ATOM TRANSFER RADICAL POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE INDUCED BY Rh^{I}(CYCLOOCTA-1,5-DIENE) COMPLEXES

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Rh(I)(diene) complexes, di(μ-docosanoato)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)] (**1**) and bis(μ-4-methylphenolato)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)] (**2**) are introduced as a new class of catalysts for the atom transfer radical polymerization (ATRP) of vinyl monomers and provide new example of an involvement of rhodium compounds in radical reactions. Single complexes **1** and **2** promote a controlled radical polymerization of methyl methacrylate and styrene affording a medium to good yield of high-molecular-weight polymers with polydispersity index, M_w/M_n, values ranging from 1.45 to 1.65. However, the initiator efficiency found for these reaction systems is rather low, from 0.04 to 0.20. The addition of $(Bu)_2NH$ to these polymerization systems has a remarkable positive influence on the catalyst activity and the polymerization control, particularly, in the systems involving complex **1**, for which approximately tenfold increase in the initiator efficiency, up to 0.85, and decrease in the polydispersity index, to the value 1.27, has been observed. Dissociation of dinuclear Rh(I)(diene) species to the mononuclear ones is suggested as an important part of the mechanism lying behind the effect of $(Bu)_2NH$ additive.

Keywords: Atom transfer radical polymerizations; Controlled radical polymerizations; Methyl methacrylate; Rhodium diene complexes; Styrene.

The development of chain-polymerization methods that enable consecutive enchainment of monomer units without any termination and chain-transfer reactions has been a primary goal of synthetic polymer chemistry in the last fifty years[1]. Such techniques, now known as controlled or living polymerizations, allow high to precise molecular weight control and synthesis of polymers with variety molecular architecture[2]. During the last two

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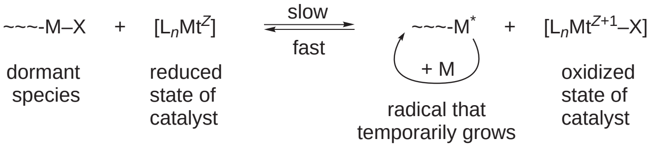
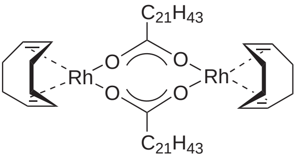
decades, high progress has been made in a control over the termination in radical polymerization to achieve the persistent radical effect. The most representative techniques developed are: (i) free radical polymerization controlled by a stable nitroxyl radical such as 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO)[3], (ii) atom transfer radical polymerization (ATRP)[4,5] and (iii) reversible addition-fragmentation chain transfer polymerization (RAFT)[6]. In particular ATRP has attracted great attention in the past few years due to its applicability to both styrene and methacrylic monomers, its simple set-up and its remarkable tolerance to functional groups. This polymerization is controlled *via* a metal-mediated redox process, in which a low-oxidation-state transition-metal complex acts as a carrier to facilitate fast exchange between a small amount of growing radicals and their dormant, alkyl halide form (Scheme 1). A high variety of transition-metal complexes has been successfully used in ATRP, mainly complexes of Cu, Fe, Ni, Pd, Ru and Re [7].



Scheme 1

Four-coordinate rhodium(I) complexes are known to act as catalysts in a variety of transformations such as hydrogenation, hydroformylation, hydrosilylation, isomerization and polymerization processes[8]. Chiral Rh(I) phosphane complexes have also been introduced as efficient catalysts for the addition of CCl_3Br to styrene and oct-1-ene *via* a radical process, which is known in the literature as the Kharash reaction or atom transfer radical addition reaction[9]. Percec[10] and Jérôme[11] independently took advantage of a close relationship between the Kharash reaction and ATRP by employing the Wilkinson catalyst, $[RhCl(PPh_3)_3]$, in the ATRP of styrene (Sty) and methyl methacrylate (MMA), respectively. Poor control of the ATRP was found for Sty with $SOCl_2$ initiator (polydispersity index M_w/M_n = 1.7–3.2). Better results were obtained for ATRP of MMA with 2,2′-dichloroacetophenone initiator (M_n up to 200 000 and M_w/M_n about 1.5). Although these results are not the best ones, they indicate that Rh(I) phosphane complexes can act as ATRP catalysts. Therefore, it is reasonable to examine other Rh(I) complexes as to their ATRP activity and to try to find and/or develop complexes, which provide a better control of the ATRP process.

