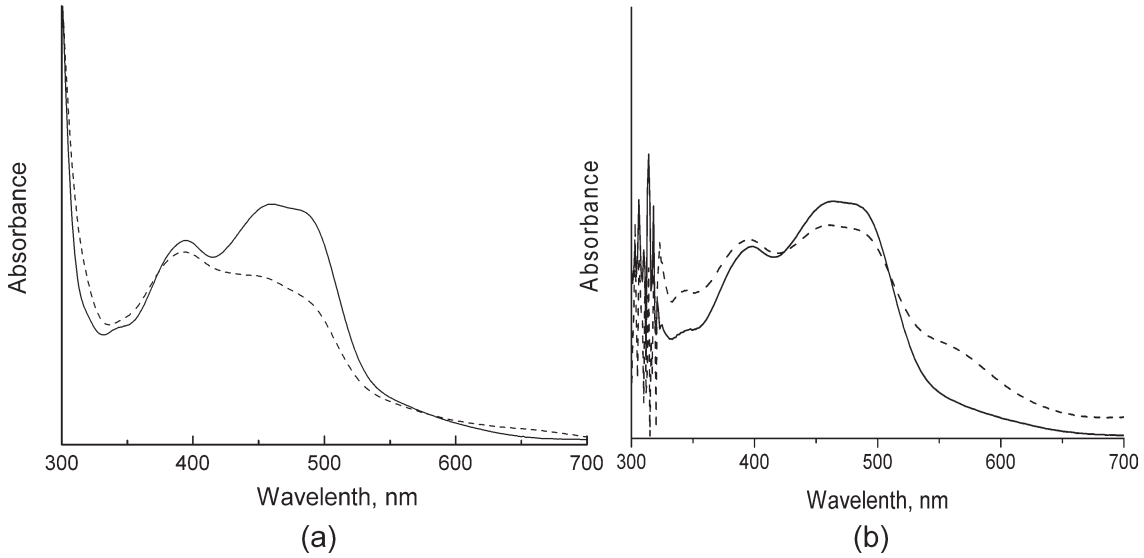

FIGURE 14 UV–vis spectra of the polymerization mixtures ($[HEMA]_0/[\mathbf{IIb}]_0/[EBiB]_0 = 200/1/1$) in methanol (a) and acetone (b) at 50°C: solid line—initial spectra; dashed line—after 8 h of the reaction.

3 h the reaction correspondingly, that is, when the polymerizations were practically completed, are presented in Figure 15 as solid and dotted lines. The spectra of the polymerized jelly-like systems were of poor quality. To improve the quality of the spectra, the polymerized samples were dissolved in MeOH (dot-lined spectra in Fig. 15). As can be seen from the figure spectrum of the "after polymerization" mixtures closely resembled the spectrum of the original catalyst. Thus, both complexes demonstrated quite high stability under conditions of water polymerization, but the comparison was not absolutely correct because of different reaction times (1.5 h for **IIa** and 3 h for **IIb**). Extended storage of **IIa** during further 3 h under these conditions revealed spectral changes very similar to those observed in MeOH. Such higher stability of **IIb** in water solution permits to explain why this catalyst was able to mediate the polymerization until high conversions even when used in low concentrations.

Our attempts to study the stability of the pure complexes in degassed deuterated solvents, such as methanol, acetone and water, at polymerization temperatures by ^{1}H NMR spectroscopy illustrated that the changes observed were quite slow in comparison with the polymerization rates and difficult to interpret. In all the studies, the signals from the original complexes remained the principal ones, some new signals which appeared in the aromatic area were of low intensities. Additionally, the appearance of free MeCN and formation of

