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ARTICLE

Comprehensive Modeling Study of Nitroxide-Mediated Controlled/Living Radical Copolymerization of Methyl Methacrylate with a Small Amount of Styrene

Julien Nicolas,*,† Laura Mueller,‡,§,⊥ Charlotte Dire,§,⊥ Krzysztof Matyjaszewski,‡ and Bernadette Charleux*,§,⊥

†*Laboratoire de Physico-Chimie, Pharmacotechnie et Biopharmacie, Université Paris-Sud, UMR CNRS 8612, Faculté de Pharmacie, 5 rue Jean-Baptiste Clément, 92296 Châtenay-Malabry, France,* ‡*Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213,* §*UPMC Université Paris 6, UMR 7610, Laboratoire de Chimie des Polymères, 4 place Jussieu, 75252 Paris cedex 05, France, and* ⊥*CNRS Université Paris 6, UMR 7610, Laboratoire de Chimie des Polymères, 4 place Jussieu, 75252 Paris cedex 05, France*

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ABSTRACT: This article presents a comprehensive kinetic study of the SG1 nitroxide-mediated copolymerization of methyl methacrylate with a small percentage of styrene using the PREDICI software. The aim of this study was to confirm the results from a previous publication showing that a living polymerization can be achieved for this system. The PREDICI simulations based on the penultimate unit effect model were also able to give a better insight into the complex mechanism of nitroxide-mediated controlled radical copolymerization. The model showed the copolymerization kinetics and the evolution of the number average molar mass, the fraction of living and dead chains, and the concentration of the four types of alkoxyamines and propagating radicals with monomer conversion. It was applied for different initial percentages of styrene and different initiator concentrations.

Introduction

With the advent of controlled/living radical polymerization (CRP),[1] the field of polymer chemistry has considerably expanded, which has led to the synthesis of new macromolecular architectures and materials with attractive properties. CRP methods are based on two general mechanisms, either reversible termination (e.g., nitroxide-mediated polymerization, NMP,[2] and atom transfer radical polymerization, ATRP[3,4]) or reversible chain transfer (e.g., iodine-transfer polymerization, ITP,[5,6] macromolecular design via the interchange of xanthate, MADIX,[7] and reversible addition−fragmentation chain transfer, RAFT[8,9]) or a combination of both (e.g., organo-tellurium[10] or cobalt-mediated[11,12] radical polymerizations). Each technique has been thoroughly studied to elucidate their respective mechanistic and kinetic aspects, but much work remains due to the wide variety of systems and monomers. It should be emphasized that most of the kinetic studies were devoted to homopolymerization and block copolymer formation.[13,14] In contrast, much less attention has been paid to the random copolymerization mechanism. The copolymer composition and composition distribution received more interest due to the potential properties and applications of such materials (e.g., copolymers exhibiting a composition gradient are of high technical importance).[15] Several articles have focused on the monomer reactivity ratios for CRP and their potential differences as compared to classical free-radical copolymerization.[16−29] Specifically, the establishment of the cross-propagation equilibrium and also the choice of adequate conditions to determine the reactivity ratios were studied. In contrast, reports on the copolymerization kinetics are very scarce.[18,23] For instance, Kubo et al.[30] determined the chain transfer constant for the dithioacetate-mediated living radical random copolymerization of styrene and methyl methacrylate at 40 °C. The kinetics for CRP based on reversible termination, in particular NMP, were also studied: a theoretical expression for the average activation−deactivation equilibrium constant was developed, considering both the terminal model and the implicit penultimate unit effect (IPUE) model.[31] It is possible to use this information to give a full theoretical description of the copolymerization kinetics based on the average propagation rate constant and the reversible termination of the propagating radicals.

The development of this theoretical description prompted a study on a particular system of interest for NMP, the copolymerization of methyl methacrylate (MMA) and styrene (Sty). The NMP of methacrylates does not exhibit the features of a controlled system, typically reaching a low conversion plateau in a short time period. This is due to extensive irreversible termination of the propagating radicals caused by the large activation−deactivation equilibrium constant and β-hydrogen transfer from the propagating radical to the nitroxide. Both reactions are predominant over reversible deactivation by TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy)[32,33] and by SG1 (*N*-*tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide),[34−38] but their respective magnitude depends on the nitroxide. The copolymerization of methyl methacrylate and styrene is much better controlled.[39] In particular, a small amount of styrene (below 10 mol %) is sufficient to convert the uncontrolled SG1-mediated homopolymerization of methyl methacrylate into a well-controlled and living copolymerization.[31,40] The presence of styrene leads to a drastic reduction of the overall concentration of propagating radicals and the formation of polymer chains with a MMA-Sty-SG1 terminal sequence.[40] In other words, styrene promotes the reversible deactivation of the propagating radicals by SG1 and the impact of the side reactions is decreased. Moreover, due to the incorporation of styrene as an isolated terminal subunit and to the steric effect of the penultimate MMA unit,

*Corresponding authors. E-mail: julien.nicolas@u-psud.fr (J.N.); bernadette.charleux@upmc.fr (B.C.). Telephone: +33 1 46 83 58 53 (J.N.). Fax: +33 1 46 61 93 34 (J.N.). Telephone: +33 1 44 27 50 70 (B.C.). Fax: +33 1 44 27 70 89 (B.C.).

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Scheme 1. Kinetic Scheme Used for the PREDICI Simulation of the Copolymerization of Methyl Methacrylate ($i, j, k = 1$) with a Small Amount of Styrene ($i, j, k = 2$) at 90 °C Initiated by the BlocBuilder alkoxyamine (RN)[a]

