In Situ Nitroxide-Mediated Polymerization of Styrene Promoted by the *N-tert*-Butyl-α-isopropylnitrone/BPO Pair: ESR Investigations

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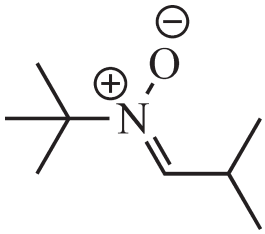
ABSTRACT: The styrene polymerization initiated by benzoyl peroxide (BPO) in the presence of *N*-tert-butyl-α-isopropylnitrone as nitroxide precursor is well-controlled provided that a prereaction between the nitrone and BPO is carried out in suitable conditions prior to polymerization at a higher temperature. Electron spin resonance (ESR) spectroscopy was implemented to probe the nitroxides formed during both steps, that is, the prereaction and polymerization, and to get crucial information regarding the structure of the nitroxides responsible for the polymerization control. ESR studies combined with first principles calculations have evidenced that nitroxides observed during the prereaction in the presence of styrene and during the polymerization steps consist of a mixture of two macronitroxides. One is formed by the addition of a growing polystyrene chain to the nitrone as would be expected. However, the second one results from the addition of a polystyrene chain to *tert*-butyl nitroso that is *in situ* formed presumably by decomposition of the first macronitroxide type. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1786–1795

KEYWORDS: ESR/EPR; kinetics (polym.); calculations; living polymerization; nitroxide mediated polymerization; styrene; electron spin resonance; nitroxide; controlled radical polymerization

INTRODUCTION Nitroxide-mediated polymerization (NMP) is one of the most efficient controlled radical polymerization (CRP) techniques that allows the precise synthesis of well-defined (co)polymers.[1–3] NMP greatly developed within the past few years with the discovery of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as an effective mediator for the CRP of styrene.[4] As then, considerable progresses have been made by extending the NMP possibilities to other monomers such as acrylates (including some functional acrylates),[5–8] acrylamides,[5,9,10] acrylonitrile,[5] methacrylates (with some limitations)[2,11–15] but also some dienes such as isoprene.[16–18] Such advances were made possible by the development of more efficient nitroxides and parent alkoxyamines.

Fortunately, few nitroxides and alkoxyamines are commercially available, that allow giving access to various polymer architectures quite easily. However, the range of NMP regulators is not broad such that organic synthesis has thus to be implemented for the preparation of nitroxides or alkoxyamines of different reactivity. This might be a limitation for implementation of NMP in industry, especially when process costs are the main criteria to be considered. Therefore, few research groups, both in academia and industry, have contemplated *in situ* NMP processes,[2] thus the direct formation of NMP regulators (nitroxides and alkoxyamines) within the polymerization medium from hopefully cheap (and ideally commercially available) precursors, including nitrones,[16,19–29] nitroso compounds,[12,30,31] sodium nitrite,[11,32,33] nitric oxide,[12] secondary amines,[24,34,35] and hydroxylamines.[36] In addition to a low cost, these precursors must provide the radical polymerization with a degree of control comparable to preformed nitroxides or alkoxyamines.

Amongst these *in situ* NMP processes, the *N-tert*-butyl-α-isopropylnitrone (Scheme 1) was one of the most powerful



SCHEME 1 Structure of Nit.

precursors for nitroxides used for CRP. The *N-tert*-butyl-α-isopropylnitrone (noted "Nit")/benzoyl peroxide (BPO) system was well-suited to the synthesis of various block copolymers, such as poly(styrene)-*b*-poly(styrene-co-acrylonitrile) (PS-*b*-PSAN), poly(styrene)-*b*-poly(*n*-butyl acrylate) (PS-*b*-PnBuA) but also poly(styrene)-*b*-poly(isoprene) (PS-*b*-PIP).[16] To be efficient, a prereaction between Nit, the free radical initiator (BPO) and styrene had to be first implemented at 85 °C for 4 h before increasing the temperature to 110 °C.[16]

In order to go a step further in the macromolecular engineering using this *in situ* NMP technology, a better understanding of the type of nitroxides formed is required. In the first report,[16] preliminary electron spin resonance (ESR) studies did not allow to elucidate their structure.

This article reports on an ESR study of this system with the purpose to collect basic information on the structure of *in situ* formed nitroxides that are responsible for the control of the polymerization. Theoretical structural and ESR results are also reported for supporting the different hypotheses.

EXPERIMENTAL

Materials

Styrene (Sty, Aldrich, 99 + %) was dried over CaH_2 and distilled before use in order to remove the stabilizer. *N-tert*-butyl-α-isopropylnitrone (Nit) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) were synthesized as reported elsewhere.[5] BPO (Fluka, 75%) was used as received. Liquids were transferred under argon by syringes or stainless steel capillaries through rubber septa.

Styrene Polymerization in the Presence of Nit

A mixture of Nit (0.1109 g, 7.75×10^{-4} mol) and BPO (0.1168 g, 3.62×10^{-4} mol) was degassed by three argon-*vacuum* cycles. Distilled and degassed styrene (8 mL, 6.98×10^{-2} mol) was added, and the reaction medium was heated at 85 °C for 4 h. The medium was then heated at 110 °C for polymerization. Samples were regularly withdrawn from the polymerization medium to monitor the polymerization kinetics. Monomer conversion was calculated by gravimetry after elimination of the unreacted monomer under reduced pressure at 70–80 °C overnight and taking into account the initial amounts of BPO and nitrone.