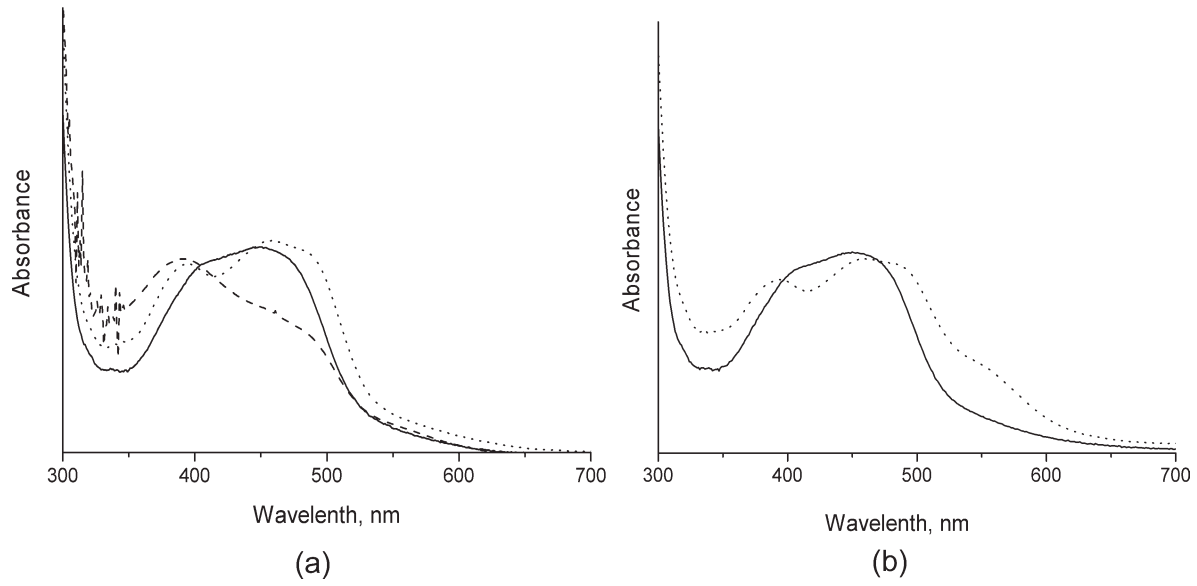

FIGURE 15 UV–vis spectra of the polymerization mixtures in water ($[HEMA]_0/[\mathbf{II}]_0/[EBiB]_0 = 200/1/1$) with **IIa** complex (a) and with **IIb** (b) at 40 °C: solid line—initial spectra; dotted line—after 1.5 h with **IIa** and 3 h with **IIb**; dashed-dotted line—after 3 h with **IIa**.

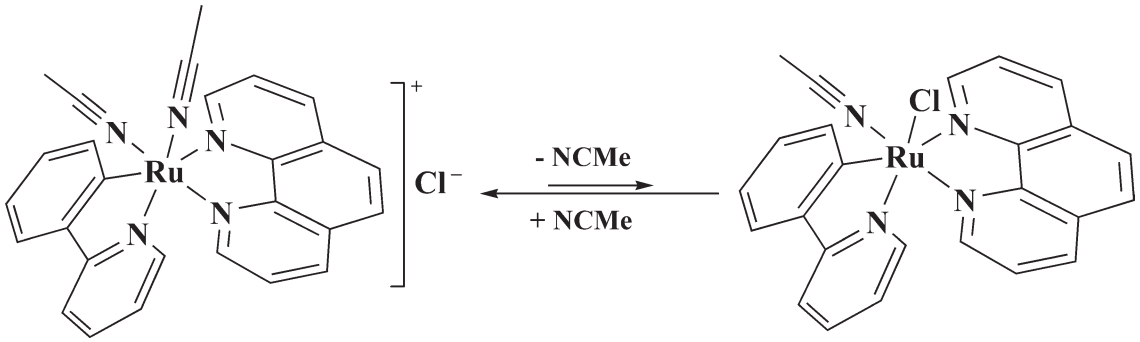

FIGURE 16 Rearrangement proposed for complex **Ib**.

possible ruthenium(III) species were also always detected. The loss of the original complex due to the probable oxidation in acetone and water was slower than in methanol.

Mechanistic Approach

As the complexes **II** are coordinatively saturated, in order to be active in ATRP they should lose one of the ligands, either MeCN or one of the bidentate, phen or phpy, ligands. The importance of release of the ligand was confirmed by the experiments with an excess of coordinative MeCN. As acetonitrile is a more labile ligand, the logical route involves its liberation. Moreover, free MeCN in the system was detected by ^{1}H NMR. Substitution of acetonitrile by methanol in **IIa** has been reported to lead to an abrupt decrease of the reduction potential.[33] Therefore, the complex should become more active in ATRP but also much more sensitive to oxidative destruction; this indeed was observed during the polymerizations in MeOH. It would be logical to propose a similar scheme for polymerization in acetone or water with the substitution of acetonitrile by acetone or water molecules. However, we could not exclude participation of the bidentate ligands, as similar complexes, but bearing only the bidentate ligands, can be very active ATRP catalysts.[35]

Furthermore, the influence of the anion moiety on the catalytic behavior of the complexes detected in this study was very strong and complicated and could not be explained in terms of simple dissociation. We assume that the complex **IIb** with Cl^- may undergo ligand rearrangement, and the two forms, cationic and neutral, exist in equilibrium as can been seen in Figure 16.

