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Nitroxide-Mediated Polymerization: The Pivotal Role of the k_d Value of the Initiating Alkoxyamine and the Importance of the Experimental Conditions

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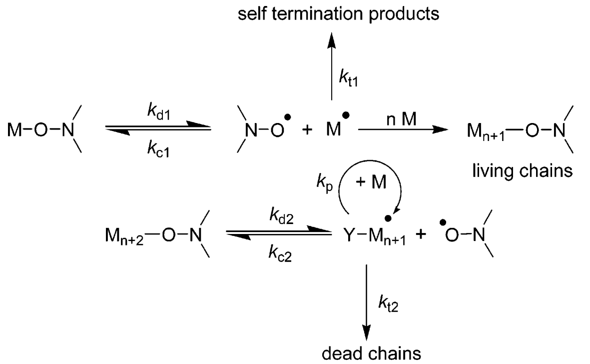
ABSTRACT: In nitroxide-mediated polymerization, NMP, the role of the initiation and therefore the role of the initiating dissociation rate constant k_{d1} on the control and livingness of a styrene and *n*-butyl acrylate polymerization was investigated. Different polymerizations were carried out, initiated with two different alkoxyamines based on the same nitroxide (**1•** or SG1). Kinetic modeling studies using the PREDICI software are used to explain these results. The use of a new tertiary SG1-based alkoxyamine **1a** instead of the secondary SG1-based alkoxyamine **1b** improved the control of the polymerization of both styrene and *n*-butyl acrylate. In particular, the polymerization of *n*-butyl acrylate can be carried out without adding any extra initial amount of nitroxide and the controlled polymerization of styrene at 90 °C is now possible. The complete kinetic analysis showed that the main role of the alkoxyamine with a high dissociation rate constant is to produce quickly in situ an extra amount of free nitroxide, which is necessary to obtain a good control of a polymerization. Moreover, we linked theoretically the threshold k_{d1} value necessary to have a good controlled and living polymerization in a true monocomponent system with the value of the propagation rate constant k_p. This new statement ($k_p/k_{d1} \leq 6.0 \times 10^5$ L·mol^{-1}) has to be added to Fischer's equations to determine the optimum experimental conditions to obtain a successful polymerization. Furthermore, the results showed clearly the importance of the experimental procedure (heating with a ramp of temperature or not, purity of the monomers and the vessels) to obtain a successful living/controlled polymerization.

Introduction

Since Rizzardo et al.[1] showed that it was possible to prepare well-controlled and living (homo-, co)polymer by radical polymerization in the presence of nitroxyl radical as controlling agent, numerous studies on the mechanism[2,3] and the kinetics[4−11] of the nitroxide-mediated polymerization (NMP) have been carried out. The breakthrough made by Fischer's group when it showed that the kinetics of the NMP were based on the persistent radical effect (PRE) (Scheme 1)[12] made possible the development of models of polymerization. The development of kinetic models for ideal NMP,[4,5,13] for NMP in the presence or in the absence of an extra amounts of nitroxide,[6,9,14] for NMP when side reactions are accounted for,[15] for NMP when additives are used, and so on,[14] allows the estimate of the conversion (ln [M]$_0$/[M]), of the final polydispersity index PDI$_\infty$, and of the dead polymer fraction $\phi_{90\%\ \mathrm{conv}}$.[4−7] Equations 1−3 are given for the ideal case.

Scheme 1



$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = \frac{3}{2}k_p\left(\frac{k_{d2}[\mathrm{I}]_0}{3k_{c2}k_{t2}}\right)^{1/3} t^{2/3} \tag{1}$$

with [I]$_0$ the initial alkoxyamine concentration, [M]$_0$ the initial

$$\mathrm{PDI}_\infty = 1 + \frac{[\mathrm{I}]_0}{[\mathrm{M}]_0} + \left(\frac{\pi k_p{}^3[\mathrm{I}]_0}{k_{d2}k_{c2}k_{t2}}\right)^{1/2} \tag{2}$$

$$\phi_{90\%\ \mathrm{conv}} = \left(\frac{2k_{d2}k_{c2}\ln 10}{k_{c2}k_p[\mathrm{I}]_0}\right)^{1/2} \tag{3}$$

monomer concentration, and [M] the instantaneous monomer concentration.

All these equations and models are based on a set of rate constants of the NMP basic reactions (Scheme 1), which are k_{d2} and k_{c2}, the decomposition and the recombination rate constants of the macroalkoxyamine, respectively, the self-termination rate constant k_{t2} of the propagating alkyl radical, and the polymerization rate constant k_p. Because k_{t2} and k_p are given for a radical and a monomer, it appeared that the values of k_{d2} and k_{c2} were the crucial parameters to control. Therefore, it prompted several groups to develop new nitroxides and to study the structural effects influencing k_d and k_c.[1,16−31] It steamed up that k_d was the most important parameter because it varies on a wider range (10^{-10} s^{-1} < k_d < 1 s^{-1} at 120 °C).[18,22−24,32,33] than k_c does (10^5 L mol^{-1} s^{-1} < k_c < 10^9 L mol^{-1} s^{-1}, from

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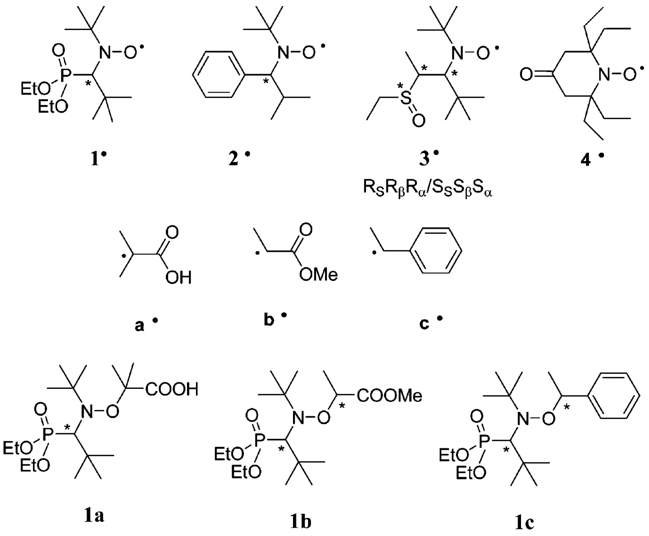
Scheme 2



room temperature to 120 °C).[33−37] From these studies, the use of an initiating alkoxyamine exhibiting a close structure of the dormant species became a rule of thumb, therefore it triggered a race to alkoxyamines (based on new nitroxide fragment) displaying high k_d values to perform polymerization at lower and lower temperatures.[18−19,21,23,24,26] During that period, our group developed two nitroxides, **1•** (SG1) and **2•** (TIPNO, Scheme 2),[17] which were revealed to be efficient for NMP experiments. In 1999, Hawker et al.[19] promoted the TIPNO-based alkoxyamines as efficient controlling agents for the polymerization of styrene and acrylate monomers, with the presence of an extra amount of TIPNO for the acrylates polymerization as well as several other monomers. In the same time, we showed that the alkoxyamine **1b** was at least as efficient as TIPNO derivatives and often even better than this latter for styrene and acrylate monomers.[20,38]

The race to new sophisticated efficient nitroxides becomes a hard task to overcome as many structures are now accessible from literature; we then decided rather to work on the initiation step to improve this process. Among the numerous SG1-based alkoxyamines prepared in our laboratory, the alkoxyamine **1a**, based on a methacrylic acid moiety, has become, at that time, the most potent and versatile alkoxyamine ever prepared.[21,39−41] These preliminary results showed that, contrary to the theory, the influence of the initiation and in particular the influence of the dissociation rate constant of the initiating alkoxyamine seemed to be crucial to obtain a controlled polymerization.

To have a better understanding of this phenomenon, we have compared first the styrene (S) and *n*-butyl acrylate (BA) polymerizations initiated with different alkoxyamines based on the same nitroxide (SG1 or **1•**). The different alkyl moieties (secondary or tertiary stabilized radicals) strongly influenced the rate of dissociation of the initiating alkoxyamine and allowed us to observe the difference obtained in the control and living character of the polymerization. Second, the use of the highly labile alkoxyamine **1a** has stressed the influence of the experimental conditions/procedure (ramp of temperature or not, vessel size, monomer purity, etc.) on the success of a controlled polymerization.

All experimental results have been compared successfully with kinetic modeling studies realized with the PREDICI software and highlighted the interest of highly labile alkoxyamines. The good agreement between experiments and modeling studies has prompted us to determine using this developed model a new systematic statement linking the initiation step and the characteristics of the system to obtain a well-controlled polymerization.

Experimental Section

Alkoxyamine **1b** and styrene were provided by ARKEMA and used as received. Alkoxyamine **1a** was either prepared following the literature[42] or provided by ARKEMA; both samples gave the same results. Alkoxyamine **1c** was prepared as already described.[43] *n*-Butyl acrylate (BA) and *t*-butylbenzene (*t*-BuPh) were purchased from Aldrich and used as received. Conversion was estimated by ^{1}H NMR experiments on a 300 Avance Bruker spectrometer ($CDCl_3$ as solvent, 300 MHz, chemical shifts were given relative to TMS (internal reference)) at the "Spectropole de RMN" of Marseille. ESR experiments were carried out on a MS100 Magnetech spectrometer. Number-average molecular mass, M_n, and weight-average molecular mass, M_w, were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump equipped with three "Styragel" columns (HR 3 (4.6 mm × 300 mm, separation between 500 and 30 000 g·mol^{-1}), HR 4 (4.6 mm × 300 mm, separation between 5000 and 600 000 g·mol^{-1}), and HR 5 (4.6 mm × 300 mm, separation between 2000 and 4×10^6 g·mol^{-1})) and two detectors: UV/visible (Waters 486) and RI (Waters 2414). Measurements were performed in tetrahydrofuran THF at room temperature, with a flow of 1 mL·min^{-1}. Calibration was based on polystyrene standards and Mark−Houwink parameters (PS $K = 0.011$ mL·g^{-1}, $\alpha = 0.725$; PBA $K = 6.895 \times 10^{-3}$ mL·g^{-1}, $\alpha = 0.75$).

Typical Homopolymerization Experiment. A 60 mL degassed (20 min nitrogen bubbling) bulk solution of styrene and **1a** (1.14 g, 3 mmol) in a 100 mL three-neck round-bottom flask, fitted with septum, condenser, and temperature probe, was heated to 120 °C (in the solution) with a 30 min ramp temperature (20−120 °C) under N_2 atmosphere, with vigorous magnetic stirring. Sampling was performed at even time intervals to determine the monomer conversion. All samples were analyzed by GPC. The polymer mixture was poured in ethanol, the precipitate filtered off, and then dried under vacuum (5×10^{-2} mbar). After 4 h, the final conversion was 81% and the M_n was 17 300 g·mol^{-1} with a PDI = 1.17. The conditions and the results of the other polymerizations are stored in Table 1.

