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Controlled radical polymerization of styrene in the presence of lithium molybdate(V) complexes and benzylic halides

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Abstract

The new lithium molybdate(V) complexes [LiMo(NAr)$_2$(*C–N*)R] (*C–N* = $C_6H_4(CH_2NMe_2)$-2; R = (*C–N*) (**5**), Me (**6**), CH_2SiMe_3 (**7**), *p*-tolyl (**8**)), have been generated in situ from reaction of the corresponding molybdenum(VI) complexes [Mo(NAr)$_2$(*C–N*)R] (*C–N* = $C_6H_4(CH_2NMe_2)$-2; R = (*C–N*) (**1**), Me (**2**), CH_2SiMe_3 (**3**), *p*-tolyl (**4**)) with *n*-BuLi. The nature of these radical anions was studied by EPR spectroscopy. The spectra of toluene solutions of in situ prepared complexes **5**–**8** revealed the presence of two different paramagnetic species, i.e. a molybdenum compound with distinct g_{iso}- and A_{iso}-values and an unidentified radical with a sometimes strong signal at $g = 1.986 \pm 0.001$, lacking any hyperfine coupling. Extended Hückel calculations on the crystal structure of **5** showed that the single electron occupies a molybdenum centered orbital, merely $d_{x^2-y^2}$ in character. In situ prepared complexes **5**–**8** were successfully applied in the atom transfer radical polymerization (ATRP) of styrene using benzyl chloride as the initiator. The efficiency of the benzyl chloride initiator is rather poor (6–18%). Reaction of the lithium molybdate(V) complex **5** with (α-chloroethyl)benzene and (α-bromoethyl)benzene resulted in the formation of **1**, LiCl and LiBr, respectively. The molecular weights as well as the molecular weight distributions show that the catalytic system, BzCl/**5**–**8**, catalyses styrene polymerization successfully but does not exercise much control over the polymerization reaction due to the poor initiator efficiency of benzyl chloride and probably the extreme air-sensitivity of the lithium molybdate(V) compounds. The unidentified radical ($g = 1.986 \pm 0.001$) is unable to initiate radical polymerization but possibly influences the ATRP activity.

Keywords: Molybdate; Alkylimido; EPR spectroscopy; MO calculations; Styrene polymerization

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1. Introduction

The 'living/controlled' [1] character of atom transfer radical polymerization (ATRP) makes it possible to synthesize well-defined polymers [2] because irreversible side reactions like chain transfer or chain termination are suppressed. In these polymerization reactions the problem of radical coupling and disproportionation is circumvented by the reversible reaction of the polymer radicals with a persistent radical to a dormant species, see Eq. (1). The high degree of control arises from a permanent low concentration of radicals, which suppresses bimolecular termination processes. Thermodynamically the equilibrium in Eq. (1) must be on the side of the dormant species (left) while kinetically the equilibrium reactions must be faster than the rate of propagation in order to get polymer chains with comparable length [3].

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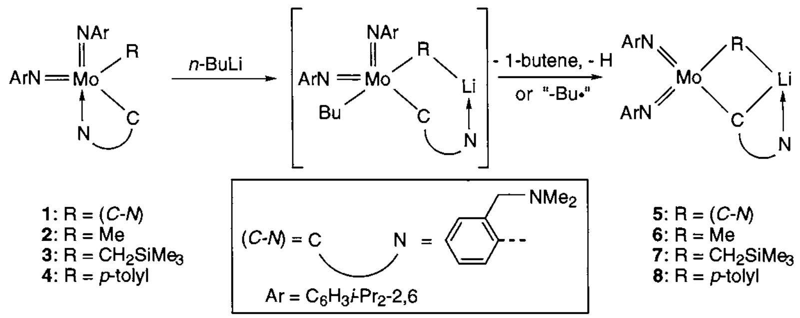
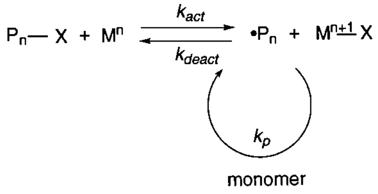


Scheme 1. Synthesis of the paramagnetic lithium molybdate(V) complexes **5**–**8**.



P_n— X	dormant species
M^n	metal complex
$\bullet P_n$	growing polymer chain
$M^{n\pm1}X$	persistent radical species

(1)

Although bimolecular decomposition always occurs, it becomes negligible because of the persistent radical effect [3a,4], if the persistent radical species is stable. The final molecular weight of the polymer is determined by the amount of initiator.