In the last decade, various dinuclear bridge Rh(I)(diene) complexes have been used as catalysts for stereospecific polymerization of substituted acetylenes to cis-transoid polyvinylenes[12]. Remarkable tolerance to various solvents and functional groups of monomers is a characteristic feature of these catalysts, such that they can operate even in the presence of atmospheric oxygen, water, amines and alcohols. Therefore, as a part of our effort in searching for new ATRP catalytic systems[13] we tested two current complexes of this class, $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ and $[\{Rh(cod)\}_2(\mu\text{-}OCH_3)_2])$ (where cod is $\eta^2{:}\eta^2$-cycloocta-1,5-diene), in the ATRP of styrene. Since we found poor or no ATRP activity of these complexes, we have synthesized novel Rh(I)(diene) complexes with phenoxo and acyloxo bridge ligands (Chart 1), which we found to show rather good ATRP activity. The results on ATRP of Sty and MMA (Scheme 2) obtained with these complexes are the subject of the present communication.



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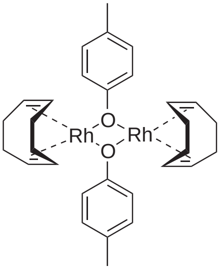

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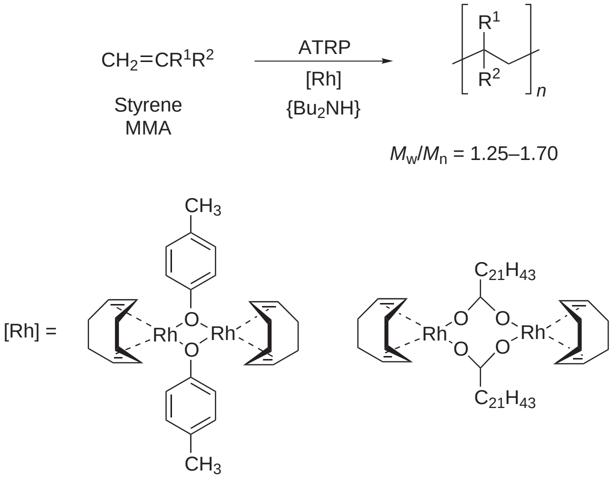
CHART 1



SCHEME 2

EXPERIMENTAL

Materials and Methods

Styrene (Sty), and methyl methacrylate (MMA) (both Acros, 99%) were distilled from CaH_2 and stored under nitrogen atmosphere at –18 °C. The initiators, (1-bromoethyl)benzene (Aldrich, 99%) and methyl 2-bromo-2-methylpropanoate (Aldrich, 99%) were used without further purification as toluene solutions (0.05 mol dm^{-3}). Tetrahydrofuran (THF), (Riedel–deHaen, 99.5%) was distilled from Cu_2Cl_2 and CaH_2 and stored under argon. Dichloromethane and hexane were dried over P_2O_5 and, after distillation, stored over 4 Å molecular sieve. Sodium acetate (Lachema, Czech Republic) was dried in the molten state under vacuum. Acetone (Lachema, Czech Republic) was distilled from $KMnO_4$ to remove reducing compounds. Potassium superoxide KO_2 and cycloocta-1,5-diene (Aldrich), $RhCl_3·3H_2O$ (Safina, Czech Republic), docosanoic acid, silver nitrate, aqueous ammonium hydroxide (30%) and ethanol (all Lachema, Czech Republic) were used as supplied. Di(μ-chloro)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)], $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$, was prepared from $RhCl_3·3H_2O$ using literature[14] procedures. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian ^{UNITY}Inova FT-NMR instrument and the chemical shifts (δ, ppm) are referenced to TMS for ^1H NMR and to the solvent ($CDCl_3$, δ 76.99 ppm) for ^{13}C NMR spectra. Coupling constants are given in Hz. Raman spectra (wavenumbers in cm^{-1}) were recorded on a Bruker Equinox 55 FRA 106/S Raman spectrometer (laser: λ = 1064 nm, 100 mW) with solid complexes. Molecular-weight characteristics of polymers were determined by the size-exclusion chromatography ($CHCl_3$, 25 °C) using a Shimadzu CLASS-VP™ system equipped with three serial columns (PSS SDV; length 30 cm; i.d. 8 mm; 10^3, 10^4, 10^5 Å); calibration was done with polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards.

