2204 *Macromolecules* **2010**, *43*, 2204–2212
DOI: 10.1021/ma902774s

Macromolecules
ARTICLE

Toward Nitroxide-Mediated Photopolymerization

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Received December 16, 2009; Revised Manuscript Received January 28, 2010

ABSTRACT: A new alkoxyamine (methyl 2-((4-benzoylphenyl)((1-methoxy-2-methyl-1-oxopropan-2-yl)oxy)-amino)-2-methylpropanoate **4**) bearing a chromophore group directly linked to the aminoxyl function is proposed as a photoiniferter. This original compound decomposes under UV irradiation to generate the corresponding alkyl and nitroxide radicals. Drastic changes of the photophysical or photochemical properties of the starting chromophore are noted. Laser flash photolysis experiments showed both a singlet state cleavage and an efficient shortening of the triplet state lifetime of **4**. MO calculations suggest a C−O bond homolytic dissociation under UV irradiation through both S_1 and T_1 pathways. However, an ESR study evidences that both N−O and C−O homolysis occur under UV irradiation. The efficiency of **4** as a conventional photoinitiator is close to that of 2,2′-dimethoxyphenyl acetophenone. When **4** was used as a photoiniferter in nitroxide-mediated photopolymerization (NMP^2), a linear growth of the poly(*n*-butyl acrylate) chain, reaching 80% of conversion in < 500 s, is observed combined with a reinitiation of the photopolymerization after the end of the irradiation: this is the first report showing a at least partial NMP^2 process.

Introduction

Photopolymerization represents a rapidly emerging field in the material science area. The actual growth of this market is ~7% each year. The photochemical process is characterized by important advantages because thin films can be polymerized very rapidly (< 1 s) with UV lamp irradiation. For polymer synthesis, coatings, inks, photoresists, dual-cure systems, and so on, the photopolymerization reaction is now recognized as particularly interesting and powerful.[1] This is also an ecological alternative to thermal processes because no volatile organic compounds (VOC) are released in this technology. However, the main drawback of the photochemical processes is related to the lack of control for the final polymer properties and the difficulty to prepare block copolymers. To overcome this problem and open a large range of applications for photopolymers, Otsu et al.[2] developed dithiocarbamate compounds called photoiniferters (see an example in Scheme 1), which are able to initiate and control the polymer growth. With these systems, the synthesis of complex architecture polymers (block, star, or amphiphilic polymers, etc.) exhibiting new properties (optic, reinforcement, chemical compatibilization, surface modification, etc.) becomes possible. Despite very encouraging results, the method developed by Otsu suffers from severe limitations.[3] Dithiocarbamyl radicals dimerize and initiate extra chains. Up to now, no other efficient controlled radical photopolymerization system has been described despite the industrial and academic growing needs in this field. To overcome the drawbacks mentioned above, the present article will propose an original alkoxyamine as a representative of a new family of photoinitiator-controller for nitroxide mediated photopolymerization (NMP^2).

Nitroxide radicals have been already extensively used as controlling agent in nitroxide-mediated polymerization (NMP).[4] Basically, during the NMP, the initiation step occurs through the homolysis of an alkoxyamine under thermal conditions (Scheme 2). This homolytic dissociation leads to a transient carbon-centered radical that acts as the initiator and to a nitroxide radical that plays the role of the controlling agent. The NMP process is based on the persistent radical effect, and the propagation step is described as the reversible dissociation between macroalkoxyamine (dormant species) and the active species, which are the carbon-centered propagating radicals. Owing to the stability of their alkoxyamine end group, the dormant macromolecules can be isolated and further used as macroinitiators under thermal condition for the polymerization of a different monomer and therefore afford the preparation of diblock copolymers.

Very few studies have been devoted to the photodissociation properties of alkoxyamines, which would allow the possibility of NMP^2. Scaiano et al.[5] first tested different TEMPO-based alkoxyamines (where TEMPO is 2,2,6,6-tetramethylpiperidinyloxy-4-yl radical) whose homolysis was photosensitized by a xanthone (Xa) triplet state or a pyrene (Py) excited singlet state. The quenching of the excited states is observed, but only a few alkyl radicals were generated (in the presence of xanthone exclusively). Yoshida[6−10] also investigated the photopolymerization of various monomers in the presence of TEMPO derivatives or their corresponding alkoxyamines using a photoacid generator (bis(alkylphenyl)iodonium hexafluorophosphate (BAI)) to produce radicals. Nevertheless, this mechanism remains unclear because the role of the BAI is not elucidated. To enhance the efficiency of the energy transfer between the chromophore and the C−O bond, Neckers et al.[11] designed new alkoxyamines bearing different chromophores covalently linked to the TEMPO−OH moiety (see, e.g., the alkoxyamine **1**−**3**, Scheme 1). With both the xanthone and the benzophenone moiety, a rapid quenching of the excited state during LFP experiments was

