Macromolecules **2005,** *38,* 27−32

Controlled Radical Polymerization of Styrene by Quinone Transfer Radical Polymerization (QTRP)

Jean-Raphaël Caille,[†] Antoine Debuigne,[‡] and Robert Jérôme*,[‡]

Solvay Research and Technology, rue de Ransbeek 310, B-1120 Brussels, Belgium, and
Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

Received July 15, 2004; Revised Manuscript Received October 26, 2004

ABSTRACT: Radical polymerization of styrene falls under control when conducted at 100 °C in the presence of an *ortho*-quinone, e.g., phenanthrenequinone (PhQ), and a catalytic amount of cobalt(II) acetylacetonate. Criteria for a controlled chain polymerization are fulfilled at least until 50% of monomer conversion, i.e., molar mass increasing with monomer conversion, molar mass predictable from the styrene/quinone molar ratio, linear time dependence of $\ln([M]_0/[M])$, and effective resumption of styrene polymerization by preformed oligopolystyrene. A tentative mechanism is proposed for this new system designated as quinone transfer radical polymerization (QTRP).

Introduction

Controlled radical polymerization of vinyl monomers has been widely investigated for the past decade, with the purpose to synthesize macromolecules with well-defined molecular characteristics under not very demanding conditions. The common feature of all controlled radical polymerizations relies on a reversible activation−deactivation process. As a result of it, the instantaneous radical concentration is decreased, and the ratio of the apparent rate constants of propagation and termination (k_p/k_t) is substantially increased at the benefit of the lifetime of the chains and the control of their length.

Several approaches have been reported, i.e., the nitroxide-mediated or alkoxyamine-initiated polymerization (NMP),[1] the atom transfer radical polymerization (ATRP),[2] and the reversible addition−fragmentation chain transfer (RAFT).[3] However, each of these well-known strategies has limitations, which justifies that a constant effort is devoted to any possible improvement.

This paper aims at reporting on a new method able to impart control to the radical polymerization of styrene (sty), which is based on a complex of phenanthrenequinone (PhQ) and cobalt(II) acetylacetonate. The basic reaction is the oxidation of an organometallic species,[4] particularly $Co(acac)_2$,[5] by an *ortho*-quinone with formation of a persistent radical centered on an oxygen atom (Scheme 1). The first series of experiments is conducted on the assumption of a counter-radical-mediated polymerization mechanism. The second part of this contribution is devoted to a much more attractive catalytic mechanism.

Experimental Section

Materials. Styrene (Aldrich, >99%) was dried over calcium hydride, degassed by several freeze−thawing cycles before being distilled under reduced pressure, and stored under nitrogen. Toluene (tolu) was dried over sodium and degassed by bubbling of nitrogen for 15 min. Phenanthrenequinone (PhQ) (Aldrich, >99%) and cobalt(II) acetylacetonate (Merck, >98%) were used as received.

Scheme 1

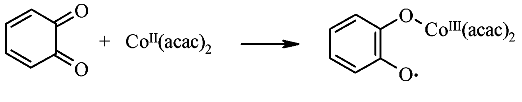


Table 1. Bulk Radical Polymerization of Styrene at 100 °C[a]

entry	additives	time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,theor}/M_{n,SEC}$	M_w/M_n
1	no additive	6	18	440 000	/	1.8
2	$Co(acac)_2$	23	27	340 000	0.04	2.2
		31	47	310 000	0.07	2.2
3	PhQ	45	30	80 000	0.17	2.2
		53	41	78 000	0.24	2.2
		76	59	85 000	0.32	2.1
		93	66	85 000	0.36	2.1
4	$Co(acac)_2$, PhQ	43	16	9 900	0.74	1.2
		50	22	11 800	0.85	1.2
		66	38	15 500	1.12	1.3
		74	45	16 200	1.26	1.3
		96	57	17 300	1.50	1.5

[a] (**1**) Styrene; (**2**) $[Co(acac)_2]/[Sty]$: 1/440; (**3**) [PhQ]/[Sty]: 1/440; (**4**) $[PhQ]/[Co(acac)_2]/[Sty]$: 1/1/440.

