Living/Controlled Radical Polymerization of Ethyl and *n*-Butyl Acrylates at 90 °C Mediated by β-Sulfinyl Nitroxides: Influence of the Persistent Radical Stereochemistry

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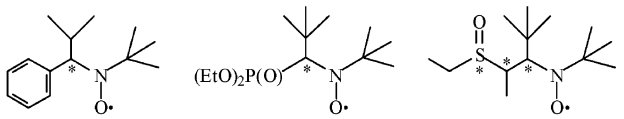
ABSTRACT: Herein we report the living/controlled radical polymerization of ethyl and *n*-butyl acrylates mediated by β-sulfinyl nitroxides at temperatures below 90 °C. This study examined the effect of the persistent radical stereochemistry on the polymerization kinetics of ethyl acrylate. Experiments were carried out in the presence of alkoxyamines based on 1-phenylethyl transient radicals bearing a 4-hydrogen or a 4-(methyl carboxylate) group, and two enantiomerically pure mixtures of *N*-*tert*-butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide (BESN); i.e., a 1:1 $S_SR_\beta R_\alpha/R_SS_\beta S_\alpha$ and a 1:1 $R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$ racemic mixtures. The dissociation rate constants (k_d) of the alkoxyamines and poly(ethyl acrylate) chains capped by both nitroxide racemic mixtures were determined by ESR spectroscopy measurements. Kinetic and ESR studies of ethyl acrylate polymerization experiments allowed the determination of the equilibrium constants (K^{90}) and the rate constants of combination (k_c^{90}) for each system. The rate constants of combination were found to be slightly dependent on the nitroxide stereochemistry whereas an order of magnitude difference was observed for the rate constants of dissociation. Then, well-defined poly(ethyl acrylate) and poly(*n*-butyl acrylate) were prepared, at 90 °C, from alkoxyamines based on the $R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$ nitroxide diastereomers.

Introduction

Since the first report from Rizzardo et al.,[1] living/controlled radical polymerization mediated by nitroxide free radicals has been shown to be a versatile method for the preparation of well-defined polymeric materials.[2−9] Many studies have proved the efficiency of this technique for the synthesis of polymers with well-defined architectures, composition and functionality, either in bulk or in dispersed media.[10−16] However, synthetic efforts to prepare more efficient nitroxides are still required, to extend this process to a wider range of monomers and architectures, using lower temperatures. Extensive reports using α,α′-*tert*-alkylated nitroxides have demonstrated the ability to control the radical polymerization of styrenic monomers.[17−22] However, slow rates of polymerization, equivalent to the rate of styrene thermal polymerization, were generally observed without the utilization of an additive.[23−25] The polymerization of (meth)acrylates mediated by *tert*-alkylated nitroxides has also been studied but generally resulted in unsatisfactory control, due to inhibition or disproportionation reactions.[26−29] A significant improvement in this field was achieved by the introduction of α-hydrogenated nitroxides (Scheme 1) such as *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) or *N*-*tert*-butyl-*N*-(2-methyl-1-phenylpropyl) nitroxide (TIPNO) which allow for the living/controlled radical polymerization of a wider range of monomers. In the case of styrene, their use results in a rate of polymerization that depends on the initial alkoxyamine concentration and is higher than the rate of thermal polymerization.[30−33] However, the high temperature (T > 115 °C) required in these systems complicates the control of the polymerization as the contribution from side reactions (e.g., thermal initiation) is more significant. *N*-*tert*-butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide (BESN, Scheme 1), a new stable

Scheme 1



TIPNO **SG1** **BESN**

α-hydrogenated nitroxide, allowed for the synthesis of well-defined polystyrene chains with a rate of polymerization higher than the rate of thermal polymerization of styrene even at temperatures below 90 °C.[34] However, extensive details were not given on the stereochemistry of the BESN persistent radical involved in this previous study (nitroxide **4**). This work focuses on the synthesis and characterization of the different BESN nitroxide diastereomers and examines the effect of nitroxide stereochemistry on the kinetics of ethyl and *n*-butyl acrylates' bulk polymerization at 90 °C. The synthesis and reactivity of chiral nitroxides and alkoxyamines have been previously studied by Braslau et al.,[35,36] but only the kinetics of styrene polymerization in the presence of the trans isomer of 2,5-diphenylpyrrolidin-1-oxyl (DPPO) have been reported by Sogah et al.[37] A factor of 3 difference between alkoxyamines derived from the two enantiomers of SG1 has been reported previously for the rate constants of dissociation and the equilibrium constants, but these differences did not result in a significantly different polymerization efficiency.[32,38,39] Herein we describe the complete resolution of the stereochemistry of BESN β-sulfinyl nitroxides and its effects on the polymerization kinetic parameters of ethyl acrylate (K^{90}, k_c^{90}, and k_d^{90}). One alkoxyamine, based on $R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$ BESN diastereomers and 1-phenylethyl radical, has been studied in the living/controlled polymerization of *n*-butyl acrylate at 90 °C, and the equilibrium constant (K^{90}) for this system has been determined.

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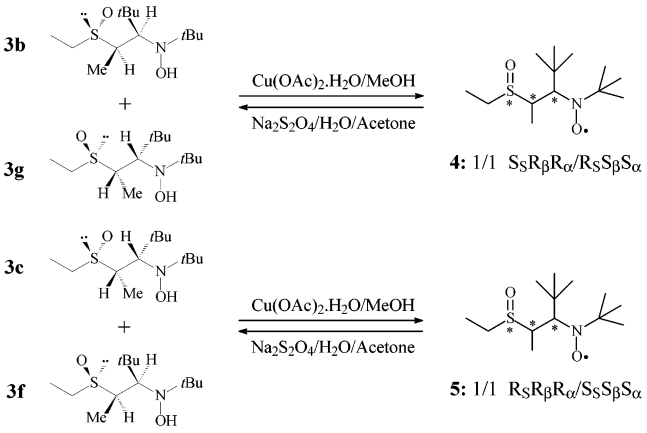
Scheme 2