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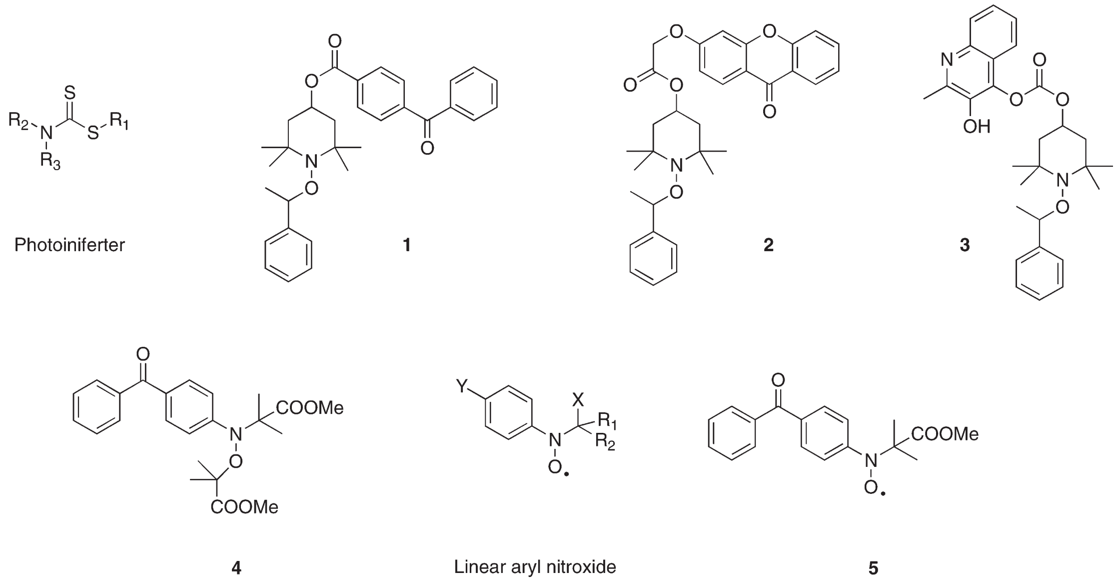
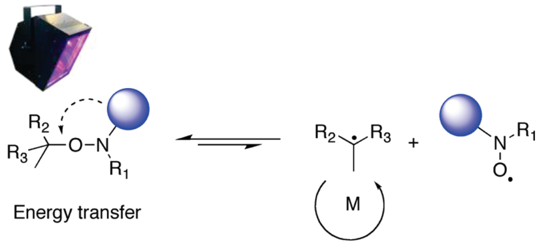
Scheme 1. Nitroxides and the Corresponding Alkoxyamines



Scheme 2. Nitroxide Mediated Photopolymerization (NMP^2) Mechanism



observed, but the detection of the alkyl radical was not easy. The photopolymerization of methyl methacrylate in the presence of **2** exhibits one of the criteria of a controlled polymerization (i.e., the M_n is linked to the amount of the initiating alkoxyamine), but the final polymer was not photoreactive under irradiation conditions, indicating a nonliving character. Similarly Scaiano et al.[12] used a quinoline as chromophore (Alkoxyamine **3**, Scheme 1). The photolysis between 300 and 400 nm in acetonitrile showed a first-order increase in the nitroxide concentration in the electron spin resonance (ESR) cavity in agreement with the unimolecular decomposition of the alkoxyamine. Their first attempt to photopolymerize styrene was encouraging, even if the polydispersity index was quite large (i.e., PDI = 1.6). A more detailed study with this kind of alkoxyamine is needed to conclude about the efficiency of this compound for both the controlled and living character of the polymerization.

Beause the energy transfer from the sensitizer ("antenna") to the C−O bond is not found to be efficient enough in these previous works, a new approach where the chromophore group is directly linked to the aminoxyl function will be developed here to facilitate the homolysis of the alkoxyamine (Scheme 2). In this way, the photochemical and photophysical properties of the chromophore will be much more strongly affected (UV absorption spectrum, singlet and triplet state lifetimes, intersystem crossing quantum yield, dissociation quantum yield, etc.) than when using separated chromophore and alkoxyamine fragments. In the present article, the photochemical behavior in NMP^2 of the original alkoxyamine **4** (Scheme 1) exhibiting such properties will be examined. Alkoxyamines synthesis as well as their photochemical properties and their use in the polymerization of both a conventional curing system (a multifunctional acrylate monomer for coating industry) and *n*-butyl acrylate are presented hereafter.

Experimental Section

Materials. 2-Bromo-2-methyl-propionic acid methyl ester (99+%), CuBr (98%), Cu(0) (powder, 99+%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-diethylenetriamine (PMDETA, 99+%), and *n*-butyl acrylate (BA, 99+%) were purchased from Aldrich and used as received. Solvents (benzene, diethyl ether, pentane) were purchased from SDS and used as received. The 4-nitrosobenzophenone was prepared according the procedure of Defoin.[13] The alkoxyamine **1** was prepared as described by Neckers et al.[11] All reactions were monitored by analytical thin layer chromatography (TLC) plates and analyzed with 254 nm UV light, phosphomolybdic acid solution, or both.