A number of low oxidation state metal complexes like ruthenium(II) [5], copper(I) [6], iron(II) [7] and nickel(II) [8] are known to be effective ATRP catalysts. These catalysts influence the equilibrium between dormant and active species and all have an accessible one-electron redox couple that promotes atom transfer. All are able to accept a halide ligand, have low affinity for alkyl radicals and contain a metal with low Lewis acidity. For effective initiation the initiation rate must be faster or comparable to the propagation rate and an alkyl halide must be used that structurally resembles the monomer [2a].

High oxidation state transition metal complexes, although often highly Lewis acidic, might result in faster polymerization reactions and suppressed side reactions by influencing the equilibrium mentioned in Eq. (1). Therefore, we studied the application of the newly developed lithium molybdate(V) complexes of general formula [LiMo(NAr)$_2$(*C*–*N*)R] (*C*–*N* = $C_6H_4(CH_2NMe_2)$-2; R = (*C*–*N*) (**5**), Me (**6**), CH_2SiMe_3 (**7**), *p*-tolyl (**8**)) as catalysts for the ATRP of styrene using benzyl chloride as the initiator. Although the lithium molybdate(VI) halide compounds (formed after one electron oxidation of the corresponding lithium molybdate(V) complexes) are no odd electron species (as in the other metal containing persistent radical species) [5–8], the lithium molybdate(VI) halide compounds are good halide donors and are able to reform the dormant species (see Eq. (1)), deactivation step with k_{deact}.

2. Results

2.1. Synthesis of catalysts

The molybdenum(VI) complexes [Mo(NAr)$_2$(*C*–*N*)R] (*C*–*N* = $C_6H_4(CH_2NMe_2)$-2; R = (*C*–*N*) (**1**), Me (**2**), CH_2SiMe_3 (**3**), *p*-tolyl (**4**)) were synthesized via the reaction of [Mo(NAr)$_2$Cl$_2$(DME)] with half an equivalent of [Zn(*C*–*N*)$_2$] and subsequent transmetallation reactions with RLi or RMgCl, according to literature procedures [9]. These complexes react with *n*-BuLi in toluene and eventually form the paramagnetic Mo(V) molybdate species with general formula [LiMo(NAr)$_2$(*C*–*N*)R] (*C*–*N* = $C_6H_4(CH_2NMe_2)$-2; R = (*C*–*N*) (**5**), Me (**6**), CH_2SiMe_3 (**7**), *p*-tolyl (**8**)) (see Scheme 1).

Compound **5** can be isolated as a dark crystalline material while complexes **6**–**8** are brown, very soluble oils. The solid state structure of **5** has been elucidated by single-crystal X-ray analysis and reveals two bridging (*C*–*N*) ligands (via C_{ipso} of the *C*–*N*-ligands) between the molybdenum and lithium centers while the two imidoaryl groups on the molybdenum center are bonded perpendicularly to the C_{ipso}–Mo–C_{ipso} plane [9].

Spectroscopic characterization of the clear brown toluene solutions of **5**–**8** by NMR only showed very broad residual solvents peaks but lacked any resonances related to **5**–**8**, corroborating the presence of a paramagnetic molybdate(V) species. This conclusion was supported by the results of the EPR measurements of toluene solutions of these compounds which revealed the presence of two different paramagnetic species, i.e. one molybdenum compound showing the characteristic six line splitting pattern [10] due to $^{95}Mo + ^{97}Mo$ (both isotopes having $I = 5/2$ and combined natural abundance of 25%) around a central line arising from ^{98}Mo ($I = 0$, 75% natural abundance), with various g_{iso}- and

dance of 25%) around a central line arising from ^{98}Mo ($I = 0$, 75% natural abundance), with various g_{iso}- and

A_{iso}-values (vide infra) and one, sometimes, strong signal at $g = 1.986 \pm 0.001$ which shows no hyperfine coupling.

During the reaction of **1**–**4** with *n*-BuLi the formation of 1-butene, which must result from β-H elimination reactions, is detected. This indicates that at least part of the *n*-butyl nucleophiles were bonded to the Mo-center. In fact, in the presence of 1,2-dimethoxyethane (DME), the intermediate lithium organomolybdate(VI) complexes [Li(DME)$_n$Mo(NAr)$_2$(*C*–*N*)(*n*-Bu)(R)] (R = Me, CH$_2$SiMe$_3$, *p*-tolyl; $n = 1$–2), formed by the reactions of **2**–**4** with *n*-BuLi, can be isolated and spectroscopically characterized at temperatures below −10°C[1]. Because the amounts of 1-butene formed during the reactions in toluene were not quantitative, β-H elimination may not be the only pathway that eventually leads to the formation of **5**–**8**. The Mo–H complexes[2] which must have been formed after β-H elimination, are presumably unstable and will form **5**–**8** after H-elimination. Alternative routes involve direct butyl radical formation[3] after Mo–C bond cleavage or innersphere single electron transfer between **1**–**4** and *n*-BuLi clusters [11].