The rearrangement of this kind involving the chloride ligand has been observed for ruthenium (II) complexes.[59] We propose that the equilibrium shown in the scheme strongly shifts to the ionic form because the neutral form was not detected by traditional methods, but the shift may be altered depending on the solvent. The neutral form may exist in higher concentrations in less polar solvents and also participate in the catalysis. This rearrangement could not be achieved in **IIa** bearing PF_6^- anion, and this explains the unusual difference between the complexes. The hypothesis was indirectly confirmed by polymerization kinetics carried out in the presence of NaCl (1.5 equiv relatively to the catalyst). The polymerizations mediated by **IIa** were not practically affected by NaCl in all solvents investigated. They were slightly slower but the effect was negligible. The effect of the presence of NaCl on the polymerizations catalyzed by **IIb** in MeOH and water was also insignificant in terms of the rate and controllability, but the polymerization in acetone was almost two times slower. Addition of a salt increases static dielectric constant (ε) of the solvent[60] that should lead to a better dissociation of the ionic complexes. Complex **IIb** exists predominantly in the form of free ions in more polar MeOH and water, but in less polar acetone a proportion of ion pairs is relatively higher. The addition of NaCl decreased the concentration of the ion pairs and thus impeded the proposed rearrangement, and the polymerization rate became similar to that in MeOH.

However, we do not have enough experimental evidence to categorically demonstrate this mechanism, and further studies on the effect of the counterion with complexes bearing only strongly bound bidentate phen or bpy ligands are in the process in our group, and hopefully these will provide more insight into the influence of the counterion.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA, Aldrich 98%) was purified by passing through a column filled with basic alumina to remove the inhibitor. Ethyl 2-bromoisobutyrate (EB*i*B) 98%, 1-phenylethyl bromide (PEB) 97%, methanol (99.8%), deuterated dimethyl sulfoxide (DMSO-d_6), and methanol (CD_3OD) were used as received from Aldrich. Amberlite IRA-400(Cl) ion exchange resin was also purchased from Aldrich. Water (J.T. Baker) was previously degassed by three freeze-pump-thaw cycles and filled with argon before use.

Amberlite Activation

Each Amberlite column for the anion exchange was prepared as follows: commercial Amberlite (50 g) was washed twice with MeOH, decanted, and poured into a chromatography column. Then, it was washed with water, 5 M aqueous NaCl, water, 1 M aqueous HCl, three times with water, and twice with MeOH (200 mL for each wash).[61]

Synthesis of the Ruthenium Complexes

The complexes $[Ru(o\text{-}C_6H_4\text{-}2\text{-}py)(phen)(MeCN)_2]PF_6$ and $[Ru(\eta^6\text{-}C_6H_6)(C_6H_5\text{-}o\text{-}CH_2NMe_2)(MeCN)]PF_6$ were prepared according to the literature.[32,33] The catalyst with chloride

anion, [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]Cl, was prepared by the ion exchange reaction as described below: [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6 (100 mg, 0.15 mmol) was deposited on the Amberlite previously activated by 4 mL of acetone and eluted with MeOH. The fractions collected (10 fractions, 20 mL each) were evaporated to dryness, and the residue was analyzed by ^{1}H NMR, ^{31}P NMR, IR, and MS. Fractions 1–7 contained the pure desired complex. The [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]Cl complex had the same characteristic signals in ^{1}H NMR spectrum as its precursor: (CD_3CN) 9.70 (dd, 1H), 8.71 (dd, 1H), 8.28 (dd, 1H), 8.22–8.13 (m, 3H), 8.16 (d, 1H), 8.02 (d, 1H), 7.85 (td, 2H), 7.46 (td, 1H), 7.36–7.32 (m, 2H), 7.27 (dd, 1H), 7.10 (td, 1H), 6.57 (td, 1H), 2.28 (s, 3H, $NCCH_3$), 2.06 (s, 3H, $NCCH_3$). Therefore, all 16 aromatic protons and two acetonitrile ligands are present in the spectrum. Additionally, no PF_6^- signals at 143 ppm in ^{31}P NMR and at 834 cm^{-1} in IR were detected. MS: 518 $[(M+H)\text{-}Cl]^+$ (14%), 477 $[(M^+ + H)\text{-}(MeCN+Cl)]^+$ (22%), and 436 $[(M+H)\text{-}(2MeCN+Cl)]^+$ (86%). All these analyses confirmed the ionic structure of the complex. In contrast to the precursor, [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]Cl was well soluble in water.