Synthesis of Rh Complexes **1** and **2**

Di(μ-docosanoato)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)] (**1**)

The complex was prepared by the reaction of $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ with 10 equivalents of silver docosanoate. The last compound was prepared by gradual adding a hot solution (50 °C) of docosanoic acid (800 mg, 2.4 mmol) in ethanol (50 ml) to a hot solution (50 °C) of silver nitrate (510 mg, 3.0 mmol) in aqueous ammonium hydroxide. The precipitated silver salt was washed with water to remove non-reacted silver nitrate, then extracted in a Soxhlet extractor with ethanol to remove traces of non-reacted docosanoic acid and the obtained silver salt was dried in vacuum for 12 h. Then water (30 ml) and $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ (100 mg, 0.2 mmol) were added to the silver salt under argon atmosphere and the resulting suspension was sonicated for 15 min until formation of AgCl was observed. Water was then removed from the suspension on a vacuum rotary evaporator, crude product was dissolved in THF (100 ml) and the side product, AgCl, was filtered off. The filtrate was concentrated to *ca* 5 ml and the concentrated solution was cooled to 4 °C to allow crystallization of **1**. Yield: 161 mg (72%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 4.05–4.15 (m, 8 H, cod); 2.55–2.90 (m, 8 H, cod); 2.05–1.91 (m, 4 H, CH_2 adjacent to COO); 1.90–1.70 (m, 8 H, cod); 1.45–1.01 (m, 76 H, CH_2); 0.88 (t, J = 6.8, 6 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): 185.30 (2 C, COO bridge); 80.60 (4 C, CH, cod); 73.57 (4 C, CH, cod); 37.49 (2 C, CH_2 acid); 31.92 (2 C, CH_2

acid); 31.12 (4 C, CH_2 cod); 30.6 (4 C, CH_2 cod); 29.70–29.14 (32 C, CH_2 acid); 26.25 (2 C, CH_2 acid); 22.68 (2 C, CH_2 acid); 14.10 (2 C, CH_3). Raman spectrum: 2881 s, 2847 s, 1707 s, 1468–1439 s, 1296 s, 1132 s, 1062 s, 891 m, 781 m, 724 m, 652 m, 518 s, 500 s, 401 m. Formula weight 1101.34 g mol^{-1}.

Bis(μ-4-methylphenolato)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)] (**2**)

Potassium superoxide (100 mg, 1.41 mmol) was suspended in CH_2Cl_2 (5 ml) under argon. A solution of $[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$ (100 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) was slowly added within 15 min and the reaction mixture was allowed to react under stirring for 3 h. During the first hour, the color of the mixture changed from orange to dark green and back to orange. After 3 h, the unreacted KO_2 and formed KCl were filtered off using the standard Schlenk technique and a solution of 4-methylphenol (71 mg, 0.66 mmol) in CH_2Cl_2 (1 ml) was added to the orange filtrate. Then the mixture was concentrated to a quarter of its volume under vacuum and hexane (15 ml) was slowly added, and the mixture left to crystallize overnight at 0 °C. A yellowish crystalline solid was filtered off, washed with cold hexane and dried in vacuum. Yield: 94 mg (70%). ^1H NMR (400 MHz, $CDCl_3$, 25°C): 6.89–6.85 (m, 4 H, arom); 6.83–6.67 (m, 4 H, arom); 3.16 (s, 8 H, CH cod); 2.38–2.24 (m, 8 H, CH_2 cod); 2.16 (s, 6 H, CH_3); 1.40–1.30 (m, 8 H, CH_2 cod). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): 158.18 (2 C, arom, adjacent to O); 130.03 (2 C, arom, adjacent to CH_3); 128.87 (4 C, arom); 122.23 (4 C, arom); 74.60 (d, J = 15.3, 8 C, CH cod); 30.04 (8 C, CH_2 cod); 20.56 (2 C, CH_3). Raman spectrum: 3041 vs, 3022 vs, 2996 s, 2921 s, 2837 s, 1606 vs, 1468 s, 1375 m, 1253 vs, 1210 m, 783 m, 769 m, 487 m, 402 s, 302 vs, 115 vs. Formula weight 636.44 g mol^{-1}.