Instrumentation. ^1H (300.13 MHz) and ^{13}C (75.44 MHz) NMR spectra in $CDCl_3$ were recorded on a Bruker AC-300 spectrometer using 5 mm o.d. tubes. Chemical shifts were reported as δ values in parts per million (ppm) relative to residual $CHCl_3$ as internal reference (^1H: δ7.26, ^{13}C: δ77.23), and coupling constants (J) were reported in hertz (Hz). Peak multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), and q (quartet). Hydrogen multiplicity (C, CH, CH_2, CH_3) information is obtained from DEPT experiments.

Elemental analyses were performed at the Service Commun de Microanalyse de l'Université d'Aix-Marseille 3 using a Thermo Finnigan EA 1112. The experiments were carried out under a N_2 atmosphere and are analyzed with the Eager 300 software.

ESI-MS experiments were performed with a QStar Elite mass spectrometer (Applied Biosystems SCIEX, Concord, ON, Canada) equipped with an electrospray ionization source operated in the positive ion mode. The capillary voltage was set at 5500 V, and the cone voltage was set at 80 V. In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight (oa-TOF) mass analyzer. Air was used as the nebulizing gas (25 psi). Analyst software version 2.1 was used for instrument control, data acquisition, and data processing. Accurate mass measurements were performed using two reference ions from a poly(ethylene glycol) internal standard (m/z 367.2690 and m/z 425.3108). Standards solutions were prepared in THF, further diluted using a methanolic solution of ammonium acetate (3 mM), and finally mixed with the sample prior to ionization. Direct sample introduction was performed at a 10 μL/min flow rate using a syringe pump.

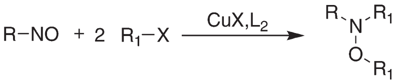
Synthesis of Alkoxyamine Methyl 2-((4-Benzoylphenyl)((1-methoxy-2-methyl-1-oxopropan-2-yl)oxy)amino)-2-methylpropanoate 4. Under an inert atmosphere, a solution of 4-nitrosobenzophenone (4.7 mmol, 1.0 g) and 2-bromo-2-methyl-propionic acid methyl ester (14.1 mmol, 2.57 g) in benzene (10 mL) was added to a deoxygenated mixture of CuBr (14.1 mmol, 2.03 g), PMDETA (28.2 mmol, 4.92 g), and Cu(0) (14.1 mmol, 901.7 mg) in benzene (10 mL). After 24 h of stirring at room temperature, the mixture was filtered off on Celite, diluted with diethyl oxide, and then washed with water to extract copper-based compounds. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent at RT under reduced pressure, the crude product was purified by silica gel column chromatography (pentane/ether 1:1). Alkoxyamine **4** (1.3 g, 3.14 mmol, yield = 66%) was obtained as a red oil. ^1H NMR ($CDCl_3$, 300.13 MHz, δ): 1.24−1.48 (m, 12 H), 3.35 (s, 3 H), 3.72 (s, 3 H), 7.29−7.86 (m, 10 H). ^{13}C NMR ($CDCl_3$, 75.47 MHz, δ): 21.2 (CH_3), 23.5 (CH_3), 23.9 (CH_3), 24.1 (CH_3), 51.4 ($-O-CH_3$), 51.8 ($-O-CH_3$), 68.4 ($(COOMe)(CH_3)_2-C-N$), 81.6 ($(COOMe)(CH_3)_2-C-O$), 124.8, 128.1, 129.7, 132.1, 134.5, 137.6, 152.5 (aryl carbons), 172.7 ($-C{=}O$), 173.5 ($-C{=}O$), 195.7 ($-C{=}O$). ESI-HRMS calcd for $C_{23}H_{27}NO_6$ $[M + H]^+$: 414.1911; found: 414.1912. Anal. Calcd. for $C_{23}H_{27}NO_6$ (413.464): C, 66.81; H, 6.58; N, 3.39. Found: C, 66.34; H, 7.04; N, 3.15.

Polymerization Experiments. The photopolymerization of BA was carried out in a sealed glass tube (sample thickness: 1 mm) after Ar bubbling under irradiation with the UV light of a Xe−Hg lamp (Hamamatsu, L8252, 200 W). The monomer conversion was directly followed by real time FTIR spectroscopy in the near-infrared spectral region as usually done for thick samples (4700−4800 cm^{-1}). The number-average molecular weights (M_n) and polydispersity index (PDI = M_w/M_n) were determined by size exclusion chromatography (SEC) using a Waters 515 HPLC pump equipped with 2 columns (PSS SDV LINEAR M 5 μm) and two detectors: UV/visible (Waters 486) and DRI (Waters 2414). Measurements were performed in tetrahydrofuran (THF) at room temperature with a flow rate of 1 mL min^{-1}. Toluene was used as a flow rate marker. Calibration was based on polystyrene standards (kit EasyCal from Polymer Laboratories; M_n between 580 and 377 400 $g \cdot mol^{-1}$) and Mark−Houwink parameters (PS $K = 11.4 \times 10^{-3}$ mL g^{-1}, $\alpha = 0.716$; PBA $K = 12.2 \times 10^{-3}$ mL g^{-1}, $\alpha = 0.70$).[14]