Homolytic dissociation of the BlocBuilder® alkoxyamine[36]	$RN \xrightarrow{k_{d0}} R^{\bullet} + N^{\bullet}$
Recombination of the BlocBuilder® alkoxyamine[50]	$R^{\bullet} + N^{\bullet} \xrightarrow{k_{c0}} RN$
Homotermination of the 2-(hydroxycarbonyl)prop-2-yl radical[51]	$R^{\bullet} + R^{\bullet} \xrightarrow{k_{t0}} RR$
Addition of the 2-(hydroxycarbonyl)prop-2-yl radical onto M^i [52]	$R^{\bullet} + M^i \xrightarrow{k_{p0^i}} RM^i$
Reversible combination of the $RM^{i\bullet}$ radical adduct with SG1[51]	$RM^{i\bullet} + N^{\bullet} \xrightarrow{k_{cR^i}} RM^iN$
Homolytic dissociation of the SG1-terminated RM^iN alkoxyamines[36,53]	$RM^iN \xrightarrow{k_{dR^i}} RM^{i\bullet} + N^{\bullet}$
Homotermination between $RM^{i\bullet}$ radical adducts[51]	$RM^{i\bullet} + RM^{j\bullet} \xrightarrow{k_{tR^iR^j}} RM^iM^jR$
Addition of the $RM^{i\bullet}$ radical adduct onto M^j [54,55]	$RM^{i\bullet} + M^j \xrightarrow{k_{pR^ij}} PM^iM^{j\bullet}$
Addition of the $PM^iM^{j\bullet}$ propagating macroradical onto M^k [54,55]	$PM^iM^{j\bullet} + M^k \xrightarrow{k_{pijk}} PM^jM^{k\bullet}$
Reversible combination of the $PM^{j\bullet}$ propagating macroradical with SG1[36,56]	$PM^{j\bullet} + N^{\bullet} \xrightarrow{k_{cj}} PM^jN$
Homolytic dissociation of the SG1-terminated PM^jM^kN alkoxyamine[36, 40,53,57]	$PM^jM^kN \xrightarrow{k_{djk}} PM^jM^{k\bullet} + N^{\bullet}$
Irreversible termination between a $PM^{j\bullet}$ and a $PM^{k\bullet}$ propagating macroradical by disproportionation [58,59,60]	$PM^{j\bullet} + PM^{k\bullet} \xrightarrow{k_{tdjk}} P_{dead}$
Irreversible termination between a $PM^{j\bullet}$ and a $PM^{k\bullet}$ propagating macroradical by combination [58,59,60]	$PM^{j\bullet} + PM^{k\bullet} \xrightarrow{k_{tcjk}} P_{dead}$
β-hydrogen transfer from a $PM^{j\bullet}$ propagating macroradicals to the nitroxide SG1[38]	$PM^{1\bullet} + N^{\bullet} \xrightarrow{k_{\beta Htr}} P_{\beta Htr} + NH$

[a] $N^{\bullet}$ = SG1 free nitroxide, NH = hydroxylamine, $R^{\bullet}$ = 2-(hydroxycarbonyl)prop-2-yl radical, M = monomer unit, P = polymer chains, P_{dead} = polymer chains terminated by coupling or disproportionation, and $P_{\beta Htr}$ = polymer chains terminated by β-hydrogen transfer from the propagating radicals to the free nitroxide.

dissociation of the ~MMA-Sty-SG1 macroalkoxyamine takes place at a much lower temperature than that of the polystyrene-SG1 counterpart. Consequently, the polymerization can be efficiently performed below 90 °C (typically in the 70−90 °C temperature range). These copolymerization results have a high impact on the development of NMP as they allow extension of the technique to the controlled polymerization of methacrylic acid[41] and other methacrylic esters[42] along with access to derived block copolymers.[41,43] The use of styrene in methacrylate polymerization was also employed in ATRP, either in miniemulsion[44] or in solution,[45] to improve crossover initiation efficiency in block copolymer synthesis using AGET (activator generated by electron transfer) and ARGET (activator regenerated by electron transfer) ATRP, respectively.

Although experimental work has been done to support the conclusions,[40] some parameters remain uncertain, such as the molar fraction of living chains and the respective concentrations of the various propagating radicals and alkoxyamines (four different species when the penultimate unit effect is considered). These parameters have a great influence on the polymerization kinetics and on the living character of the polymerization. In this article, the SG1-mediated copolymerization of MMA and Sty using the PREDICI software was comprehensively studied. The aim of this work is to confirm the experimental results, to give a better understanding of the complex mechanism of controlled radical copolymerization, and to gain new insight on how the copolymerization system can be improved.

Experimental Part

Simulations were performed using a simulation package PREDICI version 6.3.1 from CiT GmbH. The model implemented into PREDICI was built on the basis of the reaction steps describing the individual chemical reactions, with the kinetic parameters (as shown in Scheme 1 and in Table SI-1 in the Supporting Information) and the initial concentrations of all reaction components (Table 1). PREDICI performed a numerical time integration of the resulting systems of differential equations for the given final reaction time.[46−48]

Results and Discussion

1. Validation of the PREDICI model by Comparison with Experimental Data. The PREDICI model for the SG1-mediated copolymerization of MMA and Sty was constructed on the basis of kinetic and thermodynamic parameters from literature (see Scheme 1 and details given in the Supporting Information). The penultimate unit effect model was considered for calculating the rate constants of propagation (implicit model) and for the dissociation rate constants of the macroalkoxyamines, whereas the terminal model was used for recombination reactions with the nitroxide. For none of the kinetic parameters were the conversion and chain-length effects taken into account, although termination between propagating radicals may be affected.[49] The model was compared with experimental data in order to validate its relevance. In this section, the previously published results of the SG1-mediated bulk copolymerizations of MMA with Sty at 90 °C were considered.[31] The percentage of styrene was progressively increased from 0 to 8.8 mol % with a constant BlocBuilder alkoxyamine concentration. The model was then compared with experimental data using variable alkoxyamine concentrations ranging from 1.37×10^{-2} M to 1.10×10^{-1} M, with a constant styrene concentration of 8.8 mol %. All experimental conditions are shown in Table 1.

Table 1. Experimental Conditions for the SG1-Mediated Bulk (Co)Polymerizations of Methyl Methacrylate and Styrene Initiated by the BlocBuilder Alkoxyamine at 90 °C (from Ref 31)

expt	[methyl methacrylate], M	[styrene], M	initial molar fraction of styrene (f_{S0})	initial concentration of alkoxyamine, 10^{-2} M	initial concentration of SG1 nitroxide,[a] 10^{-3} M
1	8.48	0.82	0.088	2.73	2.74
2	8.92	0.41	0.044	2.72	2.75
3	9.14	0.20	0.021	2.73	2.74
4	9.36	0	0	2.73	2.74
5	8.49	0.81	0.088	11.0	11.0
6	8.49	0.82	0.088	1.37	1.36

[a] $[SG1]_0/[\text{alkoxyamine initiator}]_0 = 0.10$.

