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SG1 Nitroxide Analogues: a Comparative Study

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Due to a specific balance between steric, polar, and stabilization effects, SG1 nitroxide and its corresponding alkoxyamine BlocBuilder MA are now well recognized as two of the most potent compounds in nitroxide-mediated polymerization (NMP). In this work, alternatives to SG1, based on various aldehydes, were targeted using structure–reactivity relationships already developed by our group. Compared with SG1, we show that the substitution of the *tert*-butyl group on the carbon α to the aminoxyl function by a 2-ethylhexyl group led to a new nitroxide (ETHEXNO), which exhibited an half-life time at 120°C similar to SG1 and a slightly slower k_d for the alkoxyamine (2–3 times lower than the SG1). The styrene polymerization mediated by the ETHEXNO nitroxide has a similar behaviour to the one mediated by the SG1 in terms of livingness and control but the kinetics is affected (2–3 times lower). Concerning the *n*-butyl acrylate polymerization, an unexpected overheating occurred at 120°C, which led us to perform the polymerization in toluene at 100°C. The slow kinetics impedes the use of this nitroxide as a good alternative to SG1 and shows that the structure of the SG1 nitroxide is already delicately optimized and finding good alternatives is not straightforward.

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Introduction

With the development of living and/or controlled radical polymerization (CRP) techniques,[1] such as nitroxide mediated polymerization (NMP),[2–5] atom transfer radical polymerization (ATRP),[6–9] and reversible addition–fragmentation chain transfer (RAFT),[10–13] the control of the structure and architecture of vinyl polymers that exhibit specific properties is now possible in many cases. NMP has received great interest since the pioneering work of Rizzardo and coworkers,[4] and the subsequent development of this technique by Georges et al.[2] has shown that well controlled and living polystyrene can be prepared using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) radical. This nitroxide and its derivatives are successfully applied for the controlled polymerization of styrenic monomers at 120°C or higher. However, the main drawback of TEMPO-mediated polymerization lies in the difficulty to control the acrylate derivatives.[3] A new generation of acyclic nitroxides (among them the *N*-*tert*-butyl-2-methyl-1-phenylpropyl nitroxide[14] (TIPNO) and *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1)[15,16]) bearing a β-hydrogen was subsequently designed to overcome this difficulty.

Over the past decade, Arkema in collaboration with our group has developed a complete controlled polymer technology, which derives from a basic alkoxyamine trademarked as BlocBuilder MA based on the SG1 nitroxide.[17–19] This technology enables the design of polymers with very different architectures and compositions such as block copolymers, functionalized macromolecules, graft copolymers, gradient copolymers, hybrid organic and/or inorganic systems, star polymers, polymer brushes, etc. The enormous commercial potential of this simplistic chemistry could be used in various markets including encapsulation and release of active compounds, oil and lubricant additives, dispersion stabilizers (cosmetics, inks, paints, and mineral content), the modification of surface properties (e.g., adhesives and coatings), the modification of mass properties (e.g., impact strength and improvement of optical qualities), microelectronics, compatibilization, composites, etc.[18]

Despite the significant progress made in the synthesis of the BlocBuilder MA (Scheme 1),[20] the understanding of its radical reactivity,[21] its post-polymerization end-group removal,[22] and its use in complex macromolecular architecture synthesis,[23] one of our main interests is to improve its technology in terms of fundamental knowledge related to the efficiency of this compound.

This has led us to investigate the synthesis of new SG1-like nitroxides and their corresponding alkoxyamines using various aldehyde reactants that exhibit different steric properties and polarity compared to the pivaldehyde used in the SG1 synthesis. The choice of aldehyde is dictated using different structure–reactivity relationships already established by our group for the determination of the dissociation and recombination rate constants k_d and k_c, respectively. These rate constants are known to be the key parameters in NMP.[24,25] Once the nitroxides and the alkoxyamines have been synthesized, they are tested in the bulk polymerization of styrene and *n*-butyl acrylate and their efficiency compared with the reference SG1 nitroxide and BlocBuilder MA alkoxyamine.

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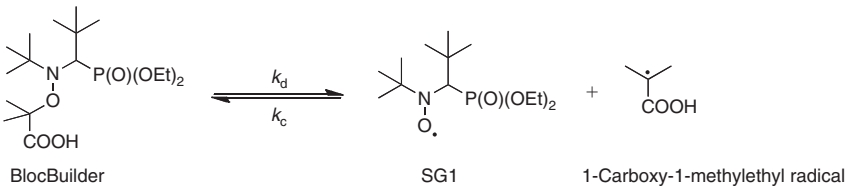


Scheme 1. Decomposition of the BlocBuilder MA alkoxyamine.

Results and Discussion

Design of New Nitroxides and Alkoxyamines

The main equilibrium between dormant and active species is the key step in the NMP process. If the equilibrium constant $K = k_d/k_c$ (with k_d the dissociation rate constant and k_c the recombination rate constant) is too high, the nitroxide acts only as a spectator and the macroradical concentration is close to the classical steady-state value. If the K value is too low, the polymerization is inhibited.[24,25] The needs of estimated values of k_d for designing new polymerization experiments led our group to develop a structure–reactivity relationship based on the 1-phenyl-ethyl alkyl radical and various nitroxides. Marque et al.[26,27] developed a linear multiparameter relationship based on the polar Hammett constant σ_L and on the Taft-type steric constant E_s to take into account the two main parameters, that is the polarity and the bulkiness of the two alkyl groups attached to the aminoxyl function. For non-cyclic nitroxides, steric hindrance around the nitroxide moiety is too high. As such, the molecule adopts a new conformation to relieve the steric strain and, therefore, the steric effect cannot be determined as the sum of the Taft-type steric constant E_s of the two alkyl groups attached to the aminoxyl function. A levelled steric effect should then be used.[28] The equations used to estimate the k_d value are summarized below:

$$\log k_d\ [s^{-1}] = -5.88(\pm 0.16) - 3.07(\pm 0.28) \times \sigma_L - 0.88(\pm 0.04) \times E_S \quad (1)$$

with $\sigma_L = \sum_{i=1}^{6} \sigma_L(R_i)$ and $\sigma_L(R_i)$ the Hammett constant σ_L of the six groups linked to the two carbons adjacent to the aminoxyl function and

$$E_S = -2.104 + 3.429 \times r_1 + 1.978 \times r_2 + 0.649 \times r_3 \quad (2)$$

with r_i the individual steric constant of the $C(R_1)(R_2)(R_3)$ group bearing by the nitrogen and which is the part carrying the hydrogen atom in the β position and/or the largest group. It has to be mentioned that the larger the R_i group, the smaller r_i, thus r_1 corresponds to the small size group, r_2 to the medium size group, and r_3 to the large size group.