Living Fraction (LF) Estimation Procedure.[44] Nondegassed *t*-BuPh 10^{-4} M solutions of polymer and **1•** standard were filled in 5 mm o.d. tubes. Tubes were sealed off, and a blank scan at room temperature was recorded for the polymer sample. That sample was heated to 120 °C for 2 h (>95% decomposition), then cooled to room temperature. A spectrum was recorded and compared to the **1•** standard. By experience, such procedure gives an absolute error smaller than 5%.

Kinetic Modeling Procedure. In Scheme 3 are taken into account the significant reactions involved in both the styrene and the *n*-butyl acrylate polymerizations. However, experimental results show that, for the polymerization of styrene, the removal of alkyl or polymer radicals (eq 12 in Scheme 3) do not need to be taken into account. Besides, the thermal self-initiating reaction (eq 13 in Scheme 3) is useless in the case of the *n*-butyl acrylate polymerization. For the sake of the simplicity, the penultimate effect was disregarded, and because several reactions are similar, it was assumed that the rate constants were chain length independent although such an assumption is not true for k_d,[45] k_p,[46] k_t,[47] and certainly, k_c. Rate constants and Arrhenius parameters are listed in Table 3.[48−57]

Results and Discussion

Kinetic Profiles: Experiment vs Theory. In comparison with the theory, the polymerizations were carried out in the same conditions: in bulk and a constant temperature (120 °C). For the styrene (S) polymerization in the presence of **1b**, as predicted by Fischer[3−7] and observed by many authors,[20,38,58,59] value of the slope α (eq 14) close to 0.66 for entry 4 (Table 1) is

Table 1. Experimental Conditions and Results of the Bulk Polymerizations of Styrene and *n*-butyl Acrylate Mediated with 1a, 1b, and 1c at 120 °C or 90 °C

entry	monomer[a]	initiator[b]	**1•**[c]	temp (°C)[d]	ramp[e]	time (min)[f]	conversion (%)[g]	M_n/M_{nth} (g·mol^{-1})[h]	PDI[i]	α[j]	LF (%)[k]
1	S	**1a**	no	120	yes	240	81	17 300/16 200	1.17	1.07	78
2	S	**1a**	no	120	no	240	90	24 600/18 000	1.12	1.00	72
3	S	**1b**	no	120	yes	205	74	16 200/14 800	1.33	0.99	81
4	S	**1b**	no	120	no	240	75	13 500/15 000	1.31	0.69	*l*
5	S	**1a**	no	90	yes	1875	57	9900/11 400	1.23	0.95	94
6	S	**1a**	no	90	no	3900	58	11 200/11 600	1.23	0.69	*l*
7	S	**1b**	no	90	yes	4190	78	14 200/15 600	1.65	0.77	93
8	S	**1b**	no	90	no	2920	65	13 000/13 000	1.55	0.60	
9	S	**1c**	no	90	yes	1708	55	10 400/11 000	1.17	0.66	90
10	BA	**1a**[m]	no	120	no	*l*	*l*	*l*	*l*	*l*	*l*
11	BA	**1a**	no	120	yes	180	71	14 800/14 200	1.40	1.10	90
12	BA[n]	**1a**	no	120	yes	60	85	19 000/17 000	1.3	1.2	*l*
13	BA[o]	**1a**	no	120	yes	95	92	20 400/18 400	1.3	1.1	*l*
14	BA	**1b**	5	120	yes	240	69	14 400/13 800	1.35	1.08	*l*
15	BA	**1b**	5	120	no	240	65	12 400/13 000	1.36	1.07	*l*
16	BA	**1a**	no	90	yes	3105	80	12 000/16 000	1.39	1.04	*l*
17	BA	**1b**	5	90	yes	5215	64	10 300/12 800	1.26	0.94	*l*

[a] Bulk experiment with styrene (S) or *n*-butyl acrylate (BA). [b] [alkoxyamine]$_0$ = 5 × 10^{-2} mol L^{-1} unless otherwise mentioned. [c] Amount (% of [alkoxyamine]$_0$) of extra free **1•** added to the solution. [d] Heating regulated oil bath, ±2 °C. [e] In the case of a ramp, the solution was heated from room temperature to the polymerization temperature in roughly 30 min. In the case of the absence of ramp, the flask was sunk in a preheated oil bath at the polymerization temperature. [f] Time of polymerization. [g] Conversion (*C*) in monomer when the polymerization was stopped. The conversion was measured by ^{1}H NMR. [h] Molar mass estimated by GPC, see Experimental Section. Targeted M_n of 20 000 g mol^{-1}. [i] PDI at the end of the polymerization. [j] Slope of Ln(Ln([M]$_0$/[M])) = *f* (Ln(*t*)) eq 14, see text. [k] Amount of living polymer determined by EPR as described in ref 44. [l] Not determined. [m] No control, see text. [n] Distilled BA with 50 ppm of MEHQ. [o] Distilled BA.

Scheme 3

$$SG1-R \xrightarrow{k_{d1}} SG1+R^{\bullet} \qquad (4)$$

$$SG1+R^{\bullet} \xrightarrow{k_{c1}} SG1-R \qquad (5)$$

$$R^{\bullet}+R^{\bullet} \xrightarrow{k_{t1}} dead \quad products \qquad (6)$$

$$M+R^{\bullet} \xrightarrow{k_{add}} RM^{\bullet} \qquad (7)$$

$$n \quad M+RM^{\bullet} \xrightarrow{k_{p}} RM_n^{\bullet} \qquad (8)$$

$$SG1+RM_n^{\bullet} \xrightarrow{k_{c2}} SG1-M_nR \qquad (9)$$

$$SG1-M_nR \xrightarrow{k_{d2}} SG1+RM_n^{\bullet} \qquad (10)$$

$$RM_n^{\bullet}+RM_n^{\bullet} \xrightarrow{k_{t2}} dead \quad products \qquad (11)$$

$$RM_n^{\bullet}+Inhibitor \xrightarrow{k_{Inh}} M_nH+Inh^{\bullet} \qquad (12)$$

$$3 \quad M \xrightarrow{k_{self}} 2 \quad R^{\bullet} \qquad (13)$$

expected, exhibiting the typical behavior due to the persistent radical effect.

$$\ln\left(\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right) = \beta + \alpha \ln \mathbf{t} \qquad (14)$$

Therefore, **1b** plays the role expected for an alkoxyamine, that is, a slow and permanent build-up of **1•** along the polymerization. For the polymerizations of *n*-butyl acrylate (BA) in the presence of **1b** (entry 15, Table 1), values of α close to 1 are observed as expected from the theory for typical experiments performed in the presence of excess of nitroxide **1•**.[6,9,14] In this case, the kinetics of the polymerization do not rest, in the strict sense, on the persistent radical effect but rather on a reversible scavenging.

When **1a** was used as initiator for the styrene or *n*-butyl acrylate at 120 °C without free excess of nitroxide **1•**, unexpected behaviors of polymerization were observed. For the styrene polymerization (entry 2, Table 1), the value of the slope α is close to 1, meaning that the mechanism involved is not based on the persistent radical effect but on a reversible scavenging process similar to a polymerization carried out in the presence of free nitroxide. For the *n*-butyl acrylate polymerization (entry 11, Table 1), no exotherm is observed (see BA polymerization section) and the control is achieved[21] without any free excess of **1•**, the value of the slope α being still close to 1. Such values (for styrene and *n*-butyl acrylate) are typical for experiments conducted in the presence of an excess of nitroxide. Great care has been given for checking the purity of **1a** (NMR and elemental analysis). However, it has to be mentioned that alkoxyamine **1a** ($t_{1/2}$ = 15 h at room temperature (RT))[39,42] decomposes quickly in solution and a concentration of 10^{-7} M ([**1a**] = 10^{-4} M) of **1•** was detected in ca. 10 min at RT. Hence, these results suggest that the main role of **1a** is to afford quickly and at low temperature the excess of **1•** required to control the polymerization of BA and, to a lesser extent, the polymerization of the styrene (see hereafter). That is, the control of styrene or BA polymerization is easily achieved using a monocomponent system, without any free excess of free nitroxide **1•** involving a reversible scavenging process.

Styrene Polymerization

Temperature Effect. The polymerization can be started either by heating the solution from room temperature to the polymerization temperature (30 min temperature ramp, RT to 120 °C) or by sinking the flask in a preheated oil bath at the polymerization temperature (no ramp). Both cases can yield quite different results depending on the initiating alkoxyamine **1a** or **1b**. Indeed, for the polymerization of styrene in the presence of **1a**, when the flask was sunk in the preheated oil bath (120 °C) or when the temperature ramp was applied, the polymerization rates were similar (Figure 1a, entries 1 and 2 in Table 1), but an induction time was observed with the temperature ramp procedure, leading to a higher needed polymerization time for the same monomer conversion. The mechanism involved is a reversible scavenging process (the value of the slope α being still close to 1). Furthermore, when the flask was sunk in the preheated oil bath, a larger M_n (Figure 1b, (without T ramp), entry 2 in Table 1) was obtained. For the ramp experiment, the