Characterization. Molar mass and polydispersity of polystyrene were determined by size exclusion chromatography (SEC), with THF as an eluent at 40 °C, with a Hewlett-Packard 1090 liquid chromatograph (four columns HP PL gel 5 μL: 10^5, 10^4, 10^3, and 10^2 Å) connected to a Hewlett-Packard 1037 refractive index detector. Polystyrene standards, with a narrow molar mass distribution, were used for calibration.

General Recipe for the Styrene Radical Autopolymerization in the Presence of PhQ and $Co(acac)_2$. 20.8 mg of PhQ (1.0×10^{-4} mol) was dissolved in 5.0 mL of degassed styrene (44×10^{-3} mol) under nitrogen with the formation of an orange-colored solution. 1.0 mL of a $Co(acac)_2$ solution in toluene (10^{-6} mol/mL) was added with a syringe under nitrogen, and the reaction medium was heated at 100 °C under stirring. After a few minutes, the color changed from orange to green, although no polymerization occurred for 24 h. Then the coloration slowly vanished parallel to a substantial increase in the solution viscosity. Samples were picked out at different reaction times, and the styrene conversion was determined by gravimetry after elimination of the residual monomer in vacuo at 80 °C (Table 2, entry 2).

The same reaction was also conducted with different amounts of $Co(acac)_2$ (solutions of $Co(acac)_2$ in toluene: $S_1 = 10^{-5}$ mol/mL; $S_2 = 10^{-6}$ mol/mL; $S_3 = 10^{-7}$ mol/mL). When a stoichiometric amount of $Co(acac)_2$ (25.7 mg, 1.0×10^{-4} mol) was used, the metal derivative was added as a solid.

[†] Solvay Research and Technology.

[‡] University of Liège.

* To whom correspondence should be addressed: Tel (32) 4-3663565; fax (32) 4-3363497; e-mail rjerome@ulg.ac.be.

10.1021/ma048561o CCC: $30.25

Table 2. Styrene Polymerization at 100 °C in the Presence of Phenanthrenequinone and Catalytic Amounts of $Co(acac)_2$[a]

entry	$[Co(acac)_2]/[PhQ]$	time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,theor}$ (g/mol)	$M_{n,theor}/M_{n,SEC}$	M_w/M_n
1	0.1	46	17	7 500	7 700	1.03	1.22
		53	23	9 800	10 500	1.07	1.21
		70	37	14 200	16 800	1.18	1.24
		77	45	15 100	20 500	1.36	1.26
		94	54	16 600	24 600	1.48	1.30
		123	66	16 600	30 000	1.81	1.42
2	0.01	28	6	3 300	2 700	0.82	1.30
		45	26	11 700	11 800	1.01	1.28
		52	32	13 700	14 600	1.07	1.29
		73	44	17 700	20 000	1.13	1.31
		165	77	18 500	35 000	1.89	1.50
3	0.001	46	17	12 300	7 700	0.63	1.78
		53	22	13 700	10 000	0.73	1.80
		70	34	16 700	15 500	0.93	1.78
		77	38	17 400	17 300	0.99	1.80
		94	45	19 100	20 500	1.07	1.80
		123	57	22 500	25 900	1.15	1.78

[a] Sty/tolu = 5/1 (v/v). (**1**) $[PhQ]/[Co(acac)_2]/[Sty]$: 1/0.1/440; (**2**) $[PhQ]/[Co(acac)_2]/[Sty]$: 1/0.01/440; (**3**) $[PhQ]/[Co(acac)_2]/[Sty]$: 1/0.001/440.

Synthesis of a Low Molar Mass Polystyrene Macroinitiator in the Presence of PhQ and $Co(acac)_2$. Degassed styrene (40.0 mL, 350×10^{-3} mol) was added to PhQ (416 mg, 2.0×10^{-3} mol) under nitrogen. A $Co(acac)_2$ solution in toluene (2.0 mL of S_1, 2×10^{-5} mol) was then added to the reaction medium with a syringe under nitrogen, and the medium was heated at 100 °C for 72 h. After this period, the initially green reaction medium was discolored. The polymer was diluted with THF, purified by repeated precipitation in methanol, filtered, and dried in vacuo at room temperature (conversion = 28%, M_n = 4300 g/mol, M_w/M_n = 1.40).