Results and Discussion

Synthesis of *β*-Sulfinyl Nitroxides and Alkoxyamine Derivatives. The synthesis of *β*-sulfinyl nitroxides, by nucleophilic addition of α-lithiated sulfoxides to prochiral nitrones and subsequent oxidation of the *β*-sulfinyl hydroxylamine intermediates, has been previously described.[40] Such nucleophilic additions have been widely studied and are known to be highly diastereoselective for the low-temperature synthesis of hydroxylamines bearing one chiral center.[41,42] The three chiral centers of BESN, i.e., the sulfoxide functionality and the α and *β* carbon atoms (with respect to the nitrogen atom), may yield up to eight (2^3) theoretical diastereomers (Scheme 1). Experimentally, BESN synthesis leads to a 1:1 mixture of nitroxide **4** ($R_f = 0.20$) and nitroxide **5** ($R_f = 0.26$) as red liquids which can be partially purified by column chromatography. To determine the specific stereochemistry of each nitroxide, X-ray experiments were carried out on the corresponding *β*-sulfinyl hydroxylamines. Single crystals were grown after reduction of nitroxides **4** or **5** by sodium dithionite in a 1:1 water/acetone mixture and subsequent crystallization under an argon atmosphere. Crystal structures highlighted the presence of a racemic mixture for both hydroxylamines; i.e., a 1:1 mixture of $S_SR_\beta R_\alpha$ (**3b**)/$R_SS_\beta S_\alpha$ (**3g**) diastereomers from nitroxide **4**, and a 1:1 mixture of $R_SR_\beta R_\alpha$ (**3c**)/$S_SS_\beta S_\alpha$ (**3f**) diastereomers from nitroxide **5** (Scheme 2). *β*-Sulfinyl hydroxylamines **3b,g** and **3h,f** crystallize alternately, forming intermolecular hydrogen bonds between sulfoxide and hydroxyl functions. These various conformations lead to different physical and chemical properties for nitroxides **4** and **5** (e.g., NMR shifts, ESR couplings, R_f) which are related, as suggested by the crystal structures, to the orientation of the sulfoxide dipole toward the nitroxide moiety. The ESR spectra of nitroxides **4** and **5** represented in Figure 1, exhibit the same structure factors ($g = 2.0061$) and an unexpected shift of 1.1 G for nitrogen hyperfine coupling constants; $a_N = 14.7$ G for nitroxide **4** and $a_N = 13.6$ G for nitroxide **5**. Since the strongly polar sulfoxide functional group is too far from the nitroxide moiety to allow any significant inductive effect, it is the spatial interactions between both functions that result in a modification of the delocalization of the spin radical on the neighboring α-nitrogen atom (Scheme 3). The stereochemistry of hydroxylamines **3b,g,h,f** is related to the four diastereomers obtained after the α-lithiation of prochiral diethyl sulfoxide **1** (Scheme 4). The bulkiness of *tert*-butyl substituents forces each diastereomer of α-lithiated diethyl sulfoxide to undergo one single

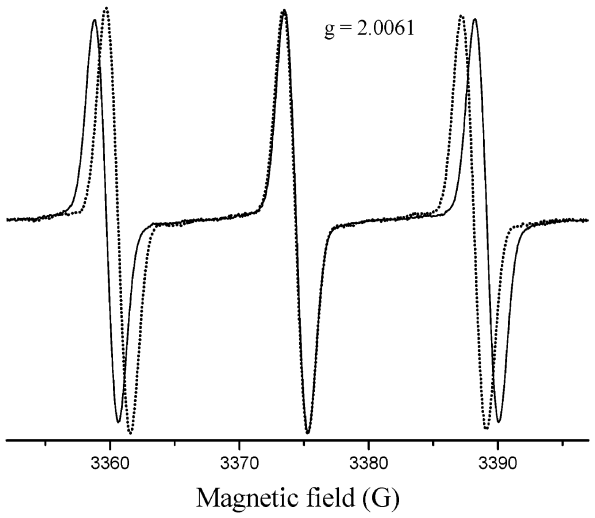
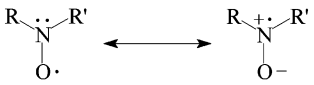
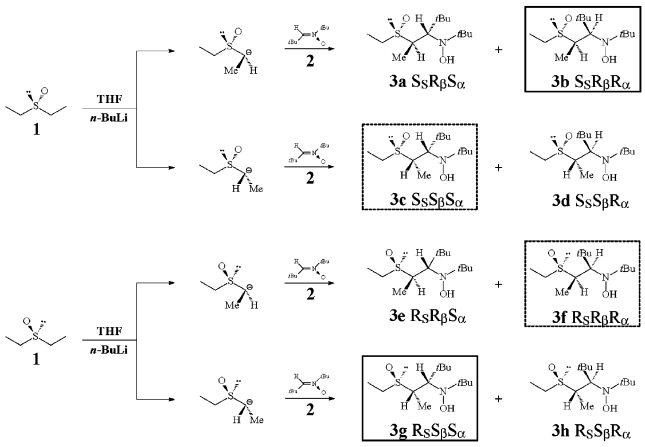


Figure 1. ESR spectra of nitroxides **4** (solid) and **5** (dot) in benzene at room temperature.

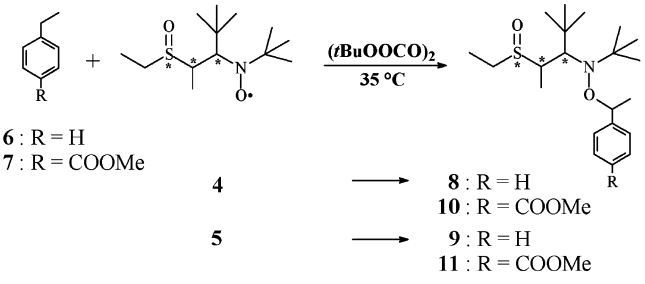
Scheme 3



Scheme 4



Scheme 5



pathway of addition to prochiral *N*-*tert*-butyl-α-*tert*-butyl nitrone **2**. Thus, despite the presence of four diastereomers, the synthesis of BESN remains still highly diastereoselective.

Alkoxyamine derivatives of nitroxides **4** and **5** were synthesized by a room-temperature spin trap coupling mediated by di-*tert*-butyl peroxalate (Scheme 5).[27,43] Contrary to the nitroxide derivatives, corresponding alkoxyamines (with or without the ester function) could be easily separated by column chromatography. Similar yields were obtained by using the ATRA method,[44] however the reaction time at room temperature was

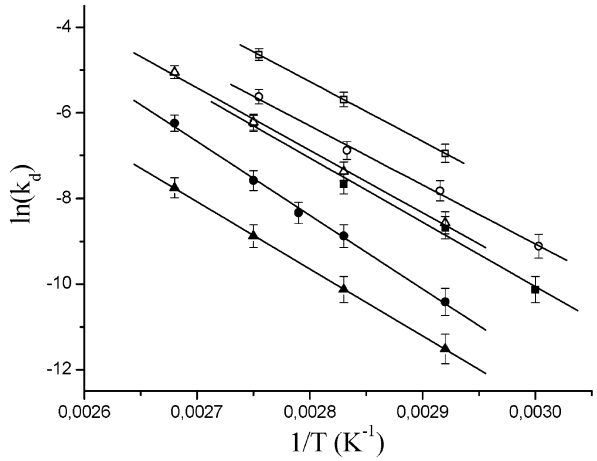


Figure 2. Temperature dependence of unimolecular initiators rate constants of dissociation (k_d) in ethyl acetate, [galvinoxyl] = 1×10^{-3} mol L^{-1}: (□) [**11**] = 0.2×10^{-3} mol L^{-1}; (○) [**9**] = 0.2×10^{-3} mol L^{-1}; (△) [**12**] = 0.2×10^{-3} mol L^{-1} (M_n = 35 400 g mol^{-1}, PDI = 1.6); (■) [**10**] = 0.2×10^{-3} mol L^{-1}; (●) [**8**] = 0.2×10^{-3} mol L^{-1}; (▲) [**13**] = 0.2×10^{-3} mol L^{-1} (M_n = 36 100 g mol^{-1}, PDI = 1.2).

considerably longer and the copper species prevented the monitoring of conversion by ESR spectroscopy. For each nitroxide, two kinds of alkoxyamines based on transient radicals derived from ethylbenzene and 4-ethyl methyl benzoate have been synthesized, characterized and studied in the bulk polymerization of ethyl and *n*-butyl acrylates at 90 °C.