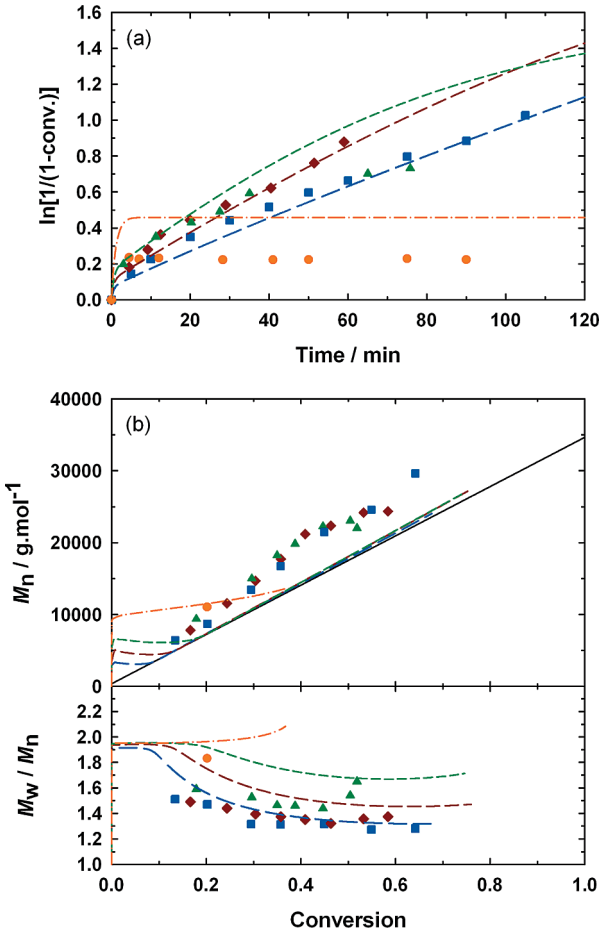

Figure 1. SG1-mediated controlled radical bulk polymerization of methyl methacrylate initiated by the BlocBuilder alkoxyamine ([BlocBuilder]$_0$ = 2.73 × 10^{-2} M) at 90 °C with 10 mol % of free SG1 as a function of the initial amount of styrene: (■) expt **1**, f_{S0} = 0.088; (◆) expt **2**, f_{S0} = 0.044; (▲) expt **3**, f_{S0} = 0.022; (●) expt **4**, f_{S0} = 0. Key: (a) ln[1/(1 − conv)] vs time (conv = overall conversion); (b) number-average molar mass, M_n, and polydispersity index, M_w/M_n, vs conversion; the dotted-lines correspond to the modeling studies (long dash, f_{S0} = 0.088; medium dash, f_{S0} = 0.044; short dash, f_{S0} = 0.021; dash−dot, f_{S0} = 0), and the full line represents the theoretical M_n.

In Figure 1, the monomer conversion versus time was plotted along with the evolutions of the number-average molar mass, M_n, and the polydispersity index, M_w/M_n, as a function of the overall monomer conversion for both experimental and simulated data for experiments **1**−**4**, Table 1. The simulations matched well with the experimental values for the highest amounts of styrene. For the homopolymerization of MMA initiated by the BlocBuilder alkoxyamine (f_{S0} = 0, experiment **4**), the predicted monomer conversion quickly reached a plateau and the polymerization stopped to yield a polydisperse PMMA homopolymer with M_n close to the theoretical value. A similar finding was observed experimentally, however, the simulated final conversion was significantly higher than that of the experimental one. This was attributed to an uncontrolled temperature increase in the reaction medium during the initial stage of polymerization, as it is an exothermic process. The increase in temperature led to a greater concentration of primary radicals due to an increased quantity of dissociated alkoxyamine, and therefore more termination to stop the experimental polymerization at an earlier conversion. In contrast, when 2.1 mol % of styrene was initially added to the reaction, monomer conversion increased progressively with time. A linear evolution of molar mass and lower polydispersity indexes were observed. When the initial styrene proportion was further increased (f_{S0} = 4.4 and 8.8 mol %), the simulated conversions were comparable to those of the corresponding experiments with a decrease of the conversion rate owing to a reduction of both the average rate constant of propagation and the average activation−deactivation equilibrium constant.[31] The polydispersity indexes decreased accordingly (the higher the initial styrene content, the lower M_w/M_n). The evolution of M_n with monomer conversion matched well with theoretical values for the simulation, but the experimental values of M_n were above the theoretical line. This could be due to the fact that PREDICI takes into account all species, including very short (dead) oligomers, while SEC analyses do not consider all species (due to the position of the low-molar mass integration limit and differences in refractive index); or impurities may have been present in the alkoxyamine used for the experimental points, which would also lead to values of M_n above the theoretical line. Moreover, in ref 31, the SEC analyses of our copolymers were performed with a polystyrene calibration and were not optimized.

Experiments with variation of the alkoxyamine initial concentration (i.e., different target molar masses) were compared with the kinetic model (experiments **1**, **5**, and **6**, Table 1). Increasing the alkoxyamine concentration (while keeping the same $[SG1]_0/[\text{alkoxyamine}]_0$ ratio) led to an increase in the experimental polymerization rate. It was, however, anticipated that reactions performed with a similar $[SG1]_0/[\text{alkoxyamine}]_0$ ratio should exhibit the same polymerization rate, irrespective of the initial alkoxyamine concentration.[61] The observed behavior was explained by the concentration of free SG1, insufficient to avoid the existence of early irreversible termination reactions: the proportion of released SG1 was higher when $[\text{alkoxyamine}]_0$ was decreased (due to the persistent radical effect).[62,63] Theoretical modeling of these experiments gave exactly the same trend, i.e. predicted first-order kinetic plots almost perfectly matched experimental data (Figure 2). Besides, a good agreement was obtained for both the evolution of M_n and that of M_w/M_n with monomer conversion (note that, regarding the M_n values, the same comments as for Figure 1 also apply here).

Assessment of the copolymerization model was considered satisfactory, especially regarding the large number of