Resumption of the Styrene Polymerization by a Polystyrene Macroinitiator and $Co(acac)_2$. The polystyrene macroinitiator (0.43 g, 1.0×10^{-4} mol, M_n = 4300 g/mol, M_w/M_n = 1.40) was dissolved in degassed styrene (5.0 mL, 44×10^{-3} mol) under nitrogen. A $Co(acac)_2$ solution in toluene (1.0 mL of S_2, 10^{-6} mol) was then added to the reaction medium with a syringe under nitrogen, and the medium was heated at 100 °C. The same reaction was conducted in the absence of $Co(acac)_2$. Samples were regularly withdrawn from the polymerization medium, and the monomer conversion was calculated as before.

Results and Discussion

Polymerization of Styrene in the Presence of PhQ and a Stoichiometric Amount of $Co(acac)_2$. Styrene undergoes spontaneous polymerization (autopolymerization) at high temperature.[6] Bulk polymerization of styrene at 100 °C results in high molar mass polystyrene with a broad molar mass distribution in a completely uncontrolled manner, as reported in Table 1 (entry 1).

However, when conducted in the presence of a stoichiometric mixture of cobalt(II) acetylacetonate and PhQ, the course of the styrene autopolymerization is deeply modified (Table 1, entry 4). Indeed, a polymer with a much lower molar mass and a narrow molar mass distribution is formed under these conditions. Moreover, the molar mass of polystyrene increases first with the monomer conversion and then deviates from this ideal behavior (Figure 1, ◆). At low conversion, the experimental molar mass is in good agreement with the theoretical value calculated on the assumption that the cobalt–quinone complex is the control agent. Beyond 50% conversion, the polymerization is uncontrolled, dead chains accumulate in the polymerization medium, the polydispersity increases, and $M_{n,SEC}$ stops increasing (see the evolution of the $M_{n,SEC}$ in Table 1).

Before drawing conclusions about the control capacity of the PhQ/Co^{II} two-component system, it is desirable to check that neither the quinone nor the Co^{II} complex can control the radical polymerization of styrene. Table 1 (entries 2 and 3) shows that polymerization is deprived of control when only one constituent (particularly, $Co(acac)_2$) of the supposed polymerization mediator is used. Moreover, phenanthrenequinone inhibits the styrene polymerization before providing broadly polydispersed polystyrene. So the mediating species results from the reaction of the quinone with Co^{II}, as was anticipated when the experiments were devised.

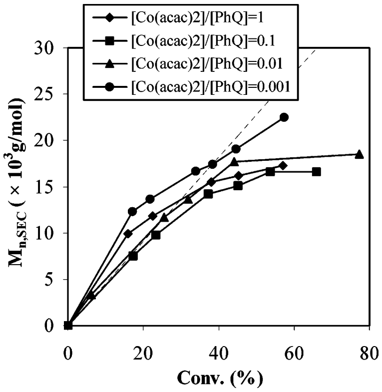


Figure 1. Dependence of molar mass on monomer conversion for the styrene polymerization at 100 °C in the presence of phenanthrenequinone and various amounts of $Co(acac)_2$. [PhQ]/[Sty]: 1/440; sty/tolu: 5/1 (v/v) (Table 1, entry 4 and Table 2). The dotted line shows the theoretical dependence.

Kinetics of the styrene autopolymerization at 100 °C, in the presence of Co^{II} and phenanthrenequinone, is first order in monomer as assessed by the linear dependence of $\ln([M]_0/[M])$ on time (Figure 2). In the first stage of the reaction, no polymerization occurred. During this induction period, the persistent cobalt–quinone radical is a trap for the radicals spontaneously formed by styrene at 100 °C. The polymerization is thought to start when the persistent radicals have been consumed, in such a way that the active radicals/dormant species equilibrium is established. The key step of the control process would be the reversible rupture of the labile carbon–oxygen bond between the cobalt–quinone complex and the polystyrene chain, as shown in Scheme 2.