The dissociation rate constant values could lie in the range of 10 and 10^{-10} s^{-1} between 20 and 120°C, and then is really the main parameter to be tuned.[29] Nevertheless, the recombination rate constant k_c, whose value could only vary between 10^5 and 10^8 $L\,mol^{-1}\,s^{-1}$ over the same temperature range,[30,31] could also lead to drastically different behaviours for the control and the livingness of the polymerization.[32] The estimation of the k_c value by such structure–reactivity relationships should then bring more insight. This study was also performed by Marque and coworkers,[27,33,34] who determine Eqn 3[29] that links the k_c value between styryl radicals and the molecular descriptors σ_L and $E_{S,tot}$ for different nitroxides.

Table 1. Electrical Hammett constants σ_i and modified Taft steric constants r_i used in Eqns 1–3

R	σ_i	r_i
Me	−0.01	0
*t*Bu	−0.01	−2.46
H	0	0.32
$P(O)(OEt)_2$	0.32	−1.22
CCl_3	0.36	−2.98
*i*Pr	0.01	−1.08
2-Ethylhexyl	0.01	−1.4

$$\log k_c\ [M^{-1}\,s^{-1}] = 10.35(\pm 0.11) + 0.47(\pm 0.17) \times \sigma_L + 0.43(\pm 0.02) \times E_{S,tot} \quad (3)$$

with $E_{S,tot}$ the total steric constant taking into account the two groups attached to the nitrogen. In that calculation, only the four α,α′ substituents that flank the aminoxyl function have to be taken into account for the steric demand. One methyl of the *tert*-butyl group attached to the nitrogen and the β-hydrogen are located in the same plane as the aminoxyl function and does not interfere in the recombination.

The equations described above were then used to determine the k_d and k_c values of different nitroxides bearing a R_1 group incorporated from several aldehyde reactants (Tables 1 and 2). These parameters were compared with the reference SG1 (Table 2).

Among the various aldehydes, isobutyraldehyde, 2,2,2-trichloracetaldehyde or chloral, and 2-ethylhexanal were found to be an interesting alternative to pivalaldehyde. These aldehydes are commercially available and give similar k_d and k_c values. The nitroxide based on chloral has a similar steric hindrance but a strongly different polarity, whereas the opposite occurs with both isobutyraldehyde and 2-ethylhexanal.

To compare theoretically the behaviour of all these nitroxides, we used the phase diagram approach developed by Fischer.[24,35,36] The double logarithmic plot of k_d versus k_c is depicted in Fig. 1. This diagram does not take into account the penultimate effect,[31] which is known to decrease generally the k_c value by one order of magnitude.

The close theoretical k_c and k_d values for the four nitroxides (the points have a close localization in the phase diagram) shows that their efficiency in the NMP of styrene, and hopefully of *n*-butyl acrylate, should be similar.

Synthesis of New Nitroxides and Alkoxyamines

The β-phosphorylated nitroxides were prepared as previously described[16,37] and the synthetic route is shown in Scheme 2.

Table 2. Total electrical Hammett constants σ_L and modified Taft steric constants E_S and E'_S used for the calculation of the dissociation and recombination rate constants k_d and k_c, respectively

Nitroxide	σ_L	E_S	Theoretical k_d (120°C) [s^{-1}]	E'_S	Theoretical k_c [$M^{-1}\,s^{-1}$]
3a (SG1)	0.28	−5.016	4.7×10^{-3}	−7.476	8.9×10^{6}
3b (*i*Pr-SG1)	0.3	−3.935	4.6×10^{-4}	−6.395	2.6×10^{7}
3c (Chloral-SG1)	0.65	−5.354	6.8×10^{-4}	−7.814	9.5×10^{6}
3d (ETHEXNO)	0.3	−4.329	1.0×10^{-3}	−6.788	1.8×10^{7}

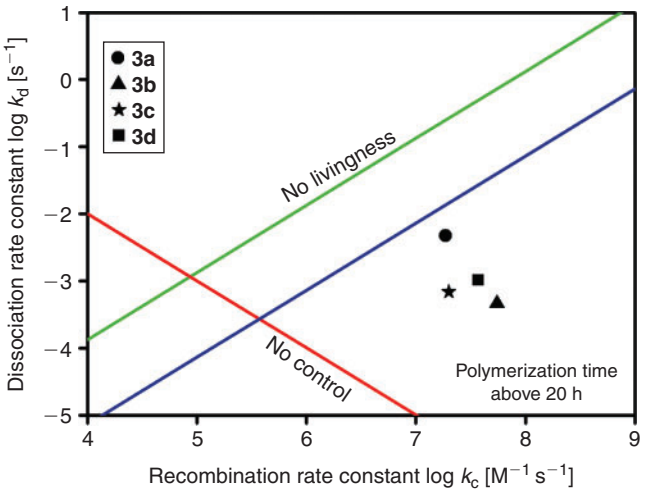


Fig. 1. Phase diagram for a the styrene polymerization at 120°C ($k_p = 2050\,M^{-1}\,s^{-1}$; $k_t = 1.5 \times 10^8\,M^{-1}\,s^{-1}$; $[Alkoxyamine]_0 = 0.05\,M$; Limit criteria $\Phi_{lim} = 0.3$, $\delta_{lim} = 0.3$, and $t_{90} = 20\,h$).

First the imines **1b**–**d** were prepared from *tert*-butylamine and the desired aldehyde by reductive condensation in one high-yielding step. In situ addition of diethyl phosphate, followed by boron trifluoride etherate, catalyzed the reaction under ambient atmosphere to give the corresponding aminophosphonate **2b**–**d**. The aminophosphonates were then oxidized in the presence of *meta*-chloroperbenzoic acid (mCPBA) to synthesize the desired nitroxides **3b**–**d**.

