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Polymer 48 (2007) 1875–1883

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Kinetics of nitroxide-controlled radical polymerization during the non-stationary state

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Received 17 March 2006; received in revised form 24 January 2007; accepted 9 February 2007

Abstract

The activation–deactivation equilibrium of nitroxide-controlled radical polymerization of styrene at 123 °C was investigated. For this purpose the reaction solution was examined time dependently during the initial phase of the polymerization by using an SEC column combination providing a very good separation of the low-molecular weight species. By time-dependent measurement of the alkoxyamine concentration the activation rate of the alkoxyamines PhEt-TIPNO (*N*-*tert*-butyl-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine) $k_{act} = 3.2 \times 10^{-3}\ s^{-1}$ and PhEt-BIPNO (*N*-*tert*-butyl-*N*-(1-isopropyl-2-methyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine) $k_{act} = 6.4 \times 10^{-3}\ s^{-1}$ can be determined directly.

Considering the Persistent Radical Effect theory, the measurement of the free nitroxide concentration allows to determine the pseudo-equilibrium constant of dissociation/combination between dormant and active species for polystyryl-TIPNO and polystyryl-BIPNO, $K = 7.5 \times 10^{-9}$ mol/L and 1.08×10^{-8} mol/L, respectively.

Keywords: Alkoxyamine; Controlled radical polymerization; Persistent radical effect

1. Introduction

Controlled radical polymerization includes a group of polymerization techniques suitable to synthesize polymers of well-defined architectures. The three main methods of controlled radical polymerization are Stable Free Radical Polymerization (SFRP) [1], Atom Transfer Radical Polymerization (ATRP) [2] and Reversible Addition–Fragmentation Chain Transfer Polymerization (RAFT) [3]. In all cases controlled radical polymerization contains a reversible activation process of "dormant" polymer chains. In the RAFT mechanism, the dormant polymer chain is attacked by the propagating radical. An exchange reaction between propagating chain and dormant chain takes place, while in Atom Transfer Radical Polymerization (ATRP) the active species are generated by a reversible redox process catalyzed by a transition metal.

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

In the case of nitroxide-controlled radical polymerization the dormant chain, P_nN, dissociates – with the rate constant k_d – into a stable nitroxide ($N^{\bullet}$) and a growing polymer chain ($P_n^{\bullet}$) (Eq. (1)). The growing polymer chain can be again deactivated by the free nitroxide with the rate constant k_c or undergo termination reactions. The rate of activation of the alkoxyamine is very important with regard to a steady state quasi-equilibrium between activated and dormant polymer chains. Fukuda already examined this activation process of the PS-TEMPO/styrene system by means of a Size Exclusion Chromatographic (SEC) peak separation method [4,5]. The activation process was started with a macroinitiator ($M_n = 1700$, PDI = 1.11) at different temperatures. A constant volume of the reaction solution was injected into the SEC system. In order to increase the radical concentration an additional initiator (*tert*-butyl hydroperoxide) was added. Thus when analyzing the reaction mixture in the SEC a bimodal distribution was observed. The first peak

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doi:10.1016/j.polymer.2007.02.016

represented the macroinitiator that had not been activated and the second peak represented the activated polymer chains with higher molecular weight. By separating the bimodal SEC curves into two peak areas, the relative concentrations of the primary macroinitiator ($S_{t=0}$) and the concentration of the not yet activated macroinitiator (S_t) could be determined as a function of time. According to Eq. (2) the activation rate constant k_{act} could be determined by the first order plot of these two peak ratios ($S_t = \mathrm{P}_n\mathrm{N}$) vs. time. Subsequently it was applied as a first order activation rate (Eq. (3)). A single straight line passing through the origin could be observed.

$$\ln(S_{t=0}/S_t) = k_{\mathrm{act}}t \tag{2}$$

$$\mathrm{P}_n\mathrm{N} \xrightarrow{k_{\mathrm{act}}} \mathrm{P}_n^{\bullet} + \mathrm{N}^{\bullet} \tag{3}$$

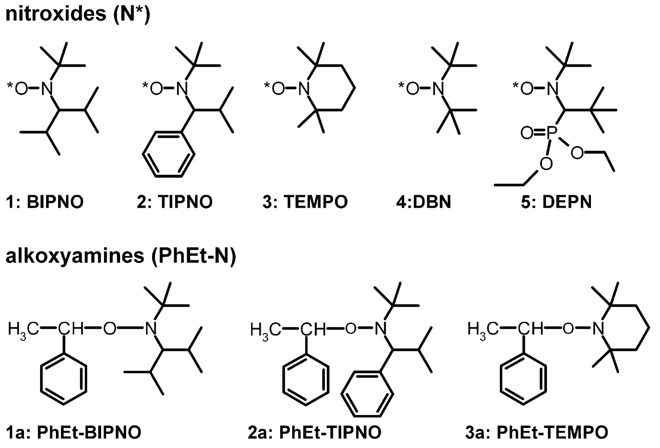
Fukuda determined the Arrhenius parameters of the activation of a PS_{16}-TEMPO macroinitiator with $k_{\mathrm{act}} = 3.0 \times 10^{13}\ \mathrm{s}^{-1} \exp(-124\ \mathrm{kJ\ mol}^{-1}/RT)$ [4]. Furthermore Fukuda investigated the activation rates of the systems styrene/DBN [6], styrene/DEPN (also known as SG1) [6] and *tert*-butyl acrylate/DBN [7] (Scheme 1). Benoit et al. used the SEC peak separation method for the investigation of the styrene/DEPN system as well [8]. A problem of the SEC peak separation method is the fact that the assigned macroinitiator also contains inactive, already terminated, polymer chains. For the investigations Fukuda considered 4–5% of inactive chains [4,6], which were determined from chain extension experiments [5].