Polymerization Procedure

Polymerization experiments were made under argon in glass tubes provided with magnetic stirrer and three-way stopcock. Polymerizations of MMA at the monomer/Rh mole ratio 800 catalyzed with **1** and **2**, respectively, in the presence of Bu_2NH were carried out as follows. A weighed amount of catalyst corresponding to six polymerization mixtures (38.7 mg of **1** or 22.3 mg of **2**, *i.e.*, 0.0351 mmol of given Rh-bridged complex) was dissolved in solution of Bu_2NH in toluene (6 ml of 0.047 M solution, *i.e.*, 0,282 mmol) and MMA (6 ml, 56.2 mmol) and solution of initiator in toluene (2.80 ml of 0.05 M solution, *i.e.*, 0.140 mmol) were added under argon. Resulting solution was under argon distributed to six glass ampoules (2.45 ml to each), which were then heated to 85 °C. After a given time period, the ampoule was cooled, its content diluted with $CHCl_3$ and formed PMMA was precipitated with heptane under vigorous stirring. Isolated polymer was dried under vacuum at 50 °C and the polymer yield was determined by gravimetry. Polymerization of Sty was carried out in the same way at the temperature of 110 °C and formed PS was precipitated with methanol. In the experiments without Bu_2NH cocatalyst, a weighed amount of catalyst was dissolved in toluene instead of Bu_2NH solution in toluene. In experiments with the monomer/Rh ratio of 100, the added volume of monomer was reduced to one eighth and volume of toluene was increased to reach the same final volume of the reaction mixture as in the experiment with the monomer/Rh ratio of 800.

RESULTS AND DISCUSSION

In the first set of experiments, we examined the ability of catalysts **1** and **2** to control the polymerization of MMA and Sty at the initiator/Rh mole ratio 2 and the monomer/Rh mole ratio 100 using methyl 2-bromo-2-methylpropanoate and (1-bromoethyl)benzene as the initiator for MMA and Sty, respectively. Results of these experiments are shown in Figs 1 to 3. As can be seen from Fig. 1, all tested polymerization systems obey the first-order-kinetics law satisfactorily. It is also evident that the rate of polymerization is not simply correlated with monomer and catalyst structure. Catalyst **1** provides moderate yield of PMMA (39% after 24 h) and medium yield of PS (56%) while catalyst **2** provides high yield of PMMA (76%) but medium yield of PS (48%). ATRP activity of **1** and **2** in polymerization of Sty is comparable while in polymerization of MMA, activity of **2** is approximately two times as high as that of **1**.

Dependence of the number-average molecular weight, M_n, of formed polymers on the monomer conversion is shown in Fig. 2. Continuous increase in M_n value is observed for all tested systems, which provides clear evidence that the polymer molecular weight is controlled during polymerization. Also the continuous decrease in the polydispersity index of formed polymer as the monomer conversion increases (Fig. 3) points to an effective control of the polymer molecular weight. On the other hand, the determined M_n values of all prepared polymers are substantially higher than the