The nitroxide *N*-*tert*-butyl-*N*-[2-ethyl-(1-diethoxyphosphoryl) hexyl] nitroxide **3d** or ETHEXNO was obtained as an orange oil with 60% overall yield after purification. Unlike this nitroxide, the nitroxide *N*-*tert*-butyl-*N*-[1-(diethoxyphosphoryl)-2-methyl-propyl] nitroxide **3b** or *i*Pr-SG1 and the nitroxide *N*-*tert*-butyl-*N*-[1-(diethoxyphosphoryl)-2,2,2-trichloroethyl] nitroxide **3c** or Chloral-SG1 were obtained with low (20%) and very low (<5%) yield, respectively. A deeper investigation of the synthesis of nitroxide **3b** led to the conclusion that this nitroxide is suroxidized to the unstable *N*-oxo-ammonium derivative. Concerning the Chloral-SG1 **3c**, the presence of two electron-withdrawing groups on the same carbon α to the nitrogen atom drastically decreases the nucleophilicity of the N atom and probably reduces its ability to react readily with peroxides or other oxidizing agents.

To evaluate the possibilities offered by the ETHEXNO nitroxide, we prepared two different alkoxyamines. First we synthesized one with a phenyl-ethyl alkyl moiety to mimic the polystyrene chain end and to determine the kinetic rate constants used in the propagation step. Second we prepared one with a 1-carboxy-1-methylethyl alkyl moiety to obtain a highly labile alkoxyamine[38] and for comparison with BlocBuilder MA. The ETHEXNO-based alkoxyamines have been synthesized using the atom transfer radical addition method developed by Matyjaszewski et al.[39] In this method, the radical $R^{\bullet}$ is generated by copper(I) reduction of the corresponding organic halide RX. Thus, alkoxyamines arise from the recombination of the nitroxide with this alkyl radical (Scheme 3).

All the alkoxyamines were obtained as mixtures of diastereoisomers and were not separated since their reactivities are similar (see below). The alkoxyamine **4a** was obtained as an oil in 40% yield. The alkoxyamine **4b** was precipitated in pentane and was obtained in 65% yield as a white powder.

Electron Paramagnetic Resonance (EPR) Studies

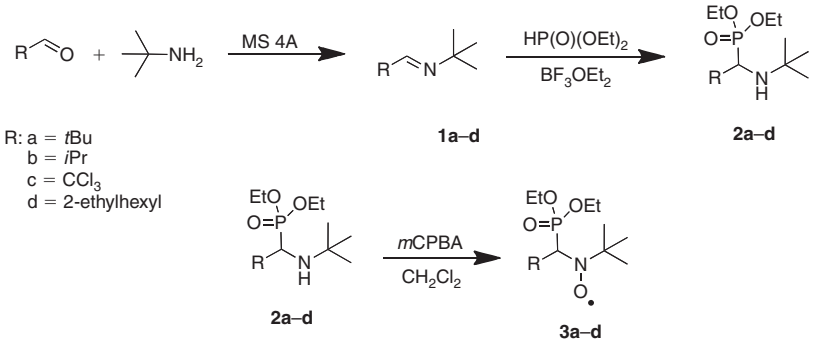
The nitroxides were studied by EPR and the hyperfine splitting coupling constants are summarized in Table 3.

The hyperfine splitting coupling constants for the phosphorous and nitrogen atom of nitroxides **3b** (*i*Pr-SG1) and **3d** (ETHEXNO) are very close to the one of nitroxide **3a** or SG1 ($a_P = 46.2$ G, $a_N = 13.6$ G). The hyperfine splitting coupling constants of the nitroxide **3c** or Chloral-SG1 are more dissimilar ($a_P = 34.4$ G, $a_N = 12.5$ G) since the high electron-withdrawing group trichloromethyl induced a change in the electronic density of the aminoxyl part.

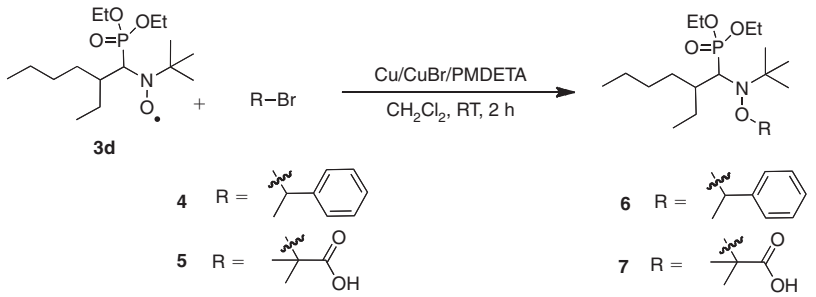
Concerning the nitroxide **3b**, a hyperfine splitting coupling constant to the β-hydrogen atom was resolved. This means that the dihedral angle between the planes N–C_α–H_β and C_α–N–$2p_z$ is less close to 90° compared with SG1. Nitroxides bearing hydrogen atoms on the carbon adjacent to the aminoxyl function usually decay through a bimolecular process to yield a nitrone and a hydroxylamine. Because of its specific conformation, the β-hydrogen of the SG1 is eclipsed by the bulky *tert*-butyl alkyl group. This conformation explains its stability, and prevents the disproportionation of the SG1. In the case of nitroxide **3b**, the difference in steric strain leads to a higher instability and prevents its use in NMP. The nitroxide **3d** (ETHEXNO) was found to be the nitroxide most similar to SG1.

The thermal stability of the ETHEXNO nitroxide was determined by monitoring the intensity of its EPR spectrum as a function of time at a given temperature (i.e., 120°C). This stability was similar or even better than that of SG1 since the half-life time at 120°C under argon atmosphere was found to be 19 h (15 h for SG1) and 21 h under aerated conditions (20 h for SG1).

The experimental rate constants k_d were measured using either the plateau of the increasing ESR nitroxide signal or the decay of the ^{31}P NMR signal, in the presence of phenylhydrazine as an alkyl radical scavenger. The advantage to perform the measurement by ^{31}P NMR is that the dissociation rate constants of different diastereoisomers could be determined separately.[40] For each alkoxyamine three runs were carried out in *tert*-butylbenzene as solvent. The average k_d value and the



Scheme 2. Synthesis of β-phosphorylated nitroxides.



Scheme 3. Synthesis of β-phosphorylated nitroxide-based alkoxyamines.