For film polymerization experiments, a given photoinitiator (PI) (1% w/w) was dissolved into a bulk oligomer/monomer formulation based on 75/25 w/w epoxyacrylate/tripropyleneglycoldiacrylate (Ebecryl 605 from Cytec). To get a good reproducibility of the experiments, thin samples with low PI optical densities were used. These experimental conditions allow a good dissipation of the heat produced during the polymerization reaction and avoid any internal filter effects. The laminated films (25 μm thick) deposited on a BaF_2 pellet were irradiated with the polychromatic light of a Xe−Hg lamp (Hamamatsu, L8252, 150 W). These experiments were carried out under laminated conditions. The evolution of the double-bond content was continuously followed by real-time FTIR spectroscopy (Nexus 870, Nicolet).[15] The experimental conditions were described in detail in ref 15. 2,2′-Dimethoxy-2-phenyl acetophenone (Irgacure 651,Ciba Spec. or Esacure KB1, Lamberti) was used as a reference.

Laser Flash Photolysis Experiments. Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser (λ_{exc} = 355 nm, 9 ns pulses; energy reduced down to 10 mJ, from Powerlite 9010 Continuum) and an analyzing system consisting of a pulsed xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer.[16]

Scheme 3. Alkoxyamine Synthesis Using a Nitroso Compound



Electron Spin Resonance Experiments. ESR spectra were recorded at room temperature, unless otherwise specified, on a Bruker ESP 300 ESR spectrometer at 9.5 GHz (X-band) employing 100 kHz field modulation and a microwave power of 10 mW, equipped with a variable temperature unit Bruker ER 4111 VT. The magnetic field strength and microwave frequency were measured with a Bruker ER 035 M NMR gaussmeter and a Hewlett−Packard 5350B frequency counter, respectively. The UV irradiations were performed with a 1000-W UV Xe−Hg Oriel lamp (Newport Corp., CA).

ESR spin trapping experiments were carried out on a X-Band spectrometer (MS 200 Magnetech). The radicals generated during the irradiation of the investigated compounds are trapped by phenyl-*N*-tbutylnitrone (PBN). Irradiation was carried out in the cavity (TE102) of the spectrometer with the light of a Hg−Xe lamp (Hamamatsu, L8252, 150 W) through a filter to cut the light below 310 nm.

Computational Procedure. Molecular orbital calculations were carried out with the Gaussian 03 suite of programs.[17] The different structures were fully optimized in the density functional theory framework (at B3LYP/6-31G* level). The bond dissociation energies (BDEs) were calculated as the energetic difference between the radicals and the starting molecules. Both N−O and C−O BDEs were calculated.

Results and Discussion

Alkoxyamine Synthesis. Linear aryl nitroxides (such as **5**, Scheme 1) and their corresponding alkoxyamines have a UV absorption in the 300−400 nm range because of the delocalization of the nitrogen lone pair with the phenyl moiety. Because of its unusual photochemical properties, these latter compounds could possibly act as a PI for NMP^2. Among the numerous nitroxides prepared in the literature, very few examples deal with nitroxides of type **5**.[18−20] Usually, their synthesis is not convenient, and most nitroxides are only persistent,[21] which make the preparation of the alkoxyamines very difficult. To obtain the alkoxyamines based on nitroxides **5**, we followed a one-step procedure originally developed by Grubbs et al.[22,23] This method presents the advantage of avoiding the isolation and purification of the nitroxide and consists only of the reaction of a nitroso compound in the presence of 2 equiv of alkyl radical generated in situ from the corresponding alkyl halide (Scheme 3).

Reaction of the alkyl halide in the presence of the Cu(I)Br/Cu(0)/PMDETA complex was used as a convenient source of alkyl radicals. In this system, the first equivalent of the generated alkyl radical reacted with the nitroso derivatives to afford in situ the corresponding nitroxide. The latter compound trapped a second alkyl radical to produce the desired alkoxyamine. We chose the benzophenone (BP) moiety because of its availability and its well-known efficiency as a chromophore. The synthesis of the nitroso-based benzophenone was straightforward using the procedure of Defoin.[13] The 2-bromo-2-methyl-propionic acid methyl ester was chosen both to increase the steric hindrance close to the aminoxyl function and to lower the BDE (C−O) of the corresponding alkoxyamine, as already demonstrated with SG1-based alkoxyamine.[24,25] The reaction of the 4-nitrosobenzophenone and 3 equiv of 2-bromo-2-methyl-propionic acid methyl ester and 4-nitrosobenzophenone gave the alkoxyamine **4** in 66% yield (Scheme 4) after purification.