A similar experiment was carried out after the Nit and BPO prereaction at 85 °C in toluene (8 mL). Eight milliliter of distilled and degassed styrene was substituted for toluene at 110 °C (*cfr. supra*).

ESR Spectroscopy

ESR spectra were recorded with a Bruker ER 100 spectrometer operating with an X-band standard cavity (υ ca. 9.24 GHz) (ER 041 XG microwave bridge) and interfaced to a Bruker Aspect data system. Temperature was controlled by a Bruker variable temperature unit. The nitroxide concentrations were measured by double integration of the ESR signal, and the data were calibrated with TEMPO solutions in benzene.

ESR Parameters

Center of magnetic field = 3289 G and 2375.3 G; sweep width = 60 and 9 G; modulation frequency = 100 kHz; modulation amplitude = 0.5 G; time constant = 1.25 ms; power: 2 mW. A variable receiver gain was used, depending on the nitroxide concentration.

ESR Study of the Nit/BPO Prereaction Medium in Toluene

Nit (0.1109 g, 7.75×10^{-4} mol) and BPO (0.1168 g, 3.62×10^{-4} mol) were dissolved in 8 mL of toluene. Approximately 0.5 mL of the reaction medium was added in an ESR quartz tube (o.d. 5 mm) capped by a teflon stopper. The sample was degassed by three freeze-pump-thaw cycles and kept under argon. It was inserted in the cavity of the spectrometer and heated at 85 °C. The ESR spectra were recorded during 4 h.

ESR Study of the Styrene Polymerization After the Nit/Initiator Prereaction in Styrene

Nit (0.1109 g, 7.75×10^{-4} mol) and BPO (0.1168 g, 3.62×10^{-4} mol) were dissolved in 8 mL of toluene. The mixture was heated for 4 h at 85 °C. Then, toluene was removed under vacuum at 30 °C and then the residue was dissolved by 8 mL of degassed styrene. Approximately 0.5 mL of the reaction medium was finally added in an ESR quartz tube (o.d. 5 mm) capped by a teflon stopper. The sample was degassed by three freeze-pump-thaw cycles and kept under argon. It was inserted in the cavity of the spectrometer and heated at 110 °C.

ESR study of the Nit/Initiator/Styrene Prereaction and Polymerization Steps

Nit (0.1109 g, 7.75×10^{-4} mol) and BPO (0.1168 g, 3.62×10^{-4} mol) were dissolved in 8 mL of styrene. Approximately 0.5 mL of the reaction medium was added in an ESR quartz tube (o.d. 5 mm) capped by a teflon stopper. The sample was degassed by three freeze-pump-thaw cycles and kept under argon. It was inserted in the cavity of the spectrometer and heated at 85 °C for 4 h while recording ESR spectra. After this period of time, the tube was heated at 110 °C and ESR spectra were regularly recorded.

Characterizations

^1H NMR spectra were recorded in $CDCl_3$ with Bruker AM 250 and 400 MHz spectrometers at room temperature. Size exclusion chromatography was carried out in THF at 45 °C with a HS chromatograph equipped with a Cfloam isotactic pump 301, a SFD autosampler S 5200 P and a SFD refractive index detector 2000 [columns PL gel 5 μm (10^5, 10^4, 10^3, and 100 Å)] and calibrated with polystyrene standards. The flow rate was 1 mL/min.

ESR Simulations

Simulations of the ESR experimental spectra were performed using winsim software. Winsim is available free of charge from Public Electron Paramagnetic Resonance Software Tools (P.E.S.T) at the following internet link http://www.niehs.nih.gov/research/resources/software/tools/index.cfm.[37]

Theoretical and Computational Aspects

To interpret the experimental data, the hyperfine coupling constants (HFCCs)—implicitly, the isotropic HFCCs—were calculated using first principles methods, of which the performance has been assessed in a recent investigation.[38] Indeed, due to the impact of electron correlation, the need to employ extended basis sets, and their sensitivity to the surrounding, accurate evaluation of HFCCs is a difficult task.[39–57] Thus, the results reported here were obtained using a density functional theory (DFT) approach combining the B3LYP hybrid exchange-correlation functional and the EPR III basis set[58] whereas the effects of the solvent were described using the polarizable continuum model and the integral equation formalism (IEFPCM).[59,60] The geometries were optimized by using the B3LYP functional and the 6-311G* basis set. The potential energy surface was sampled to detect the stable conformers. When there exist more than one stable conformer with relative energies within a few kcal/mol, an averaging procedure based on the Maxwell-Boltzmann (M-B) distribution is performed to get the average molecular properties. These relative energies were evaluated at the MP2/6-311G* level of approximation. Provided a linear regression [HFCC (predicted, mT) = 0.9261 HFCC (B3LYP/EPRIII, mT) + 0.4277] is applied for correcting for systematic errors, the HFCCs of nitroxide compounds are estimated with an accuracy of 0.05 mT for the N atoms.[38] Similar performance was achieved in other investigations based on DFT calculations. [39–53,61–63] All calculations were performed using the Gaussian 03 package.[64]