Fischer showed that nitroxide-controlled radical polymerization follows the kinetics of the Persistent Radical Effect (PRE) [9–14]. This kinetic model was developed for the idealized case so that no side reactions appear and the rate constants show a chain length independence. A radical formation by thermal self-initiation was not considered. Kinetics implying the Persistent Radical Effect include that the concentrations of the growing radical chains $\mathrm{P}_n^{\bullet}$ and the free nitroxides are not stationary (Eqs. (4) and (5)).

$$[\mathrm{N}^{\bullet}] = \left(3k_{\mathrm{t}}K^2[\mathrm{RN}]_0^2\right)^{1/3}t^{1/3} \tag{4}$$

$$[\mathrm{P}^{\bullet}] = \left(\frac{K[\mathrm{RN}]_0}{3k_{\mathrm{t}}}\right)^{1/3}t^{-1/3} \tag{5}$$

Here k_{t} is the rate constant of bimolecular termination, $[\mathrm{RN}]_0$ is the concentration of the assigned alkoxyamine and $K = k_{\mathrm{d}}/k_{\mathrm{c}}$ is the equilibrium constant of the reversible activation (Eq. (1)). The theory of the Persistent Radical Effect was validated experimentally by Boutevin et al. [15]. The polymerization of styrene was accomplished at 123 °C in the presence of different concentrations of PhEt-DEPN (**5**) (Scheme 1). Considering the theory of the Persistent Radical Effect the equilibrium constant $K = 6.1 \times 10^{-9}$ mol/L for the styrene/DEPN system (SG1) could be determined. A significant influence of the concentration of the assigned alkoxyamine on the polymerization rate was observed, which is already described by Benoit et al. [8]. The Persistent Radical Effect theory was re-evaluated by Tang et al. [18] and a new equation for the evolution of persistent radicals was derived (Eq. (6)). Contrary to Eq. (4), this equation contains the consumption of the employed alkoxyamine upon release of the nitroxide.



Scheme 1. Structures of the nitroxides and alkoxyamines.

$$K^2k_{\mathrm{t}}t = \frac{[\mathrm{RN}]_0^2}{[\mathrm{RN}]_0 - [\mathrm{N}^{\bullet}]} + 2[\mathrm{RN}]_0\ln\frac{[\mathrm{RN}]_0 - [\mathrm{N}^{\bullet}]}{[\mathrm{RN}]_0} - \left([\mathrm{RN}]_0 - [\mathrm{N}^{\bullet}]\right) \tag{6}$$

However, the styrene/TEMPO system does not show a dependence of the polymerization rate on the concentration of the alkoxyamine [16]. The reason for this is a very small equilibrium constant K of the styrene/TEMPO system. Fukuda calculated a crossing time of 100 s (120 °C and $[\text{PhEt-TEMPO}]_0 = 10^{-2}$ mol/L) [17]. For this reason the PhEt-TEMPO mediated polymerization shows similar conversion to the autopolymerization of styrene.

In this paper we investigated the nitroxide-controlled radical polymerization of styrene under the influence of BIPNO (**1**) (2,2,5-trimethyl-4-(isopropyl)-3-azahexane-3-oxyle), TIPNO (**2**) (2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyle) and TEMPO (**3**) (Scheme 1). The polymerizations were initiated with the corresponding alkoxyamines PhEt-BIPNO (**1a**) (*N*-*tert*-butyl-*N*-(1-isopropyl-2-methyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine), PhEt-TIPNO (**2a**) (*N*-*tert*-butyl-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine) and PhEt-TEMPO (**3a**).

Hawker et al. [20] synthesized a series of acyclic α-hydrogen bearing nitroxides and the corresponding alkoxyamines which enabled the controlled radical polymerization of a wide range of monomers. An important representative of this class of nitroxides is TIPNO (**2**) and its corresponding alkoxyamine PhEt-TIPNO (**2a**).

We have described [22] the synthesis of the new α-hydrogen bearing nitroxide BIPNO (**1**) and its corresponding alkoxyamine PhEt-BIPNO (**1a**) for stable free radical polymerization. Styrene and *n*-butylacrylate were polymerized in bulk in the presence of the new nitroxide. In our work, the kinetics of the activation process of this novel alkoxyamine

BIPNO is to be investigated and to be compared to the kinetics of TIPNO and TEMPO.

We enhanced the method of Fukuda and analyzed the reaction solutions by means of a SEC-column combination, which realizes a good separation within the low-molecular weight range. A very sensitive UV-detector was used to measure the concentration of the assigned low-molecular weight alkoxyamine [RN] and the free nitroxide [N$^\bullet$] (released by the dissociation of the alkoxyamine). Thus the determination of k_{act} is possible by using an alkoxyamine. Consequently the peak separation, which is necessary when using the method of Fukuda, can be avoided. To verify our method we also examined the activation of the styrene/TEMPO system.

Additional to the activation process of the alkoxyamines the control of polymerization is influenced by the equilibrium between the nitroxides and the macroradicals. Boutevin et al. [15] have determined the equilibrium constant for the styrene/DEPN system by analyzing the monomer conversion and applying the PRE theory.

Charleux et al. [19] developed a new experimental procedure named RNR–PLP–SEC (Radical Nitroxide Recombination–Pulsed Lamp Polymerization–Size Exclusion Chromatography) for the determination of the combination rate k_c. The styrene/DEPN system has also been examined.

In this work we determined time dependently the free nitroxide concentration for the styrene/TIPNO and styrene/BIPNO systems. Subsequently we applied the re-evaluated PRE theory [18] in order to determine the pseudo-equilibrium constant of dissociation/combination between dormant and active species.