Determination of the Rate Constants of Dissociation (k_d) by ESR Spectroscopy. The rate constants of dissociation (k_d) of alkoxyamines **8**−**11** and poly(ethyl acrylate) chains **12**,**13**, which release either BESN nitroxides **4** or **5**, have been determined by ESR spectroscopy experiments.[45] Ethyl acetate solutions of an alkoxyamine (macro)initiator (0.2 mol L^{-1}) and excess galvinoxyl (1 mol L^{-1}) were heated under argon at temperatures between 60 and 100 °C. Galvinoxyl was used to irreversibly trap the transient radicals released during alkoxyamine dissociation, thus suppressing the backward combination reaction. Under these conditions, the released nitroxide concentration follows the first-order law described by relation 1, $[P-X]_0$ being the initial alkoxyamine concentration and $[X^\bullet]$ the nitroxide concentration at a given time.

$$\ln(([P-X]_0 - [X^\bullet])/[P-X]_0) = -k_d t \qquad (1)$$

The rate constants of dissociation (k_d) were determined from the slopes of the first-order plots of nitroxide concentrations vs time at each temperature. From the corresponding Van't Hoff plots (Figure 2), the Arrhenius parameters (A/s^{-1} and E_a/kJ mol^{-1}) were determined. Data reported in Table 1 show that independent of the transient radical structure, the rate constants of dissociation of unimolecular initiators capped by nitroxide **5** are 1 order of magnitude higher than their analogues capped by nitroxide **4**. The different orientation of the sulfoxide group with respect to the nitroxide moiety, for each racemic mixture also affects the activation energy of the C−O bond homolysis; E_a is always lower for nitroxide **5** than for nitroxide **4**. As reported in the literature,[46] the transient radical structure has a significant effect on the rate constant of dissociation which decreases, for a given nitroxide, according to the following order: k_d(−CH(CH_3)PhCOOCH_3) > k_d(−CH(CH_3)Ph) > k_d(−CH(CH_3)COOC_2H_5). The introduction of the withdrawing *p*-ester group enhances the radical stabilization compared to 1-phenylethyl radical and leads to a k_d evolution which correlates with the reactivity order given by the Arnold scale for benzylic radicals ($\sigma_{\alpha,COOMe^\bullet} = 0.043 > \sigma_{\alpha,H^\bullet} = 0$). Conversely, ethyl acrylate radicals are less bulky and less stabilized than styryl radical derivatives, resulting in a lower value of k_d. The different alkoxyamines were then tested in the living/controlled polymerization of ethyl acrylate at 90 °C. As the stereochemistry of the persistent radical played a key role in the polymerization kinetics, the results presented in the following sections are divided according to the nitroxide structure.

Table 1. Arrhenius Parameters and Dissociation Rate Constants at 90 °C for Alkoxyamine (Macro)Initiators in Ethyl Acetate

alkoxyamine	nitroxide	A (s^{-1})	E_a (kJ mol^{-1})	k_d^{90} (s^{-1})
8	**4**	3.2×10^{17}	145	5.0×10^{-4}
9	**5**	1.1×10^{14}	114	3.4×10^{-3}
10	**4**	3.2×10^{15}	126	1.8×10^{-3}
11	**5**	2.1×10^{13}	106	9.8×10^{-3}
12	**4**	2.2×10^{15}	133	1.4×10^{-4}
13	**5**	1.7×10^{15}	124	2.1×10^{-3}

Kinetic and ESR Studies of Ethyl Acrylate Polymerization at 90 °C in Bulk Mediated by Nitroxide 4. Before discussing the kinetic behavior of ethyl acrylate polymerization, it has to be noted that while this monomer is generally described as a monomer with no autopolymerization, a polymer is formed by simple heating. The polymer yield is not rigorously reproducible and seems to depend on the storage time after distillation. Consequently, this side reaction can modify the monomer consumption for experiments carried out from different monomer batches.

The bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **8** and **10** was characterized by following the evolution of the conversion index and the nitroxide concentration with time. For a better understanding of the kinetic results, all of the data were plotted and examined simultaneously. For polymerizations mediated by alkoxyamine **10**, the conversion index (Figure 3) increases linearly, with an induction period being observed for the experiment containing an initial amount of nitroxide **4** (□; 0.4 mol %). This induction period occurs because the initial free nitroxide limits the dissociation of the alkoxyamine, and consequently the initiation and propagation reactions as well, by trapping almost all alkyl radicals generated in the medium. The linear evolution of the conversion index with time is generally observed in processes involving an external source of transient radicals or an initial excess of persistent radicals.[6,8] The ESR monitoring of nitroxide concentration during the polymerizations (Figure 4) indicates that the presence of self-initiating species rapidly leads to a decrease and a stabilization of the persistent radical concentration. This additional generation of transient radicals explains not only the linear variation of the conversion index but also the higher polymerization rate compared to that observed in experiments mediated by alkoxyamine **8**. In this last case, the evolution of conversion index with time is quite different; it follows the theoretical relation 2 established for the polymerization of monomers without additional initiation.[8]

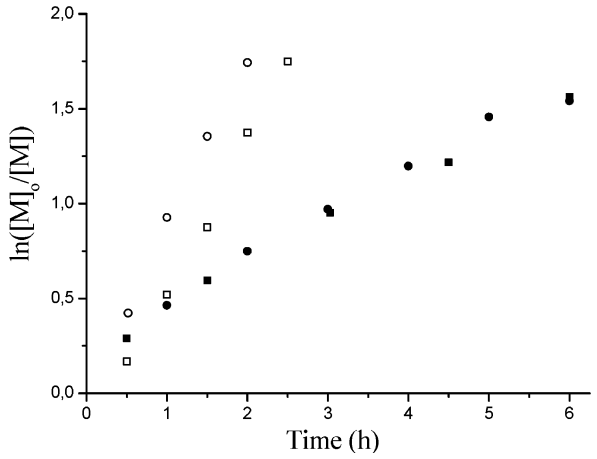


Figure 3. Conversion index vs time for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **8** and **10**: (■) [**8**] = 8.0 × 10^{-3} mol L^{-1}; (●) [**8**] = 15.0 × 10^{-3} mol L^{-1}; (□) [**10**] = 15.2 × 10^{-3} mol L^{-1}, [**4**] = 6.0 × 10^{-5} mol L^{-1}; (○) [**10**] = 15.3 × 10^{-3} mol L^{-1}.