Photochemical Properties and Excited State Processes. The UV−visible absorption spectrum of alkoxyamine **4** in acetonitrile is depicted in Figure 1. As for the BP chromophore,[26]

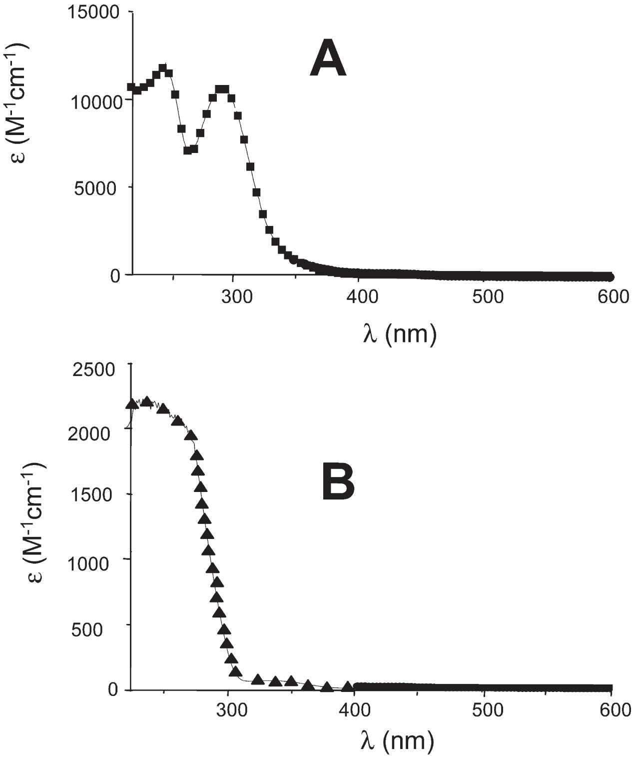
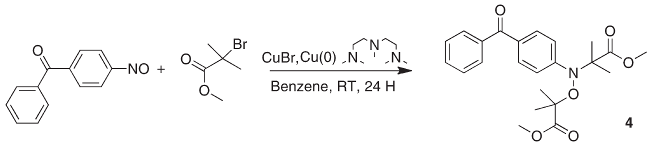


Figure 1. UV−visible absorption spectra of (A) **4** and (B) **1** in acetonitrile. (See Scheme 1 for the structures.)

Scheme 4. Synthesis of Alkoxyamine 4



it exhibits a significant $\pi-\pi^*$ absorption band at $\lambda \approx 290$ nm and a weak shoulder corresponding to a n-π^* transition at $\lambda \approx 340$ nm. Compared with BP (λ ($\pi-\pi^*$) = ~250 nm), the absorption is, however, red-shifted, which outlines the change of the absorption properties induced by the alkoxyamine substitution. Contrary to **1**−**3**, the chromophore properties are different between the unsubstituted (BP) and the final (**4**) compound. From these results, the new proposed alkoxyamine absorbs in a more convenient spectral range.

Laser flash photolysis (LFP) experiments performed on **4** lead to a transient characterized by an intense absorption at 525 nm (Figure 2). This transient can be confidently ascribed to the triplet state of this compound: (i) this species is efficiently quenched by methylnaphthalene (a well-known triplet energy acceptor) and (ii) the corresponding absorption spectrum is similar to that observed for the benzophenone moiety.[26] A residual species is also observed (Figure 2) with a lifetime > 10 ms. Interestingly, the initial absorption of this species is not affected by the oxygen despite the fact that the triplet state is quenched. This probably demonstrates that this transient is mainly produced from a short-life singlet state (S_1). The contribution of a minor triplet state cleavage cannot be ruled out because the triplet state lifetime (~1.5 μs) is shorter than that for BP (6 μs under our experimental conditions).