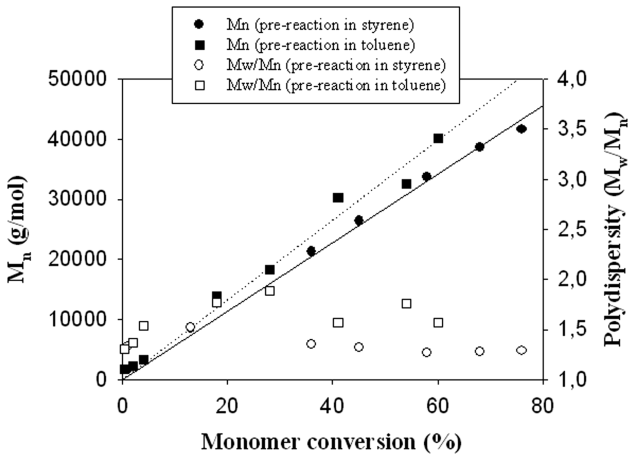


FIGURE 1 Dependence of number average molar mass ($M_{n,SEC}$) on the monomer conversion for the bulk radical polymerization of styrene (styrene/Nit: 90/1) at 110 °C after Nit/BPO prereaction at 85 °C for 4 h in styrene and in toluene ([Nit] = 9.7×10^{-2} M; [BPO] = 4.5×10^{-2} M; Nit/BPO: 1/0.5).

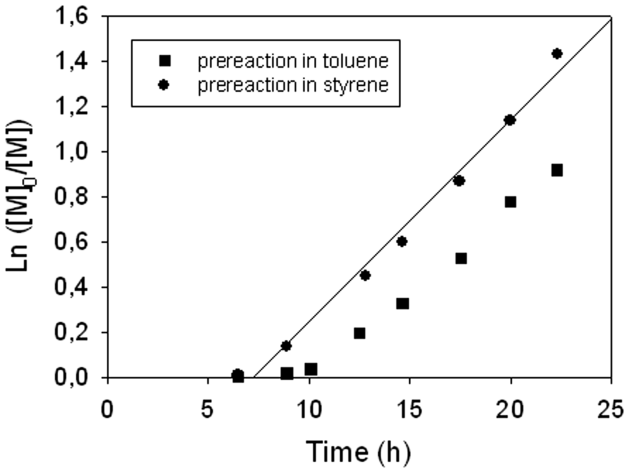


FIGURE 2 Time dependence of ln ($[M]_0/[M]$) for the bulk radical polymerization of styrene (styrene/Nit: 90/1) at 110 °C after the Nit/BPO prereaction at 85 °C for 4 h in styrene and in toluene ([Nit] = 9.7×10^{-2} M; [BPO] = 4.5×10^{-2} M; Nit/BPO: 1/0.5).

RESULTS AND DISCUSSION

Kinetic Analysis

Styrene was polymerized at 110 °C in the presence of Nit and BPO after prereaction in styrene at 85 °C for 4 h to preform the nitroxides and alkoxyamines before the polymerization was initiated at 110 °C. Under these conditions, linear evolution of molecular weight with monomer conversion was observed and a linear time dependence of ln ($[M]_0/[M]$), as well (Figs. 1 and 2).[16] A long induction period (~6–7 h) was also observed before the polymerization started, and the polydispersity was narrow (~1.3). It is essential to identify the nitroxides and alkoxyamines formed *in situ* that are responsible for the polymerization control. This analysis is however complex, because more than one radical results from the BPO thermolysis (Ph· and PhCOO·), and can react with Nit and styrene (Scheme 2). Various types of nitroxides and alkoxyamines are thus expected to be formed during the prereaction in styrene.

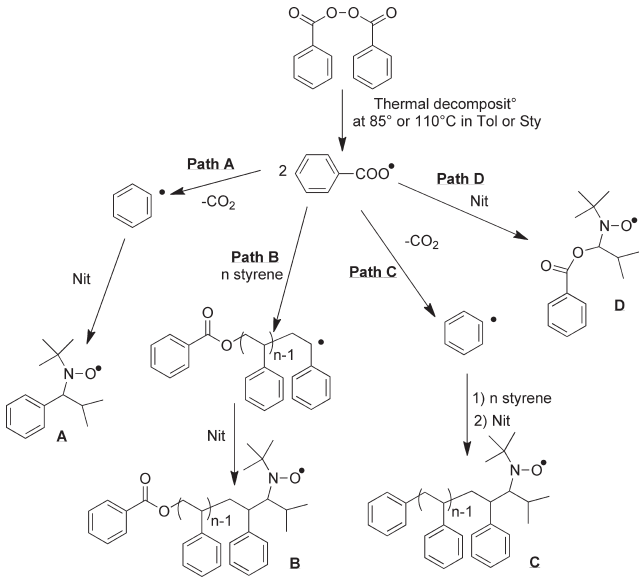
To limit the number of possible nitroxides and parent alkoxyamines, styrene was replaced by toluene in the prereaction. Although the molecular weight increased linearly with the conversion (Fig. 1), this substitution resulted however in a higher polydispersity (Fig. 1) together with a longer induction period of time (Fig. 2).

ESR Analyses

Nit/BPO Prereaction at 85 °C in Toluene Followed by Styrene Polymerization at 110 °C

First BPO and Nit were heated directly in ESR cavity in toluene at 85 °C in a pre-reaction period. A strong ESR signal was immediately obtained [Fig 3(a)] which remained unchanged during the whole prereaction period.