The origin of the singlet resonance with $g = 1.986 \pm 0.001$ is still unknown. The EPR signal from the(se) unidentified compound(s) is stable for days and is formed independently of the solvent used. The radical is not molybdenum centered since the characteristic six line hyperfine splitting is absent. Because the reactions of **1**–**4** with *n*-BuLi result in products with similar spectroscopic properties we believe that **6**–**8** are structurally related to **5**.

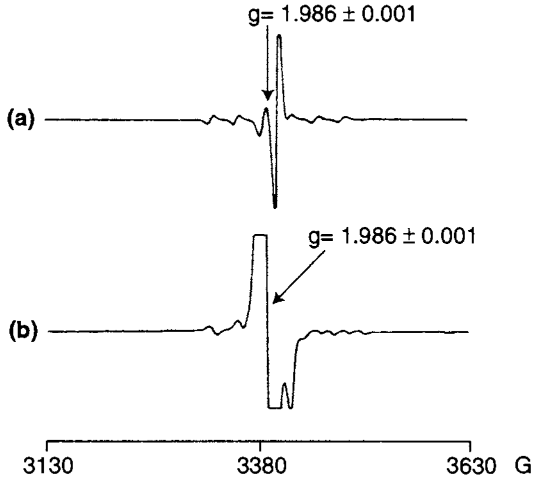


Fig. 1. EPR spectra of in situ prepared **5** (b) and **8** (a) in toluene.

Table 1
Experimentally determined EPR parameters for lithium molybdate(V) complexes (**5**–**8**) in toluene

	5	**6**	**7**	**8**
Conc. (mM)	8	10	8	15
g_{iso}	1.972	[a]	1.977	1.976
A_{iso} (G)	34.65 ± 0.05	[a]	30.16 ± 0.08	30.65 ± 0.05

[a] Hyperfine coupling unresolved because the Mo(V) spectrum was coinciding with a strong resonance peak at $g = 1.986 \pm 0.001$.

2.2. EPR and extended Hückel calculations

Fig. 1 shows the EPR spectra of in situ generated **5**, **7** and **8** in toluene. These spectra clearly show the characteristic six line spectra around a central line caused by the interaction of the Mo nucleus ($I = 0$ and $I = 5/2$) with the unpaired electron while hyperfine interaction of the nitrogens is not visible [12].

The line widths of the spectra vary between 7 and 8 G and further experiments showed that these line broadenings are not caused by spin–spin interactions. An increase of the concentration from approximately 8 mM to 20 mM does not lead to a change in the spectrum. The hyperfine coupling constant, A, is given by the splitting between the sequential lines. These lines are not equally spaced, e.g. splittings are typically ranging between 30 and 40 G, and a second order perturbation expansion in the hyperfine constant A is required to determine the accurate values of the g-factor and A [13]. From the experimental spectra the widths and line positions were taken and fitted (see Table 1). The sign of A can not be determined from the spectra.

Addition of air to the toluene solutions of **8** reduces the intensity of the singlet resonance ($g = 1.986 \pm 0.001$) with 30%, whereas the signal of the molybdenum compound is reduced by almost 90%. Finally, a strong solvent effect on the hyperfine coupling of **5** was observed.

These EPR results show that the unpaired electron in the molybdenum complexes is strongly interacting with the molybdenum nucleus. The location of this electron is supported by the results of the extended Hückel calculations[4] using the X-ray data of the structure of **5**. These calculations showed the HOMO of the complex

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[1] The complexes [Li(DME)$_n$Mo(NAr)$_2$(C–N)(*n*-Bu)(R)] (R = Me, CH$_2$SiMe$_3$, *p*-tolyl; $n = 1$–2) can be isolated as yellow solids at temperatures below 0°C, but decompose in deuterated solvents at ambient temperature.

[2] We were unable to detect traces of the 'Mo–H' species during the process of β-H elimination (monitored by NMR), probably due to the instability of the Mo–H bond.