2. Experimental section

2.1. Materials

tert-Nitrobutane (Lancaster), isobutyraldehyde (Lancaster), zinc (Lancaster), 2-bromopropane (Lancaster), magnesium (Riedel de Haen) and copper acetate (Fluka) were used as received. Diethyl ether and tetrahydrofuran were distilled from sodium before use. All other chemicals were used as received. For the polymerizations, styrene (BASF) was distilled under reduced pressure.

2.2. Synthesis

2,2,5-Trimethyl-4-(isopropyl)-3-azahexane-3-oxyle (**1**: BIPNO) and its corresponding alkoxyamine *N*-*tert*-butyl-*N*-(1-isopropyl-2-methyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine (**1a**: PhEt-BIPNO) were synthesized following the procedure given by Schmidt-Naake and Bothe [21]. 2,2,5-Trimethyl-4-phenyl-3-azahexane-3-oxyle (**2**: TIPNO) was synthesized in 35% overall yield following the procedure given by Hawker and coworkers [20]. *N*-*tert*-Butyl-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine (**2a**: PhEt-TIPNO) was produced using the same procedure as PhEt-BIPNO (**1a**). The data of characterization (NMR spectroscopy) was in agreement with reported values. PhEt-TEMPO (**3a**) was synthesized according to Miura and Yoshida [23] using di-*tert*-butyl diperoxyoxalate [16] as an α-H-abstracting reagent.

2.3. Procedure for the polymerizations

The polymerizations were carried out in sealed glass ampoules, which were filled with 1 mL reaction solution at 123 °C under nitrogen atmosphere. Samples of one series were taken at different times, cooled down in an ice bath, and dissolved in exact 1 mL of THF (1:1). The dissolved reaction solutions were injected directly into the SEC system. After SEC measurement polystyrene was precipitated into methanol and dried in vacuum to constant mass for determination of the conversion.

2.4. Characterization

The determination of the low-molecular weight species and the molecular weight distributions was carried out by means of a Size Exclusion Chromatography system with the following components: pump WATERS 510, autosampler WATERS WISP 712, photo-array detector Waters PDA 996. The spectra were recorded with a frequency of 1 Hz and a resolution of 4.8 nm. 1× Ultrastyragel 100 Å and 2× Ultrastyragel 500 Å were used as columns. THF was used as eluent, with a flow rate of 1.0 mL/min and a temperature of 25 °C. For the determination of the low-molecular weight species 15 μL of the reaction solutions was injected.

3. Results and discussion

3.1. Controlled free radical polymerization in presence of BIPNO and TIPNO

A new acyclic α-hydrogen bearing nitroxide, 2,2,5-trimethyl-4-(isopropyl)-3-azahexane-3-oxyle (BIPNO) (**1**), based on the structure of TIPNO (**2**), was synthesized in our earlier work [22]. In this work, a comparative study between nitroxide-controlled radical polymerization reactions with BIPNO (**1**), TIPNO (**2**) and TEMPO (**3**) will be performed.

Styrene was polymerized in the presence of the alkoxyamines PhEt-BIPNO and PhEt-TIPNO. The polymerizations were carried out at 123 °C with different concentrations of the alkoxyamines under bulk condition. Fig. 1 shows the $\ln([M]_0/[M])$ vs. time plot of the styrene polymerization with 0.05 mol/L PhEt-BIPNO (**1a**) in comparison to polymerizations with PhEt-TIPNO (**2a**) or PhEt-TEMPO (**3a**) under the same conditions.

Comparing the conversion–time behaviour, it seems apparent that the polymerization rate of the styrene polymerization in the presence of PhEt-BIPNO or PhEt-TIPNO is higher than in the case of PhEt-TEMPO. The induction period that can be observed in the TEMPO system is reduced by the use of the new BIPNO-based alkoxyamine. Moreover, for PhEt-BIPNO and also for PhEt-TIPNO an influence of the alkoxyamine concentration on the polymerization rate can be observed.

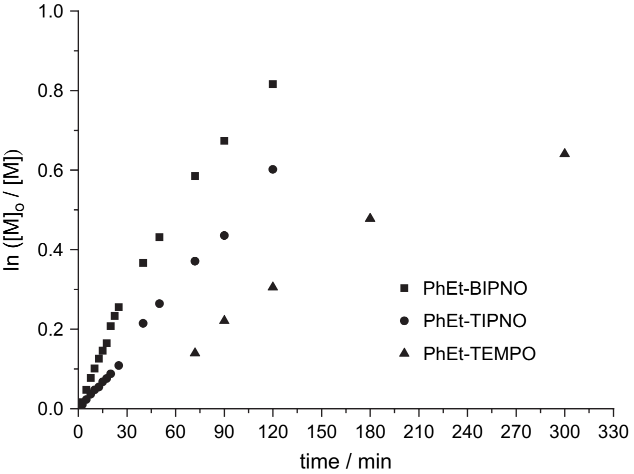


Fig. 1. $\ln([M]_0/[M])$ vs. time plot for styrene polymerization (bulk, 123 °C, 0.05 mol/L PhEt-BIPNO, PhEt-TIPNO and PhEt-TEMPO).