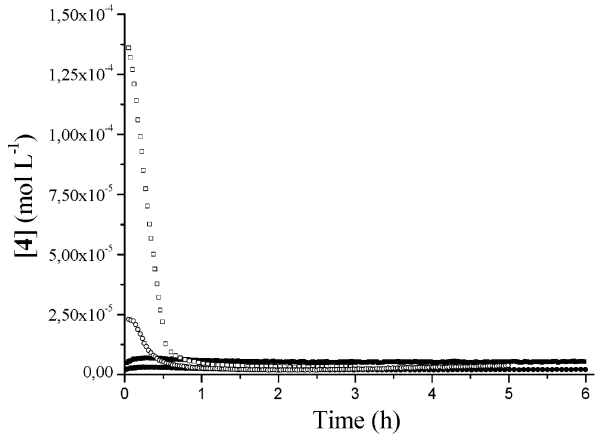


Figure 4. Nitroxide **4** concentration vs time for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **8** and **10**: (■) [**8**] = 8.0 × 10^{-3} mol L^{-1}; (●) [**8**] = 15.0 × 10^{-3} mol L^{-1}; (□) [**10**] = 15.2 × 10^{-3} mol L^{-1}, [**4**] = 6.0 × 10^{-5} mol L^{-1}; (○) [**10**] = 15.3 × 10^{-3} mol L^{-1}.

$$\ln([M]_0/[M]) = (3k_p/2)(K[P{-}X]_0/3k_t)^{1/3}t^{2/3} \qquad (2)$$

Thus, for both experiments the linear fits of $\ln(\ln[M]_0/[M])$ vs $\ln(t)$ give a similar time exponent equal to 0.68. However, an increase of the alkoxyamine concentration does not lead to a marked increase of the polymerization rate, as expected from relation 2. The effect of the alkoxyamine concentration is evidenced by the evolution of the persistent radical concentration (Figure 4) which, after the early stage of the polymerization, reaches different stationary states (Table 2). The very low level reached ($[X^\bullet]_{stat} \sim (3{-}7) \times 10^{-6}$ mol L^{-1}) indicates that the equilibrium constant between active and dormant species should be very low. It also implies that a small initial amount of free nitroxide may noticeably affect the variation of the monomer conversion with time.[8] This may be the origin of the differences observed for the monomer consumption in the two sets of experiments. To quantify this assumption, the different equilibrium constants (K^{90}) were evaluated from relation 3. The use of this relation is justified by the steady states reached by both persistent and transient radical concentrations, after 1 h of polymerization.

$$K^{90} = [P^\bullet]_{stat}[X^\bullet]_{stat}/[P{-}X]_0 \qquad (3)$$

$$k_c^{90} = k_d^{90}/K^{90} \qquad (4)$$

The values of $[P^\bullet]_{stat}$ were calculated from the slopes of the linear fits of conversion index vs time ($\alpha = k_p^{90}[P^\bullet]_{stat}$ for $t > 1$ h), using $k_p^{90} = 61\,000$.[47] The rate constants of combination (k_c^{90}) were calculated from relation 4 and the values of k_d^{90} determined by ESR spectroscopy, for the dissociation of poly(acrylate) chains capped by nitroxide **4**. The data listed in Table 2 show that the four experiments carried out with ethyl acrylate and nitroxide **4**, give a similar value for the equilibrium constant ($K^{90} \sim 6 \times 10^{-13}$ mol L^{-1}). This low value confirms the hypothesis concerning the effect of a small initial amount of free nitroxide on the evolution of monomer consumption; for $[X^\bullet] > (3K[P{-}X]_0k_t/k_p)^{1/2} \sim 10^{-6}$ mol L^{-1} a linear variation can be observed.[8] A comparison of the kinetic parameters to those previously reported for the polymerization of styrene in the presence of alkoxyamine **8**,[34] shows that the rate constants of dissociation are within the same range ($k_d^{90} \sim 3.6 \times 10^{-4}$ s^{-1} in benzene and $k_d^{90} \sim 1.4 \times 10^{-4}$ s^{-1} in ethyl acetate) whereas 3 orders of magnitude separate the equilibrium constants ($K^{90} \sim 5 \times 10^{-10}$ mol L^{-1} for styrene and $K^{90} \sim 6 \times 10^{-13}$ mol L^{-1} for ethyl acrylate). This large difference is mainly due to the combination reaction, highly favored in the case of polyacrylate radical;[48] this radical presents a greater reactivity due to the lower steric hindrance and stabilization than the polystyryl radical ($k_c^{90} \sim 6 \times 10^5$ L mol^{-1} s^{-1} for styrene and $k_c^{90} \sim 2 \times 10^8$ L mol^{-1} s^{-1} for ethyl acrylate).

Figure 5 shows that the number-average molecular weights reached the theoretical values only after a relatively high monomer consumption. For all experiments, below conversions of 50−60%, the experimental molecular weights are higher than the targeted values. This behavior is related to the low value of the rate constant of dissociation compared to the high rate constant of propagation ($k_p^{90} \sim 70 \times k_p^{90}$ of styrene).[47,49] This considerably shortens the reaction time of polymerization experiments and means that the initial amount of alkoxyamine is totally dissociated when the polymerization has already reached high conversion. During this period of time, the consumed monomer is distributed among a smaller fraction of chains than expected at such conversion. The polydispersity index is then poorly controlled, this phenomenon being amplified in the case of experiments with alkoxyamine **10** by the presence of an external source of transient radicals as established theoretically.[8]

Kinetic and ESR Studies of Ethyl Acrylate Polymerization at 90 °C in Bulk Mediated by Nitroxide 5. The bulk polymerization of ethyl acrylate at 90 °C in the presence of alkoxyamines **9** and **11** has been studied for two initial alkoxyamine concentrations. The graph representing the conversion index vs time (Figure 7) shows an evolution close to the $t^{2/3}$ variation predicted by relation 2. The time exponent of the power law, determined from the linear fits of the plot representing $\ln(\ln[M]_0/[M])$ vs $\ln(t)$, varies between 0.6 and 0.7. In all experiments, the polymerization rate, and therefore the concentration of transient radical, becomes almost constant after one to 2 h of reaction. However, the general trend is only slightly dependent on the initial alkoxyamine concentration. This observation, as shown

Table 2. Kinetic Parameters for the Bulk Polymerization of Ethyl Acrylate at 90 °C Mediated by Alkoxyamines 8 and 10

alkoxyamine	$[P-X]_0$ (mol L^{-1})	$[P^{\bullet}]_{stat}$ (mol L^{-1})	$[X^{\bullet}]_{stat}$ (mol L^{-1})	K^{90} (mol L^{-1})	k_d^{90} (s^{-1})[a]	k_c^{90} (L mol^{-1} s^{-1})
8	8.0×10^{-3}	9.6×10^{-10}	5.3×10^{-6}	6.4×10^{-13}	1.4×10^{-4}	2.2×10^{8}
8	15.0×10^{-3}	1.1×10^{-9}	7.7×10^{-6}	6.0×10^{-13}	1.4×10^{-4}	2.3×10^{8}
10	15.2×10^{-3}	3.6×10^{-9}	3.2×10^{-6}	7.6×10^{-13}	1.4×10^{-4}	1.8×10^{8}
10	15.3×10^{-3}	4.0×10^{-9}	2.9×10^{-6}	7.6×10^{-13}	1.4×10^{-4}	1.8×10^{8}

[a] k_d values for poly(ethyl acrylate) chains capped by nitroxide **4**.

