Modeling the Product Composition During Controlled Radical Polymerizations with Mono- and Bifunctional Alkoxyamines

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Summary: The objective of this paper is to present a kinetic model for simulating the nitroxide controlled radical polymerization initiated with mono- and bifunctional alkoxyamines. The model approach was validated by experimental data. The simulated product composition mainly depends on the equilibrium constants K ($=k_d/k_c$) of dissociation/combination reaction between dormant and active species. Our investigations include polymerizations under stationary state conditions (nitroxide TEMPO) and in the kinetic regime of persistent radical effect (nitroxide BIPNO). Combination reactions of the propagating radicals cause loss of functionality and dormant chains. The applied Monte Carlo approach provides detailed information about the microstructure of the reaction products.

Keywords: alkoxyamine; controlled radical polymerization; Monte Carlo simulation

Introduction

The controlled radical polymerization includes a group of polymerization techniques which are suitable to synthesize polymers of well defined architectures. The three main methods of the controlled radical polymerization are the Nitroxide-Mediated Polymerization (NMP), the Atom Transfer Radical Polymerization (ATRP) and the Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT). In all cases the controlled radical polymerization contains a reversible activation process of "dormant" polymer chains. In the case of nitroxide controlled radical polymerization the dormant chain, PnN, dissociates into a growing polymer chain ($P_n^{\bullet}$) with the rate constant k_d and a stable nitroxide (N) (Equation 1). The growing polymer chain can be deactivated again by the free nitroxide with the rate constant k_c or undergo termination reactions.

$$P_nN \underset{k_c}{\overset{k_1}{\rightleftharpoons}} P_n^{\bullet} + N \qquad (1)$$

The polymerizations were initiated with the corresponding alkoxyamines RN. Alkoxyamines with more than three nitroxide groups can be used for synthesis of star polymers following the "Core-First" approach.[1,2] By using bifunctional alkoxyamines (NRN) the synthesis of triblock copolymers in two steps is possible. Gnanou et al.[3] synthesized poly(styrene-*block*-*n*-butylacrylate-*block*-styrene) triblock copolymers using a dialkoxyamine as initiator. Triblock copolymer particles comprising a poly(n-butyl acrylate) first block and polystyrene or poly-(methyl methacrylate) second blocks were synthesized by nitroxide-mediated controlled radical emulsion polymerization by Charleux et al.[4]. The bifunctional alkoxyamines based on the nitroxide SG1 were used in both cases as initiator.

The termination reactions of the propagating polymer chains ($P_n^{\bullet}$) generate a mixture of dead (D_n) and dormant (P_nN) polymer chains during the nitroxide controlled radical polymerization.

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If the polymerization is carried out with bifunctional alkoxyamines, the dormant polymer chains are terminated with nitroxides on both chain ends (NP_nN). The termination reactions produce dead chains (D_n) and dormant chains with reduced functionality (P_nN, monofunctional).

Applying the kinetic model of the nitroxide controlled radical polymerization initiated with mono- (RN) and bifunctional (NRN) alkoxyamines we are able to investigate the product composition during the polymerization.

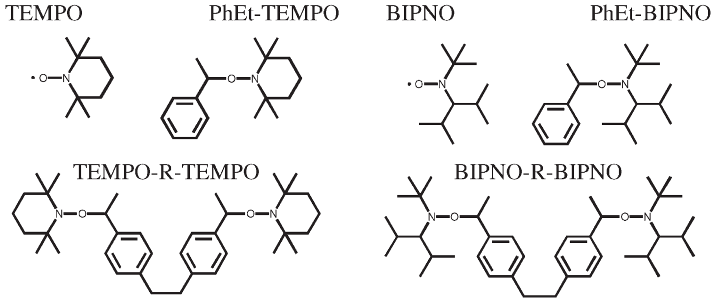
With our simulations we examined the nitroxide controlled homopolymerization of styrene at 123 °C under the influence of nitroxides with different activation rates k_d and equilibrium constants K ($=k_d/k_c$) of dissociation/combination reaction between dormant and active species. Stationary state conditions were achieved during the polymerization with TEMPO ($K = 2.1 \cdot 10^{-11}$ mol/L).[5] For this reason the TEMPO mediated polymerization shows a similar polymerization rate to the autopolymerization of styrene.