Table 3. Hyperfine splitting coupling constants of the different nitroxides in *tert*-butylbenzene (5×10^{-4} M)

Nitroxide	Hyperfine splitting coupling constants
3a (SG1)	a_N 13.6 G, a_P 46.2 G
3b (*i*Pr-SG1)	a_N 13.9 G, a_P 49.6 G, a_H 1.2 G
3c (Chloral-SG1)	a_N 12.5 G, a_P 34.4 G
3d (ETHEXNO)	a_N 13.8 G, a_P 46.8 G

Table 4. Dissociation rate constant k_d and activation energy E_a for the TIPNO, SG1, and ETHEXNO based alkoxyamines

Alkoxyamine	k_d (120°C) [s^{-1}]	E_a [kJ mol^{-1}]
Styryl-SG1	5.5×10^{-3} [41]	124.5[41]
6	1.3×10^{-3}	129.9
BlocBuilder MA	0.3[38]	111.7[38]
7	8.5×10^{-2}	116.2
Styryl-TIPNO	3.3×10^{-3} [43]	129.6[43]

activation energy are reported in Table 4. The activation energy E_a was estimated using $A = 2.4 \times 10^{14}$ s^{-1}. The estimated E_a value given in Table 4 corresponds to E_a averaged over the investigated temperature range. Individual values differed by less than 2 kJ mol^{-1} from the average value presented in Table 4.

The activation energies for the alkoxyamines **4a** and **4b** are 129.9 and 116.2 kJ mol^{-1}, respectively. In both cases the different diastereoisomers have the same decomposition kinetics. This is similar to the case of the styryl-SG1 alkoxyamine[41] and different from the alkoxyamines developed by Catala and coworkers.[42] These values are quite similar to the ones determined theoretically (see Table 3) and, therefore, validate the structure–reactivity relationships already developed. The comparison of these values with the literature data show that they are quite similar to those of the TIPNO nitroxide[43] (Table 4) and lower than those of SG1. This is attributable to a slower steric hindrance induced by the 2-ethyl-hexyl group compared with the *tert*-butyl group. Nevertheless the decomposition kinetics similar to the TIPNO nitroxide[43] let us consider a good efficiency for the ETHEXNO as a control agent in NMP.

Styrene and n*-Butyl Acrylate Polymerization*

The styrene polymerizations were carried out in bulk at 120°C. To compare the behaviour of the nitroxide **3d** (ETHEXNO) and SG1, the alkoxyamines bearing either the 1-phenylethyl group or the 1-carboxy-1-methylethyl moiety were used. In all cases, a linear or a quasi linear increase of the $\ln [M]_0/[M]$ was observed (Fig. 2a) even if the kinetics for the alkoxyamines bearing the ETHEXNO nitroxide were close to two times slower than the ones obtained with the SG1-based alkoxyamines. We have already shown that for the BlocBuilder MA alkoxyamine and for the styryl-SG1 alkoxyamine the kinetics do not follow a $t^{2/3}$ law as the acrylate-based SG1 alkoxyamines but a first order kinetics because of the important release of nitroxide during the quick establishment of the persistent radical effect.[38] It is the reason why we plot $\ln [M]_0/[M]$ versus time on Fig. 2. A closer look of the kinetics ($\ln(\ln([M]_0/[M]) = f(\ln t))$) of the polymerization initiated with alkoxyamines **6** and **7** showed that polymerization initiated by **7** followed first order kinetics and the one initiated by **6** a $t^{2/3}$ law. The dissociation rate constant of **6** is low enough to obtain a slow establishment of the PRE as already observed with the Monams alkoxyamine in ref. [38]. The tertiary 1-carboxy-1-methylethyl radical in the case of alkoxyamine **7** increases the rate of dissociation and this compound behaves