Polymerization of Styrene in the Presence of PhQ and Various Amounts of $Co(acac)_2$. However, further investigations have called the proposed mechanism into question. Indeed, the polymerization control

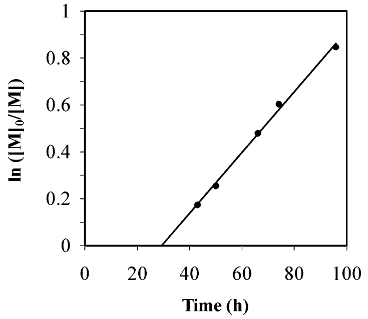
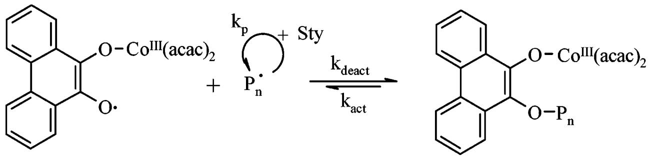


Figure 2. Plot of ln([M]$_0$/[M]) vs time for the styrene autopolymerization at 100 °C in the presence of stoichiometric amounts of PhQ and Co(acac)$_2$. [PhQ]/[Co(acac)$_2$]/[Sty]: 1/1/440 (Table 1, entry 4).

Scheme 2



persists when styrene is polymerized in the presence of PhQ and various catalytic amounts of Co(acac)$_2$ (Table 2). At low conversion, the molar mass increases linearly with conversion (Figure 1), whereas the polydispersity (M_w/M_n) is quite low (Table 2). Moreover, the experimental molecular weight determined by SEC is close to the theoretical value calculated on the assumption that PhQ is the "control agent". This agreement is confirmed by the $M_{n,theor}/M_{n,SEC}$ ratio, which is close to unity (Table 2). Nevertheless, as was the case for experiments conducted in the presence of stoichiometric amounts of the cobalt complex and PhQ, the experimental molar masses deviate from the theoretical values at higher conversion (beyond 50% conversion), and the molar mass distribution becomes broader. Formation of additional radical species by styrene self-polymerization all along the process can be an explanation for this phenomenon. The agreement between experimental and theoretical molar masses at high styrene conversion is better at [Co(acac)$_2$]/[PhQ] molar ratio as low as 0.001 (although with a higher polydispersity). In contrast, the data fit better a controlled polymerization at low conversion when the [Co(acac)$_2$]/[PhQ] ratio is 0.1. A [Co(acac)$_2$]/[PhQ] ratio of 0.01 seems to be a good compromise between the control of molecular parameters (M_n, M_w/M_n) and the lower amount of metal required.

Kinetics of the styrene autopolymerization at 100 °C, in the presence of PhQ and a catalytic amount of Co^{II}, is first order in monomer. Figure 3 shows a linear dependence of ln([M]$_0$/[M]) on time for the styrene polymerization carried out in the presence of PhQ and 1% of Co(acac)$_2$. Moreover, an induction period of time is observed in all the experiments during which quinone is thought to be consumed by the in situ formed radicals as assessed by the discoloration of the reaction medium. Then oligomers are formed, and the solution viscosity increases as the polymerization goes forward. Qualitatively, the same sequence of events is noted when the styrene polymerization is conducted only in the presence of PhQ, i.e., induction period, disappearance of the orange color of PhQ, oligomers formation, and, in this case, uncontrolled growth of the chains. The kinetics of the styrene polymerization is essentially independent of the catalytic amount of Co(acac)$_2$ used.