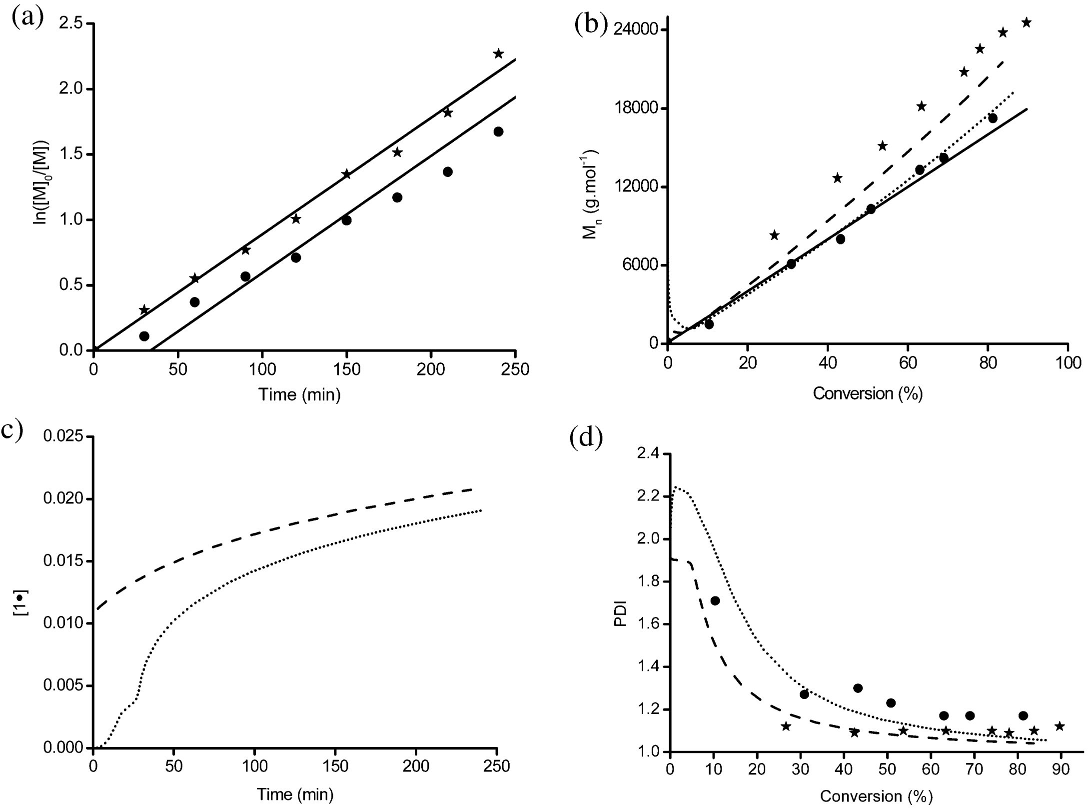


Figure 1. Bulk polymerization of styrene at 120 °C mediated by alkoxyamine **1a** with ramp (●, ···) and without ramp (★, - - -) of temperature: (a) evolution of ln([M]$_0$/[M]) vs *t*, (b) evolution of the experimental molar masses (M_n, symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (—) vs conversion, (c) modeled evolution of **1•** vs t (d) Evolution of the polydispersity indexes (PDI, symbols) and the modeling PDI (dotted and dashed lines) vs conversion.

evolution of the M_n with the conversion agrees perfectly with the theoretical evolution (Figure 1b, (T ramp**)**), whereas for the no-ramp experiment, the M_n are roughly 20% higher (Figure 1b, without T ramp), which means a 0.8 efficiency of the initiating alkoxyamine **1a**. This difference is accounted for by the high lability of alkoxyamine **1a** ($E_a = 112.3$ kJ·mol^{-1}, $k_{d1} = 0.3$ s^{-1} at 120 °C).[39,42] Then, in a very short time ($t = 7$ s for 90% decomposition), a high concentration of alkyl radical was generated and the self-termination reaction for the alkyl radical **a•** (eq 6, Scheme 3, $k_{t1} \approx 10^9$ L mol^{-1} s^{-1} at 120 °C)[60] competed with the alkoxyamine reformation (eq 5, Scheme 3, $k_{c1} = 5 \times 10^7$ L mol^{-1} s^{-1} at 120 °C)[36] and the addition of **a•** onto the styrene ($k_{add} = 1.0 \times 10^4$ L mol^{-1} s^{-1} at 120 °C).[61] Then, less macro-alkoxyamine was formed than the initial concentration of **1a** and, therefore, a lesser efficiency of **1a**. While a ramp was applied, the homolysis of **1a** occurred smoothly ($t_{1/2} = 18$ h at room temperature, $t_{1/2} = 207$ s at 75 °C),[39,42] then the concentration of radical **a•** was kept at a low enough level to make the self-termination reactions and the addition/reformation reactions competition negligible and, subsequently, observed an efficiency of 1 for **1a**. The simulation of the **1•** evolution vs time given by Scheme 3 shows that, with a ramp, the **1•** concentration grew slowly (≈20% in 3000 s), whereas without a ramp, roughly 20% of **1•** were generated in a very short time period what agrees well with the 0.8 efficiency experimentally observed (Figure 1c). Furthermore, modeling studies based in Scheme 3 confirm the importance of k_{d1}, and the main role of **1a** is to generate quickly in situ a sufficient excess of **1•** to keep the polymer self-termination reaction at a low level and then improved the molar mass control and the polydispersity. On the other hand, despite the large excess of **1•** due to the no-ramp heating, the polymerization (entry 2, Table 1, Figure 1a) rate is similar to the rate of polymerization carried out in the absence of temperature ramp, but a higher time of polymerization is needed (entry 1, Table 1, Figure 1a) due to both: (i) the induction period due to the ramp duration (30 min) where no polymerization could occur (The formed macroalkoxyamines are stable during this step), and (ii) a higher initial monomer conversion (without ramp) due to a high propagating radical concentration.

When these procedures were applied to polymerization of the styrene in the presence of **1b** as initiating alkoxyamine at 120 °C (entries 3 and 4, Table 1), the kinetic profiles depended on the temperature procedure (Figure 2a and b). Whereas without temperature ramp, the PRE was involved, with the temperature ramp, the value of the slope α was close to 1, characteristic of the reversible scavenging process. This phenomenon could be explained by the competition between the rate of addition and of self-termination at different temperatures. Below 75−80 °C, there was practically no decomposition. Between 80 and 120 °C, considering the rate of decomposition, the ratio between the rate of propagation and the rate of self-termination was too low and then a small amount of **1•** was quickly generated. If the polymerization was carried out directly at 120 °C, the rate of propagation increased and shifted the ratio toward higher values and then the primary termination became more negligible. In the evolution of the M_n with the conversion (Figure 2c), no difference were observed for both procedures (ramp and no-ramp). Such observations were expected due to the slow homolysis of **1b** (for isomer RS/SR, $E_a = 127.8$ kJ mol^{-1} and for isomer RR/SS, $E_a = 130.8$ kJ mol^{-1}, at 120 °C, $t_{1/2}$ are 250 and 619 s, respectively),[32] which allowed keeping the concentration of the alkyl radical **b•** at a very low level, making the competition between the self-termination of **b•** and

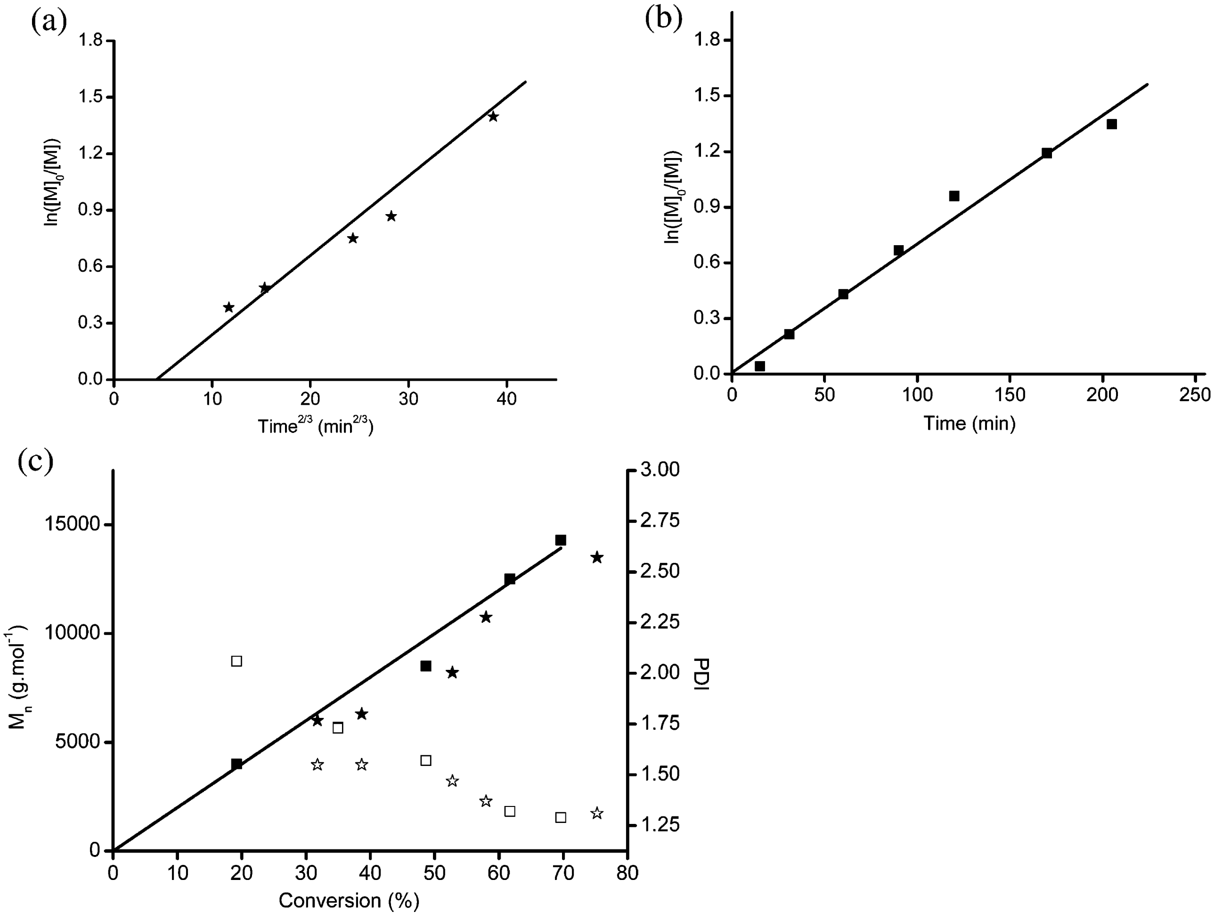


Figure 2. Bulk polymerization of styrene at 120 °C mediated by alkoxyamine **1b** with ramp (■, □) and without ramp (★, ☆) of temperature: (a) evolution of $\ln([M]_0/[M])$ vs $t^{2/3}$, (b) Evolution of $\ln([M]_0/[M])$ vs t, (c) evolution of the experimental molar masses (M_n, filled symbols), polydispersity indexes (PDI, empty symbols), and theoretical M_n (—) vs conversion.

both the addition reaction of **b•** onto the styrene and the alkoxyamine reformation unimportant.

Although the evolution of the kinetic (Figure 3a) and the evolution of M_n versus conversion were similar for alkoxyamine **1a** and **1b** (Figure 3b), the PDI values were higher with **1b** (ca. 1.3) at 120 °C than those obtained with **1a** (ca. 1.1) (entries 1, 2, 3 and 4 in Table 1) and well reproduced by the modeling studies (Figure 3c).