This triplet of doublet observed had a pattern characteristic of a nitroxide bearing a proton in the β position of the nitrogen. The HFCCs (simulated, entry 1 Table 1) A_N = 14.67 G and A_H = 2.70 G (g = 2.0058) were representative of the



SCHEME 2 Possible nitroxides formed in the Nit/BPO/styrene system.

TIPNO (nitroxide **A**, Scheme 2; entry 5 Table 1) and known as an effective NMP regulator for the CRP of various vinyl monomers.[5] ESR spectrum of original TIPNO, obtained from the procedure of Hawker et al.[5] is shown in Figure 4(a). The formation of that nitroxide was consistent with the expected thermal cleavage of BPO followed by decarboxylation and spin trapping of resulting phenyl radical by Nit (**Path A**, Scheme 2). DFT calculations predict $A_N = 15.01$ G and $A_H = 2.15$ G (entry 1 Table 2).

After the prereaction, toluene was removed and replaced by styrene. The mixture was then brought to 110 °C to initiate the polymerization. The initial ESR signal of TIPNO vanished at once and immediately a much more complex ESR spectrum, which changed with time, was obtained, suggesting the formation of new and different radical species [Fig. 3(b–d)]. These spectra were accounted to be the superimposition of a triplet and a triplet of doublet (entry 2, Table 1). The intensity of the three lines ESR signal increased all along the course of the experiment while the intensity of the six lines signal progressively decreased. The triplet signal was present since the beginning although it was not clearly visible [Fig. 3(b)]. It should be pointed out that the three lines exhibit a really large line width.

Tentative explanation of this observation is the following. It has to be noted that, after 4 h of prereaction at 85 °C in toluene, approximately 37 mol % of BPO still remained.[67] Therefore when BPO decomposed in styrene at 110 °C, other radical species are obtained because BPO produced radicals (Ph· and PhCOO·) that are able to react with Nit but also with styrene. In the latter case, the growing polystyryl radical chains add to the spin trap, leading to polymers nitroxide end capped of various lengths (macronitroxides). A complex mixture of new nitroxides as macronitroxides **B** and **C** (Scheme 2, **Path B** and **C**) might therefore account for the

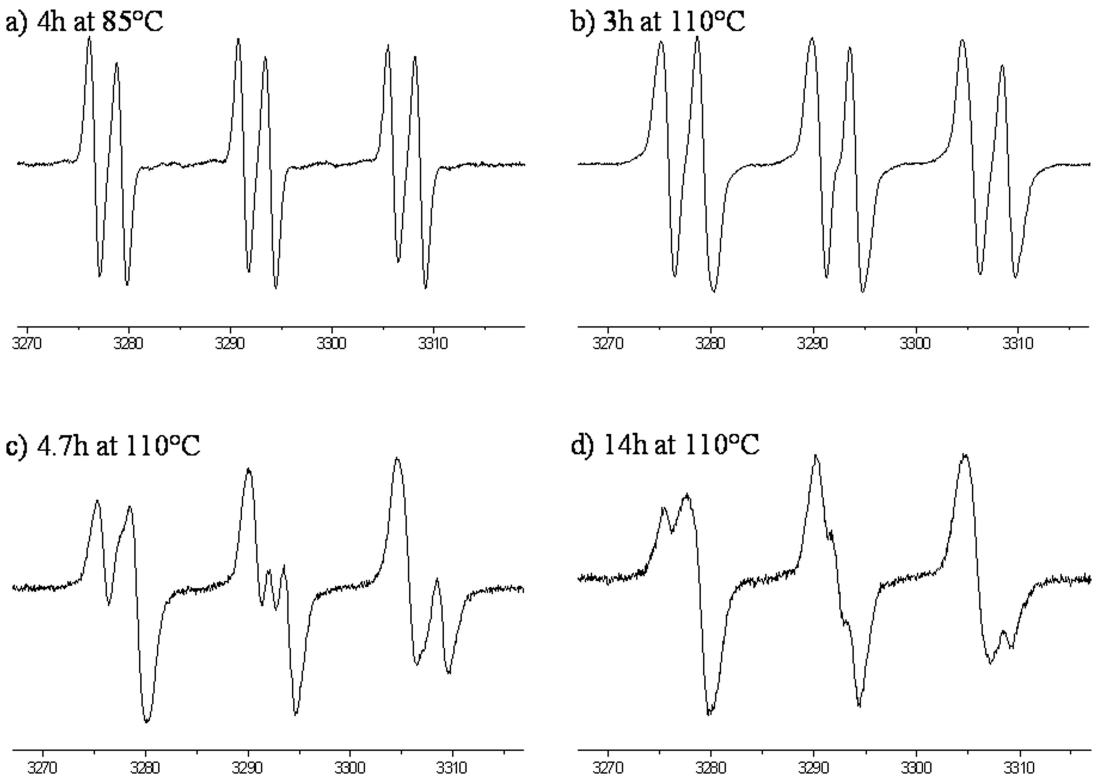


FIGURE 3 Evolution of the ESR signal observed in the Nit/BPO/styrene system prereaction during 4 h at 85 °C in toluene; (b), (c), (d) in styrene at 110 °C (after the prereaction in toluene).