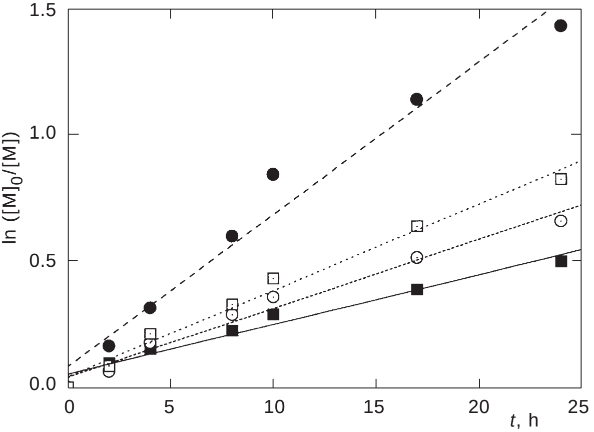


FIG. 1

First-order kinetic plots for polymerization of MMA and Sty induced by complexes **1** and **2** at the monomer/Rh mole ratio 100 (for conditions see Table I): ■ **1**-MMA, ● **2**-MMA, ❑ **1**-Sty, ❍ **2**-Sty theoretical ones and dependences of M_n on the monomer conversion are not linear, which indicates low efficiency of the initiator transformation to growing chains (Table I) and participation of undesired processes.

To obtain further insight into the reaction mechanism and kinetics, we carried out another set of polymerization experiments keeping all condi-

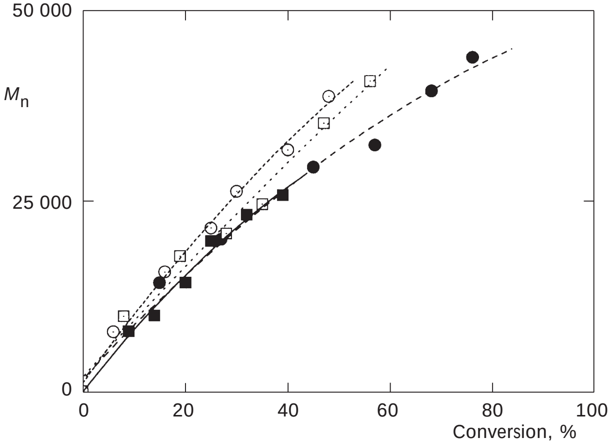


FIG. 2

Number-average molecular weight M_n of PMMA and PS as a function of the monomer conversion for polymers formed in ATRP induced by complexes **1** and **2** at the monomer/Rh mole ratio 100 (for conditions see Table I): ■ **1**-MMA, ● **2**-MMA, ❑ **1**-Sty, ❍ **2**-Sty

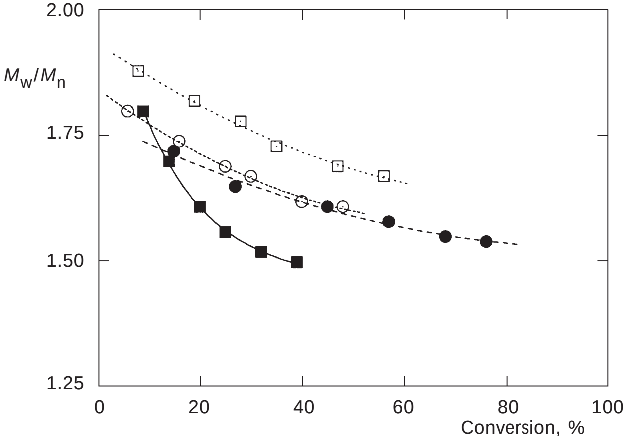


FIG. 3

Polydispersity index M_w/M_n of PMMA and PS as a function of the monomer conversion for polymers formed in ATRP induced by complexes **1** and **2** at the monomer/Rh mole ratio 100 (for conditions see Table I): ■ **1**-MMA, ● **2**-MMA, ❑ **1**-Sty, ❍ **2**-Sty tions the same as above, only increasing the monomer concentration such that the monomer/Rh mole ratio was risen from 100 to 800 and monomer/initiator mole ratio from 50 to 400. Results of these experiments are summarized in Table I together with relevant data obtained for the monomer/Rh mole ratio 100. As can be seen, the effect of increasing monomer concentration on a course of the polymerization of MMA and Sty is different. In the case of MMA polymerization, eightfold increase in the initial monomer concentration, $[M]_0$, results in a ten-fold (with **2**) to fifteen-fold (with **1**) increase in the polymer M_n value but not in an increase in the monomer conversion. As a result, values of the initiator efficiency, *f*, found for systems with the MMA/Rh mole ratio 800 are still lower than those found for the MMA/Rh ratio 100. On the contrary, only threefold increase in M_n value is observed for both Sty polymerization systems, which, how-