The higher control of the styrene polymerization in the presence of **1a** at 120 °C than using **1b** and the higher homolysis rate of **1a** lead us to reconsider the polymerization at lower temperature (90 °C). As observed at 120 °C, when the same experiments (entries 5 and 7, Table 1) were carried out at 90 °C, although the polymerization kinetics with **1a** and **1b** as initiator were similar (Figure 4a), the evolution of M_n for **1a** agreed well with the theoretical M_n as expected, whereas the evolution of M_n for **1b** showed a poorly controlled polymerization (Figure 4b). That is, with **1b**, in the first moments of the polymerization, high M_n were observed, which decreased up to 20% conversion, and then a plateau was observed (Figure 4b). Then, as shown by the modeling studies (Scheme 3 without eq 12), the dramatic difference observed between the initiation with **1a** and **1b** is due to the fast homolysis of **1a** ($t_{90\%} = 140$ s at 90 °C),[39,42] which makes the formation of the macroalkoxyamine in a short time with respect to the polymerization time ($t_{60\%} = 30$ h) (Figure 4c). While, because of the slow decomposition of **1b** ($t_{90\%} = 7$ h for the RS/SR isomer and $t_{90\%} = 18$ h for the RR/SS isomer),[32] a tiny amount of **1b** was decomposed, leading to a small amount of radicals **b•** and **1•** (Figure 4d), then higher M_n's were obtained. While the polymerization was going on, the PRE installed slowly and then the M_n decreased (Figure 4b). At 50% conversion (20 h of polymerization), all of **1b** was decomposed (Figure 4c) and was converted into macroalkoxyamines confirmed by an experimental M_n in agreement with the theoretical one (Figure 4b). The PRE was set, therefore the polymerization can occur almost in a controlled mode but with poorer PDI values than that with **1a** (Figure 4e). The heterogeneity of the MWD was due to a slow initiation, which increases drastically the PDI. Hence, for polymerization at relatively low temperature, the high lability of the initiator becomes a crucial parameter, as exemplified by the polymerization of styrene with **1a**. Whatever the procedures (ramp and no-ramp, entries 5 and 6, Table 1 and Figure 5), the efficiency of **1a** is closed to 1, which is due to a slower homolysis at 90 °C ($t = 140$ s for 90% decomposition)[39,42] than that at 120 °C ($t = 7$ s for 90% decomposition), then the concentration of radical **a•** was kept at a low enough level to make the self-termination reactions and the addition/reformation reactions competition negligible.

Then, thanks to the highly labile alkoxyamine **1a**, it is now possible to initiate polymerization of the styrene at 90 °C where the self-initiation is negligible during the polymerization time.

Living Fraction (LF). Many papers[19,62,63] are published about the preparation of controlled and living homopolymers with the evolution of the M_n as function of the conversion and the kinetics but nothing on the living character. The livingness of the first block is often proved by the preparation of the copolymer, but even if there is a shift in the GPC trace, it is difficult to quantify exactly the livingness of the polymer.[64] Furthermore, Fischer[3−7] has demonstrated that controlled polymerization does not imply

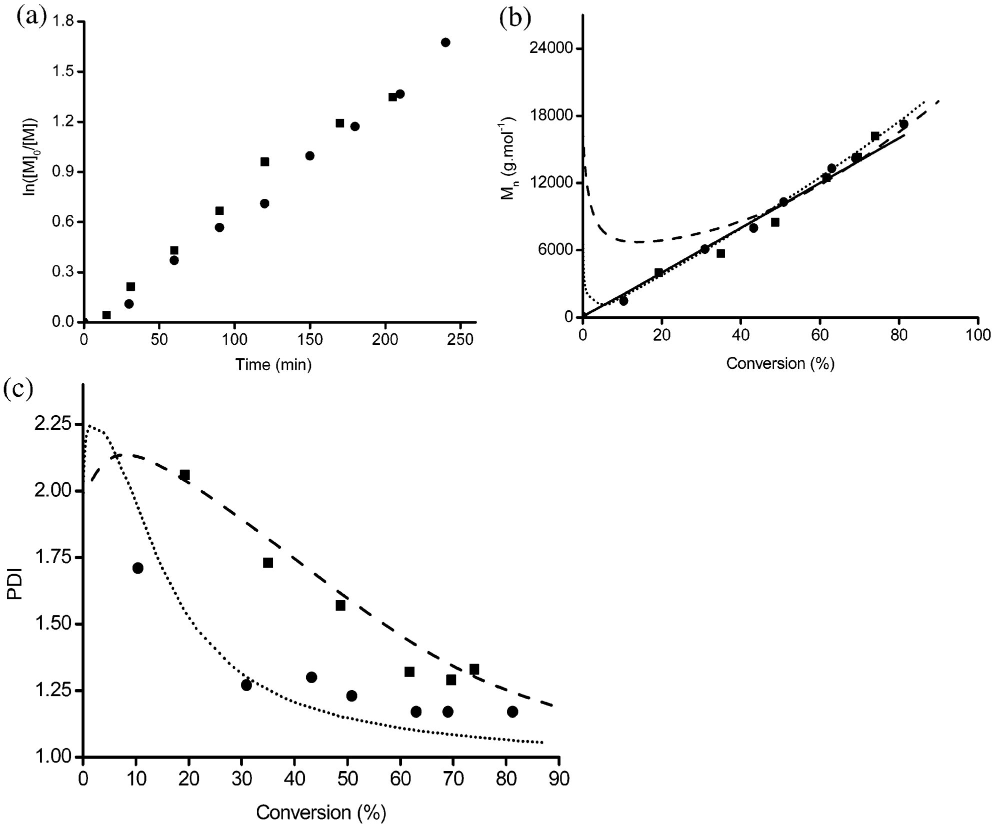


Figure 3. Bulk polymerization of styrene at 120 °C, with a ramp of temperature, mediated by alkoxyamines **1a** (●, ···) and **1b** (■, - - -): (a) evolution of the ln([M]$_0$/[M]) vs *t* (b) Evolution of the experimental molar masses (M_n, symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (—) vs conversion, (c) evolution of the polydispersity indexes (PDI, symbols) and the modeling PDI (dotted and dashed lines) vs conversion.

livingness and vice-versa. Therefore, it is regretful that more information is not provided on the livingness of the polymer. The livingness of a polymer is easily and merely determined by ESR experiments, as exemplified with PS-SG1 and PBA-SG1 polymers by Bertin et al.[44,45] Here, we provided the amount of living polymer for selected experiments, obtained from the released amount of **1•** after heating a 10^{-4} M solution of polymer in the presence of oxygen as alkyl radical scavenger. And for each experiment, the livingness was unambiguously above 70% whatever the initiators (**1a** or **1b**), the temperatures (120 °C or 90 °C), and the procedures (ramp or no ramp). Interestingly, modeling studies of the LF based in Scheme 3 show that the LF decreases with increasing conversion for the styrene polymerization (Figure 6). The predicted LFs agree well with the final LF observed (entries 1−3, 5, 7, and 9 in Table 1 and Figure 6). Therefore, it is interesting to note that higher livingness character was achieved when the polymerization of styrene was carried out at 90 °C. But in the presence of **1b** (entry 7, Table 1), the result exemplifies well the nonrelationship between the livingness and the control of the polymerization, i.e., the polystyrene prepared was highly living (LF $>$ 90 %) but poorly controlled (PDI $\approx$ 1.65), whereas with **1a (**entry 5, Table 1**)**, the same living character was obtained (LF $>$ 90%) with a good control (PDI $\approx$ 1.23).

n-Butyl Acrylate Polymerization

Hawker et al.[19] with **2•** and Gnanou et al.[38] with **1•** were the first to performed a successful controlled polymerization of *n*-butyl acrylate in the presence of 2.5−5% of an extra amount of nitroxide. However, it is almost impossible to scale up such a receipt to the industrial stage because it requires a larger amount of nitroxide to control the polymerization and the receipt must be adapted to each reactor. Such drawbacks are crippling. Therefore, it prompted several groups to develop new nitroxides such as **3•**[26,63] and **4•**,[18] able to control the polymerization of *n*-butyl acrylate without adding the extra amount of nitroxide, but results described are not well convincing in terms of industrial application due to a complex and expensive synthesis of the nitroxide and the corresponding alkoxyamine.

Temperature Effect. When **1b** was used in the presence of 5% molar of **1•**, whatever the procedure (with or without ramp, Figure 7), the kinetic profiles were similar, meaning that the initial presence of free nitroxide forced the polymerization to be control by a reversible scavenging process. This was confirmed by the slope α, of which values are close to 1 (entries 14 and 15, Table 1). When the polymerizations of *n*-butyl acrylate were carried out at 120 °C, with a ramp of temperature, and in the presence of **1a** (entry 11, Table 1) or **1b** plus 5% of **1•** (entry 14, Table 1), the polymerization was faster with **1a** than with **1b** (Figure 8a), whereas the evolution of the M_n with the conversion were almost the same for both initiators and in perfect accord with the theoretical M_n and the modeling M_n (Figure 8b), and the PDI agreed well with the modeling value given by Scheme 3 (Figure 8c). Then both receipts (alkoxyamine **1a** or alkoxyamine **1b** plus 5% of **1•**) afforded a controlled polymerization. Because of the high k_p of the *n*-butyl acrylate and the low homolysis of **1b**, the extra amount of **1•** made the alkoxyamine reformation compete with the propagation of the polymeric radical and then suppressed the overheating of the solution conducting often to an explosive regime (see hereafter). On the other hand, because **1a** is a highly labile alkoxyamine, the threshold of 3% of **1•** for which an efficient control occurred was quickly reached (Figure 8d). Then, the formation of the macroalkoxyamine can compete with the fast polymer propaga-