The synthesis of the new α-hydrogen bearing nitroxide 2,2,5-trimethyl-4-(isopropyl)-3-azahexane-3-oxyle (BIPNO), and its corresponding alkoxyamine PhEt-BIPNO for stable free radical polymerization (see Scheme 1) was described by our group.[6] The polymerization with BIPNO follows the kinetics of the persistent radical effect. We determined the equilibrium constant $K = 7.5 \cdot 10^{-9}$ mol/L by time dependent measurement of the free nitroxide concentration.[7]

Our simulations presented in this work include the monofunctional alkoxyamines (RN: 2,2,6,6-tetramethyl-1-(1-phenylethoxy) piperidine (PhEt-TEMPO), N-tert-butyl-N-(1-isopropyl-2-methyl-propyl)-O-(1-phenylethyl)-hydroxylamine (PhEt-BIPNO)) and the corresponding bifunctional alkoxyamines (NRN: 1,2-Bis{4-[1-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl]phenyl}ethane (TEMPO-R-TEMPO), 1,2-Bis(4-{1-[N-tert-butyl-N-(1-isopropyl-2-methyl-propyl)-aminooxy]ethyl}phenyl)ethane (BIPNO-R-BIPNO)) (see Scheme 1).

Computational Methods

We developed a Monte Carlo method (termed *mcPolymer*) which enables the comprehensive simulation of controlled radical polymerizations in an extremely straightforward manner. This simulation is based on the algorithm of Gillespie[8] and has been extended for the investigation of polymer species. During this simulation procedure each single molecule from a huge initial batch of molecules is accounted for throughout the entire simulated polymerization. The probability of a molecule following a distinct reaction pathway is calculated on the basis of pseudo-random numbers. This approach enables an uncomplicated implementation of reactions leading to species with sophisticated macromolecular



Scheme 1.

Structure of the nitroxides (N: TEMPO, BIPNO), the mono- (RN: PhEt-TEMPO, PhEt-BIPNO) and bifunctional (NRN: TEMPO-R-TEMPO, BIPNO-R-BIPNO) alkoxyamines.

architectures and is therefore especially suited for simulation of RAFT polymerizations.[9] The full molecular weight distributions of all the resulting polymeric materials are directly accessible. During the Monte Carlo simulation every polymer molecule is represented by one object. Thus detailed microstructure analyses are possible.

Kinetic Model

Styrene Homopolymerization

$$\text{thermal initiation :}\quad 3\ \text{styrene} \rightarrow 2\,P_1^\bullet \qquad k_{th} \tag{2}$$

$$\text{propagation :}\quad P_n^\bullet + \text{styrene} \rightarrow P_{n+1}^\bullet \qquad k_p \tag{3}$$

$$\text{transfer to monomer :}\quad P_n^\bullet + \text{styrene} \rightarrow D_n^\bullet + P_1^\bullet \qquad k_m \tag{4}$$

$$\text{termination by combination :}\quad P_n^\bullet + P_m^\bullet \rightarrow D_{n+m} \qquad k_t \tag{5}$$

Nitroxide Controlled Radical Polymerization Initiated by Monofunctional Alkoxyamine

$$\text{alkoxyamine activation :}\quad RN \rightarrow R^\bullet + N \qquad k_d \tag{6}$$

$$\text{initiation :}\quad R^\bullet + \text{styrene} \rightarrow P_1^\bullet \qquad k_p \tag{7}$$

$$\text{alkoxyamine deactivation :}\quad R^\bullet + N \rightarrow RN \qquad k_c \tag{8}$$

$$\text{chain deactivation :}\quad P_n^\bullet + N \rightarrow P_nN \qquad k_c \tag{9}$$

$$\text{dormant chain activation :}\quad P_nN \rightarrow P_n^\bullet + N \qquad k_d \tag{10}$$