TABLE 1 Simulated ESR Coupling Constants

Entry	System (Temperature)	A_N (G)	A_H (G)	Relative (%)	Time[a] (h)
1	Nit/BPO/tol. (85 °C)	14.7	2.7		
		13.5	1.3; 1.2	13	3
		14.8	3.6	87	
2	Nit/BPO/sty. (110 °C[b])	13.7	1.4; 1.2	40	4.7
		14.8	3.5	60	
		13.8	1.5;1.2	65	14
		14.8	3.3	35	
		13.9	0.8	30	0.3
		14.7	3.5	70	
3	Nit/BPO/sty (85 °C)	13.9	0.9	35	1
		14.6	3.5	65	
		13.8	1.2	55	4
		14.8	2.5	45	
		13.8	1.3	25	1
		14.8	3.5	75	
4	Nit/BPO/sty (110 °C[c])	13.8	1.2; 1.0	80	7.5
		14.8	3.4	20	
		13.8	1.2; 1.0	90	16
		14.8	3.4	10	
5	TIPNO	14.7	2.7		
6	Nit/sty (bulk, 110 °C)	13.8	1.3; 0.8; 0.7; 0.6 × 9; 0.3 × 6; 0.4 × 2		
7	Nit/PhCHBrCH$_3$/CuBr/PMDETA	13.8	1.1		
8	*t*-BuNO/BPO/sty (110 °C)	14.7	3.4		
9	*t*-BuNO/PhCHBrCH$_3$/CuBr/PMDETA[65]	14.9	3.6		
10	*t*-BuNO/(*t*-BuO)$_2$/ PhCHBrCH$_3$[66]	14.8	3.8		

[a] Time at which the ESR spectrum was recorded.
[b] After 4 h of prereaction in toluene at 85 °C.
[c] After 4 h of prereaction in styrene at 85 °C.

ESR spectrum observed. To give any clue to this hypothesis, styrene was auto-initiated at 110 °C in the presence of Nit to form macronitroxide that mimics **B** and **C** species (Scheme 2). Again the two signals described above were obtained. After 8 h at 110 °C, only the ESR signal of the triplet was observed. This signal exhibited also important line width and further shown small hyperfine splittings resolved [Fig. 4(b)]. Such resolved spectrum can be also obtained with the

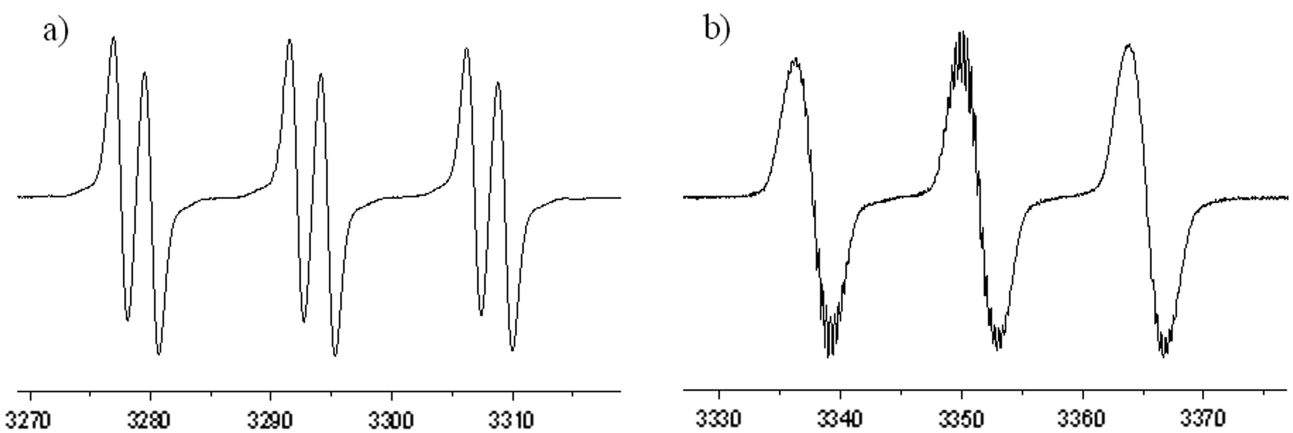
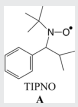
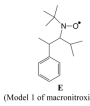
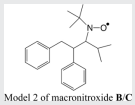
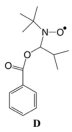
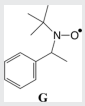


FIGURE 4 (**a**) ESR signal of original TIPNO in toluene and (b) ESR signal of nitroxide formed in bulk polymerization of styrene in the presence of Nit.

TABLE 2 Calculated ESR Coupling Constants

Entry	Compounds	A_N (G)	A_H (G)
1	 TIPNO **A**	15.01	2.15
2	 **E** (Model 1 of macronitroxide **B**/**C**)	13.67	1.29
3	 Model 2 of macronitroxide **B**/**C**	13.63	1.38
4	 **D**	13.68	0.16
5	 **G**	15.17	2.55
6	 **H** (Model of compound **F**)	15.46	2.84

Nit/BPO/styrene system if the medium is diluted with toluene and further degassed (data not shown). The large width suggested some uniform signal broadening (increase of viscosity) and/or the presence of various radical species with close coupling constant including diastereoisomeric nitroxides, and the small hfcc's of the H atoms in γ and δ positions. The experimental spectrum was therefore simulated (entry 6, Table 1) by considering only one species with one nitrogen atoms ($A_N = 13.8$ G), one hydrogen in *beta* position ($A_H = 1.3$ G), eleven (9+1+1) hydrogens in *gamma* position arising from *t*-Bu group, —$\underline{CH}(CH_3)_2$ and $\underline{CH}Ph(CH_2$—) and eight (6+2) *delta* hydrogens from *i*-propyl groups and —CHPh($\underline{CH_2}$—). This triplet was thus believed to be the macronitroxides **B** or **C** (Scheme 2) formed by addition of growing PS chains to Nit.