[3] After the reaction all volatiles were collected in a cold trap and the mixture was analyzed by NMR and GC–MS. We were unable to detect any products arising from butyl radicals (C_8H_{18} fragments or products formed after reaction of Bu$^{\bullet}$ with toluene), even when the reaction was carried out in the presence of a radical trap like TEMPO. We only observed the formation of 1-butene.

[4] Extended Hückel calculations were performed with a Wolfberg–Helmholtz constant of 1.75 and STO-6G basis set and Alvarez Collected Parameters containing a double zeta basis set.

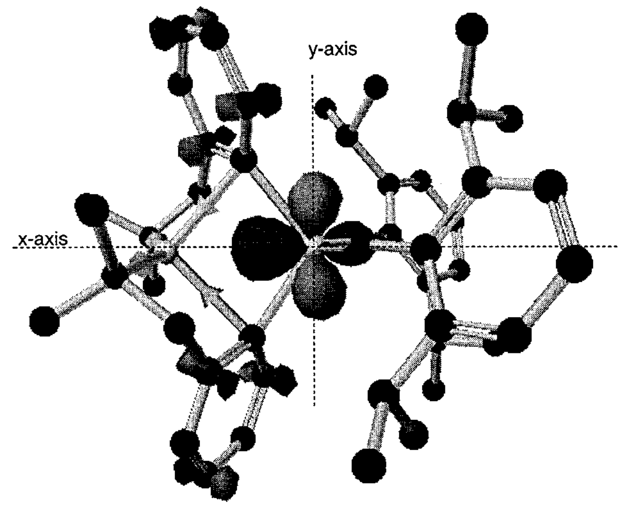


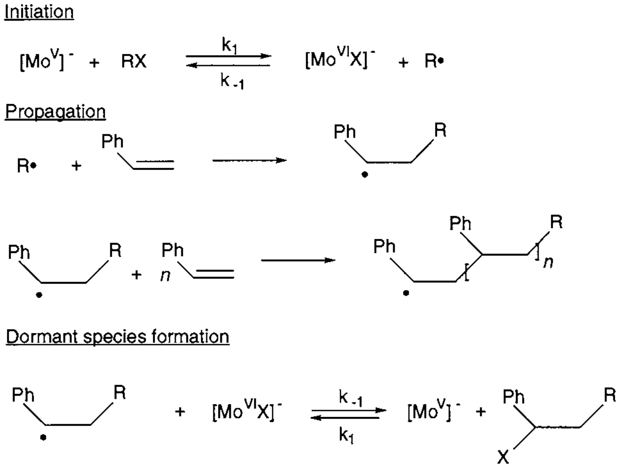
Fig. 2. The single electron in **5** occupies an orbital that is basically $d_{x^2-y^2}$ in character as calculated by extended Hückel calculations. Hydrogens are omitted for clarity.

to be a molybdenum centered, non-bonding orbital of $d_{x^2-y^2}$ character which is situated on and perpendicular to the Mo···Li axis (see Fig. 2).

Complexes **5**–**8** appear to be very sensitive towards electrophilic reagents like O_2 and vide infra (α-bromoethyl)benzene and (α-chloroethyl)benzene.

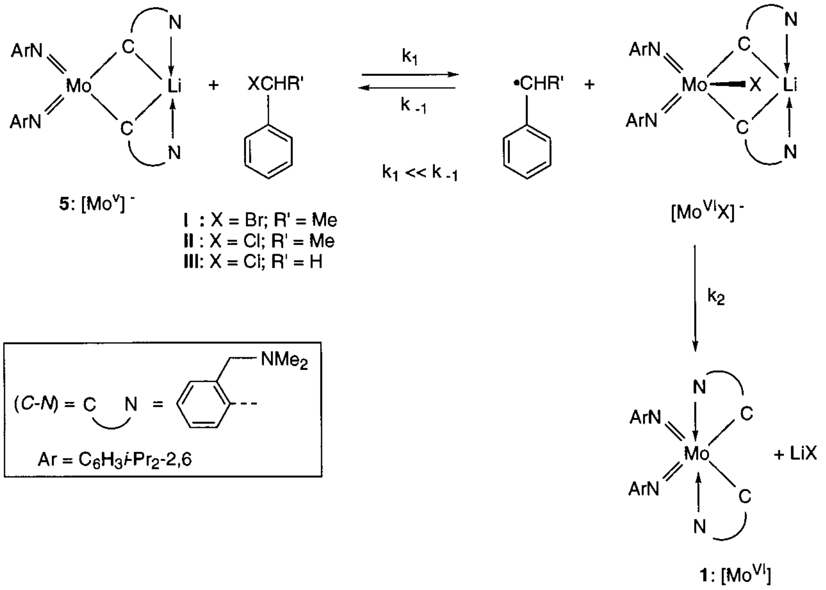
2.3. Reaction of the lithium molybdate 5 with benzyl halides

Compound **5** was reacted with different alkyl halides (**I**: (α-bromoethyl)benzene; **II**: (α-chloroethyl)benzene; **III**: benzyl chloride (BzCl)) and the reaction products were analyzed (see Scheme 2).