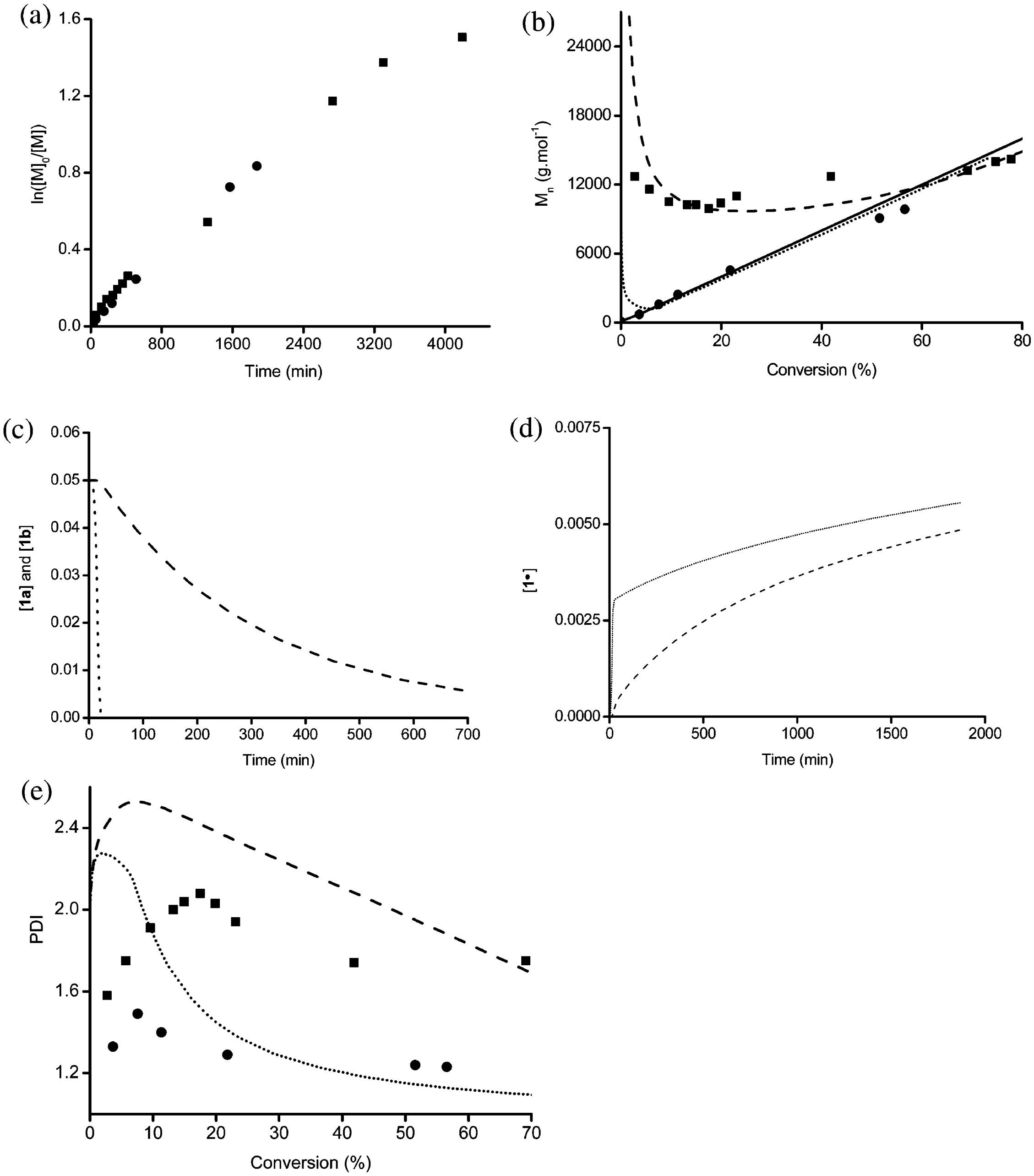


Figure 4. Bulk polymerization of styrene at 90 °C, with a ramp of temperature, mediated by alkoxyamines **1a** (●, ···) and **1b** (■, - - -): (a) evolution of the ln([M]$_0$/[M]) vs *t*, (b) evolution of the experimental molar masses (M_n, symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (—) vs conversion, (c) modeling evolution of **1a** and **1b** vs *t*, (d) modeling evolution of **1•** vs *t*, (e) evolution of the polydispersity indexes (PDI, symbols) and the modeling PDI (dotted and dashed lines) vs conversion.

tion and the polymerization can go smoothly as for **1b** with the extra amount of **1•**. The *poor* control of **1a** in the first moment of the polymerization was highlighted by the high PDI for conversions less than 20% conversion (Figure 8c). Then, considering the better control of the styrene polymerization at 120 °C without ramp procedure with **1a** (lower PDI without ramp, see Figure 1d), we reconsider the polymerization of *n*-butyl acrylate without ramp procedure. Surprisingly, an exothermic reaction was observed, leading to an uncontrolled polymerization, in disagreement to what was observed for styrene. It is noteworthy that the polymerization without a ramp of temperature was successful when a vigorous mechanical stirring was applied, and again, very high masses were observed in the very first moments of the polymerization.[65] Therefore, the evacuation of the heating due to the very exothermic (high k_p value) polymerization of BA is a major problem to take care about. All of these unexpected results led us to perform thorough kinetic modeling studies with **1a** as the initiator for the *n*-butyl acrylate polymerization with both procedures. Kinetic simulations with Scheme 3 without ramp (without eq 12) show a successful polymerization exhibiting rather low PDI, while the polymerization carried out with a ramp (without eq 12) should have failed, i.e., because of the high k_p of the BA, very high molar masses were produced in a short time and at moderate temperatures (below 60 °C), then the linearity of M_n with the conversion was only expected above 40% conversion with PDI values above 4 and up to 16 (Figure 9a and b); this was in agreement with the styrene polymerization results, that is, PDI are lower at lower conversion when there is no ramp of temperature. Furthermore, surprisingly, experimental results obtained with the ramp procedure are more in agreement with the simulation of the system without ramp (Figures 8 and 9).

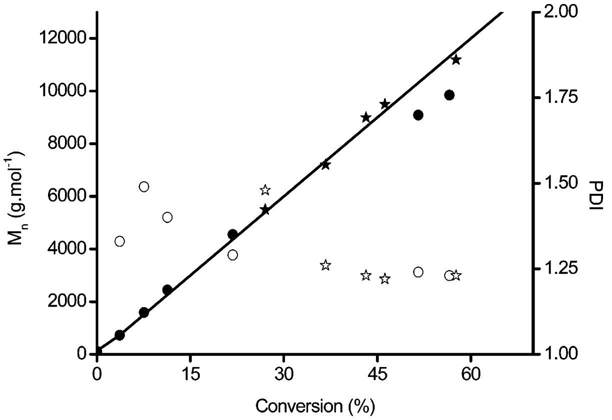


Figure 5. Bulk polymerization of styrene at 90 °C mediated by alkoxyamine **1a** with ramp (●, ○) and without ramp (★, ☆) of temperature: evolution of the experimental molar masses (M_n, filled symbols), polydispersity indexes (PDI, empty symbols), and theoretical M_n (—) vs conversion.

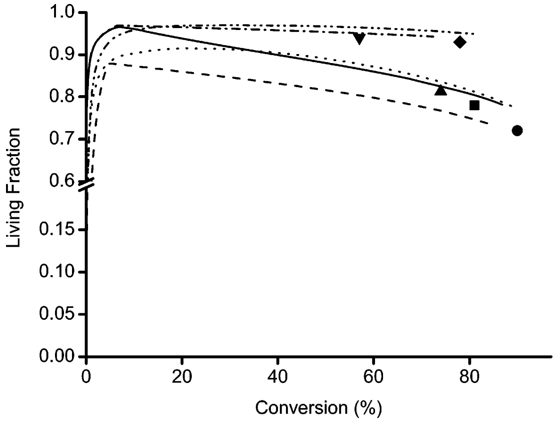


Figure 6. Living fraction vs conversion for the bulk polymerization of styrene: mediated by alkoxyamine **1a** at 90 °C (▲, —· —· —·), mediated by alkoxyamine **1b** at 90 °C (◆,—··—··—··), mediated by alkoxyamine **1a** at 120 °C with a ramp of temperature (■, —), mediated by alkoxyamine **1a** at 120 °C without a ramp of temperature (●, - - -), mediated by alkoxyamine **1b** at 120 °C (▲,···).

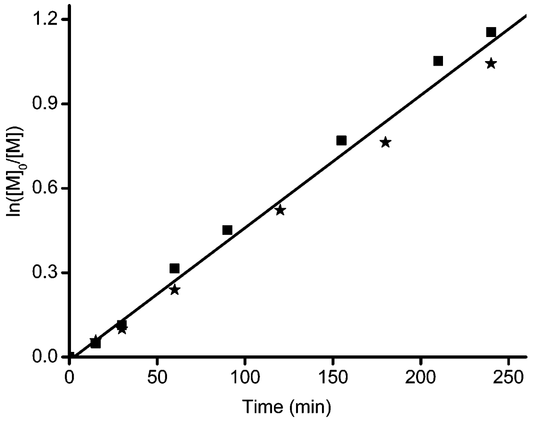


Figure 7. Evolution of $\ln([M]_0/[M])$ vs t for the bulk polymerization of *n*-butyl acrylate at 120 °C mediated by alkoxyamine **1b** with 5% of free **1** with ramp (■) and without ramp (★) of temperature.

This could be explained by the experimental procedure used. As mentioned in the Experimental Section, BA was used as received, that is, with the presence of 15−50 ppm of inhibitors. By taking into account the scavenging of alkyl or polymer radicals by the inhibitors (eq 12 in Scheme 3), we observed the expected behavior of the polymerization (Figure 9a). This assumption is then confirmed by some experiments carried out with distilled BA and distilled BA with an added amount of inhibitor (50 ppm of hydroquinone methyl ether MEHQ). With the distilled *n*-butyl acrylate, higher M_n was observed during the first instant of the polymerization (Figure 10a), whereas in the presence of inhibitors, they played their role of radical scavenging limiting the propagation reaction. Then, because of the rapid decomposition of **1a**, enough **1•** was produced to control the polymerization even at low conversion (Figure 10a and b). With distilled monomers, using the no-ramp procedure, because of the production of high M_n at the beginning, the exothermicity is quite difficult to control using only a magnetic stirring. That is why the main conclusions for the BA polymerization at 120 °C initiated by **1a** is to carry out the process with a vigorous mechanical stirring and with a double-jacket reactor and, in this case, with a no-ramp procedure. If these conditions cannot be fulfilled, the process must be carried out with nondistilled monomers, and then the ramp procedure seems to be more appropriate. To be more confident in the process, we studied the polymerization of nondistilled BA at a lower temperature (90 °C) in order to decrease the influence of the k_p value. As expected, the process is really easiest to control (no problem of exothermicity) and a true control of the polymerization is observed (Figure 11).

The Importance of the Vessel. Because of the observations mentioned above, our preliminary results were difficult to reproduce and it prompted us to study the importance of the vessel on the control of the polymerization. To our great surprise, it appeared that the polymerization of *n*-butyl acrylate, at 100 °C, was possible in the presence of alkoxyamine **1b** without any extra amount of **1•** or any other additives (entry 1, Table 2) a contrario to our long-lasted claims. In fact, when 2 mL of solution was heated into a 50 mL Schlenk tube, the huge free air volume was able to dissipate the excess of heat released by the reaction, thus the polymerization occurred rather smoothly although the polymerization was still poorly controlled but the explosive regime was never reached (entry 1, Table 2). The control cannot be obtained due to the slow setting up of the persistent radical effect even if the final experimental M_n's at high conversion are close to the theoretical ones. In the same way, when the polymerization was carried out at 100 °C in a one-fourth-filled flask (entry 2, Table 2), the free volume was still enough to dissipate the overheating of the reaction, and then the polymerization exhibited a poorly controlled character. However, when the same experiment was performed with a two-thirds- filled flask (entry 3, Table 2), an explosive regime was quickly reached and a noncontrolled polymerization occurred, as highlighted by a very broad GPC peak (from a few hundred to several tens of thousands g mol^{-1}). Should we conclude that the polymerization of the *n*-butyl acrylate (entries 1 and 2, Table 2) is possible in the presence of **1b** or the opposite (entry 3, Table 2)? Keeping in mind that the aim of the NMP is to be applied to the industrial stage, our interpretation of the results must rest on the experiment that is closer to industrial application, that is, the polymerization performed in a two-thirds-filled flask (entry 3, Table 2). Because such details are not always reported in the Experimental Sections, many nonreproducible polymerization experiments might be due to ill-described procedures.