Nitroxide Controlled Radical Polymerization Initiated by Bifunctional Alkoxyamine

$$\text{alkoxyamine activation :}\quad NRN \rightarrow NR^\bullet + N \qquad 2k_d \tag{11}$$

$$\text{initiation :}\quad NR^\bullet + \text{styrene} \rightarrow NP_1^\bullet \qquad k_p \tag{12}$$

$$\text{alkoxyamine deactivation :}\quad NR^\bullet + N \rightarrow NRN \qquad k_c \tag{13}$$

$$\text{chain deactivation :}\quad NP_n^\bullet + N \rightarrow NP_nN \qquad k_c \tag{14}$$

$$\text{dormant chain activation :}\quad NP_nN \rightarrow NP_n^\bullet + N \qquad 2k_d \tag{15}$$

$$\text{chain deactivation :}\quad P_n^\bullet + N \rightarrow P_nN \qquad k_c \tag{16}$$

$$\text{dormant chain activation :}\quad P_nN \rightarrow P_n^\bullet + N \qquad k_d \tag{17}$$

$$\text{termination by combination :}\quad NP_n^\bullet + NP_m^\bullet \rightarrow NP_{n+m}N \qquad k_t \tag{18}$$

$$\text{termination by combination :}\quad NP_n^\bullet + P_m^\bullet \rightarrow P_{n+m}N \qquad k_t \tag{19}$$

$$\text{transfer to monomer :}\quad NP_n^\bullet + \text{styrene} \rightarrow P_nN + P_1^\bullet \qquad k_m \tag{20}$$

The simulations were initialized with a predetermined total number of $5 \cdot 10^9$ individual molecules, which were assigned to the reactant species, i.e., monomer and alkoxyamine, according to their molar concentrations in the initial reaction mixture.

The calculations were performed on a multiprocessor computer DELL PowerEdge 6950 (4x AMD Opteron Athlon 8216, 16 GB RAM), running on SuSE-Linux.

Results and Discussion

Model Validation

The validation of the assigned kinetic model was performed by comparing with

Table 1.
Kinetic parameters.

Simulation Parameters	Reference
k_{th} ($L^2mol^{-2}s^{-1}$) $= 2.2 \cdot 10^5 exp(-13810/T)$	[10]
k_p ($L \cdot mol^{-1}s^{-1}$) $= 4.2658 \cdot 10^7 exp(-3910/T)$	[11]
k_t ($L \cdot mol^{-1}s^{-1}$) $= 2.12 \cdot 10^9 exp(-743/T)$	[12]
k_t monomer conversion dependent correction	[10]
k_m ($L \cdot mol^{-1}s^{-1}$) $= 2.31 \cdot 10^6 exp(-6377/T)$	[10]
k_d (s^{-1}) $= 0.001$ (TEMPO)	[5]
k_c ($L \cdot mol^{-1}s^{-1}$) $= 4.76 \cdot 10^7$ (TEMPO)	[5]
k_d (s^{-1}) $= 0.0068$ (BIPNO)	[7]
k_c ($L \cdot mol^{-1}s^{-1}$) $= 6.32 \cdot 10^5$ (BIPNO)	[7]

experimental data of BIPNO controlled polymerizations.[5,13]

The dependence of the polymerization rate on the alkoxyamine concentration $[RN]_0$ according to the persistent radical effect kinetic was well reproduced by the kinetic model (Figure 1, A).

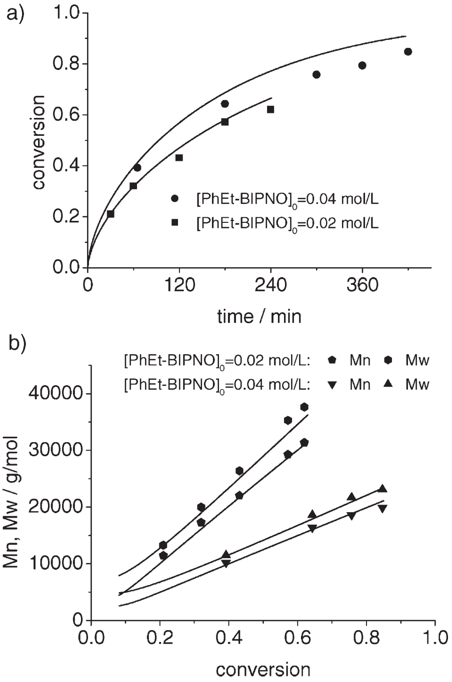


Figure 1.
Comparison of the simulation (line) with experimental data (dots),[13] variation of the alkoxyamine concentration $[RN]_0$. A: conversion-time curves; B: evolution of molecular weight (M_n, M_w) as a function of conversion.