Scheme 3. Initiation, propagation and dormant species formation.

The reaction of **I** and **II** with compound **5** resulted in the gradual formation of **1** and LiBr and LiCl, respectively. For this reaction various reaction pathways can be envisaged. Firstly, nucleophilic substitution could be expected leading to the formation of the C–C coupling product (*C–N*)-benzyl and a molybdate with an X (X = Cl, Br) ligand. Secondly, an electron transfer reaction could occur as shown in Scheme 2 in which the molybdate(V) ($[Mo^V]^-$) is oxidized to a molybdate(VI) species ($[Mo^{VI}X]^-$) with concomitant formation of a benzyl radical. This reaction is typical for the initiation step in ATRP reactions. The benzyl radicals formed react with the alkene producing product radicals. Both radicals can react back with $[Mo^{VI}X]^-$ to give **5** and the corresponding alkyl halide (dormant species, Scheme 3).



Scheme 2. Reaction of **5** with various alkyl halides.

Any dimerization reaction of the benzyl or product radicals would lead to irreversible formation of $[Mo^{VI}X]^-$ (persistent radical effect). However, we found that the reaction of the α-substituted benzyl halides **I** and **II**, respectively, with **5** resulted in the gradual formation of **1** and LiX. This forward reaction produces the neutral Mo(VI) compound (**1**) after LiX elimination. When benzyl chloride (**III**) was used, neither **1** nor LiCl was formed. Here, the equilibrium k_1/k_{-1} is on the left side and assures that the concentration of $[Mo^{VI}X]^-$ remains low and that the reaction in which **1** and LiCl are formed, is suppressed.

The reactions $[Mo^V]^- \rightarrow [Mo^{VI}X]^-$ and $[Mo^{VI}X]^- \rightarrow$ **1** have different rates. It is known that the reactivity of the alkyl halides, and thus the position of equilibrium k_1/k_{-1}, is reflected in the bond dissociation energy (BDE) of these compounds [6c]. The order of BDE in **I**–**III** is **I** < **II** < **III** (for BzCl the BDE amounts to 70 kcal mol^{-1}) [14]. The higher the BDE, the more the equilibrium will be on the left side: this implies that in the case of **I** and **II** the equilibrium k_1/k_{-1} is so far to the right side that the reaction to the Mo^{VI} species **1** is possible. For effective ATRP the equilibrium needed, has to be on the side of the dormant species. Apparently, the use of **III** realizes this and the permanent low concentration of $[Mo^{VI}X]^-$ assures that the forward reaction is suppressed. Reactions of **I**–**III** with compounds **6**–**8** gave similar results.

When styrene (St) was added to the reaction mixture ($[St]_0 = 3$ M, $[\mathbf{5}] = 0.03$ M, $[XC(Ph)HR']_0 = 0.03$ M (X = Br, Cl) in toluene at 80°C) and the polymerization was monitored, fast initial polymerization was observed but this polymerization activity ceased within 1 h, probably because recombination of the reactive radical chains occurred (see Fig. 3).

However, when St was added to the reaction mixture of **5** and BzCl ($[St]_0 = 3$ M, $[\mathbf{5}] = 0.03$ M, $[BzCl]_0 = 0.03$ M in toluene at 80°C), polymerization of styrene is still observed after 22 h (vide infra).

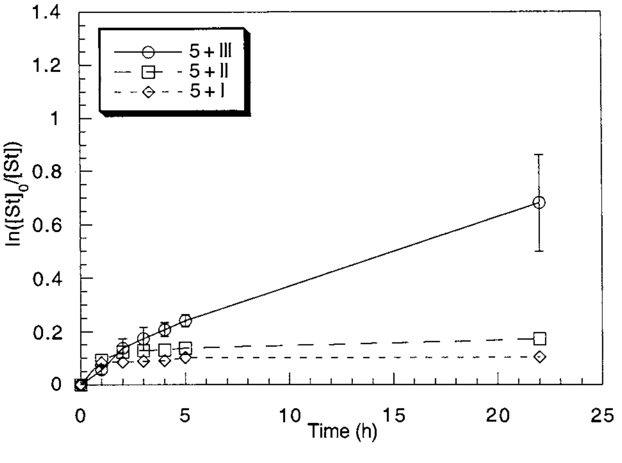


Fig. 3. Semilogarithmic plot of styrene conversion vs. time using different initiators ($[St]_0 = 3$ M, $[\mathbf{5}] = 0.03$ M, $[XC(Ph)HR']_0 = 0.03$ M in toluene at 80°C).