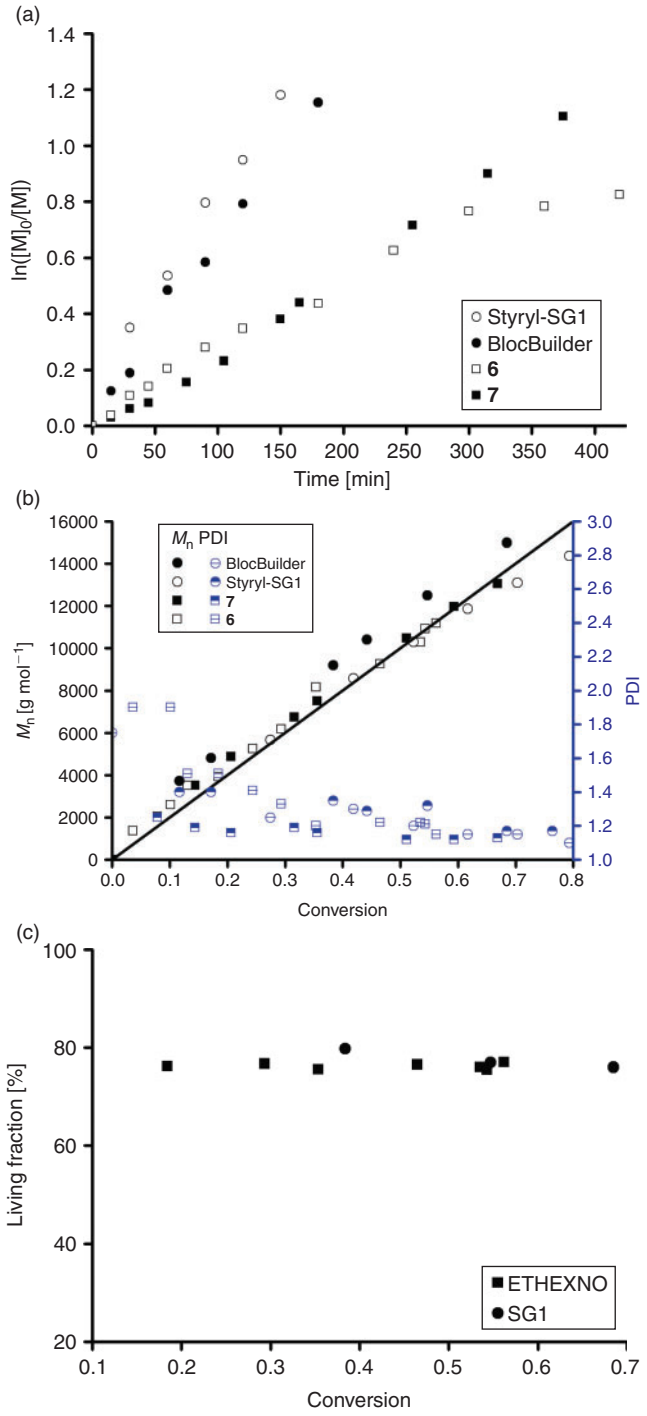


Fig. 2. (a) Experimental kinetic plot of $\ln([M]_0/[M])$ versus time for styrene bulk polymerization at 120°C initiated with various alkoxyamines attached to the SG1 and ETHEXNO nitroxide. (b) Evolution of number-average molar mass (M_n, full symbols) and polydispersity index (PDI, empty symbols) versus conversion for bulk styrene polymerization at 120°C initiated with various alkoxyamines (targeted M_n at 100% conversion = 20000 g mol^{-1}). The solid line corresponds to the theoretical M_n. (c) Evolution of the living fraction versus conversion for the bulk styrene polymerization initiated by the BlocBuilder MA and alkoxyamine **7**.

like highly labile SG1-based alkoxyamines as already observed for the Blocbuilder MA alkoxyamine.[38]

As the kinetic plot of the polymerization initiated by **6** is linear versus $t^{1/3}$, thus exhibiting the typical behaviour attributable to the persistent radical effect, this enabled us to determine the $K = k_d/k_c$ value (1.0×10^{-9} M^{-1}). Using this value and considering no chain length effect for k_d (k_d for a macromolecular species is equal to that for the 1-phenyl-ethyl moiety) the experimental k_c value could be evaluated for the macromolecular species. This value is equal to 1.3×10^6 M^{-1} s^{-1} at 120°C, which is two- to three-fold higher value than that for the SG1 nitroxide. This value is also in good agreement with the theoretical one (see Table 2), with a ratio of k_c between ETHEXNO and SG1 of two.

Concerning the evolution of the number-average molecular weight (M_n) versus conversion, for the four alkoxyamines the experimental and theoretical M_n are in good agreement (Fig. 2b) and the obtained PDI are low (<1.2 after 40% conversion). The livingness of the polymers was also checked since this characteristic is of paramount importance to prepare block copolymers essential for the preparation of nanostructured materials and telechelic polymers. The living fraction was determined by ESR as already performed in ref. [38]. Typically a 10^{-4} M solution of the polymer in *tert*-butylbenzene was heated at 120°C for 2 h in the presence of an alkyl radical scavenger and the amount of released radical was determined by comparison with nitroxide standards. For each experiment, the livingness was unambiguously above 70% and the evolution of the living fraction versus conversion is similar for the ETHEXNO and the SG1 nitroxide (Fig. 2c).

All these results show that the control and livingness of the styrene polymerization mediated by the ETHEXNO nitroxide are similar to the ones obtained with the SG1 but the kinetics are affected (2–3 times lower). This prompted us to evaluate the potential of this nitroxide to control the polymerization of *n*-butyl acrylate. Indeed these all-acrylic copolymers are of wide interest since they behave as new tough thermoplastic materials.[18]

The direct extrapolation of the experimental procedure (bulk, 120°C) developed for the BlocBuilder MA alkoxyamine to the new alkoxyamine **7** led to overheating during the polymerization process and this induced a non-controlled polymerization even if preliminary tests showed that the obtained polymer was living. In order to avoid this overheating, the reaction temperature was decreased to 100°C and the polymerization was also performed in 50 wt-% toluene. Under these conditions the kinetics is controlled, the evolution of M_n versus conversion is linear and close to the theoretical M_n and the livingness of the polymer is similar to the one obtained with SG1 (Fig. 3). Nevertheless the time needed to reach 60% of conversion is close to 13 h and the PDIs are higher than those obtained with the SG1 nitroxide (1.4 instead of 1.2). Work is in progress to understand this unusual behaviour. This result highlights again the dramatic influence of the steric hindrance in the quality of control and livingness for the NMP of acrylate derivatives.

Conclusions

Alternatives to the SG1nitroxide based on various aldehydes were considered using structure–reactivity relationships to select the most appropriate candidates. The substitution of the *tert*-butyl group on the carbon α to the aminoxyl function by a 2-ethylhexyl group led to a new nitroxide (ETHEXNO) with a close conformation as evidenced by ESR. The synthesis of both the nitroxide and the corresponding alkoxyamines were performed using the procedure already described for the SG1 and the compounds were obtained in good yields. The dissociation rate constant k_d for ETHEXNO-based alkoxyamine was