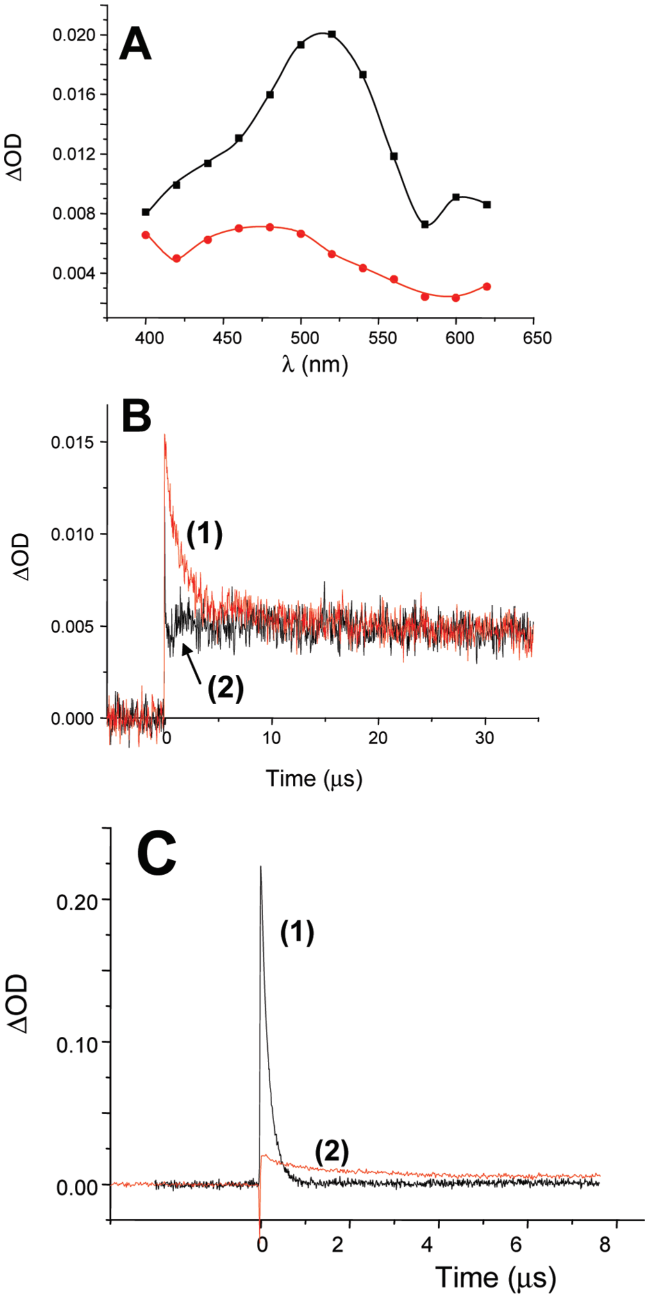


Figure 2. (A) Transient absorption spectra after laser irradiation of **4** in acetonitrile (■, $t = 0\,\mu$s; ●, $t = 15\,\mu$s). (B) Kinetics observed at 525 nm under argon (1) and under air (2). (C) Comparison of kinetics observed for benzophenone BP (under air) (1) and **4** (under argon) (2) in acetonitrile for a similar light absorption intensity.

Considering the residual maximum absorption at about 400−500 nm (very similar to that expected for the nitroxide: 452.4 nm at MPW1PW91/6-31G* level) and its insensitivity to oxygen, the residual transient is confidently ascribed to the nitroxide. This supports a C−O bond cleavage from S_1. For a similar amount of light absorbed for **4** and BP, the transient observed at 525 nm is much more intense for BP (Figure 2c). Assuming similar absorption coefficients for both triplet states, an intersystem crossing ISC (Φ_{isc}) of ~0.1 can be evaluated for **4**. For BP, as usual, Φ_{isc} is assumed to be 1.0.[26] This result demonstrates that the substitution strongly affects the ISC process. No fluorescence is observed for **4** ($\Phi_{fluo} < 10^{-3}$), confirming that the cleavage process is probably the major deactivation pathway for S_1.

Electron Spin Resonance Investigation of Alkoxyamine Photodecomposition. The interesting photochemical properties of **4** prompted us to investigate the decomposition of the

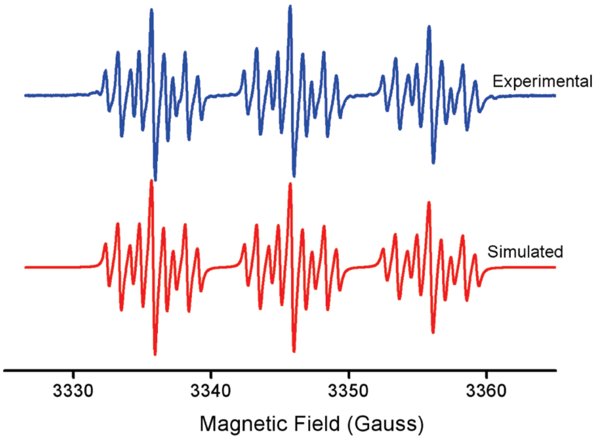


Figure 3. ESR spectrum of nitroxide **5**.

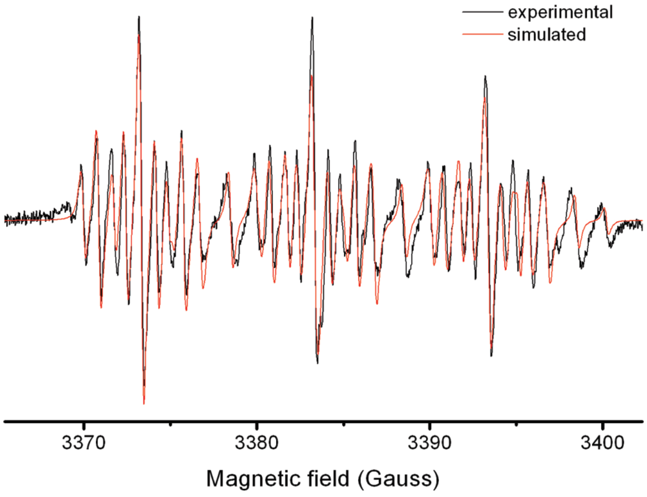


Figure 4. Comparison between the ESR spectrum recorded after 1 h of photolysis and the simulated spectrum coming from the combination of nitroxide **5** and aminyl radical **6**. (See Scheme 5.)

alkoxyamine under UV irradiation by ESR. To characterize the expected nitroxide **5** upon irradiation of the alkoxyamine, we first heated **4** (Figure 3) inside the cavity of the spectrometer. This strategy to observe the nitroxide radical was motivated by the fact that the thermal homolysis of alkoxyamine is a well-known property and because the synthesis of pure nitroxide **5** is not straightforward. A 0.1 M solution of **4** in *tert*-butylbenzene was then heated inside the cavity of the spectrometer at 120 °C in the presence of oxygen as alkyl radical scavenger. The ESR spectrum observed (Figure 3) and the hyperfine coupling constants ($a_N = 1.007$ mT, $a_{Ho} = 0.245$ mT, $a_{Hm} = 0.088$ mT, $g = 2.0057$) are consistent with a linear aromatic nitroxide structure and are in good agreement with the literature for such structure.