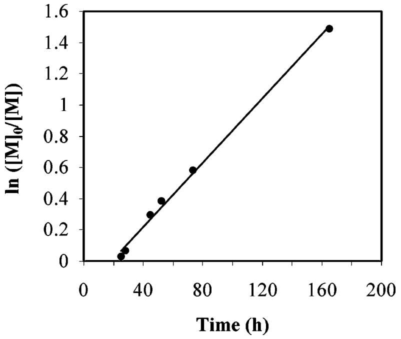


Figure 3. Plot of ln([M]$_0$/[M]) vs time for the styrene autopolymerization at 100 °C in the presence of PhQ and catalytic amount of Co(acac)$_2$. [PhQ]/[Co(acac)$_2$]/[Sty]: 1/0.01/440; sty/tolu: 5/1 (v/v) (Table 2, entry 2).

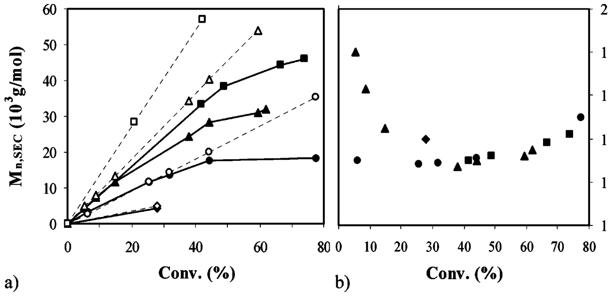


Figure 4. Dependence of (a) molar mass and (b) polydispersity on monomer conversion for the styrene polymerization at 100 °C in the presence of PhQ and catalytic amount of Co(acac)$_2$ with different [Sty]/[PhQ] ratios. (◆) [PhQ]/[Co(acac)$_2$]/[Sty]: 1/0.01/175, sty/tolu = 20/1 (v/v). (●) [PhQ]/[Co(acac)$_2$]/[Sty]: 1/0.01/440, sty/tolu = 5/1 (v/v). (▲) [PhQ]/[Co(acac)$_2$]/[Sty]: 1/0.01/870, sty/tolu = 10/1 (v/v). (■) [PhQ]/[Co(acac)$_2$]/[Sty]: 1/0.01/1310, sty/tolu = 15/1 (v/v). The dotted lines with hollow symbols show theoretical dependences.

Compared to ATRP, in which a metal salt is also used as catalyst, the concentration of the metallic species can be decreased substantially in this process without losing the control.

Polymerization of Styrene at Different [Styrene]/[PhQ] Molar Ratios. Two major effects are noted when the [styrene]/[PhQ] molar ratio is changed while keeping the amount of cobalt constant (1% of Co(acac)$_2$ compared to the quinone). First, the molar masses are determined by the [styrene]/[PhQ] ratio. Indeed, the slope of the molar mass vs conversion plot increases with the monomer/PhQ molar ratio while the polydispersity remains in the 1.3−1.6 range, as shown in parts a and b of Figure 4, respectively. Moreover, at constant styrene conversion, the discrepancy between experimental and theoretical molar masses increases with this ratio, which indicates that the synthesis of polystyrene of high molar mass by this technique might be a problem. Second, the induction period decreases with increasing the [styrene]/[PhQ] molar ratio. Because the concentration of styrene is maintained quasi-constant, the rate of production of the initiating radicals by autopolymerization is nearly the same in this series of experiments. Therefore, when the concentration of PhQ is decreased, less quinone has to be consumed before the polymerization starts, consistent with a shorter induction period (Figure 5).

Because the molar mass of polystyrene is basically controlled by the [styrene]/[PhQ] ratio, it is a reasonable hypothesis that PhQ end-caps the polystyrene chains reversibly and acts as a mediator in this CRP process.

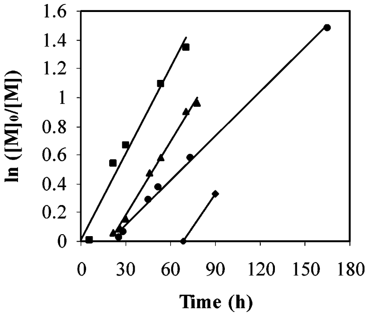


Figure 5. Plot of ln([M]$_0$/[M]) vs time for the styrene autopolymerization at 100 °C in the presence of PhQ and catalytic amount of $Co(acac)_2$ ([$Co(acac)_2$]/[PhQ] = 0.01) with different [Sty]/[PhQ] ratios. (◆) [Sty]/[PhQ] = 175, (●) [Sty]/[PhQ] = 440, (▲) [Sty]/[PhQ] = 870, and (■) [Sty]/[PhQ] = 1310.