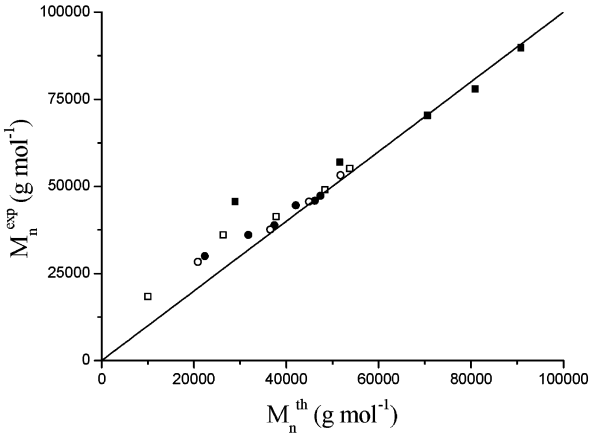


Figure 5. Experimental molecular weights vs theoretical molecular weights for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **8** and **10**: (■) [**8**] = 8.0×10^{-3} mol L^{-1}; (●) [**8**] = 15.0×10^{-3} mol L^{-1}; (□) [**10**] = 15.2×10^{-3} mol L^{-1}, [**4**] = 6.0×10^{-5} mol L^{-1}; (○) [**10**] = 15.3×10^{-3} mol L^{-1}.

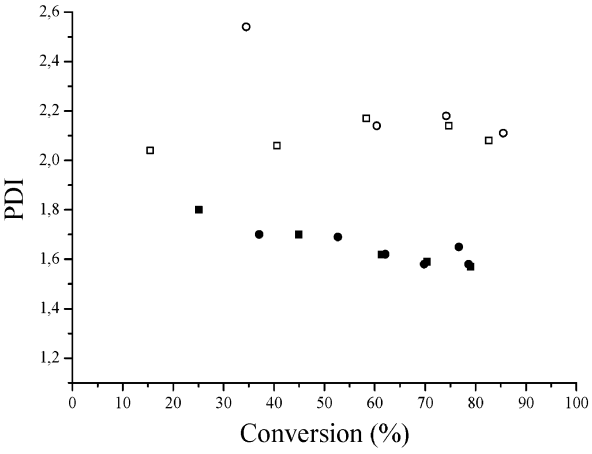


Figure 6. Polydispersity indexes vs conversion for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **8** and **10**: (■) [**8**] = 8.0×10^{-3} mol L^{-1}; (●) [**8**] = 15.0×10^{-3} mol L^{-1}; (□) [**10**] = 15.2×10^{-3} mol L^{-1}, [**4**] = 6.0×10^{-5} mol L^{-1}; (○) [**10**] = 15.3×10^{-3} mol L^{-1}.

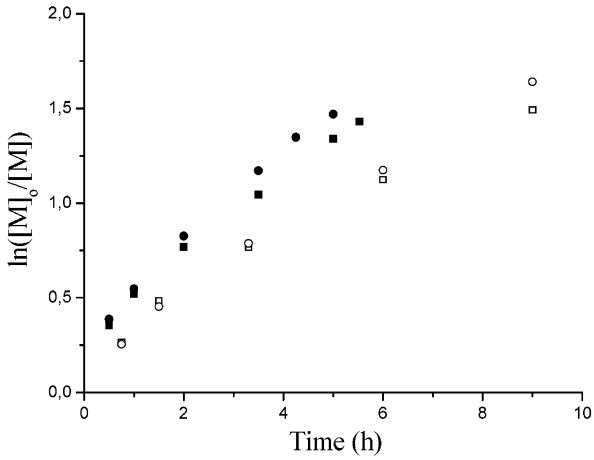


Figure 7. Monomer conversion vs time for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **9** and **11**: (■) [**9**] = 9.3×10^{-3} mol L^{-1}; (●) [**9**] = 16.9×10^{-3} mol L^{-1}; (□) [**11**] = 6.5×10^{-3} mol L^{-1} (○) [**11**] = 10.1×10^{-3} mol L^{-1}.

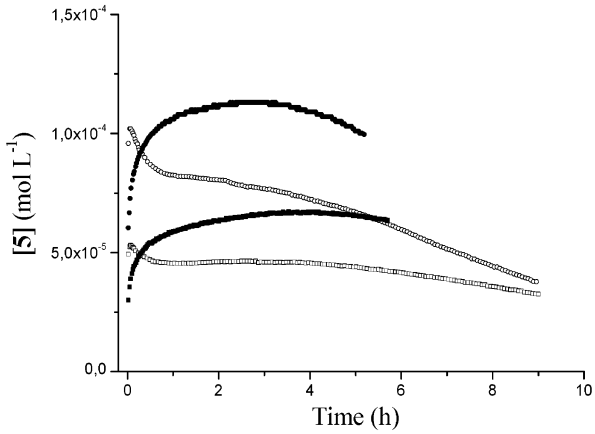


Figure 8. Nitroxide **5** concentration vs time for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **9** and **11**: (■) [**9**] = 9.3×10^{-3} mol L^{-1}; (●) [**9**] = 16.9×10^{-3} mol L^{-1}; (□) [**11**] = 6.5×10^{-3} mol L^{-1}; (○) [**11**] = 10.1×10^{-3} mol L^{-1}.

in experiments involving nitroxide **4**, can be the result of a small excess of free nitroxide at the beginning of the reaction. Therefore, the evolution of nitroxide **5** concentration during the polymerization experiment was monitored by ESR spectroscopy (Figure 8). For all experiments, nitroxide concentration reached a stationary state after one to 2 h of reaction depending on the transient radical structure. For alkoxyamine **11**, a sudden increase in the nitroxide concentration was observed at the beginning of the reaction; this can be explained by the high value of the rate constant of dissociation and probably also to a lower initiation of the monomer, due to the stabilization of the benzyl radical by the *p*-ester group. If less than 1% of these radicals are ineffective in the initiation reaction as a result of an irreversible coupling reaction, the concentration of persistent radical is then higher than the theoretical value and results in a rate of polymerization lower than expected. For alkoxyamine **9**, the nitroxide concentrations attain steady values which depend on the initial alkoxyamine concentration and remain about 1 order of magnitude higher than those observed in experiments involving nitroxide **4**. The equilibrium between nitroxide **5** and ethyl acrylate radical is shifted more to the active species than in the case of nitroxide **4**. To quantify this observation, transient and persistent radical concentrations were introduced in relations 3 and 4. Data collected in Table 3 confirm that the equilibrium constant for nitroxide **5** ($K^{90} \sim 7 \times 10^{-12}$ mol L^{-1}) is 1 order of magnitude greater than the one determined for nitroxide **4**. This difference is mainly due

Table 3. Kinetic Parameters for the Bulk Polymerization of Ethyl Acrylate at 90 °C Mediated by Alkoxyamines 9 and 11

alkoxyamine	$[P-X]_0$ (mol L^{-1})	$[P^\bullet]_{stat}$ (mol L^{-1})	$[X^\bullet]_{stat}$ (mol L^{-1})	K^{90} (mol L^{-1})	k_d^{90} (s^{-1})[a]	k_c^{90} (L mol^{-1} s^{-1})
9	9.3×10^{-3}	1.1×10^{-9}	6.7×10^{-5}	7.9×10^{-12}	2.1×10^{-3}	2.7×10^{8}
9	16.9×10^{-3}	1.2×10^{-9}	1.1×10^{-4}	7.8×10^{-12}	2.1×10^{-3}	2.7×10^{8}
11	6.5×10^{-3}	8.6×10^{-10}	4.6×10^{-5}	6.1×10^{-12}	2.1×10^{-3}	3.4×10^{8}
11	10.1×10^{-3}	7.8×10^{-10}	7.9×10^{-5}	6.1×10^{-12}	2.1×10^{-3}	3.4×10^{8}

[a] k_d values for poly(ethyl acrylate) chains capped by nitroxide **5**.