ATRP Synthesis

Homopolymerizations were conducted in solutions (HEMA/solvent = 50/50 v/v) using the Schlenk technique. In a typical experiment, [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6 (20 mg, 0.030 mmol) was added to a 25-mL Schlenk tube and degassed twice using pump-nitrogen cycles. Then, the reaction tube was filled with the solvent (0.727 mL of acetone, methanol, or methanol–water mixtures) and (0.727 mL, 6 mmol) of the monomer, which had been previously deoxygenated in dry nitrogen for 30 min. The reaction tube was filled with nitrogen, and the initiator (EB*i*B, 4.42 μL, 0.030 mmol) was introduced via a syringe. When the polymerizations were carried out in water, the order of the addition was slightly changed: the degassed catalyst [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6 was first dissolved in HEMA, and then the water was added using a degassed syringe. A homogeneous solution was formed immediately at room temperature, and the reaction tube was immersed in an oil bath preheated at the desired temperature. The polymerizations in acetone and MeOH were carried out at 50 °C and in water at 40 °C. In the majority of the experiments, the initial molar ratio of $[monomer]_0/[catalyst]_0/[initiator]_0$ = 200/1/1 was held, but in several cases different molar ratios were used. The samples were removed from the flask after certain time intervals using a degassed syringe. The conversions were determined gravimetrically, and the current monomer concentration, [M], was determined by subtraction of the amount of the polymer from the initial monomer. Several conversions in acetone were also determined by GC with *n*-decane as an internal standard by a disappearance of the monomer peak. GC results coincide well with those obtained gravimetrically. In the grand majority of the kinetic measurements, the polymer samples were dissolved in DMF and injected in the GPC equipment without purification from the catalyst although in several cases the purified samples were analyzed. Purification was achieved by passing the samples dissolved in methanol through a silica column (ø = 17 mm; *h* = 30 mm) to remove the catalyst. No difference in molecular weights and molecular weight distributions between purified and nonpurified polymer samples was detected. All kinetic measurements were repeated in triplicates.

Chain Extension Experiments

These were conducted under identical conditions to the homopolymerizations, that is, in solution HEMA/solvent = 50/50 v/v, in MeOH and MeOH/water (80/20 v/v) mixture using as a macroinitiator PHEMA previously synthesized with [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]Cl catalyst and EB*i*B initiator at 200/1/1 initial molar ratio in MeOH at 50 °C within 20–25% of conversion. The following protocol was held for the chain extension in MeOH: the PHEMA from the first polymerization was purified passing through a silica column and then dried in vacuum to remove the residual monomer and solvent. The resulting white powder-like polymer of $M_{n,GPC}$ = 13,200 and M_w/M_n = 1.31 was applied as a macroinitiator for the next polymerization of HEMA. The complex [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6 (25 mg, 0.038 mmol) and the macroinitiator (200 mg, 0.038 mmol) previously degassed were dissolved in degassed methanol (0.922 mL) with continuous stirring for ~30 min before addition of HEMA (0.922 mL, 7.7 mmol). The polymerization was conducted at 50 °C for 12 h and then stopped by cooling.

The chain extension experiment in the MeOH/water mixture was carried out in a different way without purification of the PHEMA macroinitiator, as described below. The first polymerization was also stopped after 3 h, and the sample was taken by syringe in order to determine the conversion and characterize the polymer (19% conversion, PHEMA of $M_{n,GPC}$ = 10,200 and PDI = 1.32). The Schlenk flask was connected to high vacuum system, and the liquid part of the reaction was evaporated. Then, the Schlenk tube was purged with nitrogen, and degassed MeOH was added (0.4 mL). The system was kept for 20–30 min at room temperature under stirring until complete homogenization. Then, the monomer (0.5 mL) and water (0.1 mL) were added, and the flask was merged into 50 °C oil bath for another 6 h. The polymers synthesized were purified using the same protocol as that described above for the homopolymerization.