DFT calculations carried out on two model systems representing these macronitroxides also support this assignment [$A_N = 13.67$ G and $A_H = 1.29$ G for model 1 and $A_N = 13.63$ G and $A_H = 1.38$ G for model 2, containing one more styrene unit] (Table 2, entries 2 and 3, respectively).

Nit/BPO/Styrene Prereaction at 85 °C Followed by Polymerization at 110 °C

When the prereaction was carried out in styrene, directly the two radical species obtained formerly at 110 °C and described above were detected (Fig. 5, entry 3 Table 1). Both signals intensities increased during that period. Again the doublet of triplet concealed the three lines signal at the beginning of the experiment. When the temperature was raised to 110 °C after the prereaction, these species were still present and their amounts increased during the first hours. The intensity of the triplet of doublet diminished with time while the intensity of the triplet increased (entry 4 Table 1). After 16 h of reaction, only the three lines signal was observed .

The triplet of doublet observed in the presence of styrene at 85 °C and/or at 110 °C had nitrogen coupling constant of 14.7 G and hydrogen coupling of 3.5 G. All our attempts to purify and isolate that nitroxide by eluting the reaction medium on silica column using various solvents as mobile phases were unsuccessful. In particular, the large H HFCC value is typical to a nitroxide formed by the addition of an alkyl radical to the nitrone.[68] However, the nitroxide involved was clearly neither TIPNO ($A_N = 14.7$ G, $A_H = 2.6$ G) nor macro-nitroxides **B** or **C** ($A_N = 13.8$ G, $A_H = 1.5$ G).

We therefore first considered that it might be the result of the addition of only one or a few styrene units to Nit. Nitroxide **E** (Scheme 3) that mimics **B** or **C** radical species with small oligomer tails was prepared by Atom Transfer Radical Addition of (1-bromoethyl)benzene with Nit at room temperature using CuBr/PMDETA as catalyst in *t*-butylbenzene (Table 1, entry 7). The three lines ESR signal obtained with $A_N = 13.8$ G and $A_H = 1.1$ G [$A_N = 13.67$ G and $A_H = 1.29$ G from DFT calculations] was clearly equivalent to those identified in Nit/styrene bulk system and for macro-nitroxides **B** or **C**. Unfortunately in this case, the long-range hyperfine splittings were not resolved surely in the reason of the important presence of copper salts. DFT calculations also enable to exclude compound **D** ($A_N = 13.68$ G and $A_H = 0.16$ G; entry 4 Table 2).

We then supposed the possible occurrence of a secondary spin trap species such as *tert*-butyl nitroso (*t*-BuNO) which can be formed from the degradation of nitroxides.[31,69–73] An evidence was brought by polymerizing styrene with BPO in the presence of *t*-BuNO at 110 °C in place of Nit. In that case, a triplet of doublet was found with the following splittings $A_N = 14.7$ G and $A_H = 3.4$ G (Table 1, entry 8). Various authors reported similar splitting for nitroxide **G** (Scheme 3) obtained from the thermal cleavage of corresponding styryl alkoxyamine (**G**-$\underline{CH}(CH_3)$Ph) or by spin trapping of PhC·HCH_3 by *t*-BuNO (Table 1, entries 9–10).[66,65,72] In this case, the calculations predict a slightly larger/smaller A_N/A_H than experimentally ($A_N = 15.17$ G and $A_H = 2.55$ G, compound **G**, entry 5 Table 2). In all case, the similarity of the coupling constants convinced us of the existence of macro-nitroxides **F** in our experiments. This is further substantiated by the DFT calculations on macronitroxide **H**, a model for macronitroxide **F**, which presents a large A_H value (2.84 G, entry 6 Table 2).

It is therefore suggested that *t*-BuNO is likely formed *in situ* by decomposition of macro-nitroxides **B** or **C** according to Scheme 4. However, a thermal decomposition of the nitrone into *t*-BuNO cannot be ruled out even if the parent TIPNO has shown a different decomposition pathway.[74]

The higher value of A_H coupling is an evidence of a lower steric hindrance of the substituents surrounding the nitroxyl