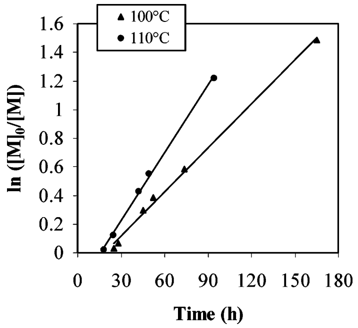


Figure 6. Plot of ln([M]$_0$/[M]) vs time for the styrene autopolymerization, in the presence PhQ and catalytic amount of $Co(acac)_2$ ([PhQ]/[$Co(acac)_2$]/[Sty]: 1/0.01/440, sty/tolu = 5/1 (v/v)) at 100 and 110 °C (Table 2, entry 2 and Table 3, respectively).

Table 3. Styrene Polymerization at 110 °C in the Presence of PhQ and $Co(acac)_2$[a]

time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,theor}$ (g/mol)	$M_{n,theor}/M_{n,SEC}$	M_w/M_n
18	2	1 100	900	0.82	1.56
25	12	4 500	5 500	1.22	1.45
42	35	11 300	15 900	1.41	1.31
49	43	12 500	19 600	1.57	1.32
94	71	13 700	32 300	2.36	1.44

[a] [PhQ]/[$Co(acac)_2$]/[Sty]: 1/0.01/440, sty/tolu = 5/1 (v/v).

Effect of Temperature. As expected and confirmed by the change in the slope of the time dependence of ln([M]$_0$/[M]), the polymerization is faster and the inhibition time is decreased when the polymerization temperature is increased from 100 to 110 °C (Figure 6). In parallel, the discrepancy between the experimental and theoretical masses at high conversion increases with the polymerization temperature, in contrast to the polydispersity which remains unchanged (see entry 2 in Table 2, and Table 3).

Resumption of the Styrene Polymerization by a Polystyrene Macroinitiator. To support the hypothesis that the polystyrene chains are end-capped by a PhQ unit, low molar mass chains have been synthesized using a [styrene]/[PhQ] ratio equal to 175 in the presence of a catalytic amount of $Co(acac)_2$ (conversion = 28%, $M_{n,SEC}$ = 4300 g/mol; M_w/M_n = 1.4). The polymer was precipitated in methanol before being used as potential macroinitiator for the styrene polymerization (Figure 7).

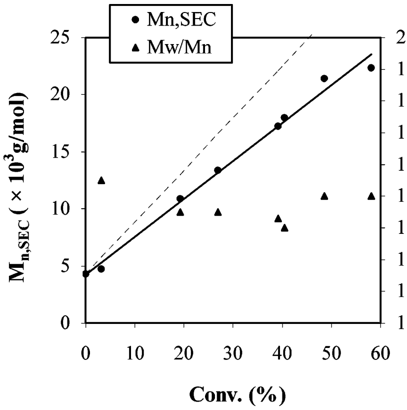


Figure 7. Dependence of molar mass and polydispersity on monomer conversion for resumption of the styrene polymerization at 100 °C by a polystyrene macroinitiator (M_n = 4300 g/mol, M_w/M_n = 1.4) in the presence of a catalytic amount of $Co(acac)_2$ ([PS macroinitiator]/[$Co(acac)_2$]/[Sty]: 1/0.01/440, sty/tolu = 5/1 (v/v)). The dotted line shows the theoretical dependence of M_n vs conversion.