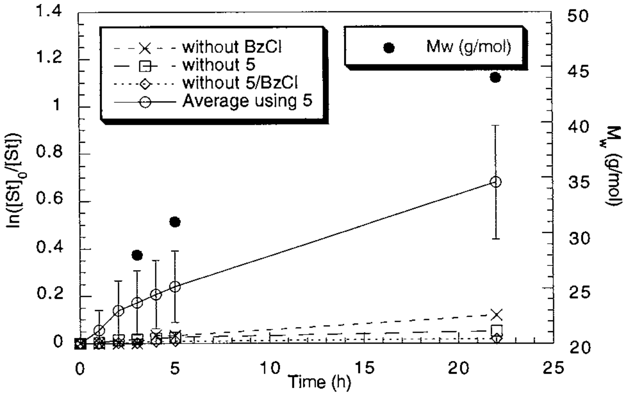


Fig. 4. Semilogarithmic plot of styrene conversion vs. time. (i) Without BzCl, (ii) without molybdenum compound (**5**), (iii) without BzCl nor **5**, and (iv) average in the presence of BzCl and **5**.

2.4. *Atom transfer radical polymerization with **5**/benzyl chloride*

In a typical experiment a mixture of in situ prepared **5** and 1 equivalent of BzCl, was added to a mixture of 30 equivalents of mesitylene (internal standard) and 100 equivalents of styrene ($[St]_0 = 3$ M, $[\mathbf{5}] = 0.03$ M, $[BzCl]_0 = 0.03$ M in toluene at 80°C). The polymerization experiments were followed by GC using mesitylene as internal standard. After 22 h the reaction was stopped and the resulting polystyrene (PS) polymers were isolated and characterized by GPC.

In order to examine the influence of the BzCl initiator and the catalyst, reactions were performed in toluene at 80°C under various experimental conditions. The semilogarithmic plot of $\ln([St]_0/[St])$ versus time is shown in Fig. 4 and the results are summarized in Table 2.

PS yields are low if polymerizations are performed without **5** (Entry 2), without BzCl (Entry 3) or without both catalyst components (Entry 1). However, with the homogeneous initiating system, **5**/BzCl, conversion reached 38% after 22 h (Entry 4). The molecular weights, determined during this experiment (Entry 4) increased during the polymerization reaction, although not linearly. The use of half the amount of $[BzCl]_0$ afforded a less active system but yielded PS with a higher molecular weight. These findings show a trend which is consistent with the fact that the initial amount of alkyl halide $[RX]_0$ determines the number of initiated chains: the polymerization rate is first order in $[RX]_0$ while the molecular weights are reciprocally dependent upon $[RX]_0$. Because the initiator efficiency is rather low ($\pm 9\%$) the influence of variations in $[BzCl]_0$ is limited.

Table 2
Styrene polymerizations in toluene with various components at 80°C

Entry	$[\mathrm{BzCl}]_0$ ($\times 10^2$ mol l^{-1})	[5] ($\times 10^2$ mol l^{-1})	% yield PS after 22 h	M_w (PDI) $\times 10^{-3}$ (g mol^{-1})
1	0	0	3	n.d.[a]
2	3	0	5	n.d.
3	0	3	11	102 (1.89)
4	3	3	38	44 (1.57)
5	1.5	3	33	51 (1.48)

[a] Not determined.

Molybdenum(V) compounds **6**, **7** and **8** were also tested for their ATRP activity with benzyl chloride as the initiator. The kinetic plots are shown in Figs. 5–7, respectively, and the results are outlined in Table 3.

The combination of BzCl and molybdenum compounds accelerates the polymerization reaction considerably. Yields of PS are in the range 38–60% and the molecular weights are high (32 000–85 000 g mol^{-1}). The PDIs are rather high (1.57–1.71) but remain constant for the different experiments. With conversions between 38 and 60%, molecular weights of the resulting PS were expected to be between 4000 and 6200 g mol^{-1} but the actual values are much higher which indicates that the initiator efficiency is poor. Only a small percentage (6–18%) of the benzyl chloride initiator is participating in the polymerization reaction. Indeed, considerable amounts of unreacted BzCl were found (GC) during and after the polymerization process[5].