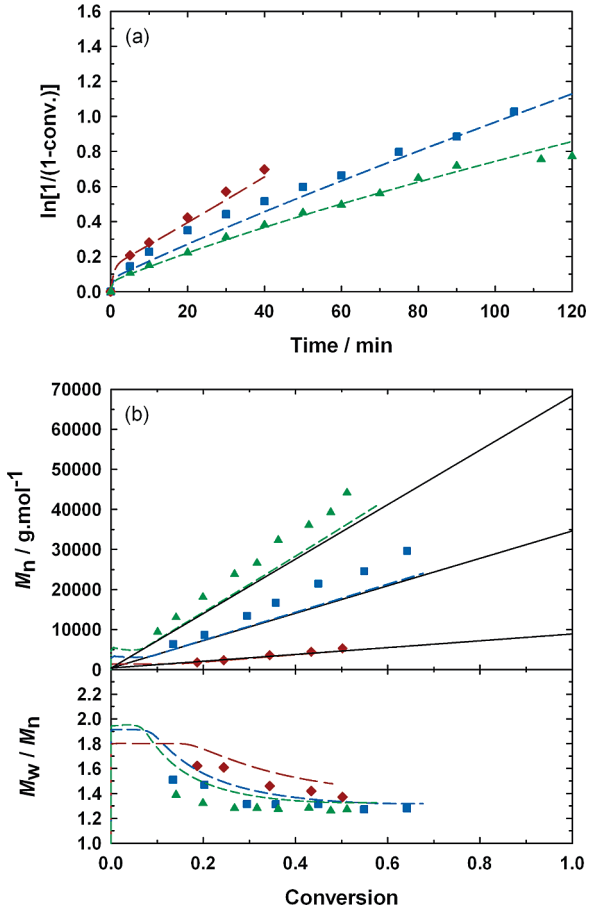

Figure 2. SG1-mediated controlled radical bulk polymerization of methyl methacrylate with a small amount of styrene (f_{S0} = 0.088) at 90 °C with 10 mol % of free SG1 as a function of the initial amount of the BlocBuilder alkoxyamine: (▲) expt **6**, [BlocBuilder]$_0$ = 1.37×10^{-2} M; (■) expt **1**, [BlocBuilder]$_0$ = 2.73×10^{-2} M; (◆) expt **5**, [BlocBuilder]$_0$ = 1.10×10^{-1} M. (a) ln[1/(1 − conv.)] vs time (conv. = overall conversion); (b) number-average molar mass, M_n, and polydispersity index, M_w/M_n, vs conversion; the dotted-lines correspond to the modeling studies (short dash, [BlocBuilder]$_0$ = 1.37×10^{-2} M; medium dash: 2.73×10^{-2}; long dash, [BlocBuilder]$_0$ = 1.10×10^{-1} M), and the full lines represent the theoretical M_n.

kinetic parameters. A very good agreement was obtained for the experiments with 4.4 and 8.8 mol % of styrene, which is the focus of a more profound discussion in the next part of this article. This model helps to understand the copolymerization process and to evaluate the concentration of all species as a function of monomer conversion.

2. Investigation of the Controlled/Living Copolymerization Mechanism. *Fraction of Living Chains.* A good agreement between simulated and experimental data on the kinetics of the copolymerization and the evolution of M_n and polydispersity index versus conversion was obtained. Thus, the model can be applied for analysis of the living character of the polymer chains during copolymerization. This is a crucial parameter for block copolymer synthesis. The living character is defined by the proportion of chains that exhibit an alkoxyamine functional group at the chain-end (called LF for living fraction), which is calculated according to eq 1 (LF1) and to eq 2 (LF2), in which i and j = 1 or 2 (methyl methacrylate = M^1, styrene = M^2), R stands for 2-(hydroxycarbonyl)prop-2-yl, N is SG1, RN is the BlocBuilder alkoxyamine, P stands for polymer chains, P_{dead} stands for polymer chains terminated by coupling or disproportionation, and $P_{\beta Htr}$ stands for polymer chains terminated by β-hydrogen transfer from the propagating radicals to the free nitroxide. In eq 1, only the polymer chains were taken into account and the alkoxyamine initiator was excluded, whereas in eq 2, the latter was considered.

$$\mathrm{LF1} = \frac{\sum_{i=1,2}[\mathrm{RM}^i\mathrm{N}] + \sum_{i,j=1,2}[\mathrm{PM}^i\mathrm{M}^j\mathrm{N}]}{\sum_{i=1,2}[\mathrm{RM}^i\mathrm{N}] + \sum_{i,j=1,2}[\mathrm{PM}^i\mathrm{M}^j\mathrm{N}] + \mathrm{P}_{dead} + \mathrm{P}_{\beta Htr}} \quad (1)$$

$$\mathrm{LF2} = \frac{[\mathrm{RN}] + \sum_{i=1,2}[\mathrm{RM}^i\mathrm{N}] + \sum_{i,j=1,2}[\mathrm{PM}^i\mathrm{M}^j\mathrm{N}]}{[\mathrm{RN}]_0} \quad (2)$$

For copolymerizations with a variable initial amount of styrene and a constant alkoxyamine concentration ([BlocBuilder]$_0$ = 2.73×10^{-2} M, experiments **1**−**4**, Table 1) the evolution of the alkoxyamine concentration, of f_S (instantaneous molar fraction of styrene in the comonomer mixture), and of both LF1 and LF2 with the overall monomer conversion are shown in Figure 3. As expected for f_{S0} = 0 (experiment **4**), a rapid decrease of LF with conversion was obtained in agreement with experimental observations from the literature (Figure 3, parts c and d).[37,38] This confirms the unstable character of the PMMA-SG1 alkoxyamine bond and the extensive irreversible termination reactions of the PMMA radicals. In contrast, for f_{S0} = 2.2−8.8 mol %, the evolution of LF with conversion was drastically different. LF decreased slowly with monomer conversion and LF = 0 was reached only at high conversions. Also, LF was higher for a given conversion when the initial proportion of styrene was higher. This indicates that the irreversible termination reactions were significantly decreased. In the presence of styrene, the LF1 vs conversion plots (calculated according to eq 1) can be divided into three distinct parts: (i) in the very first moments of the reaction, LF1 drops sharply during a short period of time because of the persistent radical effect, particularly pronounced for MMA-terminated radicals; (ii) during the period of continuous creation of new chains by BlocBuilder (Figure 3a) and due to an efficient incorporation of styrene (Figure 3b), LF1 increases due to the formation of more stable MMA-Sty-SG1 terminal sequences, and (iii) the final part is the decrease of LF1 due to the depletion of the proportion of styrene in the comonomer mixture (Figure 3b) in agreement with the reactivity ratios (see values in the Supporting Information) and the unavoidable irreversible termination reactions. Using eq 2, a more simple evolution with monomer conversion can be observed as the LF2 values continuously decrease from 1 at conversion = 0 to 0 at final conversion.

The evolution of LF with the overall monomer conversion for the copolymerizations with the same initial amount of styrene (f_{S0} = 8.8 mol %) and variable alkoxyamine concentrations ([BlocBuilder]$_0$ = 1.37×10^{-2} M, 2.73×10^{-2} M and 1.10×10^{-1} M, experiments **6**, **1**, and **5**, respectively, Table 1) is presented in Figure 4. The LF value was higher at a given conversion when a higher initial concentration of alkoxyamine was used. In particular, short chains (i.e., high [BlocBuilder]$_0$) maintained a living character up to very high conversions. LF eventually reached 0 due to the nearly complete consumption of styrene before the end of the polymerization (Figure 4b) and to side reactions affecting mainly the macroradicals with MMA chain-end.