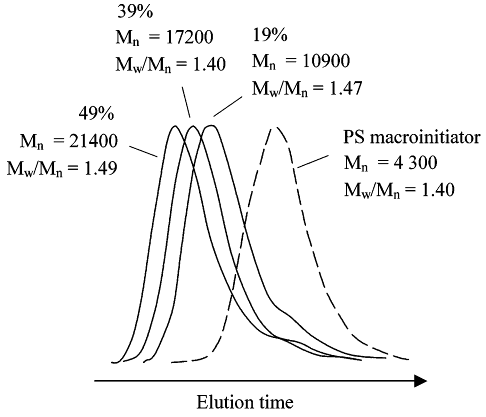


Figure 8. Evolution of SEC traces for the resumption of styrene polymerization by a polystyrene macroinitiator in the presence of catalytic amount of $Co(acac)_2$ at 100 °C ([PS macroinitiator]/[$Co(acac)_2$]/[Sty]: 1/0.01/440, sty/tolu = 5/1 (v/v)).

Figure 7 shows that the molar mass dependence on monomer conversion is linear, although with a slope which is lower than the theoretical value. Moreover, the polydispersity tends to decrease at least until 40% conversion. Although it is a qualitative observation, small amount of unreacted PS-macroinitiator can be detected by SEC (Figure 8), which strongly suggests that most of the polystyrene chains collected by precipitation in methanol have the structure of the dormant species and that their "initiation efficiency" is very high. Furthermore, the linear time dependence of ln([M]$_0$/[M]) shows no induction period, which is additional evidence that the polystyrene macroinitiator is the dormant species of the system (Figure 9). These macroinitiators are stable enough for being isolated by precipitation and filtration, dried under reduced pressure at room temperature, and used to resume the controlled radical polymerization of styrene. Unfortunately, the ^{1}H NMR analysis of polystyrene oligomers does not permit to clearly establish the structure of the dormant species because signals typical of the aromatic protons of the phenanthrenequinone end groups are hidden in the broad signal for the polystyrene chains. The addition of $Co(acac)_2$ remains however mandatory. Indeed, in the absence of this catalysis, a bimodal molecular weight distribution is observed that consists of the polystyrene macroinitiator and high molar mass polystyrene expectedly formed by the traditional (and thus uncontrolled) autopolymerization of styrene at 100 °C. It is clear that

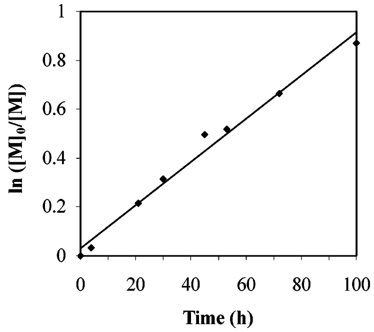
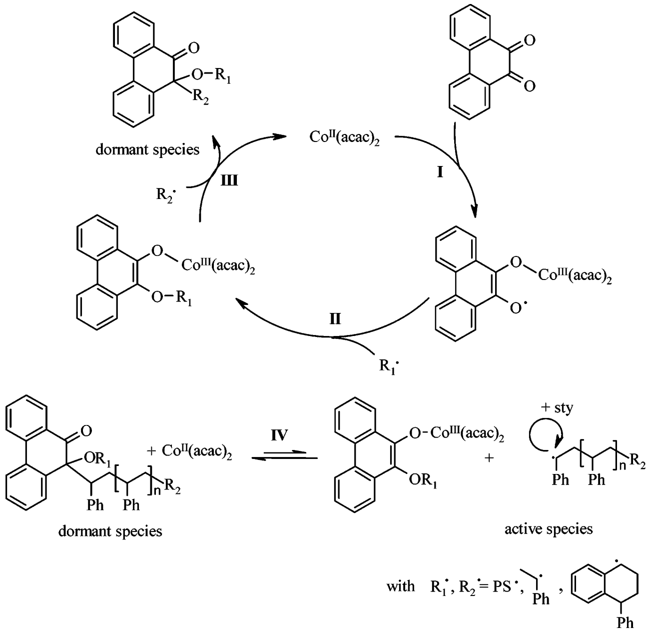


Figure 9. Plot of ln([M]$_0$/[M]) vs time for the resumption of the styrene polymerization at 100 °C by a polystyrene macroinitiator (M_n = 4300 g/mol, M_w/M_n = 1.4) in the presence of a catalytic amount of Co(acac)$_2$ ([PS macroinitiator]/[Co(acac)$_2$]/[Sty]: 1/0.01/440, sty/tolu = 5/1 (v/v)).