TABLE I

Data on polymerization of MMA (at 85 °C) and Sty (at 110 °C) induced by **1** and **2** in toluene: *Y*, relative yield of polymer; M_n and M_w, number-average and weight-average molecular weight of polymer; *f*, initiator efficiency. Reaction conditions: [**1**] = [**2**] = 2.37 mmol dm^{-3}, *i.e.*, [Rh] = 4.74 mmol dm^{-3}, $[I]_0$ = 9.46 mmol dm^{-3}, $[Bu_2NH]$ = 19 mmol dm^{-3}, $[M]_0$ = 0.475 or 3.80 mmol dm^{-3} (according to the [M]/[Rh] ratio), reaction time 24 h

Catalyst	Monomer	[M]/[Rh]	*Y*, %	$M_n{}^a \times 10^{-3}$	$M_w/M_n{}^a$	f^b
1	MMA	100	39	26	1.50	0.08
1	MMA	800	38	397	1.45	0.04
1 + Bu_2NH^c	MMA	800	95	116	1.46	0.33
1	Sty	100	56	41	1.67	0.07
1	Sty	800	23	126	1.55	0.08
1 + $Bu_2NH^{c,d}$	Sty	800	80	39	1.27	0.85
2	MMA	100	76	44	1.54	0.09
2	MMA	800	78	445	1.52	0.07
2 + Bu_2NH^c	MMA	800	87	289	1.49	0.12
2	Sty	100	48	39	1.61	0.06
2	Sty	800	60	122	1.44	0.20
2 + $Bu_2NH^{c,d}$	Sty	800	85	100	1.42	0.36

[a] Determined by SEC using the PMMA calibration for PMMA and PS calibration for PS. [b] Initiator efficiency: $f = M_{n,theor}/M_{n,exp}$ where $M_{n,theor} = ([M]_0/[I]_0)M_{mon}Y$ ($[M]_0$ and $[I]_0$ is initial concentration of the monomer and initiator, respectively, M_{mon} is molecular weight of monomer). [c] Four equivalents of Bu_2NH with respect to Rh. [d] Reaction time 20 h.

ever, exhibit diverse behavior as to the monomer conversion to polymer. In the system **1**-Sty, the polymer yield drops to less than one half upon increase in the Sty/Rh mole ratio from 100 to 800, whereas the polymer yield increases about 25% in the system **2**-Sty upon the same change. As a result, a slight increase in f value is observed for the **1**-Sty system, however, *ca* three-fold increase in f is observed for the **2**-Sty system. Nevertheless, the initiator efficiency about 0.20 achieved in the last system is not high enough for a good ATRP system. As far as polydispersity of polymers is concerned, the increase in monomer concentration results in a small decrease in the M_w/M_n value (see Table I), which also indicates that the polymerization is controlled.

The observed low values of the initiator efficiency point to a participation of some inevitable side reactions in the overall polymerization process. In general, side reactions are more probable at the beginning of polymerization till formed radicals are small and, therefore, mobile enough to escape from a solvent cage which they share with their catalyst species counterparts. In the case of dinuclear Rh-catalysts, still another, more facile mechanism of termination of growing radicals comes into consideration. Potentially, two dormant species can be activated in the same time interval in one solvent cage, each with assistance of one Rh atom of the same dinuclear Rh species. Since probability of termination of two free radicals occurring in the same solvent cage is very high, the above event can be regarded as a possible mechanism lying behind the observed low initiator efficiency. Therefore, an *in situ* dissociation of dinuclear catalyst species to the mononuclear ones can be expected to bring about a desired increase in the initiator efficiency. Dissociation of dinuclear Rh(I) complexes is known to proceed in the polymerization of substituted acetylenes induced by dinuclear Rh(diene) catalysts in the presence of various amines[15]. Besides, it is known from the literature that addition of amines to a Ru-based catalysts can favorably affect the control over ATRP process *via* appropriate stabilization of oxidized catalyst species through intermolecular interactions[16]. Therefore, we decided to examine the effect of dibutylamine, Bu_2NH, on the initiator efficiency and overall course of ARTP of MMA and Sty induced with **1** and **2** using the monomer/Rh mole ratio 800 and Bu_2NH/Rh mole ratio 4. Results of these experiments are shown in Figs 4 to 6 and selected data are included in Table I.