The theory of persistent radical effect[14] implies that the concentrations of the growing radical chains ($P_n^{\bullet}$) and the free nitroxides (N) are not stationary (Equation 21, 22).

$$[P_n^{\bullet}] = (K \times [RN]_0/(3k_t))^{1/3} \times t^{1/3} \qquad (21)$$

$$[N] = (3k_t \times K^2[RN]_0^2)^{1/3} \times t^{1/3} \qquad (22)$$

Here k_t is the rate constant of termination by combination (Equation 5), $[RN]_0$ is the concentration of the assigned alkoxyamine and $K = k_d/k_c$ is the equilibrium constant of the reversible activation (Equation 10 and 9). According to Formula 21 leads an increase in the alkoxyamine concentration $[RN]_0$ to an increase in radical concentration $[P_n^{\bullet}]$ and to higher polymerization rates consequentially.

The agreement between the simulation of the conversion dependent molecular weights (M_n, M_w) and the corresponding experimental data is satisfied up to high monomer conversions (Figure 1, B).

Time dependent BIPNO concentrations were determined experimentally by Size Exclusion Chromatography (SEC).[5] The accumulation of the nitroxide (Figure 2) BIPNO in the reaction solution agrees with the persistent radical effect theory (Equation 22). The usage of the bifunctional alkoxyamine (BIPNO-R-BIPNO) leads to higher BIPNO concentration in comparison to the monofunctional alkoxyamine (RN). At the same alkoxyamine concentration ($[RN]_0 = [NRN]_0 = 0.03$ mol/L) more nitroxide groups incorporated in the case of bifunctional alkoxyamine.

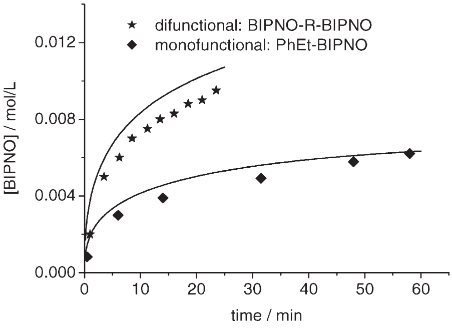


Figure 2.
Comparison of the simulation (line) with experimental data (dots),[5,13] time dependent BIPNO (N) concentration during the polymerization with mono- (RN) and bifunctional (NRN) alkoxyamine, $[RN]_0 = [NRN]_0 = 0.03$ mol/L.

The kinetic model of the BIPNO controlled radical polymerization initiated with bifunctional alkoxyamines describes the experimental data (conversion, M_n) satisfying up to high conversions (Figure 3).

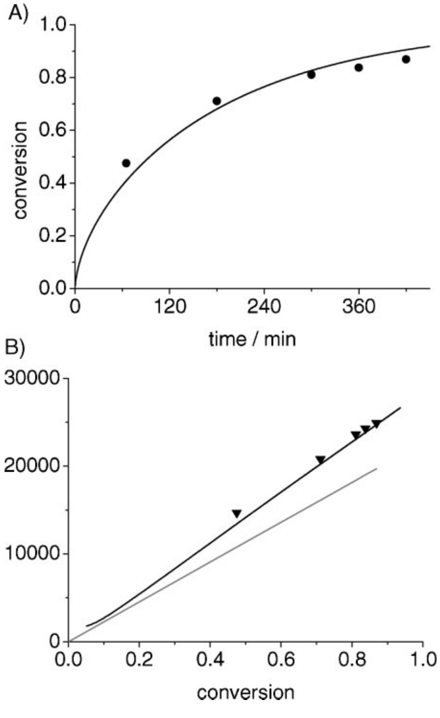


Figure 3.
Comparison of the simulation (line) with experimental data (dots),[13] $[\text{BIPNO-R-BIPNO}]_0 = 0.04$ mol/L; A: conversion-time curve; B: molecular weight (M_n) as a function of conversion; gray line: theoretically calculated molecular weight (Equation 23).