Looking at the polymerization of styrene with the alkoxyamines PhEt-TIPNO (**2a**) and PhEt-BIPNO (**1a**) more closely, a good control of the polymerization reaction could be achieved up to high conversions, i.e. a linear correlation between the number-average molecular weight M_n and the conversion is found. In Fig. 2A and B, the good agreement with the theoretically calculated molecular weight (Eq. (7)) and the low values for the polydispersity are displayed. Experimental results are summarised in Table 1.

$$M_n(\text{theoretical}) = [\text{styrene}]_0 \frac{\text{conversion}_{\text{styrene}}}{100} \frac{104.15}{[\text{RN}]_0} \tag{7}$$

Table 1
Bulk polymerization of styrene at 123 °C in presence of PhEt-BIPNO and PhEt-TIPNO, $[\text{RN}]_0 = 0.05$ mol/L

Alkoxyamine	Time (min)	Conversion (%)	M_n (g/mol)	$M_{n,\text{theor.}}$ (g/mol)	PDI
PhEt-TIPNO	40	19	3635	3553	1.22
	50	23	4233	4180	1.19
	90	35	6182	6360	1.14
	120	45	7354	8178	1.12
PhEt-BIPNO	40	31	5817	5634	1.13
	50	35	6789	6361	1.12
	90	49	9514	8905	1.09
	120	56	10,534	10,178	1.10

3.2. Investigation on low-molecular weight species (alkoxyamines, nitroxides)

The aim of this paper is to investigate the activation–deactivation equilibrium of the different nitroxide systems. The time-dependence of the concentrations of RN (PhEt-BIPNO, PhEt-TIPNO and PhEt-TEMPO) and of the free nitroxides (BIPNO, TIPNO, Tempo) at the beginning of the reaction is determined experimentally by SEC. Eq. (8) describes the initial period of the polymerization.

$$\text{RN} \underset{k_c}{\overset{k_d}{\rightleftarrows}} \text{R}^{\bullet} + \text{N}^{\bullet} \tag{8}$$

$$\text{R}^{\bullet} + \text{M} \rightarrow \text{P}_1^{\bullet}$$

For the investigation of the activation–deactivation equilibrium reaction (Eq. (8)), the reaction solution was examined time dependently during the initial phase of the polymerization by using a SEC column combination, which realized a very good separation of the low-molecular weight species. The measurement of the reaction solutions in the SEC realized a good peak separation of the alkoxyamine, the free nitroxide and the emerging polymer as shown exemplarily in Fig. 3 for a bulk polymerization of styrene at 123 °C with PhEt-BIPNO ($[\text{RN}]_0 = 0.05$ mol/L) after 3 min. The elution curves were extracted from the UV spectra of the photo-array detector at a wavelength of 254 nm.

In the elution curve (Fig. 3), the dominant peak for the elution of the growing polymer as well as the individual, smaller peaks for the oligomers consisting of up to four monomer units can be identified. The species denominated P_1N and P_2N in Fig. 3 are considered to be oligomers with the PhEt starting group, one (or two) styrene monomer unit and BIPNO

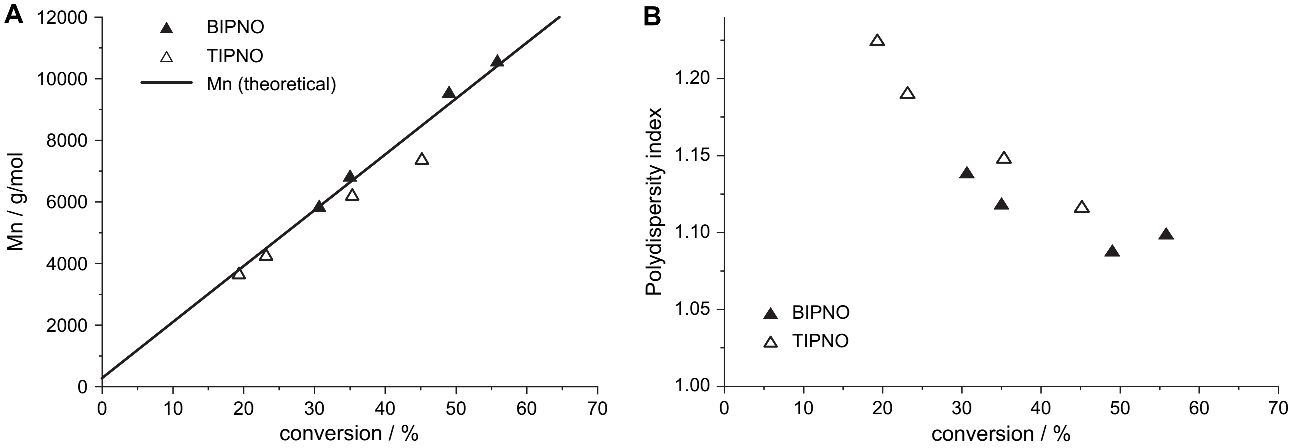


Fig. 2. Molecular weight (A) and polydispersity (B) vs. conversion plot for the polymerization of styrene in presence of PhEt-BIPNO and PhEt-TIPNO (bulk polymerization at 123 °C, $[\text{RN}]_0 = 0.05$ mol/L).

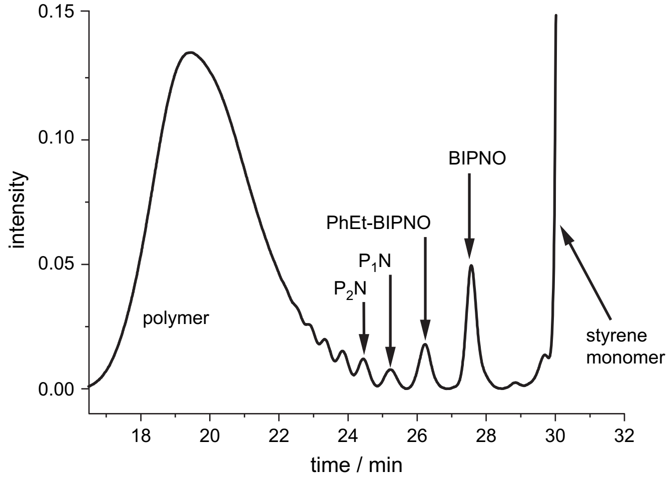


Fig. 3. SEC elution curve (UV, 254 nm) for the reaction solution of a styrene polymerization in bulk at 123 °C with PhEt-BIPNO ($[RN]_0 = 0.05$ mol/L) after 3 min.

as the nitroxide capping the chain. The differences in the elution times of the oligomers equal the time differences that occur when calibrating the SEC with styrene standards. The measured oligomers P_nN are not used for the kinetic analysis.