First-order-kinetics plots (Fig. 4) show good linearity for both monomers and both catalyst systems indicating the first-order process in monomer consumption and constant number of active species during the polymerization. The last one is further supported by the linearity of dependences of

M_n on the monomer conversion (Fig. 5), which also proves absence of transfer reactions and the presence of long-lived growing species same as continuously decreasing dependence of the polymer polydispersity index

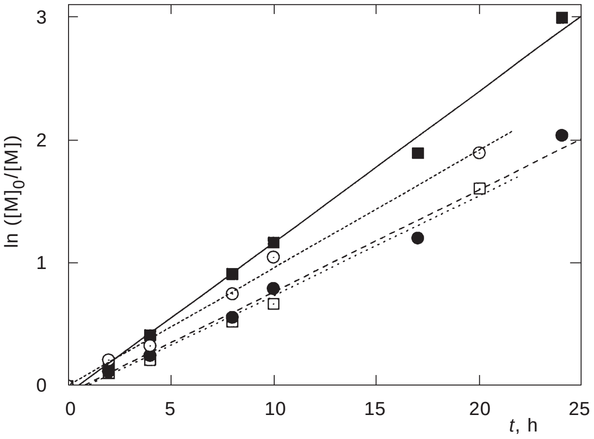


FIG. 4

First-order kinetic plots for polymerization of MMA and Sty induced by complexes **1** and **2** in the presence of Bu_2NH at the monomer/Rh mole ratio 800 and Bu_2NH/Rh mole ratio 4 (for conditions see Table I): ■ **1**-MMA, ● **2**-MMA, ❑ **1**-Sty, ❍ **2**-Sty

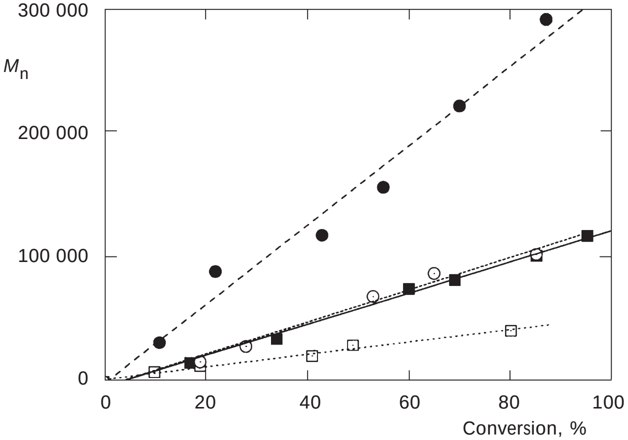


FIG. 5

Number-average molecular weight M_n of PMMA and PS as a function of the monomer conversion for polymers formed in ATRP induced by complexes **1** and **2** in the presence of Bu_2NH at the monomer/Rh mole ratio 800 and Bu_2NH/Rh mole ratio 4 (for conditions see Table I): ■ **1**-MMA, ● **2**-MMA, ❑ **1**-Sty, ❍ **2**-Sty

M_w/M_n (Fig. 6) on the monomer conversion. These results indicate clearly that all the criteria of a controlled/"living" polymerization process are fulfilled in the presence of Bu_2NH.

TABLE II
Values of apparent rate constant of polymerization, k_{app}, obtained from dependences shown in Figs 1 and 4 and ratio k_{app}/f, where f is the initiator efficiency, as a function of monomer and catalyst

Monomer	Catalyst	f	$k_{app} \times 10^6$, s^{-1}	$(k_{app}/f) \times 10^6$, s^{-1}
MMA	**1**	0.08	5.4	68
MMA	**1** + Bu_2NH	0.33	34.1	103
MMA	**2**	0.09	16.6	184
MMA	**2** + Bu_2NH	0.12	23.1	193
Sty	**1**	0.07	9.4	135
Sty	**1** + Bu_2NH	0.85	22.6	27
Sty	**2**	0.06	7.5	126
Sty	**2** + Bu_2NH	0.36	26.7	74