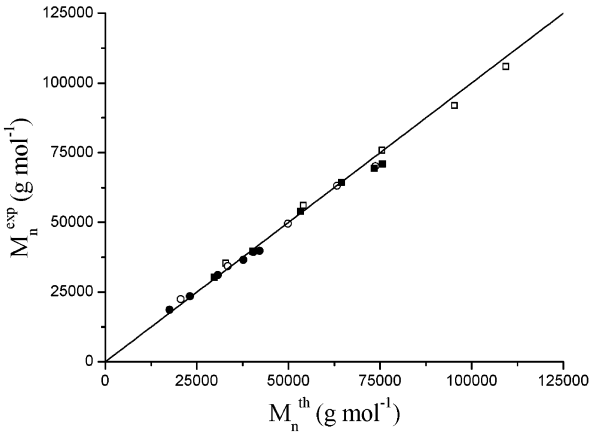


Figure 9. Experimental molecular weights vs theoretical molecular weights for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **9** and **11**: (■) [**9**] = 9.3×10^{-3} mol L^{-1}; (●) [**9**] = 16.9×10^{-3} mol L^{-1}; (□) [**11**] = 6.5×10^{-3} mol L^{-1}; (○) [**11**] = 10.1×10^{-3} mol L^{-1}.

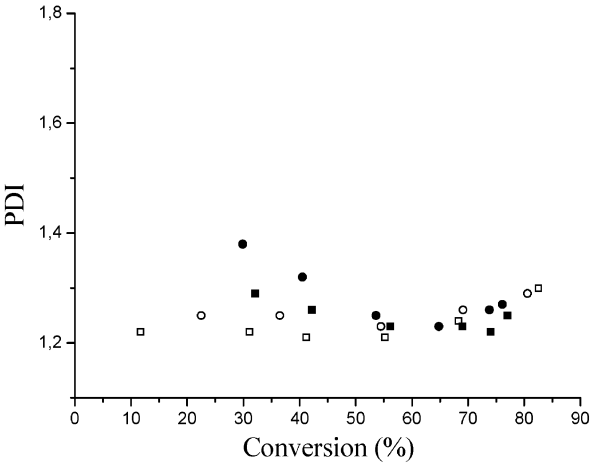


Figure 10. Polydispersity indexes vs conversion for the bulk polymerization of ethyl acrylate at 90 °C mediated by alkoxyamines **9** and **11**: (■) [**9**] = 9.3×10^{-3} mol L^{-1}; (●) [**9**] = 16.9×10^{-3} mol L^{-1}; (□) [**11**] = 6.5×10^{-3} mol L^{-1}; (○) [**11**] = 10.1×10^{-3} mol L^{-1}.

to a higher value of the rate constant of dissociation, since the rate constants of combination depend only slightly on the nitroxide stereochemistry ($k_c^{90} \sim 2 \times 10^8$ L mol^{-1} s^{-1} for nitroxide **4** and $k_c^{90} \sim 3 \times 10^8$ L mol^{-1} s^{-1} for nitroxide **5**).

Concerning the evolution of the average molecular weights with conversion, Figure 9 shows a linear increase up to 100 000 g mol^{-1}. The fast dissociation of these alkoxyamines lead to the formation of all acrylate chains at the early stage of the reaction and the molecular weights, after 1 h of polymerization, follow the theoretical linear evolution. This fast exchange between dormant and active species lead to a polydispersity index (Figure 10), which decreases to 1.2 and then slightly increases after 70% of conversion, resulting from the unavoidable accumulation of dead chains.

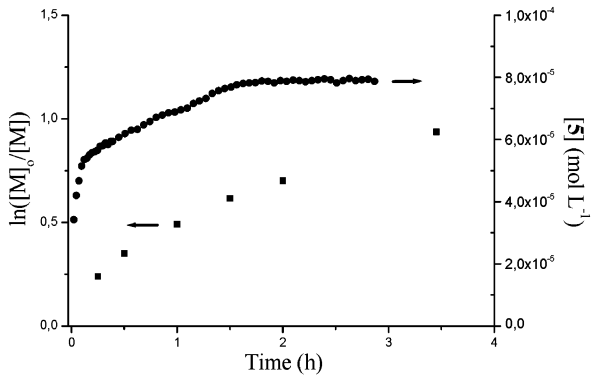


Figure 11. Monomer conversion (■) and nitroxide **5** concentration (●) vs time for the bulk polymerization of *n*-butyl acrylate at 90 °C mediated by alkoxyamine **9**: [**9**] = 8.0×10^{-3} mol L^{-1}.

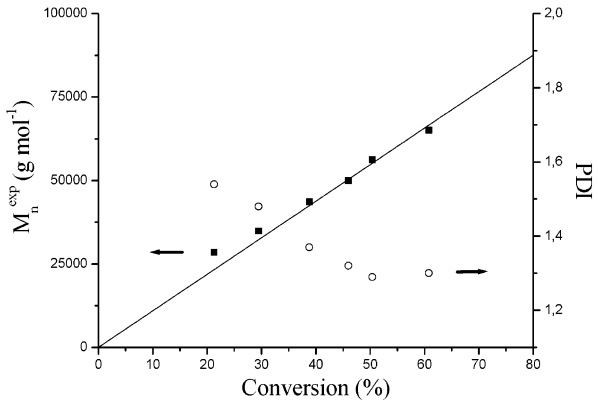


Figure 12. Experimental molecular weights (■) and polydispersity indexes (○) vs conversion for the bulk polymerization of *n*-butyl acrylate at 90 °C mediated by alkoxyamine **9**: [**9**] = 8.0×10^{-3} mol L^{-1}.

Kinetic and ESR Studies of *n*-Butyl Acrylate Polymerization at 90 °C in Bulk Mediated by Nitroxide 5. The efficient control of the polymerization of ethyl acrylate using nitroxide **5** prompted us to investigate the polymerization of *n*-butyl acrylate at 90 °C using one initial concentration of alkoxyamine **9**. The evolutions of conversion index and nitroxide concentration, shown in Figure 11, exhibit a similar trend to those observed for the polymerization of ethyl acrylate; after the first hour of polymerization, both transient and persistent radical concentrations reach stationary states. Thus, the equilibrium constant ($K^{90} = 9.0 \times 10^{-12}$ mol L^{-1}) could be determined using relation 3, with k_p = 54 100 L mol^{-1} s^{-1}.[49] This value is three times higher than the extrapolated value found in the literature for the polymerization of *n*-butyl acrylate mediated by SG1 ($K^{90} = 3.3 \times 10^{-12}$ mol L^{-1}).[33] The experimental molecular weights are in good agreement with the theoretical values, exhibiting polydispersity indices close to 1.3 (Figure 12).