The following peak represents the elution of the alkoxyamine PhEt-BIPNO. The area of this peak decreases with the reaction time (Fig. 4) and is used by us to determine the kinetics of the activation of the alkoxyamine. The free BIPNO was eluted next. The area of the peak of BIPNO increases in the activation phase of the alkoxyamine (Fig. 4). The concentration of the free nitroxide derived from the peak area can be utilized to determine the equilibrium constant of growing and dormant polymer chains (Eq. (1)) by means of the PRE theory. The assignment of these peaks was validated by separate SEC measurements of the employed alkoxyamines and nitroxides.

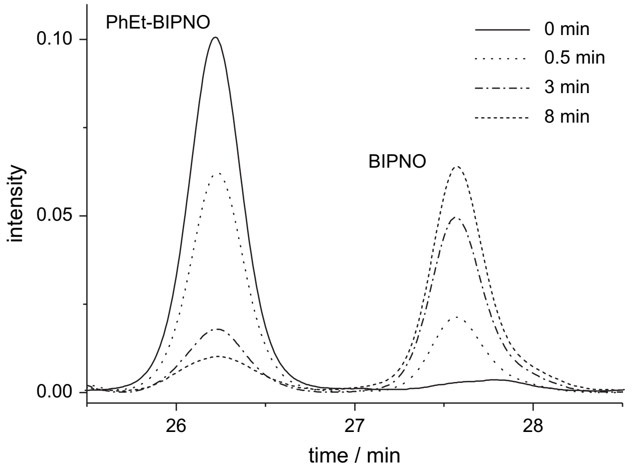


Fig. 4. Time-dependent development of the SEC elution curves for the reaction solution of a styrene polymerization in bulk at 123 °C with PhEt-BIPNO ($[RN]_0 = 0.05$ mol/L).

The last, dominant elution peak at 29.5 min is that of the styrene monomer that forms the bulk of the injected solution.

Fig. 4 shows the time-dependent decreasing value of the elution curve for PhEt-BIPNO as starting molecule for polymerization. The increase in the concentration of free BIPNO can also be identified within a time interval from 0 to 8 min. At a reaction time of 0 min no free nitroxide is present in the solution.

The elution times of the examined alkoxyamines and free nitroxides are summarised in Table 2. The free nitroxides showed a weak absorption at 430 nm.

For the determination of the absolute concentrations of the low-molecular weight alkoxyamines (RN) and free nitroxides ($N^\bullet$) calibrations were made.

Fig. 5 shows exemplarily the calibration of the nitroxide BIPNO. For the calibration of the nitroxide ($N^\bullet$) concentration, an injection of a THF solution with a concentration of 2.651×10^{-4} mol/L was carried out in steps of 10, 40, 70, 100, and 150 μL. The areas of the recorded peaks can be correlated with the concentration of alkoxyamine and nitroxide.

The intensities (RN, $N^\bullet$) of the elution curves were determined time dependently and could be transferred into concentrations using the calibration curves.

3.3. Determination of the rate constant of the alkoxyamine activation

The time-dependent alkoxyamine concentrations during the activation process at 123 °C are represented in Table 3.

Table 2
Elution times of the examined alkoxyamines and nitroxides

System	Elution time	
	Alkoxyamine [RN] (min)	Nitroxide [$N^\bullet$] (min)
TEMPO	27.1	28.8
TIPNO	25.9	27.1
BIPNO	26.2	27.5

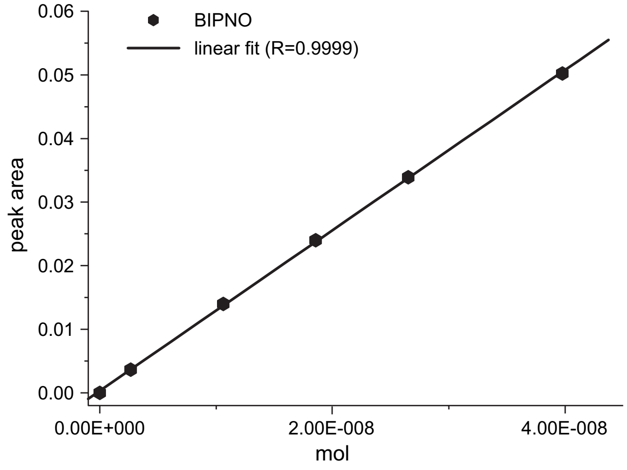


Fig. 5. Calibration of the BIPNO concentration, injection of a THF solution with a concentration of 2.651×10^{-4} mol/L was carried out in steps of 10, 40, 70, 100, 150 μL.