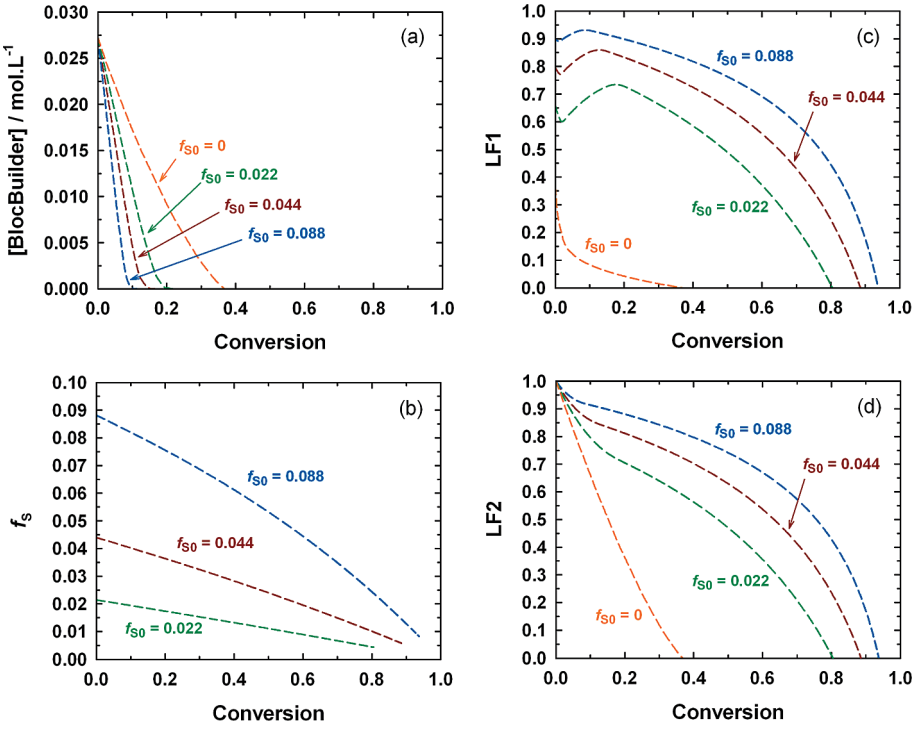

Figure 3. Modeling studies of the SG1-mediated controlled radical bulk polymerization of methyl methacrylate initiated by the BlocBuilder alkoxyamine ([BlocBuilder]$_0$ = 2.73 × 10^{-2} M) at 90 °C with 10 mol % of free SG1 and variable proportions of styrene: expt **1**, f_{S0} = 0.088; expt **2**, f_{S0} = 0.044; expt **3**, f_{S0} = 0.022; expt **4**, f_{S0} = 0. Key: (a) BlocBuilder concentration versus overall monomer conversion; (b) molar fraction of styrene in the comonomer mixture; (c) fraction of chains terminated by an alkoxyamine group, LF1, calculated according to eq 1, in which the initiator is not included; (d) fraction of chains terminated by an alkoxyamine group, LF2, calculated according to eq 2, in which the initiator is included.

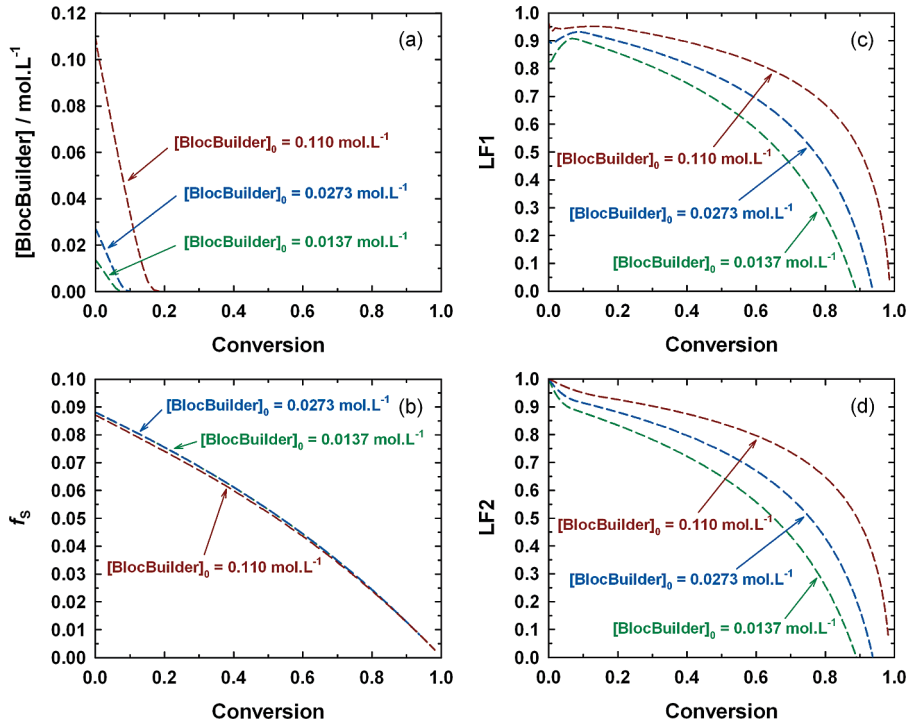

Figure 4. Modeling studies of the SG1-mediated controlled radical bulk polymerization of methyl methacrylate with a small amount of styrene (f_{S0} = 0.088) at 90 °C with 10 mol % of free SG1 as a function of the initial amount of the BlocBuilder alkoxyamine: expt **6**, [BlocBuilder]$_0$ = 1.37 × 10^{-2} M; expt **1**, [BlocBuilder]$_0$ = 2.73 × 10^{-2} M; expt **5**, [BlocBuilder]$_0$ = 1.10 × 10^{-1} M. Key: (a) BlocBuilder concentration versus overall monomer conversion; (b) molar fraction of styrene in the comonomer mixture; (c) fraction of chains terminated by an alkoxyamine group, LF1, calculated according to eq 1, in which the initiator is not included; (d) fraction of chains terminated by an alkoxyamine group, LF2, calculated according to eq 2, in which the initiator is included.