Conclusion

This study has shown that the stereochemistry of BESN β-sulfinyl nitroxide modifies the orientation of the sulfoxide group toward the nitroxide moiety, resulting in different physical and chemical properties for the two diastereomer mixtures of the nitroxide and the corresponding alkoxyamines. Kinetic and ESR studies of ethyl and *n*-butyl acrylates polymerizations clearly demonstrated the effect of BESN nitroxide stereochemistry on the kinetic parameters and consequently on their ability to control the polymerization of acrylates. Thus, the rate constant of dissociation (k_d) strongly depends on the persistent radical stereochemistry whereas the rate constant of combination (k_c) appears to be only slightly dependent. The control of ethyl and *n*-butyl acrylates has been achieved, even at temperatures below 90 °C,[50] through the use of alkoxyamines releasing the $R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$ mixture of BESN diastereomers.

Experimental Section

General Methods. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) measurements were performed on a Bruker AC 200 spectrometer at room temperature. To prevent their fast and easy oxidation in the presence of oxygen, ^{1}H NMR experiments of β-sulfinyl hydroxylamines were carried out after in-situ reduction of the corresponding nitroxides by sodium dithionite in a 1:1 D_2O/C_3D_6O mixture. ESR spectra were recorded on a Bruker ESP-300 X-band spectrometer equipped with a HP 53150A frequency meter and a Boonton microwatt meter. Nitroxide concentrations were determined by integration of the ESR spectra and calibration with a TEMPO solution in benzene. Size exclusion chromatography (SEC) was carried out at room temperature on a Shimadzu apparatus equipped with a refractometer (Shimadzu) coupled to a light scattering spectrometer Dawn DSP and five columns PL GEL (10 μm particles) (three mixed B, 10^3Å, 10^5Å), using THF as eluant (flow rate: 1 mL min^{-1}). Calibration curves obtained from poly(ethyl acrylate) and poly(*n*-butyl acrylate) standards were used to calculate the average molecular weights (M_n) and the polydispersity indexes (PDI = M_w/M_n).

Materials. 4-(Ethyl) methyl benzoate (**7**) was synthesized as described previously.[51] Tetrahydrofuran (THF) was distilled from sodium benzophenone dianion. Benzene (Aldrich, 99%) was distilled from 1,1-diphenylethylene/*n*-BuLi and stored under argon. Ethylbenzene (Aldrich, 99%) was distilled twice from calcium hydroxide and stored under argon. Ethyl acrylate and *n*-butyl acrylate (Aldrich, 99%) were distilled twice from calcium hydride prior to use and stored under argon. All other materials were used as received. β-sulfinyl hydroxylamines (**3b,c,g,f**), corresponding nitroxides (**4,5**) and alkoxyamine derivatives, (**8**−**11**) were synthesized according to the following procedures.

General Procedure for the Preparation of Nitroxides, 4,5. A solution of *N*-*tert*-butyl-α-*tert*-butyl nitrone, (**2**) (1.5 g, 9.6 mmol), in anhydrous THF (45 mL), was added dropwise to a cooled (−78 °C) stirred solution of α-lithiated diethyl sulfoxide in THF (45 mL), prepared from diethyl sulfoxide (**1**) (1.1 mL, 9.6 mmol) and *n*-BuLi (6.0 mL, 9.6 mmol). After 6 h of maintaining the cooling, the reaction was quenched with a saturated solution of ammonium chloride and extracted twice with methylene chloride. Solvents were evaporated and crude hydroxylamines were oxidized by copper(II) acetate monohydrate (0.02 g, 0.10 mmol) in methanol (50 mL) under air bubbling. Methanol was removed under vacuum, nitroxides **4** and **5** were purified by column chromatography, and the mixture of diastereomers was involved in alkoxyamine syntheses.

($S_SR_\beta R_\alpha/R_SS_\beta S_\alpha$) *N*-*tert*-Butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propylhydroxylamine, 3b,g. (835 mg, 33%). ^{1}H NMR (1:1 D_2O/C_3D_6O): δ 0.84 (s, (C**H**$_3$)$_3$CCH, 9H), 0.92 (s, (C**H**$_3$)$_3$CN, 9H), 1.14 (t, J = 7.2 Hz, C**H**$_3$CH$_2$SO, 3H), 1.31 (d, J = 7.2 Hz, C**H**$_3$CHSO, 3H), 2.68 (m, CH$_3$C**H**$_2$SO, 2H), 2.91 (s, (CH$_3$)$_3$CC**H**N, 1H), 3.23 (q, J = 7.2 Hz, CH$_3$C**H**SO, 1H).

($R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$) *N*-*tert*-Butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propylhydroxylamine, 3c,f. (835 mg, 33%). ^{1}H NMR (1:1 D_2O/C_3D_6O): δ 1.17 (s, (C**H**$_3$)$_3$CCH, 9H), 1.22 (s, (C**H**$_3$)$_3$CN, 9H), 1.45 (t, J = 7.2 Hz, C**H**$_3$CH$_2$SO, 3H), 1.52 (d, J = 7.2 Hz, C**H**$_3$CHSO, 3H), 2.71 (m, CH$_3$C**H**HSO, 1H), 3.19 (m, CH$_3$CH**H**SO, 1H), 3.60 (s, (CH$_3$)$_3$CC**H**N, 1H), 3.82 (q, J = 7.2 Hz, CH$_3$C**H**SO, 1H).

($S_SR_\beta R_\alpha/R_SS_\beta S_\alpha$) *N*-*tert*-Butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide, 4. Purification by column chromatography eluting with 1:9 cyclohexane/ethyl acetate mixture (R_f = 0.20, 800 mg, 48%). ESR (benzene): triplet, a_N = 14.7 G, g = 2.0061.

($R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$) *N*-*tert*-Butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide, 5. Purification by column chromatography eluting with 1:9 cyclohexane/ethyl acetate mixture (R_f = 0.26, 800 mg, 48%). ESR (benzene): triplet, a_N = 13.6 G, g = 2.0061.

General Procedure for the Preparation of Alkoxyamines Releasing 1-Phenylethyl Radical, 8,9. A degassed solution of a 1:1 mixture of nitroxides **4** and **5** (1.6 g, 6.1 mmol) and di-*tert*-butyl peroxalate (1.43 g, 6.1 mmol) [***Caution!*** *explosive when crystals are scratched!*] in ethylbenzene (15 mL) was stirred at 35 °C under argon during 4 h. Excess ethylbenzene was then removed under vacuum and the residue was chromatographed on silica gel eluting with a 7:3 cyclohexane/ethyl acetate mixture. After evaporation of the solvents, pure alkoxyamines, **8** and **9**, were obtained separately as pale yellow oils.

($S_SR_\beta R_\alpha/S_SS_\beta S_\alpha$) 2-Phenyl-2-(*N*-*tert*-butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide)ethane, 8. (R_f = 0.4, 852 mg, 38%). ^{1}H and ^{13}C NMR in ref 34.