Therefore, when polymerizations are carried out in inadequate conditions (flasks and magnetic stirring), a temperature ramp and the presence of inhibitors suppress the formation of the high masses and moderate the overheating, and consequently the polymerization went smoothly as observed. It is noteworthy that the polymerization of BA carried out in the presence of **1a** at

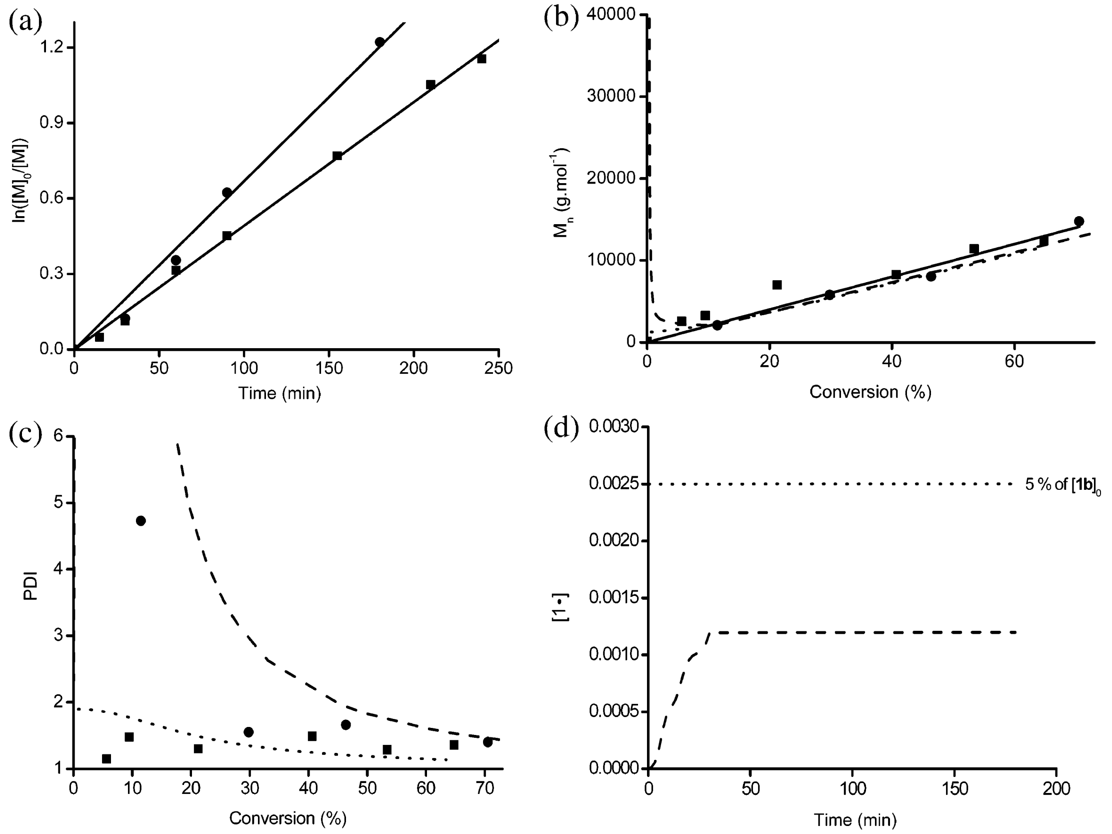


Figure 8. Bulk polymerization of *n*-butyl acrylate at 120 °C, with a ramp of temperature, mediated by alkoxyamines **1a** (●, - - -) and **1b** (■, ···): (a) evolution of $\ln([M]_0/[M])$ vs *t*, (b) evolution of the experimental molar masses (M_n, filled symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (—) vs conversion, (c) evolution of the polydispersity indexes (PDI, symbols) and modeling PDI (dotted and dashed lines) vs conversion, (d) modeling evolution of **1•** vs *t*.

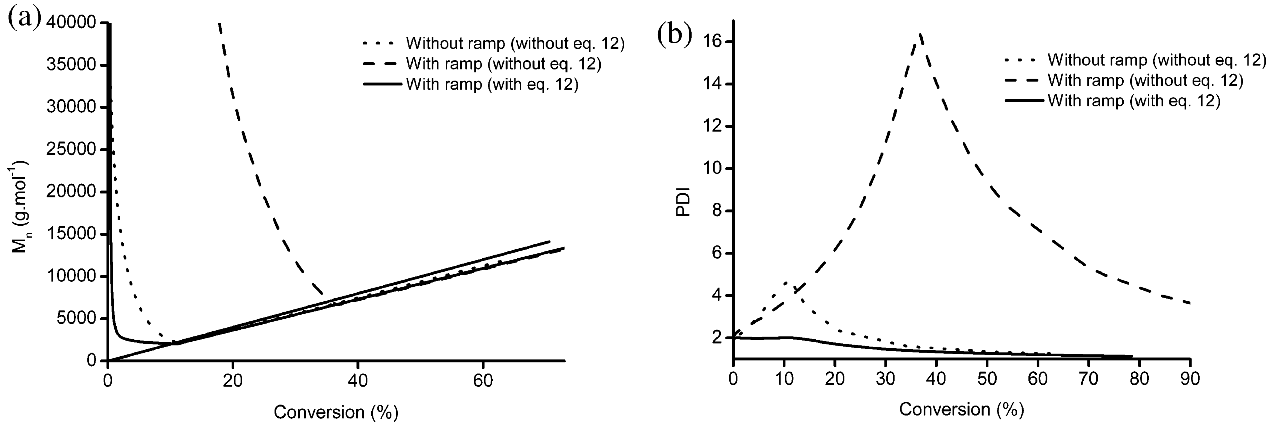


Figure 9. Bulk polymerization of *n*-butyl acrylate at 120 °C mediated by alkoxyamine **1a** with ramp and without eq 12 (- - -), without ramp and without eq 12 (—), with ramp and with eq 12 (···): (a) evolution of the modeling M_n and the theoretical M_n (—) vs conversion, (b) evolution of the modeling polydispersity indexes PDI vs conversion.

120 °C (in a round-bottom flask with an oil bath and magnetic stirring) and using distillated BA showed a poor control of the M_n and high PDI at the beginning of the polymerization (entry 13, Table 1), while the same experiment carried out with added inhibitors (50 ppm of MEHQ), a good control of M_n and low PDI values were observed (entry 12 in Table 1, Figure 10a and b) as expected from the trends given by the simulations from Scheme 3.

Living Fraction (LF). As expected by Fischer,[7] higher living fractions were obtained with BA than with styrene using **1•** due to more appropriate equilibrium constant values ($K_S = 3 \times 10^{-8}$ mol·L^{-1} and $K_{BA} = 5.5 \times 10^{-11}$ mol·L^{-1}). Close to 90% of LF was obtained when 20 000 g·mol^{-1} PBA was targeted at 120 °C. There is no advantage in this case to work at lower temperatures, mainly due to the absence of self-thermal polymerization of BA.

Modeling Studies

During the kinetic analysis of the NMP and the development of its predictive phase diagrams,[3−7] for the sake of the simplicity, Fischer disregarded the influence of the k_{d1} value of the initiating alkoxyamine and assumed, as did many authors, obviously that a successful NMP required merely an initiating alkoxyamine cleaving at least as fast as the alkoxyamine model or the macroalkoxyamine. The simulations and the experimental results presented in the above sections show unambiguously the pivotal

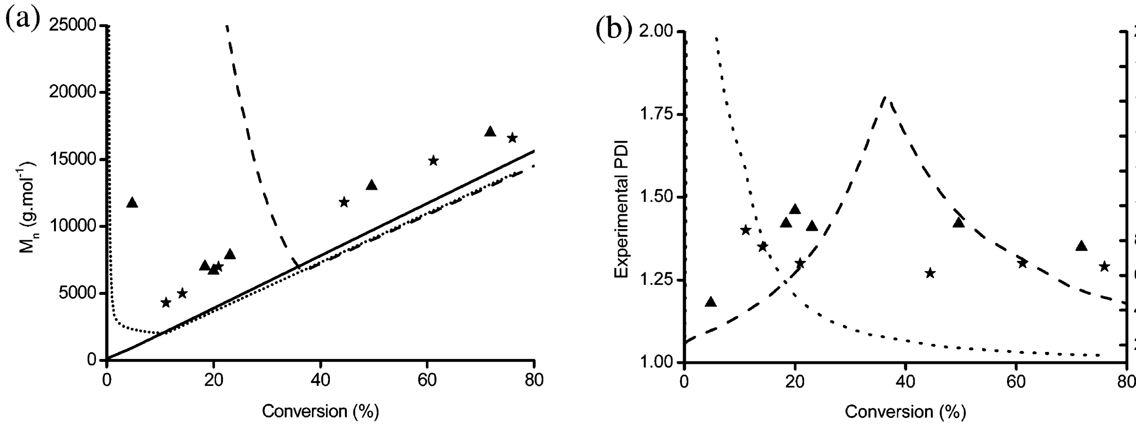


Figure 10. Bulk polymerization of *n*-butyl acrylate at 120 °C mediated by alkoxyamine **1a** with ramp with distilled monomers (▲, - - -) and with distilled monomers + inhibitors (50 ppm of MEHQ) (★, ···): (a) evolution of the experimental molar masses (M_n, symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (—) vs conversion, (b) evolution of the polydispersity indexes (PDI, symbols) and modeling PDI (dotted and dashed lines) vs conversion

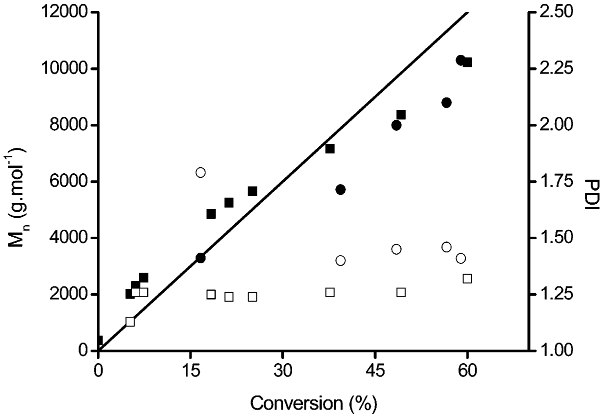


Figure 11. Evolution of M_n (fulled symbols) and PDI (empty symbols) vs conversion for the bulk polymerization of *n*-butyl acrylate at 90 °C, with a ramp of temperature, mediated by alkoxyamines **1a** (●, ○) and **1b** + 5% SG1 (■, □).