Synthesis of PMMA-*b*-PHEMA

The PMMA block was prepared previously using [Ru(*o*-C_6H_4-2-py)(phen)$(MeCN)_2$]PF_6, EB*i*B, and toluene (monomer/solvent = 50/50, v/v) as a solvent at the initial molar ratio of $[MMA]_0/[catalyst]_0/[EBiB]_0$ = 200/1/1 at 80 °C. It was shown earlier that the polymerization of MMA proceeded by "living" fashion under these conditions.[37] The polymerization was stopped after 1.5 h. Thus, synthesized PMMA was purified passing through a alumina column, characterized by GPC (M_n = 6500, M_w/M_n= 1.30) and applied as macroinitiator in the subsequent polymerization of HEMA in acetone at 50 °C during 6 h with the basic 200/1/1 initial component ratio using the same procedure as that described for the chain extension.

Characterization

NMR spectra were recorded on a Bruker Avance instrument operating at 400 MHz using d_6-DMSO, d_7-DMF, CD_3OD, CD_3CN, and D_2O as solvents. The molecular weights and molecular weight distribution of the polymers were analyzed by GPC (Waters 717 plus Autosampler) equipped with two column series of two Styrogel columns HR4E and HR5E (MW range 50 to 1×10^5 and 2×10^3 to 4×10^6, respectively) connected to a Waters 410 RI detector. The GPC measurements were conducted using 10 mM solution of LiBr in DMF as an eluent at 45 °C with a flow rate of 0.4 mL/min. PMMA standards were utilized for the GPC calibrations. UV–vis measurements were performed on a Varian Cary 400 UV–vis spectrophotometer. Concentrations of 0.20–0.22 mM of complex in solutions were used for these measurements. To get similar level of the absorption in the complex concentration, 10 μL aliquots were taken from the reaction and diluted to 2 mL with solvent. Mass spectra were obtained using a JEOL JMS-SX 102A instrument with *m*-nitrobenzyl alcohol as the matrix [FAB^+ mode, *m/z*]. Consumption of the initiator was measured by gas chromatography (GC) on a Shimadzu GC-2010 gas chromatograph equipped with RESTEK stabilwax column with *n*-decane as an internal standard.

CONCLUSIONS

The radical polymerization of HEMA catalyzed by cationic complexes of ruthenium(II), $[Ru(\eta^6\text{-}C_6H_6)(C_6H_5\text{-}o\text{-}CH_2NMe_2)(MeCN)]PF_6$ (**I**) and two $[Ru(o\text{-}C_6H_4\text{-}2\text{-}py)(phen)(MeCN)_2]^+$, bearing different counterions, PF_6^- and Cl^- (**IIa** and **IIb**), in acetone and protic media was investigated. All complexes demonstrated high activity, and the polymerization was fast and proceeded under very mild conditions achieving high conversions. The level of control was different and depended on the catalyst and the polymerization conditions. Thus, the polymerization mediated by the catalyst **I** proceeded without control, whereas the complexes **II** with both PF_6^- and Cl^- counterions were able to control the polymerization in MeOH and acetone. It was seen by chain extension experiments that the polymerization catalyzed by these two complexes proceeded in a "living" manner, and a linear block copolymer, PMMA-*b*-PHEMA, was synthesized from PMMA-Br macroinitiator.

Comparative analysis of the complexes **IIa** and **IIb** having the same structure and only differing by the type of anion demonstrated the importance of the nature of the counterion. The polymerization catalyzed by **IIb** in methanol was about twice as slow as the polymerization with catalyst **IIa**, but demonstrated better control. The polymerization accelerated significantly in the aqueous medium, but again the polymerizations with **IIb** were slower, and the variations in the polymerization rates were even larger in water than in methanol. However, the complexes behaved contrarily in aprotic solvent. The polymerization in acetone with catalyst **IIb** proceeded faster than that mediated by **IIa** under similar conditions. On the other hand, the polymerization with complex **IIb** resulted in a polymer of lower molecular weight in all the solvents. Both complexes were reasonably stable in water under the polymerization conditions, particularly complex **IIb**, which was able to mediate the polymerization of HEMA to high conversions, even with a HEMA/catalyst initial ratio equal to 2000/1. The polymerizations in water were homogeneous but proceeded in an uncontrolled manner. High activity together with good stability was shown by **IIb** in the aqua polymerization at low concentrations, and this makes it a promising candidate for controlled polymerizations of hydrophilic monomers.

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