Macroalkoxyamine Chain-End Structure. The preferential formation of stable MMA-Sty-SG1 terminal sequences is the key feature for a successful SG1-mediated copolymerization of MMA with a small amount of styrene, as evidenced by ESR analyses.[40] From the PREDICI simulations, the molar fractions of each type of macroalkoxyamine (i.e., the four

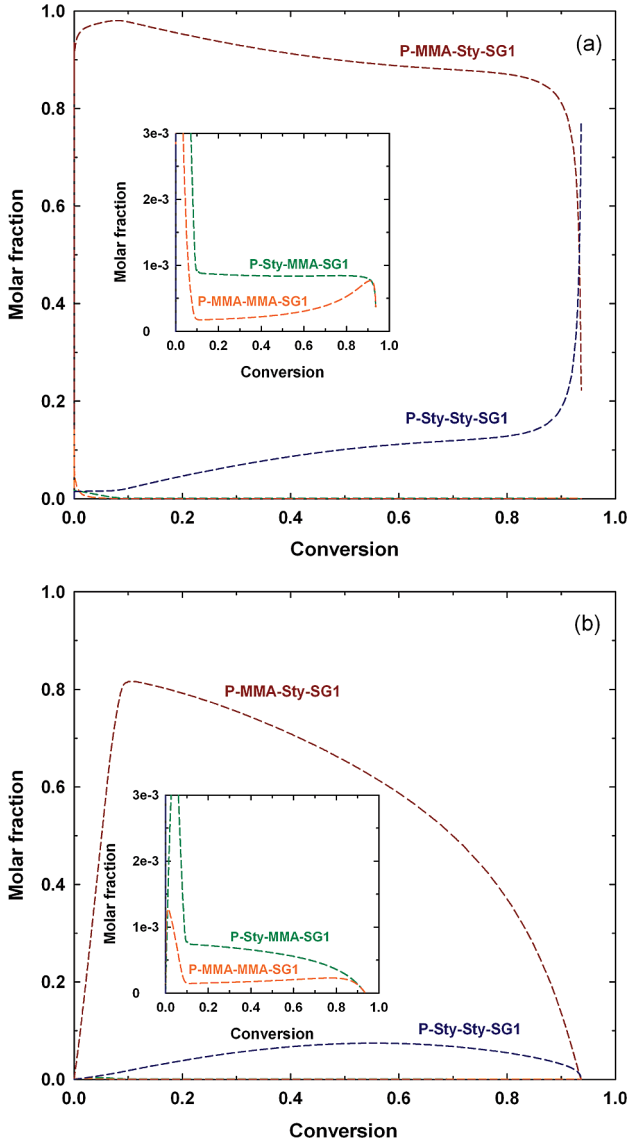

Figure 5. Modeling studies of the molar fraction of the different macromolecular species during the SG1-mediated controlled radical bulk polymerization of methyl methacrylate (MMA) initiated by the BlocBuilder alkoxyamine ($[\text{BlocBuilder}]_0 = 2.73 \times 10^{-2}$ M) at 90 °C with 10 mol % of free SG1 and a small amount of styrene (Sty, $f_{S0} = 0.088$) (experiment **1** in Table 1). Key: (a) Molar fractions are calculated on the basis of the overall macroalkoxyamine concentrations and exclude the other types of chain-ends; (b) molar fractions are calculated on the basis of the initial concentration of BlocBuilder alkoxyamine. Insets: expanded graphs of the $(0-3) \times 10^{-3}$ region.

different chain-end structures: MMA-MMA-SG1, MMA-Sty-SG1, Sty-MMA-SG1, and Sty-Sty-SG1) are represented in Figure 5 as a function of the overall monomer conversion for a typical copolymerization experiment (experiment **1**, Table 1). At the onset of the reaction, the proportion of P-MMA-Sty-SG1 macroalkoxyamine sharply increased and reached a maximum within ca. 5 min (at 8% monomer conversion). Its concentration was much higher than the other types of SG1-terminated macromolecular species, in agreement with experimental results.[40] For instance, at 40% conversion, [P-MMA-Sty-SG1] was 11 times higher than [P-Sty-Sty-SG1], 1100 times higher than [P-Sty-MMA-SG1] and 4600 times higher than [P-MMA-MMA-SG1]. The concentrations of MMA-terminated alkoxyamines initially increased, but quickly decreased to reach a low, stationary value. This is due to the poor stability of the C-ON bond, preventing accumulation of those species in the reaction medium. In contrast, the P-Sty-Sty-SG1 macroalkoxyamines accumulated in the reaction mixture due to their low dissociation rate constant at 90 °C and then they slowly disappeared (due to styrene depletion) at high monomer conversion. This is very important information for the synthesis of diblock copolymers. At low polymerization temperatures, they may induce slow reinitiation and appear as dead chains. Consequently, it might be important to avoid the presence of styrene dyads. This will narrow the concentration window for the initial amount of styrene: not too low to perform the polymerization under living conditions and not too high to avoid the accumulation of P-Sty-Sty-SG1 alkoxyamine.

Dead Chains. At the beginning of the reaction, a significant production of dead polymer chains from termination of the propagating radicals was noticed, as expected from the persistent radical effect that has been well described for NMP (Figure 6).[62] Subsequently, their concentration increased quite slowly and a molar fraction of 20% was reached at the end of the polymerization. This is within the expected range for the NMP of styrene.[64] The unsaturated polymer produced by bimolecular hydrogen transfer from the propagating radicals to the free nitroxide is the other type of dead chain.[37,38] At low conversion, their proportion remained below that of the self-terminated chains, but they increased more rapidly and became the main dead species above ca. 40% conversion. This irreversible side reaction affects essentially the macroradicals with an MMA ultimate unit and is the main event that leads to a complete consumption of the macroalkoxyamine dormant chains. This process is enhanced by the release of free SG1 in the system (i.e., resulting from macroradical self-terminations/persistent radical effect). A more complete description of the various proportions of dead chains in the SG1-mediated copolymerization of methyl methacrylate and styrene was reported previously.[38]

Concentration of the Various Propagating Radicals. Due to the large difference of the activation−deactivation equilibrium constants for the various macroalkoxyamines (see Table 2), the respective concentrations of the macroradicals followed different trends than the corresponding dormant chains. This is illustrated in Figure 7 and can be compared with Figure 5. The P-MMA-MMA$^\bullet$ macroradical concentration was the highest, whereas that of the corresponding alkoxyamine was the lowest. The P-MMA-Sty$^\bullet$ and P-Sty-MMA$^\bullet$ radical concentrations were similar to each other and were comparable to the P-MMA-MMA$^\bullet$ concentration whereas the P-Sty-Sty$^\bullet$ macroradical concentration was the lowest. All macroradical concentrations remained constant throughout the polymerization and consequently obeyed the cross-propagation equilibria after complete consumption of the BlocBuilder initiator (as shown in Figure SI-1 in the Supporting Information). Macroradicals with a methacrylate terminus can be terminated by β-hydrogen transfer to the SG1 free nitroxide. This provides an explanation for the extensive formation of dead chains even though the chain transfer constant $k_{\beta\text{Htr}}$ is rather small (Table SI-1, Supporting Information).[38] It is worth mentioning that in the absence of such a reaction the polymerization would exhibit an excellent living character, as discussed earlier.[31,38]

Concentration of Free SG1. The accumulation of free SG1 is caused by the irreversible termination between propagating macroradicals. As mentioned above, the concentration of the nitroxide is of paramount importance in the