Table 2. Conversion, Molecular Mass (M_n) and Polydispersity Indexes (PDI) in Function of the Vessels

entry	**1b**[a] (g)	BA[b] g (mL)	reactor[c] (mL)	*T*[d] (°C)	*t*[e] (min)	*C*[f] (%)	M_n[g] (g/mol)	PDI
1	0.052	1.78 (2)	S (50)	100	1000	95	14500	1.9
2	0.594	20 (22.4)	F (100)	100	1080	82	8500	2.1
3	1.782	60 (67.1)	F (100)	100	*h*	*i*	*j*	*i*

[a] No extra free nitroxide **1•**. [b] *n*-Butyl acrylate (BA). [c] For the experiments carried out in a Schlenk (S) tube, the solutions were degassed by three thaw−freeze−thaw cycles. For the experiments carried out in a flask (F), the solutions were deoxygenated by 30 min nitrogen bubbling. [d] Heating regulated oil bath, ±2 °C. [e] Any times in this Table and in the footnotes are given when the experimental temperature was reached. That occurred generally after a 20 min ramp of temperature. [f] Conversion (*C*) in monomer when the polymerization was stopped. The conversion was measured by ^{1}H NMR. [g] Molar mass estimated by GPC, see Experimental Section. Targeted M_n of 12 800 gmol^{-1}. [h] Temperature increasing steadily. Suddenly, the temperature reached 140 °C in three minutes, the solution boiled and turned yellow, and then a temperature of 210 °C was reached in five minutes. [i] Not determined. [j] The GPC was too broad to give any significant information.

role of k_{d1} on the success or the failure of a controlled polymerization, that is, when the couple (k_{d2}, k_{c2}) of the macroalkoxyamine fulfilled the requirement for successful NMP, a high k_{d1} value of the initiating alkoxyamine ensures lower PDI and polymerization without an added extra amount of nitroxide. Furthermore, the differences observed between **1a** and **1b** point out the existence of a threshold value of k_{d1}, above which the NMP can be performed successfully in a monocomponent system and which depends on the value of k_p. The modeling studies, displayed in Figure 12a, based on the Scheme 3 applied to the BA polymerization, and assuming an average value for k_{c1} and k_{add} (average from the values given for **a•** and **b•** in Table 3). As expected, **1b** (without extra amount of **1•**) is not able to control the BA polymerization, that is, there is no linear evolution of M_n with the conversion and PDI values increasing monotonically up to 4.0 (Figure 12b). The control (linear evolution of M_n with conversion) and lower PDI values are improved with increasing value of k_{d1} up to the threshold value of around 0.1 s^{-1} (linear evolution of M_n with conversion below 35% conversion and final PDI below 1.4, Figure 12a and b). Above that threshold, the BA polymerization is successfully controlled as experimentally observed with **1a**. It is important to mention that a sharp change of k_{d1} close to the threshold makes the polymerization quite different. For example, the k_{d1} of **1a** that is merely 3 times higher than the threshold value makes the polymerization controlled from 10% conversion, and the PDI shows a sharp increase (up to 4.5) and decrease down to 1.4 above 20% conversion. When k_{d1} is 10 times higher than the k_{d1} of **1a**, the control is even better and the peak of the PDI even narrower than that for **1a**. Indeed, alkoxyamine with so high a k_{d1} exhibits a half-life time shorter than 1 or 2 h at 30 °C, then immediately a large fraction is decomposed to generate a large amount of alkyl radicals. Consequently, at room temperature, the self-termination reaction of alkyl radicals should compete strongly with the addition onto the monomer and propagation of the polymer radical, then a large excess of nitroxide should be left that should scavenge all the growing polymer radicals and then should stop the polymerization until the polymerization temperature is reached. Hence, no high masses should be observed, the overheating should be reduced, and the excess of nitroxide radical required for successful NMP should be generated in situ. The modeling of the **1•** evolution shows that, with **1b**, the concentration of **1•** is always below 0.5% of **1b** concentration and that the polymerization should be almost controlled for 1% of **1•** as threshold. On the other hand, for **1a** and alkoxyamines exhibiting larger k_{d1}, a concentration above 5% is immediately observed and does not change on time (Figure 12c). Finally, the polymers prepared with highly labile alkoxyamines are expected to exhibit a lower living character (>90%) than for those prepared with less-labile alkoxyamines and an extra amount of nitroxide (>99%). However, such a tiny difference cannot be measured (Table 1) and does not matter for the final material.

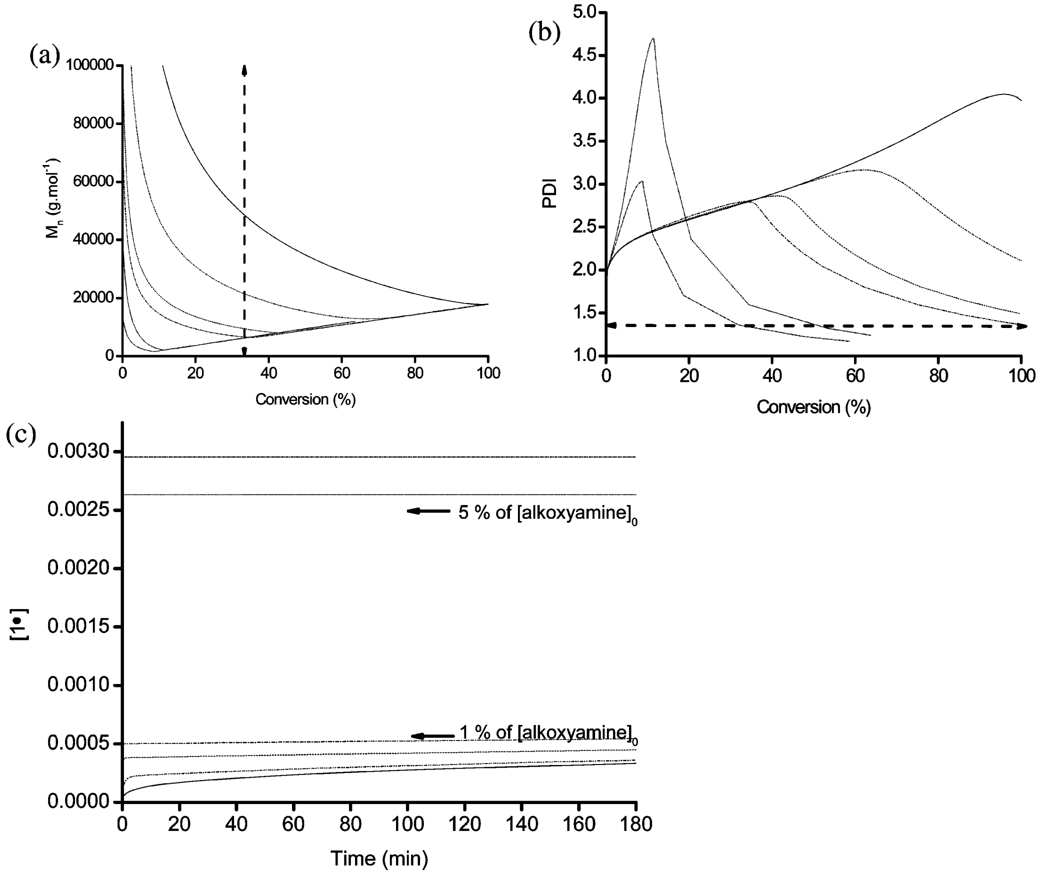


Figure 12. Simulated evolution of (a) M_n vs conversion, (b) PDI vs conversion, and (c) the concentration of **1•** vs conversion for various k_{d1} given from the slowest (full line) to the fastest: 2.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2}, 0.1, 0.3, and 3.0 L mol^{-1} s^{-1}.

Because the choice of the initiating alkoxyamine depends on both the (k_{d2}, k_{c2}) and (k_{d1}, k_p) couples, we looked for a simple relationship between k_{d1} and k_p to help for designing new alkoxyamines. Keeping the assumptions mentioned above, setting that a polymerization is successful for k_{d1} values that afford a linear evolution of M_n with the conversion from a value below 35% and with a final PDI below 1.4, choosing for values of $k_p = 2.1 \times 10^3$ (styrene), 4.0×10^4, 8.3×10^4 (BA), and 1.5×10^5 (in L•mol^{-1}•s^{-1} at 120 °C), kinetic simulations afforded 1.0×10^{-3}, 1.5×10^{-2}, 7.5×10^{-2}, and 0.3 (in s^{-1} at 120 °C) for the threshold k_{d1}, respectively. The plot k_p vs the threshold k_{d1} (Figure 13) shows a rough linear relationship, and eq 15 can be used as rule of thumb to estimate the values of the threshold k_{d1} and then predict the efficiency of a given alkoxyamine as initiating agent.

$$\frac{k_p}{k_{d1}} \leq 6.0 \times 10^5 \text{ L}\cdot\text{mol}^{-1} \qquad (15)$$

Because many assumptions have been done, more detailed simulations and experimental studies should be carried out to confirm the trends observed in Figure 13. It is noteworthy that, when the styrene polymerization carried out at 90 °C in the presence of **1a**, **1b**, and **1c** are compared (Figure 14), the evolution of the M_n's vs conversion are in good agreement with the trends displayed in Figure 12a for the BA polymerization simulations. It is noteworthy that the styrene polymerization is rather well controlled at 90 °C in the presence of **1c** (entry 9 in Table 1, Figure 14), although k_{d1} (**1c**) is only 2−5 times larger than k_{d1} (**1b**). That is, as the k_p/k_{d1} values of 2.0×10^7, 5.0×10^6, and 5.0×10^4 L•mol^{-1} for **1b**, **1c**, and **1a**, respectively, decrease, the control improves. The increase of k_{d1} leads to an improvement of the control as observed when **1a** was used as initiator.

Concluding Remarks

It appears that a successful NMP (controlled evolution of M_n with conversion, low PDI, short polymerization time, high livingness) depends of the value of the equilibrium constant as stated by Fischer.[3−7] By knowing the value of the dissociation and recombination rate constant and the characteristic rate constants for a given monomer (k_p, k_{t2}) it is theoretically possible to choose the experimental condition to have a controlled polymerization. Nevertheless, as shown for the BA−SG1 system, this requirement is not sufficient.

The examination of the living fraction for styrene and BA polymerization showed that livingness is governed by the equilibrium value but not necessarily the control. By increasing the dissociation rate constant of the initiating alkoxyamine, we have demonstrated that the control is dependent on the initiation step. The faster the initiation, the better the control. And to help for designing new alkoxyamine, we have developed a new statement (eq 15), linking k_{d1} and k_p, which should be added to the Fischer's equations (eq 1−3).

When all these requirements are fulfilled, a great care has to be taken on the procedure, heating with a ramp of temperature or not, purity of the materials, and the vessels.