Table 3
Time-dependent alkoxyamine concentration during the activation process at 123 °C

Time (s)	[PhEt-TEMPO] (mol/L)	[PhEt-TIPNO] (mol/L)	[PhEt-BIPNO] (mol/L)	[PhEt-BIPNO] (mol/L)
0	0.050	0.050	0.050	0.030
30	0.048	0.040	0.032	0.017
180	0.040	0.025	0.010	0.007
345	0.037	0.015	0.007	0.002
480	0.034	0.010	0.005	0.001
645	0.032	0.007	0.001	0.0
780	0.030	0.005	0.0	0.0
930	0.029	0.003	0.0	0.0
1080	0.024	0.002	0.0	0.0
1230	0.022	0.0	0.0	0.0

If only activation of the alkoxyamines is taken into consideration in Eq. (8) then the resulting kinetic equation is of first order (Eq. (9)). Using first order kinetics, k_{act} can be derived from Eq. (10).

$$RN \xrightarrow{k_{act}} R^{\cdot} + N^{\cdot} \tag{9}$$

$$\ln\left([RN]_0/[RN]_t\right) = k_{act}t \tag{10}$$

Analogous to the peak separation method of Fukuda [4,5] the activation rate of the different alkoxyamines can be determined from the time-dependent measurements of the alkoxyamine concentration (RN) given in Table 3 according to Eq. (10). In contrast to the peak resolution method developed by Fukuda, which is based on the use of a macroinitiator with a certain content of dead chains, the advantage of our method is that the activation of the alkoxyamines can be measured directly. Consequently a peak separation can be avoided and therefore our method needs no additional initiator to shift the peaks of the activated polymer chains. Thus the activation rate of the alkoxyamines can be determined at real polymerization conditions obtaining better results.

When plotting the term $\ln([RN]_0/[RN]_t)$ for the alkoxyamines (RN = PhEt-BIPNO, PhEt-TIPNO and PhEt-TEMPO) against reaction time t (Fig. 6), the slope of the curve represents the activation constants k_{act} according to Eq. (10). Table 4 presents the activation rates k_{act} of our investigations in comparison to the rates of different alkoxyamines and macroinitiators reported in literature.

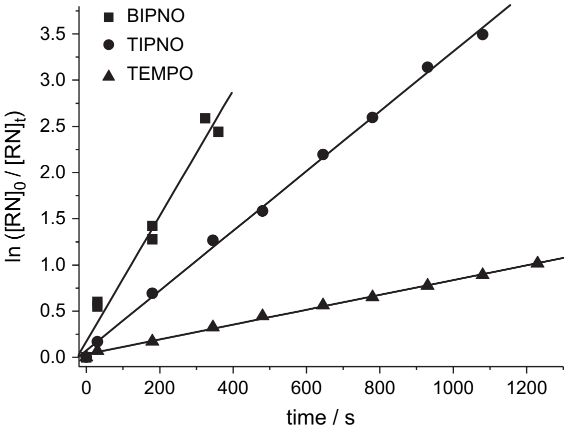


Fig. 6. Plot for the determination of the activation rate of the alkoxyamines PhEt-TEMPO, PhEt-TIPNO and PhEt-BIPNO at 123 °C.

To verify our method we also determined the activation of PhEt-TEMPO. The value of $k_{act} = 0.0008\ s^{-1}$, determined by us, is in good agreement with the results published by Fukuda ($k_{act} = 0.001\ s^{-1}$) [4,5]. The activation rate of the alkoxyamine PhEt-TIPNO determined by us is nearly identical to the results determined by Fisher et al. [24], who used ESR measurements. The value of the activation rate is comparable to that determined by Benoit et al. [8] for PhEt-DEPN ($0.0034\ s^{-1}$). PhEt-BIPNO has an activation rate twice as high as that of PhEt-TIPNO and the well-investigated PhEt-DEPN. Since the conversion of low-molecular alkoxyamines and not chain growth of a macroinitiator is detected, the chain length dependence of the activation rate typical for macroinitiators cannot be recorded. Some deviations found for the measured values for TEMPO might be explained by this fact.

3.4. Determination of the equilibrium constant of the reversible alkoxyamine activation

As a consequence of the Persistent Radical Effect, the nitroxide concentration does not remain stationary, but depends, according to Eq. (6), on the concentration of the applied alkoxyamine and the equilibrium constant for the reversible activation of the nitroxide. Determination of this constant was achieved by time-dependent measurement of the nitroxide concentration of BIPNO and TIPNO using different starting concentrations (for PhEt-BIPNO: 0.01, 0.02 and 0.03 mol/L; for PhEt-TIPNO: 0.03 and 0.05 mol/L). The concentration values of the nitroxides in the reaction mixtures (see Table 5

Table 4
k_{act} of the alkoxyamines and macroinitiators (PS: polystyrene)

Alkoxyamine	k_{act} ($10^3 \times s^{-1}$)
PhEt-TEMPO	0.8 (this work)[a]
PS-TEMPO	1.0 [4,5][b]
PS-DBN	42 [6][b]
PS-DEPN	11 [6][b]
PS-DEPN	3.4 [8][b]
PhEt-TIPNO	3.3 [24][b]
PhEt-TIPNO	3.2 (this work)[a]
PhEt-BIPNO	6.8 (this work)[a]

[a] 123 °C.
[b] 120 °C.

Table 5
Time-dependent BIPNO concentration during the activation process at 123 °C

$[\text{PhEt-BIPNO}]_0$								
0.01 mol/L			0.03 mol/L			0.05 mol/L		
Time (s)	[BIPNO] (10^{-3} × mol/L)	*bt*	Time (s)	[BIPNO] (10^{-3} × mol/L)	*bt*	Time (s)	[BIPNO] (10^{-3} × mol/L)	*bt*
30	0.5	0.002	360	3.0	0.010	30	1.3	0.001
180	0.9	0.015	840	3.9	0.023	180	3.3	0.003
345	1.4	0.028	1890	4.9	0.052	345	4.3	0.006
480	1.5	0.039	2880	5.8	0.079	480	4.8	0.008
645	1.7	0.053	3480	6.2	0.095	645	5.2	0.011
780	1.8	0.064				780	5.5	0.013
930	1.9	0.076				930	6.0	0.015
1080	2.0	0.089				1080	6.1	0.018
1230	2.0	0.101				1230	6.3	0.020
1380	2.2	0.113				1380	6.4	0.023
						2880	8.6	0.047