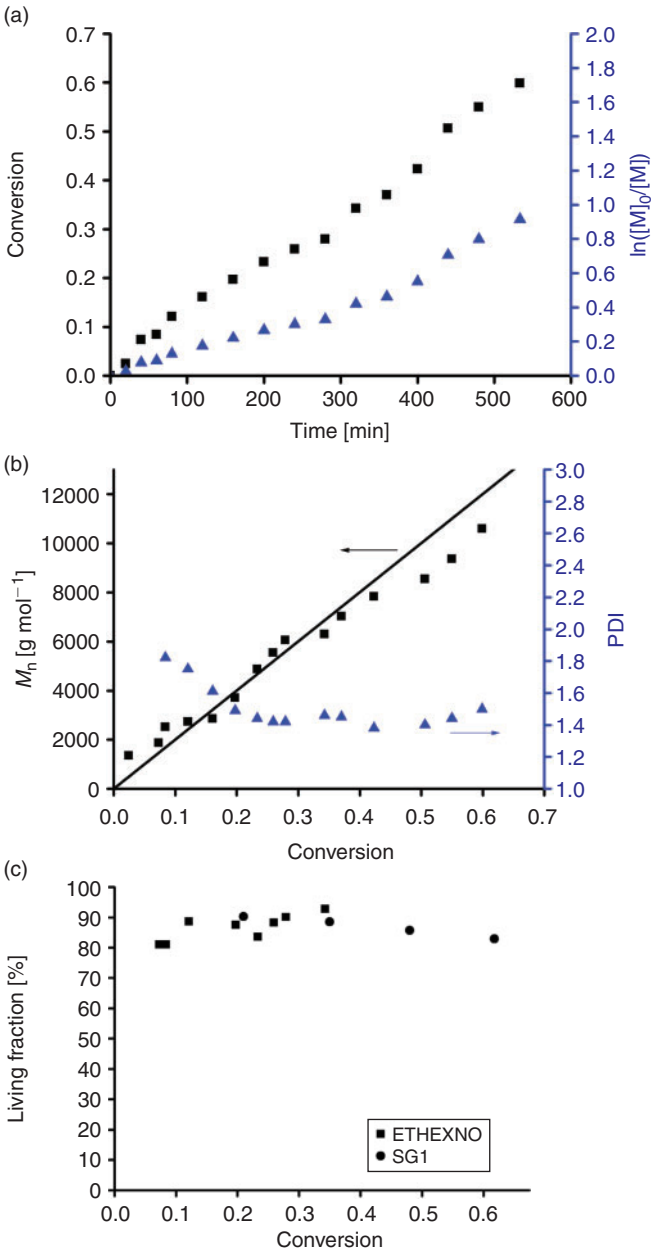


Fig. 3. (a) Experimental kinetic plot conversion and $\ln([M]_0/[M])$ versus time for the *n*-butyl acrylate polymerization (toluene 50 wt-%) at 100°C initiated with alkoxyamine **7**. (b) Evolution of number-average molar mass (M_n, square symbols) and polydispersity index (PDI, diamond symbols) versus conversion for the *n*-butyl acrylate polymerization (toluene 50 wt-%) at 100°C initiated with alkoxyamine **7** (targeted M_n at 100% conversion = 20000 g mol^{-1}). The solid line corresponds to the theoretical M_n. (c) Evolution of the living fraction versus conversion for the *n*-butyl acrylate polymerization (toluene 50 wt-%) at 100°C initiated with alkoxyamine **7**.

determined and was found to be between two and three times lower than the SG1 analogue.

The styrene polymerization mediated by the ETHEXNO nitroxide has a similar behaviour to that mediated by SG1 in terms of livingness and control but the kinetics is affected (2–3 times lower). Concerning the *n*-butyl acrylate polymerization, an unexpected overheating occurred using the common experimental procedure (bulk, 120°C), which led us to perform the polymerization in toluene at 100°C. In that case the behaviour is similar to that mediated by SG1 in terms of livingness but the control (PDI close to 1.4) is lower and above all the kinetics is strongly affected (60% conversion in 13 h). This impedes the use of this nitroxide as a good alternative to SG1. This study also highlights that the structure of the SG1 nitroxide is already a delicate compromise and it is very difficult to find other stable and efficient nitroxides to control the polymerization of styrenic and acrylic derivatives.

Experimental

Materials

All reagents were purchased from Aldrich at the highest purity level available and used without further purification unless otherwise stated. The SG1 nitroxide and the BlocBuilder MA alkoxyamine were kindly provided by Arkema. Silica gel for column chromatography was Merck silica gel 60. All reactions were monitored by analytical TLC plates and analyzed with 254 nm UV light and/or phosphomolybdic acid solution.

Analytical Techniques

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker AC-300 spectrometer using 5 mm o.d. tubes. Conversion was determined by ^{1}H NMR spectroscopy. Mass spectrometry was performed on a 3200 QTrap machine (Applied Biosystems Sciex) equipped with an atmospheric ionization source. The M_n and PDI of the samples were determined by size exclusion chromatography using a Waters 515 HPLC pump equipped with three Styragel columns (HR 3 (4.6 mm × 300 mm, separation between 500 and 30000 g mol^{-1}), HR 4 (4.6 mm × 300 mm, separation between 5000 and 600000 g mol^{-1}), and HR 5 (4.6 mm × 300 mm, separation between 2000 and 4×10^6 g mol^{-1})), and two detectors: UV/visible (Waters 486) and RI (Waters 2414). Measurements were performed in tetrahydrofuran (THF) at room temperature, with a flow rate of 1 mL min^{-1}. Calibration was based on polystyrene standards (kit EasyCal Polymer Laboratories, M_n = 1180 to 377400 g mol^{-1}). Data acquisition and processing were performed with Millenium 32 Waters software. ESR experiments were carried out on a Bruker EMX 300 spectrometer.

N-*(2-Methylpropan)-2-trichloromethyl-1-imine* ***1c***

Trichloroacetaldehyde (0.04 mol), was diluted with 10 volumes of ether and cooled to 0°C. *Tert*-butylamine (0.12 mol) was combined and titanium chloride (0.022 mol) was slowly added. The reaction mixture was strongly stirred for 2 h at room temperature. The mixture was washed with 150 mL of NaOH solution (0.75 M). The aqueous phase was extracted three times with ether and the combined organic layers were dried over magnesium sulfate. The solvent was removed under pressure to afford a yellow oil (5.7 g, 70%). δ_H 1.32 (s, 9H, C–CH_3), 7.67 (d, 1H, CH=N). δ_C 29.5 (3C, C(**C**H$_3$)$_3$), 58.1 (C–N), 95.9 (C–Cl$_3$), 152.4 (C=N).

N-*(2-Methylpropan)-2-ethylhexyl-1-imine* ***1d***

2-Ethylhexanal (0.122 mol) was cooled at 0°C in the presence of 4 Å molecular sieve (5 g). *Tert*-butylamine (0.134 mol) was then added and the reaction mixture was stirred for 4 h at room temperature. It was then filtered and residual *tert*-butylamine was removed under reduced pressure to give a colourless oil (21.7 g, 86%). δ_H 0.85 (m, 6H, CH_3CH$_2$), 1.15 (s, 9H, C–CH$_3$), 1.20–1.55 (m, 8H, CH$_2$), 2.11 (m, 1H, CH), 7.25 (d, 1H, CH=N). δ_H 11.9 (**C**H$_3$CH$_2$), 14.3 (**C**H$_3$–CH$_2$–CH$_2$), 23.1

(CH_3–**C**H_2–CH_2), 26.1 (CH_2–**C**H_2–CH_2), 29.7 (CH_3–**C**H_2–CH), 30.1 (3 × **C**H_3–C), 32.6 (CH_2–CH_2–**C**H_2), 47.4 (CH), 56.9 (C), 163.4 (CH=N).