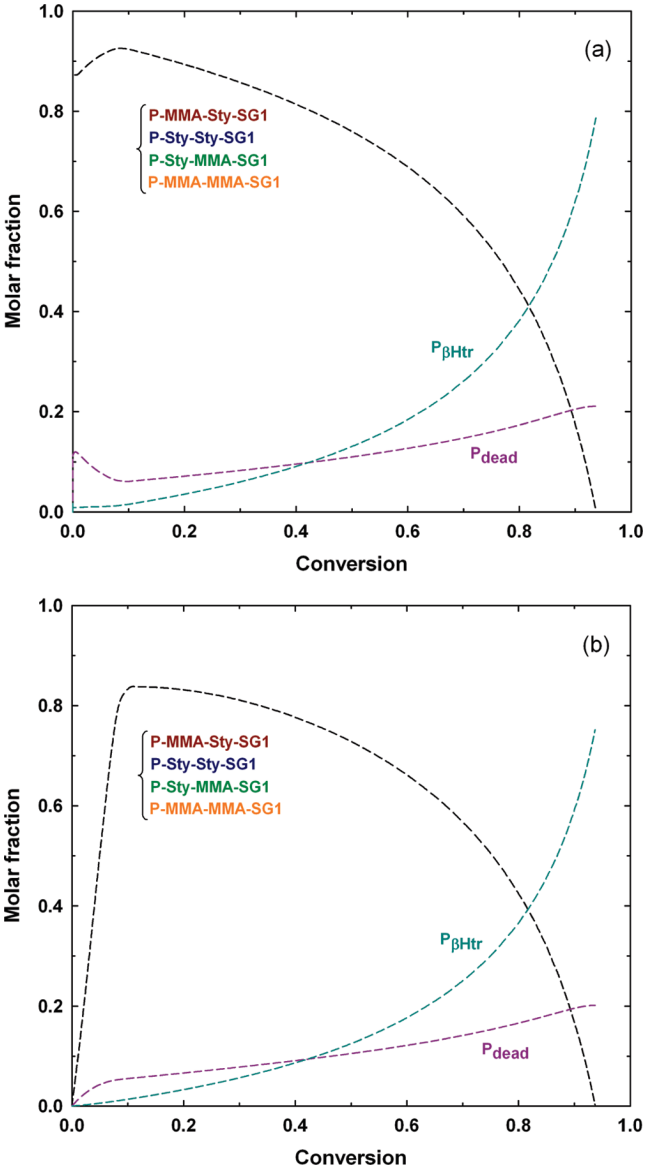

Figure 6. Modeling studies of the molar fraction of macroalkoxyamine species (P-MMA-Sty-SG1 + P-Sty-Sty-SG1 + P-Sty-MMA-SG1 + P-MMA-MMA-SG1), dead polymer chains obtained by disproportionation and combination (P_{dead}) and by β-hydrogen transfer from the propagating radical to the nitroxide ($P_{\beta Htr}$) during the SG1-mediated controlled radical bulk polymerization of methyl methacrylate (MMA) initiated by the BlocBuilder alkoxyamine ([BlocBuilder]$_0$ = 2.73×10^{-2} M) at 90 °C with 10 mol % of free SG1 and a small amount of styrene (Sty, f_{S0} = 0.088) (experiment 1 in Table 1). Key: (a) Molar fractions are calculated on the basis of the overall polymer chain concentrations; (b) molar fractions are calculated on the basis of the initial concentration of BlocBuilder alkoxyamine.

Table 2. Activation−Deactivation Equilibrium Constants for the Four Types of Macroalkoxyamines: $K_{ii} = k_d^{ii}/k_c^{i\,a}$

equilibrium constant	value (M)
K_{11}	8.36×10^{-5}
K_{21}	4.93×10^{-6}
K_{12}	7.56×10^{-9}
K_{22}	5.56×10^{-10}

[a] 1 stands for MMA and 2 for styrene; see Table SI-1 (Supporting Information) for the k_d^{ii} and k_c^{i} values.

copolymerization system since it governs the living character of the polymerization via the activation−deactivation equilibrium. It also induces formation of dead chains via

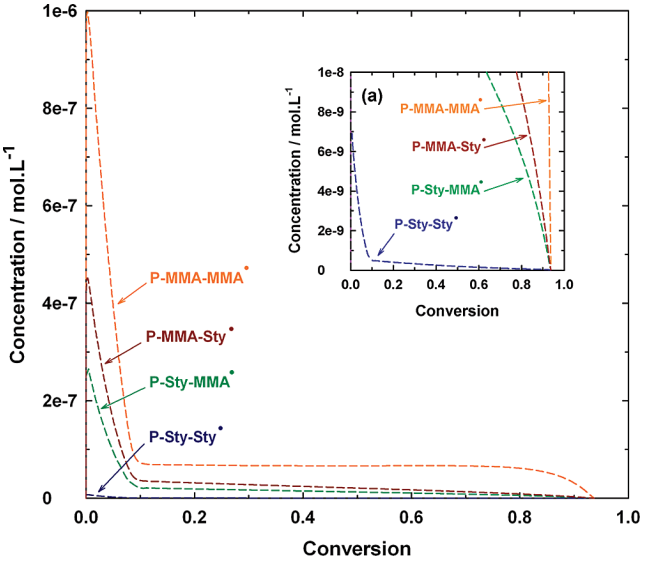

Figure 7. Modeling studies of the concentrations of the different macroradicals during the SG1-mediated controlled radical bulk polymerization of methyl methacrylate (MMA) initiated by the BlocBuilder alkoxyamine ([BlocBuilder]$_0$ = 2.73×10^{-2} M) at 90 °C with 10 mol % of free SG1 and a small amount of styrene (Sty, f_{S0} = 0.088) (experiment 1 in Table 1). Inset a: Expanded graph of the (0−1) × 10^{-8} M region.