$$M_n(\text{theoretical}) = [\text{styrene}]_0 \times \text{conversion}_{\text{styrene}} \times 104.15/[\text{NRN}]_0 \qquad (23)$$

A significant divergence appears between the theoretically expected molecular weight (Equation 23), the experimental data and also the simulated curve (Figure 3, B). That indicates a decrease of the concentration of the dormant bifunctional polymer chains ([NPnN]). The concentration of propagating chains will be determined by activating the dormant chains (Equation 15) significantly. Termination reactions of the propagating chains (Equation 18) reduce the concentration of dormant chains. This discrepancy between experimentally observed and theoretically predicted (Equation 23) molecular weight was already described by Gnanou et al.[3].

Product Composition, Polymerization with Monofunctional Alkoxyamines (RN)

For the TEMPO mediated polymerization in the stationary state a constant concentration of dormant chains (P_nN) is observed after the transition of the alkoxyamine RN into dormant chains (Figure 4, A). Concentration of the free nitroxide N remains very low on a constant level ($3 \cdot 10^{-5}$ mol/L) and dead polymer chains D_n are created steadily.

On the opposite, in the case of the polymerization controlled by BIPNO the concentration of the dormant chains tails off after reaching a maximum due to the persistent radical effect. The dormant chains (P_nN) are formed by initialization of the alkoxyamine at the beginning of the polymerization. By the persistent radical effect the concentration of propagating chains $P_n^{\bullet}$ achieves a maximum at this time (Equation 21). More termination by combination (Equation 5) takes place. Therefore, substantially more dead polymer chains D_n are generated and BIPNO concentration increases with conversion (Figure 4, B).

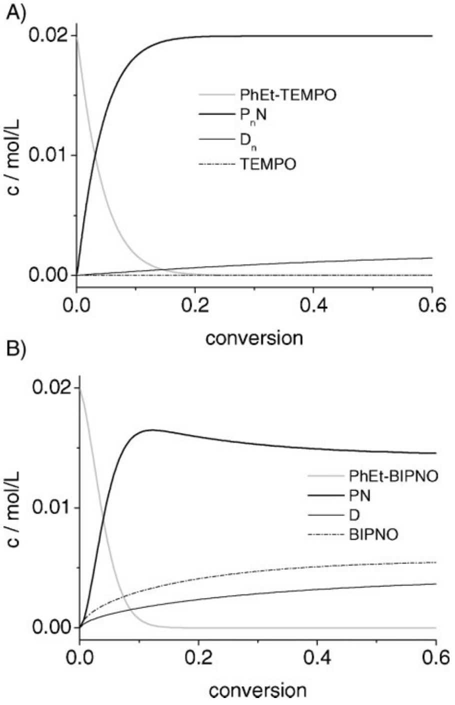


Figure 4.
Simulation of the conversion dependent product composition $[RN]_0 = 0.02$ mol/L; A: PhEt-TEMPO; B: PhEt-BIPNO.

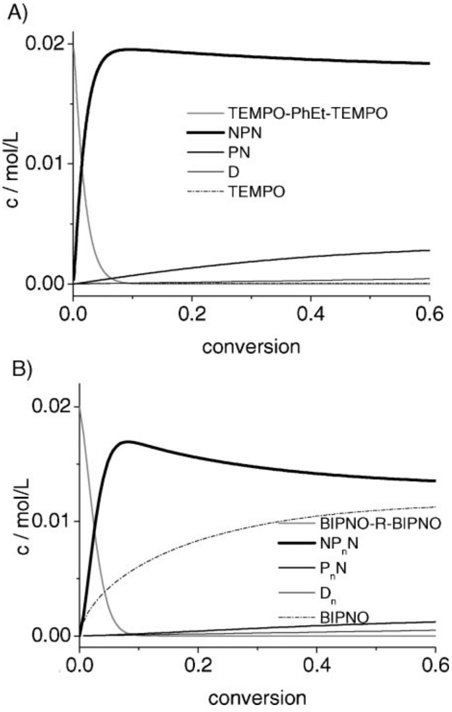


Figure 5.
Simulation of the conversion dependent product composition $[NRN]_0 = 0.02$ mol/L; A: TEMPO-R-TEMPO; B: BIPNO-R-BIPNO.