Table 6
Time-dependent TIPNO concentration during the activation process at 123 °C

$[\text{PhEt-TIPNO}]_0$					
0.03 mol/L			0.05 mol/L		
Time (s)	[TIPNO] (10^{-3} × mol/L)	*bt*	Time (s)	[TIPNO] (10^{-3} × mol/L)	*bt*
30	0.5	0.001	30	0.9	0.001
345	2.1	0.014	180	2.1	0.004
645	2.8	0.026	345	3.1	0.008
780	3.1	0.031	480	3.4	0.012
1380	3.8	0.055	645	4.1	0.016
			780	4.2	0.019
			930	4.6	0.022
			1080	4.8	0.026
			1380	5.1	0.033
			2280	5.5	0.055
			2880	6.1	0.069

and 6) were obtained by SEC after an adequate calibration was performed.

By means of the time-dependent determination of the nitroxide concentrations it is possible to determine the equilibrium constant *K* which is included in Eq. (6). The terms on the right side of Eq. (6) only depend on $[\text{N}^\bullet]$ (Eq. (11)). In order to determine *K* the function $F([\text{N}^\bullet])$ was plotted vs. *t* as can be seen in Fig. 7A and B. The slope determined by the linearization corresponds to $k_t K^2$ (Eq. (12)) for all experiments, independent of the concentration of the alkoxyamine. The equilibrium constant for the system styrene/BIPNO and styrene/TIPNO can be calculated, with k_t (styrene, 123 °C) = 3.12×10^8 L mol s^{-1} [25] (Eq. (13)).

$$F([\text{N}^\bullet]) = \frac{[\text{RN}]_0^2}{[\text{RN}]_0 - [\text{N}^\bullet]} + 2[\text{RN}]_0 \ln\frac{[\text{RN}]_0 - [\text{N}^\bullet]}{[\text{RN}]_0} - \left([\text{RN}]_0 - [\text{N}^\bullet]\right) \tag{11}$$

$$\text{slope} = k_t K^2 \tag{12}$$

$$K = \sqrt{\text{slope}/k_t} \tag{13}$$

The determined equilibrium constants of the dissociation/combination of the dormant and active species at 123 °C are:

TIPNO: 7.5×10^{-9} mol/L $\pm 1 \times 10^{-10}$ mol/L.
BIPNO: 1.08×10^{-8} mol/L $\pm 1 \times 10^{-10}$ mol/L.

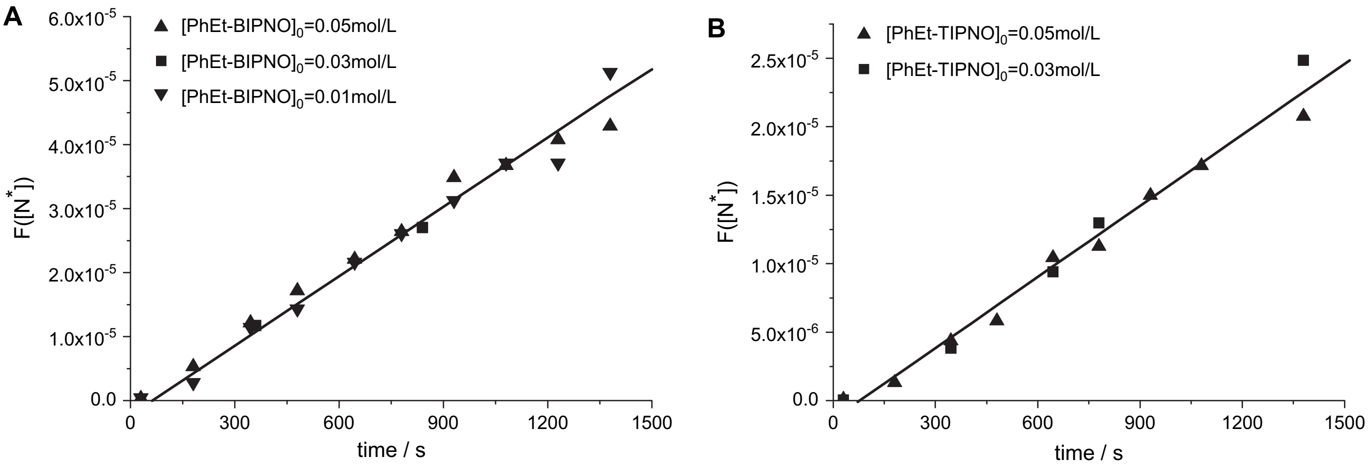


Fig. 7. Plot of $F([\text{N}^\bullet])$ vs. *t* for the determination of the equilibrium constant *K* with Eq. (13). PhEt-BIPNO (A) and PhEt-TIPNO (B).

The polymerization of styrene at 123 °C shows a significant thermal initiation. Therefore a crossover from power-law kinetics determined by the applied alkoxyamine to stationary state kinetics dominated only by thermal initiation occurs.

The time period to reach a stationary state has been discussed by Fukuda and Goto [17], according to the power-law kinetics of Fischer. The time range of validity of the power-law kinetics depends on the initiation rate R_i of the thermal polymerization, on the equilibrium constant K (determined for styrene-BIPNO and styrene-TIPNO), on the concentration of the alkoxyamine ($[\mathrm{BIPNO}]_0$ and $[\mathrm{TIPNO}]_0$) and finally on the termination rate k_t.