β-hydrogen transfer from the PMMA propagating macroradicals, yielding the corresponding hydroxylamine (SG1-H) and unsaturated polymer.[38] Modeling studies of the concentration of free SG1 (Figure 8, parts a and b) and SG1-H (Figure 8, parts c and d) (both represented as the ratio of their concentrations to [BlocBuilder]$_0$), were performed for variable initial amounts of styrene (experiments **1**−**4**, Table 1) and for variable initial concentrations of the BlocBuilder alkoxyamine (experiments **1**, **5** and **6**, Table 1). The PREDICI simulations show that when styrene was not added to the reaction medium (f_{S0} = 0, Figure 8, parts a and b), all the SG1 initially present in the BlocBuilder alkoxyamine was released either in the form of free nitroxide or in the form of SG1-H.[65] Eventually, the concentration of the alkoxyamine initiator reached zero (see also Figure 3a), in agreement with the observed absence of macromolecular alkoxyamines. The concentration of free SG1 was larger than that of SG1-H at a given conversion, indicating extensive termination due to a high concentration of propagating radicals. In contrast, when styrene was initially added to the system, the evolution of free SG1 was quite slow above ca. 20% monomer conversion. However, the SG1-H concentration increased in a continuous manner and became the major species before the end of the polymerization. Such observations were similar to those for the evolution of P_{dead} and $P_{\beta Htr}$ (Figure 6). In addition, when the initial amount of styrene was increased, the concentrations of both free SG1 and SG1-H at a given conversion were lower. Two features of the copolymerization approach should be highlighted here: (i) the presence of styrene induced a decrease in the self-termination rate via a decrease of the overall concentration of propagating radicals; (ii) for a given conversion, the less free SG1 present in the reaction medium, the less pronounced the β-hydrogen transfer is (Figure 8, parts a and c). In other words, the presence of styrene reduced the occurrence of both irreversible side reactions. Those effects were more pronounced when the initial concentration of BlocBuilder alkoxyamine was increased from 1.37×10^{-2} to 1.10×10^{-1} M (Figure 8, parts b and d).

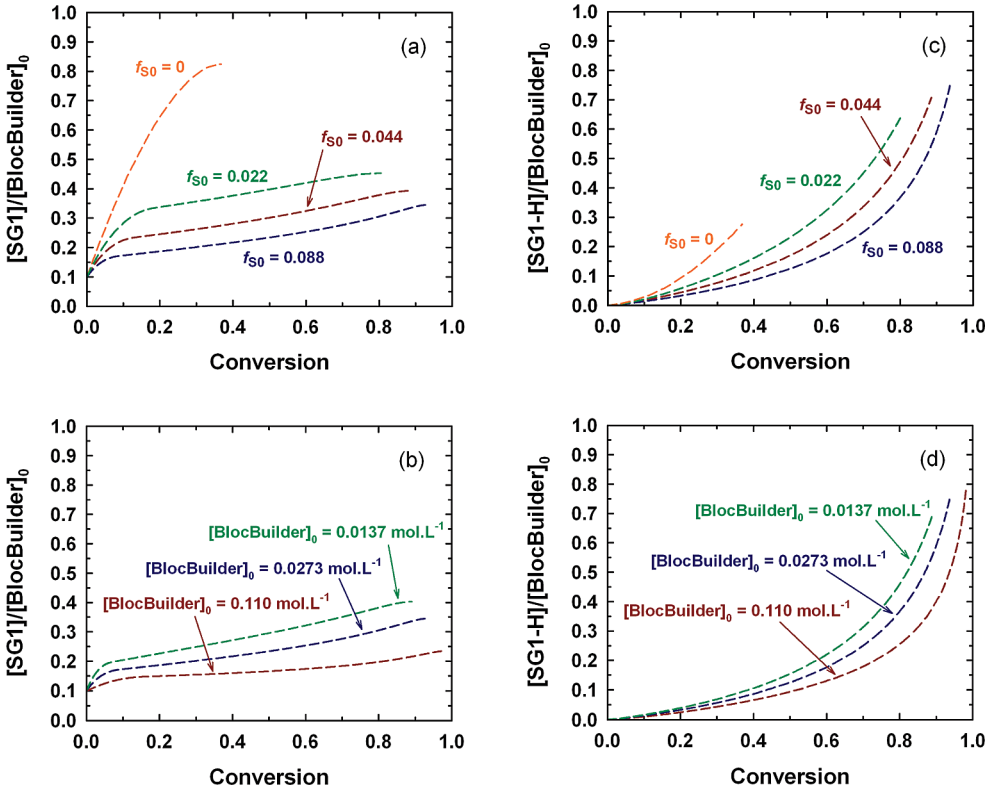

Figure 8. Modeling studies of the concentrations of free SG1 ([SG1]/[BlocBuilder]$_0$) (a, b) and formed hydroxylamine SG1-H ([SG1-H]/[BlocBuilder]$_0$) (c, d) during the SG1-mediated controlled radical bulk polymerization of methyl methacrylate (MMA) initiated by the BlocBuilder alkoxyamine at 90 °C with 10 mol % of free SG1 and a small amount of styrene (Sty). (a and c) Initial amount of styrene versus overall monomer conversion ([BlocBuilder]$_0$ = 2.73 × 10^{-2} M): expt **1**, f_{S0} = 0.088; expt **2**, f_{S0} = 0.044; expt **3**, f_{S0} = 0.022; expt **4**, f_{S0} = 0. (b and d) Initial amount of the BlocBuilder alkoxyamine versus overall monomer conversion (f_{S0} = 0.088): expt **6**, [BlocBuilder]$_0$ = 1.37 × 10^{-2} M; expt **1**, [BlocBuilder]$_0$ = 2.73 × 10^{-2} M; expt **5**, [BlocBuilder]$_0$ = 1.10 × 10^{-1} M.

Conclusion

The PREDICI model was a very useful tool to describe in detail the SG1-mediated polymerization of methyl methacrylate with and without a small percentage of styrene. It was found that the model correlated very well with previously published experimental results. Furthermore, the model was able to give precise information, otherwise inaccessible through experimental means. This included the fraction of living chains, the macroalkoxyamine chain-end structure, the structure and fraction of dead chains, the concentration of the various propagating radicals, and the concentration of free SG1. Overall, the presence of styrene was found to improve the nitroxide-mediated polymerization of methyl methacrylate. However, an increase in styrene concentration caused an increase in the P-Sty-Sty-SG1 macroalkoxyamine concentration (which only slowly reinitiated under the polymerization conditions). Therefore, it is important to identify an appropriate balance for the styrene concentration, which could be done with PREDICI, by feeding appropriately the styrene into the system via a semibatch approach. Those experiments are still in progress and will be the topic of a forthcoming article.

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Supporting Information Available: Text dicussing the model construction and choice of the rate constants, a table of the kinetic scheme and rate constants, and equations and figures showing the cross-propagation equilibria. This material is available free of charge via the Internet at http://pubs.acs.org.

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(63) From reference 62, the equation giving the concentration of released free nitroxide due to the persistent radical effect reads: $[SG1] = ([SG1]_0^3 + 3k_tK^2[P\text{-}SG1]_0^2t)^{1/3}$ with $[P\text{-}SG1]_0$ the initial concentration of alkoxyamine, k_t, the overall rate constant of termination and K, the activation-deactivation equilibrium constant. It turns out then that $[SG1]/[P\text{-}SG1]_0 = ([SG1]_0^3[P\text{-}SG1]_0^{-3} + 3k_tK^2[P{-}SG1]_0^{-1}t)^{1/3}$ is larger at a given time when $[P\text{-}SG1]_0$ is lower.
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