Second, we studied by ESR the behavior of the alkoxyamine **4** in *tert*-butylbenzene in a quartz tube upon direct UV irradiation inside the ESR cavity. The comparison of the experimental spectra with the ESR spectrum of the nitroxide **5** highlighted the presence of **5** in combination with another radical. The computer simulation of the experimental spectrum obtained after 1 h of irradiation clearly indicates the formation of two radicals species (Figure 4). From the ESR parameters (Table 1), it can be concluded that both the nitroxide and a aminyl radical **6** arising from the N−O homolytic bond and C−O bond homolysis, respectively, are generated upon irradiation of the alkoxyamine **4** (Scheme 5).

Table 1. ESR Hyperfine Coupling Constants (in mT) for 5 and 6 and Relative C−O/N−O Cleavage Yields

	relative %	a_N	a_{Ho}	a_{Hm}	g
5	75	1.007	0.245	0.088	2.0057
6	25	0.829	0.340	0.165	2.0037

To confirm this assumption, spin-trapping experiments were performed using α-phenyl-*N*-*tert*-butyl nitrone (PBN) as alkyl and alkoxyl radicals scavenger. When **4** was irradiated in the presence of PBN, two different species were observed and characterized by the following hyperfine couplings for the spin adducts: $a_N = 1.45$ mT; $a_H = 0.27$ mT and $a_N = 1.39$ mT; $a_H = 0.16$ mT. These species can be confidently ascribed to alkyl and alkoxyl radicals, respectively, because of the value of the hydrogen splitting constants.[27] A better characterization by isolation of the spin adducts is impossible because of the instability of the latter compounds.[27]

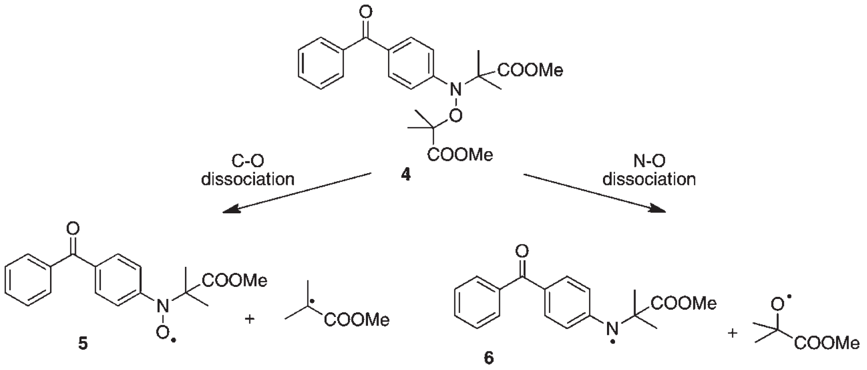
The observation of both carbon- and oxygen-centered radicals is clearly in agreement with a competition of N−O and C−O bond dissociation. The selectivity of the spin trap agent toward both primary radicals (C•, O•) does not allow a direct access to the relative N−O versus C−O pathways.

The calculated BDEs are in agreement with a competitive cleavage; that is, it is found that the BDE(N−O) is 143.0 kJ/mol and BDE(C−O) is 122.1 kJ/mol, with the difference ΔBDE = BDE (N−O) − BDE (C−O) being quite low (20.9 kJ/mol). Interestingly, for this molecule, the BDE(O−C) is lower than the BDE(N−O), which is in agreement with the observed nitroxide formation. A triplet energy (E_T) of 265 kJ/mol has been evaluated for **4** at the UB3LYP/6-31G* level. This value is close to that found for BP (288 kJ/mol), demonstrating that the corresponding excited state is probably mainly localized on the BP moiety.[26] From the calculated BDEs, both N−O and C−O cleavages are found to be exothermic because E_T > BDE. The design of molecules exhibiting a higher ΔBDE can be useful to enhance the selectivity of the C−O bond cleavage. Cleavage from S_1 is expected to be even more exothermic because $E_{S1} > E_T$.