*Diethyl [1-(*tert-*Butylamino)-2-methylpropyl] Phosphonate* ***2b***

In a two necked round-bottom flask, isobutyraldehyde (0.5 mol) was cooled to 10°C under nitrogen. *Tert*-butylamine (0.5 mol) was added dropwise and after addition the mixture was heated at 35°C for 2 h. Water was removed from the flask and 4 Å molecular sieves were added to the solution. Diethyl phosphate (0.75 mol) was then added and the mixture was heated at 40°C for 17 h. The mixture was then diluted with dichloromethane and filtered over celite. The solution was acidified to pH 3 with dilute chlorhydric acid (5% v/v) and extracted five times with dichloromethane. The aqueous phase was treated with a saturated $NaHCO_3$ solution to pH 8 and residual aminophosphonate was extracted two times with dichloromethane. The solution was dried over magnesium sulfate and the solvent removed under pressure to give a colourless oil (79.8 g, 60%). δ_P 29.9. δ_H 0.90 (t, 3H, $J_{H–H}$ 6.9, O–CH_2–CH_3), 0.91 (t, 3H, $J_{H–H}$ 6.8, O–CH_2–CH_3), 0.98 (s, 9H, C–CH_3), 1.20 (t, 3H, $J_{H–H}$ 7.1, O–CH_2–CH_3), 1.21 (t, 3H, $J_{H–H}$ 7.1, O–CH_2–CH_3), 1.96 (m, 1H), 2.80 (dd, 1H, $J_{H–P}$19.3, $J_{H–H}$ 2.9), 3.95–4.08 (m, 4H). δ_C 16.5 (d, 2C, $J_{C–P}$ 5.6, 2C, **C**$H_3$$CH_2$), 18.8 (s, 1C, **C**$H_3$CH), 19.6 (d, 1C, $J_{C–P}$ 11.2, **C**H_3CH), 30.3 (s, 3C, **C**H_3C), 31.6 (d, 1C, $J_{C–P}$ 6.4, CH_3**C**H), 50.9 (d, 1C, $J_{C–P}$ 5.9, CH_3**C**), 54.7 (d, 1C, $J_{C–P}$ 146.3, **C**H–P), 61.4 (d, 1C, $J_{C–P}$ 7.5, **C**H_2), 62.0 (d, 1C, $J_{C–P}$7.5, **C**H_2).

*Diethyl [1-(*tert-*Butylamino)-2-trichloroethyl] Phosphonate* ***2c***

Imine **1c** (0.015 mol) and diethyl phosphate (0.015 mol) were cooled at 0°C. BF_3·OEt (0.0015 mol) was added. Formation of the aminophosphonate was monitoring by TLC. Themixture was then diluted with dichloromethane and filtered over celite. The solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a white powder (5.1 g, 70%). δ_P 21.70. δ_H 1.23 (s, 9H, C–CH_3), 1.38–1.40 (t, 6H, $J_{H–H}$ 7.1, 2 × CH_3–CH_2–O), 2.35 (d, 1H, $J_{H–P}$ 19, C*H*), 4.10–4.30 (m, 4H, $J_{H–H}$ 7.1, 2 × CH_3–CH_2–O). δ_C 16.6 (d, $J_{C–P}$ 9, 2C, **C**H_3–CH_2–O), 30.7 (d, $J_{C–P}$ 40, 3C, C(**C**H_3)$_3$), 52.3 (CH_3–**C**–N), 62.8 (d, $J_{C–P}$ 9, P–**C**H–N), 63.8 (d, $J_{C–P}$ 9, 2C, CH_3–**C**H_2–O), 70.1 (Cl_3**C**).

*Diethyl [1-(*tert-*Butylamino)-2-ethylhexy] Phosphonate* ***2d***

Imine **1d** (0.054 mol) and diethyl phosphate (0.070 mol) were cooled at 0°C. BF_3·OEt (0.005 mol) was then added. The reaction mixture was stirred for an hour at room temperature. It was then filtered, dissolved in ether, and the residue was washed two times with 150 mL of 5% HCl in water. The solution was extracted three times with ether. Na_2CO_3 was added to the combined organic layers to give a basic solution (pH = 8). The solution was then extracted three times with ether. The organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure to give a colourless oil (16.5 g, 94%). δ_H 0.85–1.00 (m, 6H, C$H_3$$CH_2$), 1.15 (s, 9H, C–C$H_3$), 1.28–1.40 (t + m, 12H, $J_{H–H}$ 7.1, 2 × CH_3–CH_2–O + 3 × CH_2), 1.5–1.65 (m, 3H, 1 × CH_2 + 1 × CH), 3.15 (d, 1H, $J_{H–H}$ 19.6, CH), 4.05–4.25 (m, 4H, 2 × CH_3–CH_2–O). δ_C 12.6 (**C**$H_3$$CH_2$), 13.0 (**C**$H_3$$CH_2$$CH_2$), 22.8–23.1 ($CH_3$**C**$H_2$$CH_2$), 23.2–23.3 ($CH_2$**C**$H_2$$CH_2$), 29.8–29.9 ($CH_2$$CH_2$**C**$H_2$), 30.5–30.6 ($CH_3$**C**$H_2$CH), 30.3 (3 × **C**$H_3$C), 32.6 ($CH_2$$CH_2$**C**$H_2$), 44.6–45.1 (**C**$H_3$–$CH_2$–O), 50.2–50.4 (**C**H$CH_2$), 51.2–51.5 (C), 52.1–52.4 (**C**HCH), 61.6–61.7 (**C**H–NH), 62.4–62.5 (CH_3–**C**H_2–O). δ_P 29.38 (48%), 29.53 (52%).

General Procedure for Oxidation of Aminophosphonate into Nitroxide

Aminophosphonate (0.016 mol) was dissolved in dichloromethane (80 mL) and then cooled at 0°C. *Meta*-chloroperbenzoic acid (0.048 mol) dissolved in dichloromethane (95 mL) was added dropwise over a period of 2 h. The reaction mixture was stirred overnight at room temperature. It was then filtered and the residue was washed several times with a saturated solution of Na_2CO_3 and with a solution of 5% HCl in water. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the nitroxide.