Scheme 3



the macroinitiator cannot operate in the absence of the metallic catalyst.

Mechanism Proposal and Experimental Observations. Phenanthrenequinone is known for a long time as an efficient radical trap.[7] Particularly, PhQ is used to inhibit the radical polymerization of styrene.[8] It is thus reasonable to propose that polystyrene is end-capped by PhQ, which would be the actual polymerization mediator. The induction period of time, which is systematically observed, would be the time required for the formation of the dormant species by reaction of the quinone with radicals spontaneously formed by styrene at 100 °C. Quite interestingly, a catalytic amount of Co(acac)$_2$ is sufficient to impart a control to the styrene polymerization. On the basis of all these observations, a four-step mechanism can be proposed for the control of the radical polymerization of styrene in the presence of PhQ and a catalytic amount of Co(acac)$_2$ (Scheme 3).

I. Formation of a persistent radical by oxydo-reductive reaction of PhQ and Co(acac)$_2$, as assessed by the change of color of the reaction medium from orange, the color characteristic of PhQ, to green, the typical color for this type of radicals.

II. The persistent cobalt–quinone radicals trap the radicals $R_1^•$ spontaneously formed by the styrene autopolymerization.

III. Reaction of a second radical $R_2^•$ with the quinonoid species leads to the formation of the dormant species, releasing the metallic complex able to react with another PhQ. This permits the turnover of the catalyst until complete conversion of the PhQ, marked by the discoloration of the reaction medium.

IV. Equilibrium between dormant and active species activated by the Co(acac)$_2$ is consistent with the control imparted to styrene polymerization.

The kinetics of the three first steps governs the length of the induction period, whereas the fourth step is the actual step of control.

Conclusions

This paper has reported on a new process for the controlled radical polymerization of styrene based on an *ortho*-quinone and a catalytic amount of cobalt(II) acetylacetonate. Even though departure from ideal control is regularly observed beyond 50% conversion under these conditions, the catalytic feature of this new procedure raises optimistic forecasts. The mechanism of control, which is proposed on the basis of the experimental data collected until now, relies on a catalytic reversible homolytic cleavage of a carbon–carbon bond of substituted *ortho*-quinones. This mechanism might be tentatively designated as quinone transfer radical polymerization (QTRP). The study is now extended to additional *ortho*-quinones and metallic catalysts in order to confirm the proposed mechanism and to evaluate better the potential and limitations of this new system.

Acknowledgment. The authors gratefully acknowledge Solvay for financial support and fellowship to A. Debuigne. They are grateful to V. Bodart and F. Declercq for fruitful discussions. They are also indebted to the "Belgian Science Policy" for financial support in the frame of the "Interuniversity Attraction Poles Programme (PAI V/03)–Supramolecular Chemistry and Supramolecular Catalysis". J.-R. Caille and R. Jérôme are much indebted to O. Detaille and I. Olen for skillful assistance.

References and Notes

(1) (a) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909. (b) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4581429, 1985. (c) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (d) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373. (e) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.

(2) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (b) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (c) Granel, C.; Dubois, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1996**, *29*, 8576. (d) Patten, T. E.; Matyjaszewski, K. J. *Adv. Mater.* **1998**, *10*, 901. (e) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (e) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.

(3) (a) Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559. (b) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977. (c) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993.

(4) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45. (b) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331 and references therein.

(5) Kukes, S. G.; Prokofev, A. I.; Masalimov, A. S.; Bubnov, N. N.; Solodovnikov, S. P.; Kabachnik, M. I. *Izves. Akad. Nauk SSSR, Ser. Khim.* **1978**, *7*, 1519.
(6) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289.
(7) (a) Finley, K. T. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1974; Part 2, Chapter 17, p 963. (b) Maruyama, K.; Sakurai, H.; Otsuki, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2777.
(8) Foord, S. G. *J. Chem. Soc.* **1940**, 48.

MA048561O