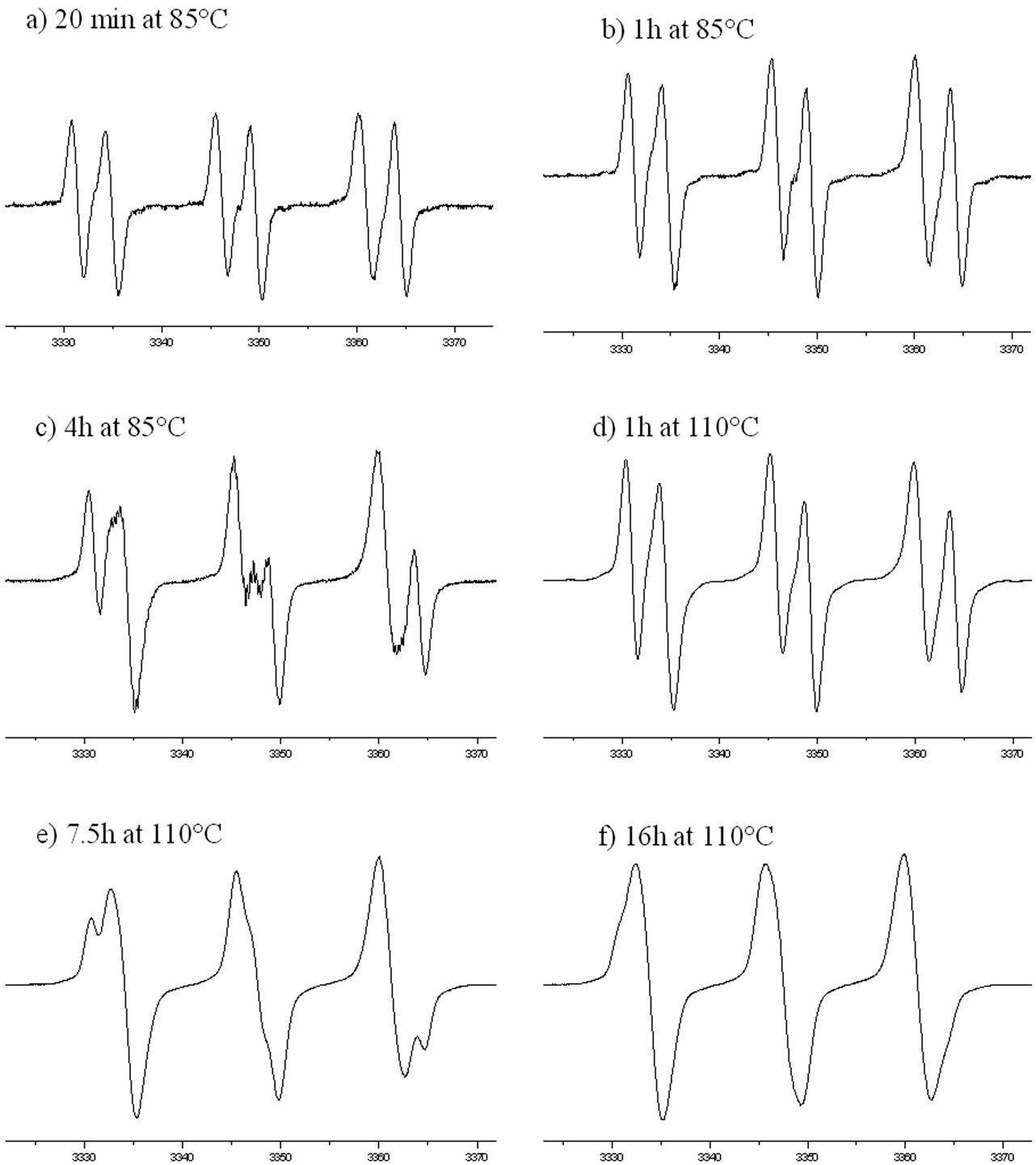


FIGURE 5 Evolution of the ESR signal observed in the Nit/BPO/styrene system (a–c), prereaction in styrene during 4 h at 85 °C; (d–f) in styrene at 110 °C (after the prereaction in styrene).

function in macronitroxide **F** compare to macro-nitroxides **B** or **C**. This reason may explain the lower stability of **F** at 110 °C which is no more observed at the end of ESR experiments. This hypothesis is in agreement with some works reporting that nitroxides with a high A_H value have poor thermal stability.[74]

CONCLUSIONS

Some of us previously reported that the *N-tert*-butyl-α-isopropylnitrone/BPO pair was well-suited to the synthesis of various block copolymers, such as PS-*b*-PSAN, PS-*b*-PnBuA but also PS-*b*-PIP.[16] To be efficient, a prereaction between the nitrone, the free radical initiator (BPO) and styrene had