The molecular weights and particularly the PDIs of the resulting polymers, shown in Table 3, show that the catalytic systems used here obey the theoretical rules that are found in other ATRP systems [2a], but poor initiator efficiency results in poor control during the polymerization reaction. Moreover, the ATRP experiments were difficult to reproduce and therefore the standard deviations of both the styrene conversions and the molecular weights are large. As **5**–**8** are very sensitive towards air, any possible air-leakage in the system may be a reason for the observed differences in reactivity of the same catalytic system. Furthermore, decomposition of the molybdenum compounds in time may be an additional problem.

The influence of the unidentified radical (with $g = 1.986 \pm 0.001$) on the polymerization appears to be modest. In polymerization experiments in which the in situ prepared molybdenum complexes are used without the BzCl initiator, only low PS yields are obtained. Apparently, the unidentified radical is not capable to initiate radical polymerization. However, because the binary systems BzCl/**5**–**8** all show similar polymerization behavior with features characteristic for ATRP [2a], the unidentified radical possibly does play a role in the ATRP activity observed. The identification and the influence of this unidentified radical on the BzCl/**5**–**8** system and the styrene polymerization is subject of future investigations.

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of dry N_2, using standard Schlenk techniques. All solvents were distilled from sodium under nitrogen, prior to use, except CH_2Cl_2, which was distilled from CaH_2. Commercially available reagents were distilled prior to use. $[\mathrm{Mo(NAr)_2}(C{-}N)\mathrm{R}]$ ($C{-}N = \mathrm{C_6H_4(CH_2NMe_2)}$-2; R = ($C$–$N$) (**1**), Me (**2**), CH_2SiMe_3 (**3**), p-tolyl (**4**)) were synthesized according to literature procedures [9]. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Bruker AC 300 spectrometer, in benzene-d_6 at room temperature (r.t.) unless otherwise indicated. GC measurements were performed on a Philips PU 4600 Gas Chromatograph with a J&W Scientific liquid-phase DB-5 column (30 m × 0.320 mm, 0.25 μm film thickness). GPC measurements were taken on a Jordi-Gel DVB Mixed Bed, 300 mm and I.D. 7.8 mm column, using a Thermo Separation Products P200 pump and UV2000 and Shodex RI-71 detectors.

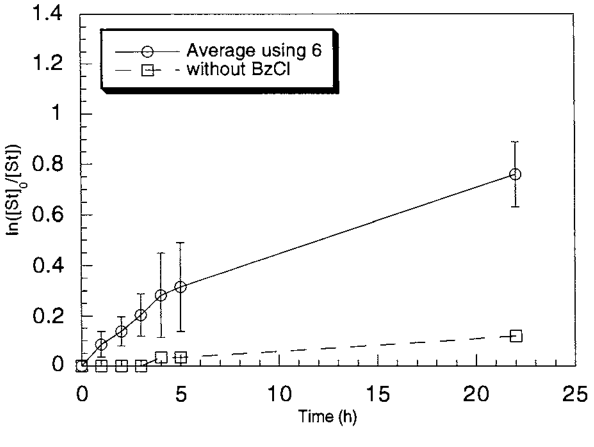


Fig. 5. Semilogarithmic plot of $\ln([\mathrm{St}]_0/[\mathrm{St}])$ vs. time with $[\mathrm{St}]_0 = 3$ M using $[\mathrm{LiMo(NAr)_2}(C{-}N)\mathrm{Me}]$ (**6**) (= 0.03 mM).

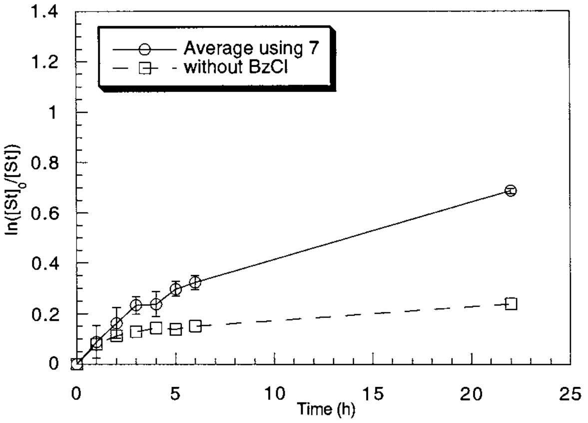


Fig. 6. Semilogarithmic plot of ln($[St]_0$/[St]) vs. time with $[St]_0 = 3$ M using $[LiMo(NAr)_2(C\text{–}N)(CH_2SiMe_3)]$ (**7**) (= 0.03 mM).