An interesting challenge for the industry is the *n*-butyl acrylate polymerization without adding an extra amount of nitroxide. Several groups claim that their alkoxyamines are able to take up the challenge. However, in our work, we have shown that the ability of an alkoxyamine to control the polymerization depends also on the procedure and the vessel! Then, when can it be claimed that an alkoxyamine wins the challenge? Keeping

Table 3. Rate Constants Used for the Kinetic Modeling Studies Using the PREDICI Software

	styrene		*n*-butyl acrylate	
	90 °C	120 °C	120 °C	refs
k_{d1} (**1a**)[a]	1.7×10^{-2} s^{-1}	0.3 s^{-1}	0.3 s^{-1}	39, 42
k_{d1} (**1b**)[b]	5.0×10^{-5} s^{-1}	1.6×10^{-3} s^{-1}	1.6×10^{-3} s^{-1}	32
k_{d1} (**1c**)[c]	2.3×10^{-4} s^{-1}	*d*	*d*	32
k_{c1} (**1a**)[e,f]		5.0×10^{6} L mol^{-1} s^{-1}		36, 48
k_{c1} (**1b**)[e]		5.0×10^{7} L mol^{-1} s^{-1}		48, 49
k_{c1} (**1c**)[e]		5.0×10^{6} L mol^{-1} s^{-1}		36, 48
k_{add} (**a•**)[g]	8.0×10^{3} L mol^{-1} s^{-1}	1.0×10^{4} L mol^{-1} s^{-1}	3.3×10^{3} L mol^{-1} s^{-1}	61
k_{add} (**b•**)[h]	3.1×10^{5} L mol^{-1} s^{-1}	4.45×10^{5} L mol^{-1} s^{-1}	1.4×10^{5} L mol^{-1} s^{-1}	50
k_{add} (**c•**)[i]	1.2×10^{4} L mol^{-1} s^{-1}	*d*	*d*	51
k_t (**a•**, **b•**, **c•**)[j]		2.0×10^{9} L mol^{-1} s^{-1}		50, 60, 61
k_p[k]	900 L mol^{-1} s^{-1}	2.05×10^{3} L mol^{-1} s^{-1}	8.3×10^{4} L mol^{-1} s^{-1}	52
k_{d2}[l]	3.1×10^{-4} s^{-1}	7.5×10^{-3} s^{-1}	1.55×10^{-3} L mol^{-1} s^{-1}	44, 45, 48
k_{c2}[m]	2.6×10^{5} L mol^{-1} s^{-1}	2.6×10^{5} L mol^{-1} s^{-1}	2.8×10^{7} L mol^{-1} s^{-1}	48, 56, 57
k_{t2}	1.5×10^{8} L mol^{-1} s^{-1}	1.8×10^{8} L mol^{-1} s^{-1}	7.34×10^{7} L mol^{-1} s^{-1}	52, 53
$k_{self-initiation}$[n]	8.8×10^{-11} L mol^{-1} s^{-1}	9.3×10^{-10} L mol^{-1} s^{-1}	*o*	54
k_{inh} (MEHQ)[p]	*q*		5×10^{6} L mol^{-1} s^{-1}	55

[a] $A = 2.4 \times 10^{14}$ s^{-1}, $E_a = 112.3$ kJ·mol^{-1}. [b] Mean values of E_a's corresponding to a 1:1 mixture of the two isomers. $A = 2.4 \times 10^{14}$ s^{-1}, $E_a = 129.3$ kJ·mol^{-1}. [c] $A = 2.4 \times 10^{14}$ s^{-1}, $E_a = 125.2$ kJ·mol^{-1}. [d] Not determined. [e] The temperature dependence of k_c often exhibits a negative slope. Then, it was assumed that the values of k_c do not vary much between 60 and 120 °C. [f] The Arrhenius parameters of k_{c1} for **1•** + **a•** are not known. Therefore, it was assumed that k_{c1} values were slightly higher than those of **1•** + the esterified form of **a•**, $k_c = 1.2-1.6 \times 10^6$ L mol^{-1} s^{-1}. [g] The k_{add} values of **a•** are not known but they were assumed to be close of those of the 2-(alkoxy)carbonylprop-2-yl radical. For the addition onto the styrene $A = 6.7 \times 10^6$ L mol^{-1} s^{-1}, $E_a = 16.5$ kJ·mol^{-1}, and for the addition onto the *n*-butyl acrylate, $A = 4.0 \times 10^6$ L mol^{-1} s^{-1}, $E_a = 19.8$ kJ·mol^{-1}. Values given in the table provide the best fits. [h] For the addition of **b•** onto styrene, $A = 7.6 \times 10^7$ L mol^{-1} s^{-1}, $E_a = 14.7$ kJ·mol^{-1}, and for the addition of **b•** onto *n*-butyl acrylate, $A = 5.0 \times 10^7$ L mol^{-1} s^{-1}, $E_a = 19.1$ kJ·mol^{-1}. [i] It has been shown that the cumyl and the benzyl radicals add onto styrene with the same rate constants. Therefore, the value of k_{add}(**c•**) was estimated with $A = 4.0 \times 10^8$ L mol^{-1} s^{-1} and $E_a = 31.5$ kJ·mol^{-1}. [j] Self-termination rate constants are not known for **a•** and are assumed close to those of 2-(alkoxy)carbonylprop-2-yl radical. Furthermore, self-termination rate constants are close to the diffusion-controlled and then exhibit very weak temperature dependence, see ref 60. Therefore, same values for k_t between room temperature to 120 °C are assumed, k_t(**a•**) ≈ k_t(**b•**) ≈ k_t(**c•**) $= 2.0 \times 10^9$ L mol^{-1} s^{-1} at room temperature. [k] For the propagating polystyryl radical, $A = 4.27 \times 10^7$ L mol^{-1} s^{-1}, $E_a = 32.5$ kJ·mol^{-1}, and for the propagating poly(*n*-butyl acrylate) radical, $A = 1.81 \times 10^7$ L mol^{-1} s^{-1}, $E_a = 17.4$ kJ·mol^{-1}. [l] For the polystyryl−SG1 alkoxyamines, we have shown that the values of k_d do not change with the chain length after an increase of 1.4 factor, that is, $E_a = 124.3$ kJ·mol^{-1}. For the poly(*n*-butyl acrylate)-SG1 alkoxyamines, we have shown that k_d increased with the chain length between $n = 0$ to $n = 370$ monomer units. The 20 000 g·mol^{-1} targeted M_n involved at the best an increase by a factor two of k_d, that is, $E_a = 127.0$ kJ·mol^{-1}. Values given in the table provide the best fits. [m] An estimate of the k_{c2} value for the cross-reaction of poly(*n*-butyl acrylate) radicals and **1•** has been given by Bertin: 2.8×10^7 L mol^{-1} s^{-1} at 120 °C, see ref 57. The values given in the table were affording the best fits. [n] For the thermal self-initiation of the styrene polymerization, $A = 2.5 \times 10^3$ L mol^{-1} s^{-1}, $E_a = 93.5$ kJ·mol^{-1}. [o] In general, it is commonly accepted that the thermal self-initiation of the *n*-butyl acrylate polymerization does not occur. [p] It was assumed that the inhibition is a complex reaction (interaction with O_2) and both alkyl, alkoxyl, or peroxyl radicals can be trapped by substituted phenols. So a mean value of 5×10^6 L mol^{-1} s^{-1} is considered. [q] The presence of inhibitors is not required to take into account the reactivity observed, see text.

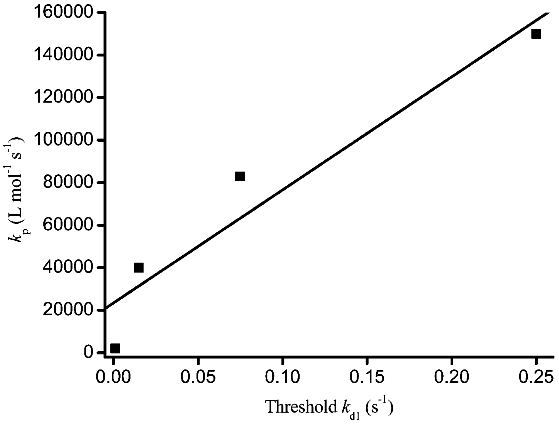


Figure 13. Plot of k_p vs threshold k_{d1}.

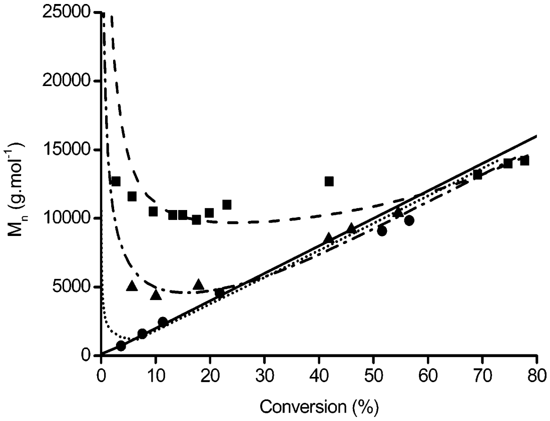


Figure 14. Evolution of the M_n vs conversion for the bulk polymerization of styrene at 90 °C mediated by alkoxyamines **1a** (●, ···), **1b** (■, - - -), and **1c** (▲, -·-·-·): experimental M_n (symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (—).

in mind that research is ultimately aimed for application at the industrial stage, although it is an exciting field for academia, claims for any success should rest on criteria as close as possible to industrial know-how, that is, more than half-filled reactors, vigorous stirring, poorly degassed solutions, and nonpurified materials. Therefore, we propose that a NMP of any monomer is claimed to be successful when the polymerization is performed with the following criteria of (i) a two-thirds-filled flask, (ii) a nonpurified monomer, (iii) a poorly degassed solution (30 min N_2 bubbling and possibly permanent N_2 flow), and when the typical features are observed, there is (i) perfect agreement between the experimental and theoretical M_n as exemplified above, (ii) high livingness (above 80% of living fraction), and (iii) polymerization performed in a reasonable time (less than 24 h).

It is noteworthy to highlight few points such as: (i) for a same nitroxide, the success or the failure of a controlled polymerization depends on the slow/fast homolysis of the initiating alkoxyamine, (ii) in general, in the first moments of the polymerization, simulations predict a better control in the absence of ramp of temperature, and (iii) regarding the ratio k_p/k_{d1} (eq 15), controlled polymerization of monomers exhibiting high k_p values can be carried out in the absence of an extra amount of **1**.

Our results highlight the pivotal role of the k_d values of the initiating alkoxyamine, that is, successful NMP experiments depend on the k_p/k_{d1} ratio (eq 15) and that it should be considered as a new requirement to be fulfilled before developing new alkoxyamines. This work confirmed the importance of the knowledge of the dissociation rate constant value for the development of the NMP and the interest in the structure−reactivity relationships developed in our group.

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