($R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$) 2-Phenyl-2-(*N*-*tert*-butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide)ethane, 9. R_f = 0.6, 785 mg, 35%. ^{1}H NMR ($CDCl_3$): δ 0.76−1,03 (m, C**H**$_3$CH$_2$SO, 3H), 1.13 (s, (C**H**$_3$)$_3$CCH, 9H), 1.18 (s, (C**H**$_3$)$_3$CN, 9H), 1.21−1.43 (m, C**H**$_3$CHSO, 3H), 1.59 (d, C**H**$_3$CHO, 3H), 2.22−2.93 (m, CH$_3$C**H**$_2$SO, 2H), 3.15−3.66 (m, CH$_3$C**H**SO, (CH$_3$)$_3$CC**H**, 2H), 4.98 (dq, CH$_3$C**H**O, 1H), 7.09−7.37 (m, aromatics, 5H). ^{13}C NMR ($CDCl_3$): δ 8.9 (s, **C**H$_3$CH$_2$SO, 1C), 13.3−14.1 (2s, **C**H$_3$CHSO, 1C), 25.2 (s, (CH$_3$)$_3$**C**CH, 1C), 29.0−29.3 (2s, (**C**H$_3$)$_3$-CCH, 3C), 30.6−30.9 (2s, (**C**H$_3$)$_3$CN, 3C), 31.8−83.8 (2s, CH$_3$**C**HO, 1C), 36.8 (s,(CH$_3$)$_3$C**C**H, 1C), 45.7 (s, **C**H$_3$CHO, 1C), 57.8 (s, (CH$_3$)$_3$**C**N, 1C), 62.2 (s, CH$_3$**C**H$_2$SO, 1C), 72.1 (s, CH$_3$**C**HSO, 1C), 127.0 (s, *p*-aromatic, 1C), 127.5 (s, **C**CHO, 1C), 128.6 (s, *m*-aromatics, 2C), 128.9 (s, *o*-aromatics, 2C). Anal. Calcd for $C_{21}H_{37}NO_2S$: C, 68.61; H, 10.15; N, 3.81. Found: C, 68.27; H, 10.34; N, 3.74.

General Procedure for the Preparation of Alkoxyamines Releasing 1-(4-Methylbenzoate)ethyl Radical, 10,11. A degassed solution of a 1:1 mixture of nitroxides **4** and **5** (1.3 g, 5.0 mmol), 4-(ethyl) methyl benzoate (**7**) (2.4 g, 10 mmol), and di-*tert*-butyl peroxalate (1.2 g, 5.0 mmol) [***Caution!*** *explosive when crystals are scratched!*] in benzene (15 mL) was stirred at 35 °C under argon during 4 h. Excess benzene was then removed under vacuum and the residue was chromatographed on silica gel eluting with a 4:1 methylene chloride/ethyl acetate mixture. After evaporation of the solvents, pure alkoxyamines **8** and **9** were obtained separately as pale yellow oils.

($S_SR_\beta R_\alpha/R_SS_\beta S_\alpha$) 2-(4-Methyl carboxylate)phenyl-2-(*N*-*tert*-butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide)ethane, 10. R_f = 0.6, 700 mg, 33%. ^{1}H NMR ($CDCl_3$): δ 0.89, 1.11 (2s, (C**H**$_3$)$_3$CCH, 9H), 1.17, 1.23 (2s, (C**H**$_3$)$_3$CN, 9H), 1.02−1.61 (m, C**H**$_3$CH$_2$SO, C**H**$_3$CHSO, C**H**$_3$CHO, 9H), 2.30−3.11 (m, CH$_3$C**H**$_2$SO, 2H), 3.72−3.86 (m, CH$_3$C**H**SO, (CH$_3$)$_3$-CC**H**, 2H), 3.88 (s, OC**H**$_3$, 3H), 5.03 (dq, CH$_3$C**H**O, 1H), 7.35 (dd, *o*-aromatics, 2H), 7.99 (dd, *m*-aromatics, 2H). ^{13}C NMR ($CDCl_3$): δ 8.0 (s, **C**H$_3$CH$_2$SO, 1C), 12.7−13.5 (2s, CH$_3$**C**HSO, 1C), 22.7−25.8 (2s, (CH$_3$)$_3$C**C**H, 1C), 28.5−28.8 (2s, (**C**H$_3$)$_3$-CCH, 3C), 30.4−31.0 (2s, (**C**H$_3$)$_3$CN, 3C), 31.0−84.4 (2s, CH$_3$**C**HO, 1C), 36.0−36.3 (2s, (CH$_3$)$_3$**C**CH, 1C), 45.6 (s, **C**H$_3$-CHO, 1C), 57.4 (s, (CH$_3$)$_3$**C**N, 1C), 61.8 (s, CH$_3$**C**H$_2$SO, 1C), 62.3 (s, CH$_3$**C**HSO, 1C), 67.4 (s, O**C**H$_3$, 1C), 126.5, 126.9, 127.5,

128.4, 144.0, 146.6 (6s, aromatics, 6C), 186.4 (s, **C**$OOCH_3$, 1C). Anal. Calcd for $C_{23}H_{39}NO_4S$: C, 64.91; H, 9.24; N, 3.29. Found: C, 64.85; H, 9.40; N, 3.38.

($R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$) 2-(4-Methyl carboxylate)phenyl-2-(*N*-*tert*-butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl nitroxide)ethane, 11. R_f = 0.3, 620 mg, 29%. ^{1}H NMR ($CDCl_3$): δ 0.89, 1.12 (2s, (CH_3)$_3$CCH, 9H), 1.17, 1.25 (2s, (CH_3)$_3$CN, 9H), 1.08−1.57 (m, CH_3CH_2SO, CH_3CHSO, CH_3CHO, 9H), 2.31−3.07 (m, CH_3CH_2SO, 2H), 3.65−3.86 (m, CH_3CHSO, (CH_3)$_3$-CC**H**, 2H), 3.88 (s, OCH_3, 3H), 5.04 (dq, CH_3CHO, 1H), 7.36 (dd, *o*-aromatics, 2H), 7.97 (dd, *m*-aromatics, 2H).

Determination of the Rate Constants of Dissociation (k_d) by ESR Spectroscopy. Ethyl acetate solutions containing excess galvinoxyl (1.0×10^{-3} mol L^{-1}) and an alkoxyamine (macro)initiator **8**−**13** (0.2×10^{-3} mol L^{-1}) were degassed by freeze−pump−thaw cycles, placed under argon and heated at temperatures between 60 and 100 °C by a thermostated flux of nitrogen. The release of the persistent radical during the alkoxyamine dissociation was monitored by ESR spectroscopy by integration of the first peak of nitroxide **4** or **5** and calibration with a known TEMPO solution in benzene.

Typical Polymerization Experiment, 13. A solution of alkoxyamine **10** (55.0 mg, 0.15 mmol) in freshly distilled ethyl acrylate (18.5 g, 185 mmol) was distributed among 10 glass tubes. The contents were degassed by freeze−pump−thaw cycles, and the tubes were sealed off under vacuum, keeping one of them to follow the polymerization by ESR spectroscopy. One tube was heated to 90 °C during 8 h, and after cooling, the polymerization medium was dissolved in THF. After evaporation of excess monomer and solvent, the polymer was freeze-dried twice in benzene. Conversion was evaluated gravimetrically, molecular weight and polydispersity index were determined by SEC (yield = 74.0%, M_n = 39 400 g mol^{-1}, PDI = 1.22).

Supporting Information Available: Tables of X-ray experimental data, positional parameters, general displacement parameters, bond distances, and bond angles for $S_SR_\beta R_\alpha$/$R_SS_\beta S_\alpha$ and $R_SR_\beta R_\alpha/S_SS_\beta S_\alpha$ β-sulfinyl hydroxylamines. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting

This article was released ASAP on 2/11/2004. Due to a production error, Scheme 2 was incorrect. The correct version was posted on 2/18/2004.

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