Product Composition, Polymerization with Bifunctional Alkoxyamines (NRN)

During the polymerization initiated with bifunctional alkoxyamines the fraction of dead polymer chains D_n is negligible (Figure 5).

In the case of the stationary state polymerization (TEMPO) the concentration of the propagating radicals is determined by thermal autopolymerization of styrene. The thermal initiated polymer chains $P_n^{\bullet}$ are able to combine with other propagating chains $NP_n^{\bullet}$ from the reversible activation equilibrium (Equation 15/14). This combination reaction (Equation 19) leads to loss of functionality and the concentration of the monofunctional dormant species P_nN increases significantly (Figure 5, A).

The activation equilibriums (Equation 15/14, 17/16) of the dormant species NP_nN and P_nN determine mainly the concentration of the propagating chains in case of the persistent radical effect kinetic (initiation with BIPNO-R-BIPNO). Terminating reactions by combination according Equation 18 do not reduce the functionality but decrease the chain concentration. Thus the molar weight increases faster than expected according to Equation 23 (Figure 3, B).

With our simulation the microstructure of the difunktional dormant polymer chains NP_nN can be investigated more precisely at 60% monomer conversion.

Table 2.
species BIPNO-P_n-BIPNO at 60% monomer conversion.

Combination steps	0	1	2	3	4
c/mol/L	0.0095	0.0028	0.0009	0.0003	0.0001
M_n/g/mol	34900	44200	53300	62500	71600

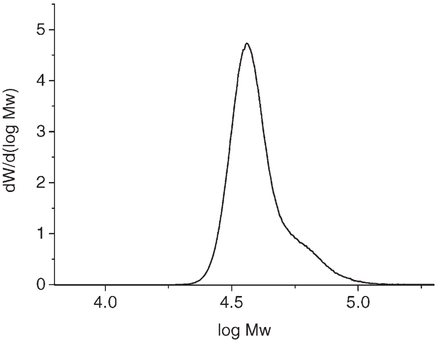


Figure 6.
Simulated molecular weight distribution of BIPNO-P_n-BIPNO at 60% monomer conversion.

TEMPO-P_n-TEMPO chains contain only a low mol fraction (0.05) of combination products according Equation 18. The fraction of combination products created from more the one combination steps is negligible.

On the opposite, in the case of the polymerization initiated by BIPNO-R-BIPNO the mol fraction of different combination products is significant; the results are summarized in Table 2.

With the number of combination steps according Equation 18 and 19 the molecular weight M_n of the dormant chains increases. Those chains are located in the high molecular weight area of the simulated molecular weight distribution (Figure 6).

In our simulation only the homopolymerization was considered. Thus the combination reactions only influence the molecular weights.

The synthesis of triblock copolymers using bifunctional alkoxyamines in principle is also possible.[1,15] This allows the synthesis of three blocks in only two steps. By the simultaneous growth of the outer blocks symmetrical triblocks are formed. In the case of block copolymerization (polymerization of the second block), combination of the outer blocks are possible. That would lead to completely different block structures.

Conclusion

Our kinetic model of nitroxide controlled radical polymerization initiated by mono- and bifunctional alkoxyamines is suitable to describe the polymerization process in accordance with experimental data. Depending on the equilibrium constants K ($=k_d/k_c$) of dissociation/combination between dormant and active species different product compositions were simulated. The loss of functionality and dormant chains due to combination reactions of the propagating chains was quantified by the Monte Carlo simulation. Additionally detailed information about the microstructure of the polymeric reaction products was received.

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