The power-law kinetics holds for $bt < 0.2$. The crossover time t_{cross} between the power-law kinetics and stationary state kinetics can be estimated by equating Eq. (14) with Eq. (15) [13,17]:

$$b = \frac{2R_i^{3/2}}{\left(k_t K^2 [\mathrm{RN}]_0\right)^{1/2}} \tag{14}$$

$$t_{\mathrm{cross}} = \frac{\left(k_t K^2 [\mathrm{RN}]_0\right)^{1/2}}{3R_i^{3/2}} = \frac{2}{3b} \tag{15}$$

Table 7 lists the values of the crossover time (t_{cross}) of the investigated alkoxyamines calculated with an initiation rate of $R_i = 1.67 \times 10^{-7}$ [26, 27] for the thermal polymerization and with k_t (styrene, 123 °C) $= 3.12 \times 10^{8}$ L mol s^{-1} [25].

Evidently, the condition of $bt < 0.2$ is met for all experimental data points with all values being lower than the crossover time. The interpretation based on the kinetics of the Persistent Radical Effect is therefore justified in all cases.

The value of the equilibrium constant K determined for styrene/TIPNO system corresponds nearly to the value $K = 6.1 \times 10^{-9}$ mol/L at 123 °C, which Boutevin et al. [15] found for the styrene/DEPN system. Benoit et al. [8] determined $K = 6.0 \times 10^{-9}$ mol/L at 120 °C for the styrene/DEPN system. Because of the nearly identical activation rate of the alkoxyamine PhEt-TIPNO $k_{\mathrm{act}} = 0.0032$ s^{-1} (this work) and PhEt-DEPN $k_{\mathrm{act}} = 0.0034$ s^{-1} (Benoit et al. [8]), a very similar polymerization behaviour is assumed when using the nitroxides TIPNO and DEPN in the controlled free radical polymerization.

The kinetic investigations of the styrene/BIPNO system, which are presented in this paper, show that the activation of the alkoxyamine PhEt-BIPNO is approximately significantly faster than that for PhEt-DEPN and PhEt-TIPNO. In addition, the equilibrium constant of the dissociation/combination of the dormant and active species of the styrene/BIPNO system is significantly higher than in case of other performed experiments of nitroxide free radical polymerizations of styrene. This high equilibrium constant opens the possibility of persistence in non-stationary state of the controlled free radical polymerization up to high conversions. In the non-stationary state we can achieve high polymerization rates. Due to fast activation, a good control of the polymerization process is possible as well.

Table 7
Crossover time at 123 °C

$[\mathrm{PhEt\text{-}BIPNO}]_0$ ($10^{-3} \times$ mol/L)	b ($10^{-5} \times \mathrm{s}^{-1}$)	t_{cross} (s)	$[\mathrm{PhEt\text{-}TIPNO}]_0$ ($10^{-3} \times$ mol/L)	b ($10^{-5} \times \mathrm{s}^{-1}$)	t_{cross} (s)
10	8.20	8130	10	0.12	5540
30	2.73	24,400	30	4.01	16,600
50	1.64	40,700	50	2.41	27,700

An important step towards the development of novel nitroxides for the controlled radical polymerization was the synthesis of acyclic α-hydrogen bearing nitroxides, like TIPNO or DEPN [1]. With synthesis of BIPNO, the structural modification of the well-known nitroxide TIPNO has a significant effect on the kinetic parameters (k_d and K) of the controlled radical polymerization of styrene. In place of the phenyl ring, a second isopropyl group was introduced, so that this nitroxide lacks a chiral α-carbon atom like TIPNO.

Modifications at the α-C-atom of the nitroxides seem to have an impact on the activation–deactivation equilibrium and on the range of suitable monomers for the controlled free radical polymerization. The reason of this influence can be attributed to stabilization of the radical and to sterical effects.

The alkoxyamine PhEt-BIPNO has been identified [22] as a suitable initiator for the controlled free radical polymerization of styrene and as an excellent initiator for the controlled free radical polymerization of *n*-butylacrylate.

Realization of the controlled free radical polymerization under non-steady state conditions up to high conversion leads to higher polymerization rates during the whole reaction process, without losing control of the polymerization. The polymerization rates can be influenced by the concentration of the alkoxyamines and due to the fast activation of the alkoxyamine (high k_d), low polydispersities can be achieved even at low monomer conversion.

4. Conclusion

The initiation kinetics of BIPNO/styrene, TIPNO/styrene and TEMPO/styrene systems were investigated by controlled free radical polymerization. The concentrations of the alkoxyamine (RN = PhEt-BIPNO, PhEt-TIPNO, PhEt-TEMPO) and of the free nitroxide ($\mathrm{N}^{\bullet}$ = BIPNO, TIPNO, TEMPO) in the initial phase of the reaction were determined experimentally by SEC.

By this new method, k_{act} can be derived from the plot of $\ln([\mathrm{RN}]_0/[\mathrm{RN}]_t)$ vs. time, similar to the work of Fukuda [4,5].

For the new PhEt-BIPNO [22] synthesized by us, a value of $k_{\mathrm{act}} = 6.8 \times 10^{-3}$ s^{-1} is experimentally determined. For PhEt-TIPNO $k_{\mathrm{act}} = 3.2 \times 10^{-3}$ s^{-1} and for PhEt-TEMPO $k_{\mathrm{act}} = 0.8 \times 10^{-3}$ s^{-1} are determined.

Furthermore, the equilibrium constant K should be determined by applying the Persistent Radical Effect. The determined equilibrium constants of the dissociation/combination of the dormant and active species at 123 °C are for TIPNO: $K = 7.5 \times 10^{-9}$ mol/L and for BIPNO: $K = 1.08 \times 10^{-8}$ mol/L.

Acknowledgement

The authors acknowledge the Deutsche Forschungsgemeinschaft for financial support within the European Graduate School "Microstructural Control in Free Radical Polymerization".

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