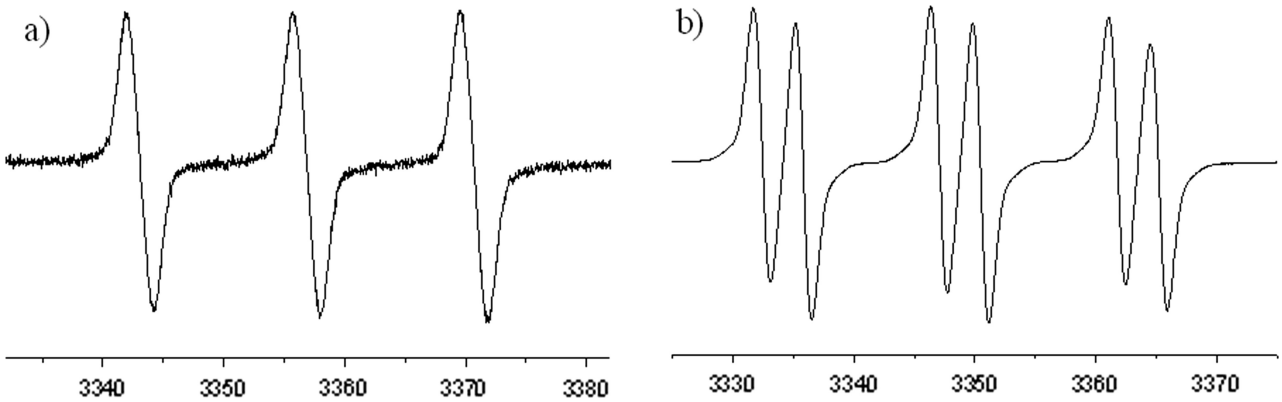
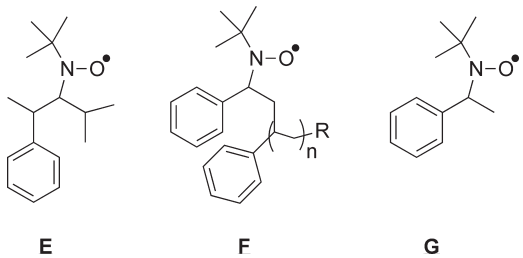
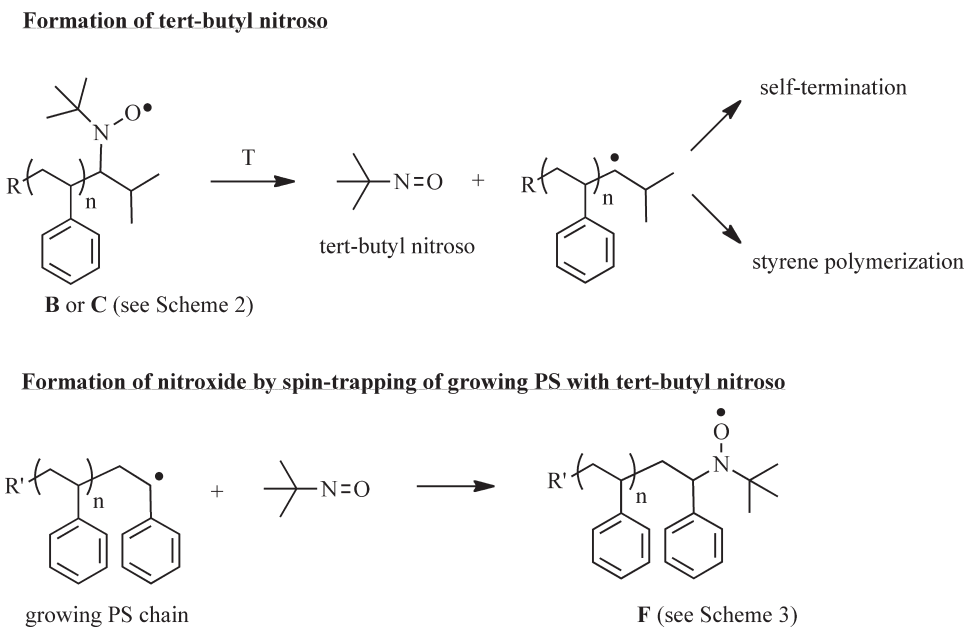


FIGURE 6 (a) ESR signal of nitroxide formed in situ from $PhCHBrCH_3$/CuBr/PMDETA in the presence of Nit and (b) ESR signal formed in t-BuNO/BPO/sty at 110 °C.



SCHEME 3 Structure of nitroxides : **E** : obtained from Nit/$PhCHBrCH_3$/CuBr/PMDETA system; **F** : formed in *t*-BuNO/BPO/styrene at 110 °C (R = —Ph or OCO-Ph); **G**: obtained in ref. [18].

to be first implemented at 85 °C for 4 h before increasing the temperature to 110 °C. When the prereaction is performed in toluene in the absence of styrene, the polymerization is still under control but the polydispersity is however higher. In this article, we study the nitroxides formed *in situ* during both the prereaction and the polymerization steps using the two different reaction pathways (prereaction in the presence or not of styrene). The objective is to get a better understanding on the structure of the nitroxides that are responsible for the polymerization control. ESR was implemented to study the nitroxides formed *in situ* during the prereaction and the polymerization steps. ESR studies have emphasized that the structure of the nitroxide is dependent on the way to perform the prereaction. These studies have also evidenced that a complex mixture of nitroxides that are not always expected is often observed that strongly complicates the interpretations. TIPNO is formed when the prereaction is carried out in the absence of styrene as the result of the trapping of phenyl radical (that comes from the decomposition of BPO) by the nitrone. A mixture of two macronitroxides is however observed when the polymerization occurs



SCHEME 4 Mechanism proposals for the formation of *t*-BuNO by decomposition of the macronitroxide **B** or **C**, and formation of macronitroxide **F** by addition of growing PS chains to *t*-BuNO.

at 110 °C after the addition of styrene at the end of the prereaction. As evidenced by ESR experiments on the polymerization medium and on model reactions, and further supported by DFT calculations, one of these macronitroxides is formed by the expected trapping of a growing polystyrene chain by the nitrone. All experiments carried out to elucidate the structure of the second macronitroxide were in line with the occurrence of a side reaction that leads to the formation of a second nitroxide precursor in the polymerization medium. Indeed *t*-BuNO is first formed *in situ* presumably by decomposition of the first macronitroxide and/or of the nitrone. This nitroso compound then leads to the second macronitroxide by trapping a growing PS chain. When the prereaction is carried out in the presence of styrene, the mixture of macronitroxides is observed both during the prereaction and the polymerization steps, and TIPNO is not detected anymore. The *in situ* NMP process described in this paper is therefore more complex than expected since the nitrone is not the only source of nitroxides. A second nitroxide precursor (*t*-BuNO) is formed during the process and also contributes to the formation of a macronitroxide that is expected to participate to the polymerization control.

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