N-tert-*Butyl*-N-*[2-ethyl-(1-diethoxyphosphoryl-2-methylpropyl)] Nitroxide* ***3b***

Purification: chromatography (pentane/ethyl acetate, 1/1). Nitroxide: orange oil (yield 26%). *m*/*z* (ESI): 336 (M^+). ESR: a_N 13.9 G, a_P 49.6 G, a_H 1.2 G.

N-tert-*Butyl*-N-*[2-ethyl-(1-diethoxyphosphoryl)-2,2,2-trichloroethyl] Nitroxide* ***3c*** *or Chloral SG1*

Nitroxide: yield <5%. ESR: a_P 34.4 G, a_N 12.55 G.

N-tert-*Butyl*-N-*[2-ethyl-(1-diethoxyphosphoryl)hexyl] Nitroxide* ***3d*** *or ETHEXNO*

Purification: chromatography (pentane/ethyl acetate, 3/1). Nitroxide: orange oil (3.2 g, yield 64%). *m*/*z* (ESI) 336 (M^+). ESR spectra: a_P 46.8 G, a_N 13.8 G.

N-tert-*Butyl*-N-*[2-ethyl-(1-diethoxyphosphoryl)hexyl]-O-(1-phenylethyl) Hydroxylamine* ***6***

PMDETA (1.6 mL, 9.0 mmol) was added to a degassed solution of CuBr (646 mg, 4.5 mmol) and copper (285 mg, 4.5 mmol) in dichloromethane, and nitrogen was bubbled through the solution for 10 min. A degassed dichloromethane solution of ETHEXNO **3d** (1.0 g, 3.0 mmol) and 1-bromoethylbenzene (441 mg, 4.5 mmol) was transferred to the mixture, which was then stirred for 2 h at room temp under nitrogen. Diethyl ether (30 mL) was added and the solid filtered off. The organic layer was washed with water until colourless and then dried with $MgSO_4$. The solvent was removed to yield a colourless oil (920 mg, 70%). δ_P 26.17 (33.2%), 26.66 (14.1%), 26.80 (17.5%), 27.41 (35.2%). δ_H 0.73–0.97 (m, 6H, C$H_3$$CH_2$), 1.18 (s, 9H, CCH_3), 1.24–1.44 (m + t, 12H, $J_{H–H}$ 7.1, 2 × CH_3–CH_2–O + 3 × CH_2), 1.54 (d, 3H, 1 × CH*–CH_3), 1.74–2.16 (m, 3H, 1 × CH_2 + 1 × CH), 3.35–3.51 (dd, 1H, $J_{H–H}$ 10.4, CH), 3.97–4.39 (m, 4H, 2 × CH_3–CH_2–O), 5.08–5.22 (m, 1H, C*H**–CH_3), 7.15–7.43 (m, 5H, –C*H*=CH–). δ_C 12.8 (**C**$H_3$$CH_2$), 15.7 (**C**$H_3$$CH_2$$CH_2$), 20.8 ($CH_3$**C**$H_2$$CH_2$), 22.6 ($CH_2$**C**$H_2$$CH_2$), 24.1 ($CH_3$$CH_2$**C**$H_2$), 25.7 ($CH_3$**C**$H_2$CH), 26.4 (3C, C(**C**$H_3$)$_3$), 30.1 ($CH_2$$CH_2$**C**$H_2$), 48.3 (**C**$H_3$–$CH_2$–O), 50.2 (**C**H$CH_2$), 55.2 (**C**HCH), 59.8 (**C**(CH_3)$_3$), 62.5 (CH_3–**C**H_2–O), 79.4 (**C**H–NH), 82.9 (**C**HCH_3), 125.1–12.6 (5C, **C**H=CH), 145.2 (C).

*2-Methyl-2-[*N-tert-*butyl*-N-*(2-ethyl-(1-diethoxyphosphoryl)hexyl)]propanoic Acid* ***7***

PMDETA (1.6 mL, 9.0 mmol) was added to a degassed solution of CuBr (646 mg, 4.5 mmol) and copper (285 mg, 4.5 mmol) in dichloromethane, and nitrogen was bubbled

through the solution for 10 min. A degassed dichloromethane solution of ETHEXNO **3d** (1.0 g, 3.0 mmol) and 2-bromo-2-methylpropionic acid (745 mg, 4.5 mmol) was transferred to the mixture which was then stirred for 1 h at room temperature under nitrogen. Diethyl ether (30 mL) was added and the solid filtered off. The organic layer was washed with 5% HCl in water two times and with water until colourless and then dried with $MgSO_4$. The solvent was removed to yield an oil which precipitated in cold pentane (755 mg, 60%). δ_P 29.50 (60%), 29.22 (13%), 26.65 (27%). δ_H 0.76–1.02 (m, 8H, $CH_3CH_2 + CH_2$), 1.18 (s, 9H, CCH_3), 1.27–1.37 (m, 12H, $2 \times CH_3$–CH_2–$O + 3 \times CH_2$), 1.51–1.56 (d, 6H, $J_{H–H}$ 8.8, $2 \times CH_3$–CH_2–O), 1.73 (s, 1H, CH–P), 3.35–3.52 (m, 1H, $J_{H–H}$ 10.5, C*H*–CH), 4.05–4.25 (m, 4H, $2 \times CH_3$–CH_2–O). δ_C 9.9 (1C, $\mathbf{C}H_3CH_2$), 13.1 (1C, $\mathbf{C}H_3CH_2CH_2$), 15.5 (1C, $CH_3\mathbf{C}H_2CH_2$), 22.1 (1C, $CH_2\mathbf{C}H_2CH_2$), 23.8 (1C, $CH_2CH_2\mathbf{C}H_2$), 25.6 (1C, $CH_3\mathbf{C}H_2CH$), 27.6 (2C, $HOOCC(\mathbf{C}H_3)_2$), 29.0 ($3 \times C(\mathbf{C}H_3)_3$), 33.1 (2C, $\mathbf{C}H_3$–CH_2–O), 49.3 (1C, $\mathbf{C}HCH_2$), 59.7 (1C, $\mathbf{C}H$–NO), 63.8 (2C, CH_3–$\mathbf{C}H_2$–O), 82.7 ($\mathbf{C}(CH_3)_3$), 91.2 (1C, $\mathbf{C}COOH$), 175.6 (1C, C=O). *m*/*z* (ESI) 423 (M^+).

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