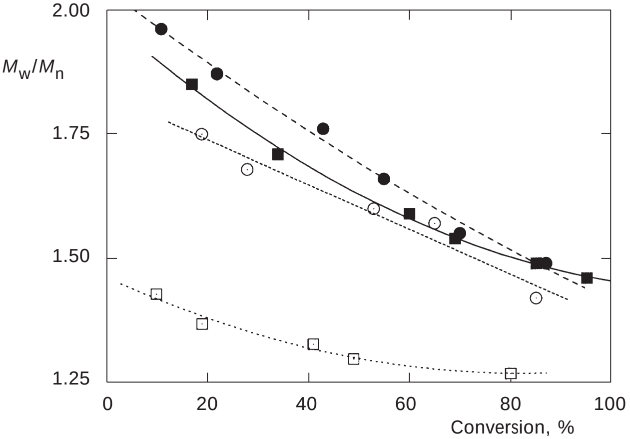


FIG. 6
Polydispersity index M_w/M_n of MMA and Sty polymers as a function of the monomer conversion for polymers formed in ATRP induced by complexes **1** and **2** in the presence of Bu_2NH at the monomer/Rh mole ratio 800 and Bu_2NH/Rh mole ratio 4 (for conditions see Table I): ■ **1**-MMA, ● **2**-MMA, ❑ **1**-Sty, ❍ **2**-Sty

A comparison of the systems with and without Bu_2NH is seen from Table I. Addition of four equivalents of Bu_2NH (in relation to Rh) to the reaction mixture (i) increases the polymer yield, (ii) decreases the polymer molecular weight, and (iii) significantly increases the initiator efficiency f in all tested polymerization systems. The highest, above ten-fold increase in the initiator efficiency (from 0.08 to 0.85) is observed for the polymerization of Sty induced with catalyst **1**, for which also the lowest polymer polydispersity index about 1.27 was achieved. Similar relative increase in the f value (from 0.04 to 0.33, *i.e.*, more then eight-fold increase) is observed for the polymerization of MMA induced with the same catalyst **1**. On the other hand, the addition of Bu_2NH to the systems containing catalyst **2** has much lower impact on the polymerization process. It gives only 80% relative increase in the initiator efficiency f: from 0.07 to 0.12 for polymerization of MMA and from 0.20 to 0.36 for polymerization of Sty. As a result, addition of Bu_2NH completely changes the order of ATRP activity of studied catalysts, as can be seen from Table I, data for the monomer/Rh mole ratio 800. In the systems without Bu_2NH additive, catalyst **2** shows better control of the polymerization process than catalyst **1**, whereas **1** is better than **2** in the presence of Bu_2NH cocatalyst.

It seems reasonable that the mechanism underlying the observed effect of Bu_2NH on ATRP induced with complexes **1** and **2** includes both the dissociation of dinuclear Rh species to mononuclear ones and the interactions of Rh species with residual Bu_2NH and other constituents of the reaction mixture, mainly monomer. It is seen from Table II, in which values of apparent rate constant of polymerization, k_{app}, and values of the constant corrected to different initiator efficiency, k_{app}/f, obtained by evaluation of kinetic plots in Figs 1 and 4 are summarized. Upon addition of Bu_2NH, value of the corrected rate constant of polymerization increases in the case of polymerization of MMA but significantly decreases in the case of Sty. Thus, it is clear that elucidation of the overall mechanism of ATRP induced by Rh(I)(diene) complexes requires further, more detailed investigation of these reaction systems, which is beyond a scope of this paper.

It can be concluded that Rh(I)(cod) complexes **1** and **2** are efficient catalysts for the ATRP of methyl methacrylate and styrene, which, however, provide polymerization systems with low initiator efficiency. This disadvantage can be eliminated to a great extent by an addition of the cocatalytic amount of dibutylamine, which results in a dramatic increase in the initiator efficiency, decrease in the polymer polydispersity and increase in the overall polymerization rate. Further investigation of Rh(I)(diene) catalysts is needed to assess their position in the ever-expanding sphere of the ATRP chemistry.

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