3.2. EPR spectroscopy

The EPR spectra were recorded at r.t. on a modified Bruker ESP 300 spectrometer operating near 9.4 GHz. The samples were enclosed in carefully sealed quartz tubes (∅ = 2 mm) developed for manipulation of liquid samples under conditions free of oxygen and water. The tubes were placed in the center of a Bruker ST1 resonator (operating in the TE_{102} mode with unloaded $Q = 3800$). The magnetic field was centered around 3380 G, with a sweep width of 500 G. The magnetic field was modulated with a frequency of 100 kHz and amplitude of 2.5 G. The microwave power was 20–40 μW, gain = 2×10^4, time constant = 5 ms, and ADC conversion time = 10 ms. The EPR spectra contain 8k field points in order to achieve good field resolution. The concentrations contained 8–15 mM of molybdenum and toluene were used as a solvent throughout. The values of the g-factor and hyperfine splitting A were extracted from the experimental EPR spectra by fitting the experimental line positions to those obtained from a perturbation expansion up to second order in the hyperfine coupling [13]. This procedure leaves the sign of the hyperfine coupling undetermined.

3.3. General polymerization procedure

Compounds **5**–**8** were prepared in situ by dissolving $[Mo(NAr)_2(C\text{–}N)R]$ ($C\text{–}N = C_6H_4(CH_2NMe_2)\text{-}2$; R = ($C$–$N$) (**1**), Me (**2**), CH_2SiMe_3 (**3**), p-tolyl (**4**)) (0.50 mmol), respectively, in toluene (8 ml) to which 0.77 ml of a 1.60 M solution of n-BuLi (0.48 mmol) was added at −78°C. The reaction mixture was allowed to warm to r.t. and was stirred overnight. After 18 h, 0.063 g of benzyl chloride (0.50 mmol) was added and the reaction mixture was stirred for 15 min.

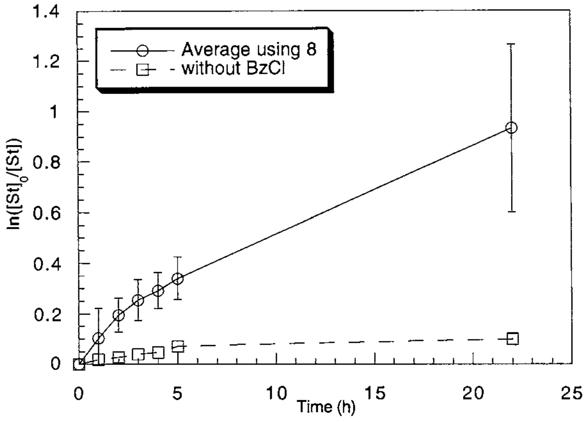


Fig. 7. Semilogarithmic plot of ln($[St]_0$/[St]) vs. time with $[St]_0 = 3$ M using $LiMo(NAr)_2(C\text{–}N)(p\text{-tolyl})]$ (**8**) (= 0.03 mM).

In a Schlenk vessel was mixed 5.21 g of styrene (50 mmol) and 1.80 g mesitylene (15 mmol) as an internal standard. The solution was warmed to 80°C and the catalyst solution was quickly added to this mixture. The polymerization reaction was followed from this point on. Samples of 0.5 ml were taken from the reaction mixture at 1 h intervals and were quenched with 5 ml of methanol. The white precipitate was removed by filtration and the clear solution was measured by GC. The reaction was stopped after 22 h by quenching with methanol. The polymer was collected, dried in vacuo and analyzed by NMR and GPC.

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Table 3
Results of ATRP of styrene using **5**–**8**

Compound	Average styrene conversion (%)[a]	M_w (g mol^{-1}) expected	$M_w \times 10^{-3}$ (g mol^{-1})[a]	PDI[a]	BzCl$_{eff}$[b] (%)
5	38 (7)	3958	44 (7)	1.57 (0.02)	9
6	55 (7)	5728	32 (3.5)	1.69 (0.04)	18
7	50 (5)	5207	85 (15)	1.62 (0.07)	6
8	60 (10)	6249	48 (7)	1.71 (0.01)	13

[a] The estimated standard deviations are shown in parentheses.

[b] Benzyl chloride initiator efficiency = M_w/M_w expected.

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