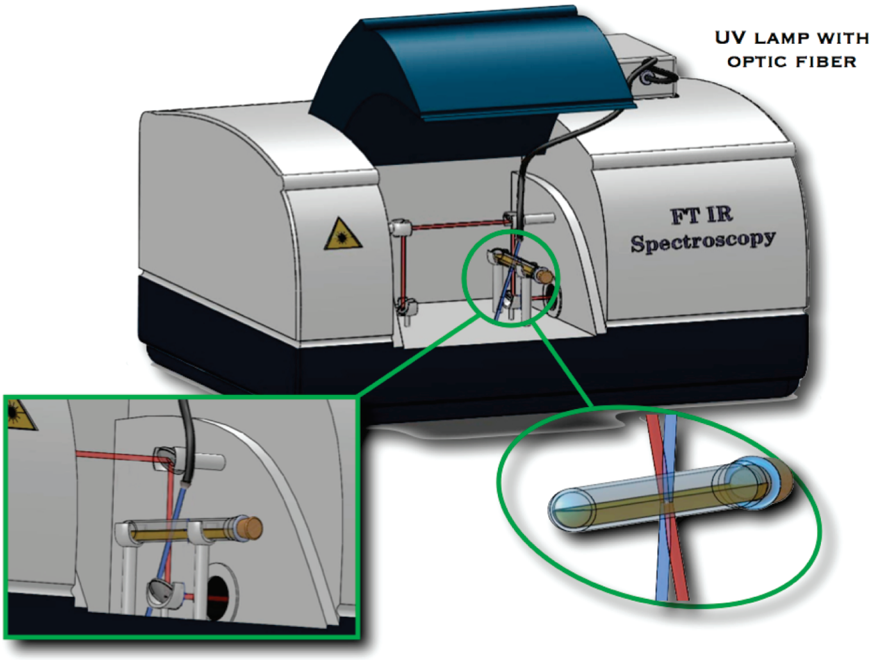
Photopolymerization experiments. *Photoinitiator Ability*. The PI ability of **4** has been evaluated for an acrylate matrix (Ebecryl 605, Cytec) (Figure 5). The behavior of **4** as a conventional PI is worthwhile because it exhibits a PI ability close to 2,2′-dimethoxyphenyl acetophenone (Irgacure 651, Ciba). This high photoinitiating ability of **4** will be useful for applications requiring both high polymerization rates and a living character for the polymer formed.

Nitroxide-Mediated Photopolymerization. As previously noticed, there are only a few studies on the possibility of alkoxyamines to control the polymerization of acrylates or styrenic derivatives under UV activation.[11,12] All of the already described alkoxyamines are based on styryl-TEMPO−OH-based compounds on which different chromophores were attached. As we were working with the benzophenone chromophore, we prepared the alkoxyamine **1** as the representative of both the work of Neckers[11] and Scaiano[12] and also as a comparative compound for the alkoxyamine **4**. The ability of the different alkoxyamines to control the photopolymerization of *n*-butyl acrylate was therefore investigated. This monomer was chosen because it does not self-polymerize under UV irradiation under our conditions. (See the Supporting Information.) The photopolymerization was carried out in a sealed glass tube (sample thickness: 1 mm) after degazing by argon bubbling. The experimental setup is schematically presented in Scheme 6.

Scheme 5. Competition between C−O and N−O Bond Cleavages



Scheme 6. Experimental Setup Used for the Nitroxide Mediated Photopolymerization Experiment



This allows us to follow online the conversion during the irradiation.

The first nitroxide-mediated photopolymerization experiments were performed using the alkoxyamine **1** as a model of the alkoxyamines previously used in the literature. The polymerization kinetic is displayed in Figure 6. A linear increase in the conversion was observed, and 30% of conversion is reached in 500 s. In the case of alkoxyamine **4**, a linear increase in ln $[M]_0/[M]$ was also observed, and more interestingly, 80% of conversion was obtained in 500 s. This represents an important increase in the rate of polymerization. By comparison, few studies were devoted to the *n*-butyl acrylate polymerization mediated by dithiocarbamate compounds,[28,29] but in these works, the time to reach conversion above 60% was usually >1 h at least.

Because the polymerization rate is higher in the case of alkoxyamine **4** compared with other photoiniferter systems (dithiocarbamates and alkoxyamine **1**) and is more similar to a classical PI system, we have to investigate if a reversible recombination reaction inducing the controlled character was occurring. Therefore, we checked if the lifetime of the alkoxyamine functionality could be prolonged in the absence of any scavenger. Photolysis experiments of 10 s in acetonitrile using a similar setup as the one used in polymerization process were carried out under aerated and inert (argon degazing) conditions (Figure 7). It is worthwhile to note that the irradiation of 10 s under aerated

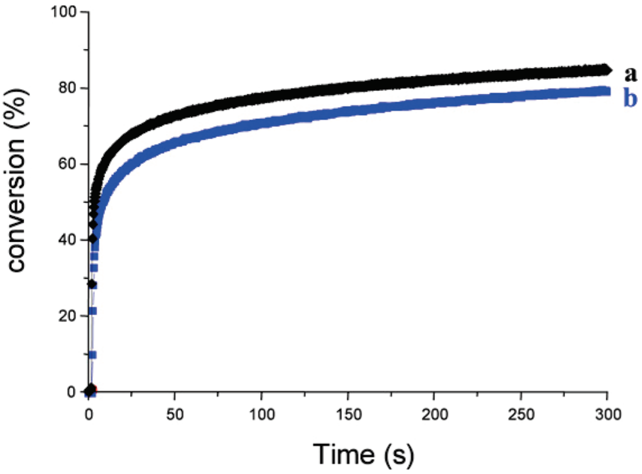


Figure 5. Conversion versus time curves for the photopolymerization of Ebecryl 605. Photoinitiating system (1% w/w): (a) Irgacure 651 (Ciba) and (b) **4**.

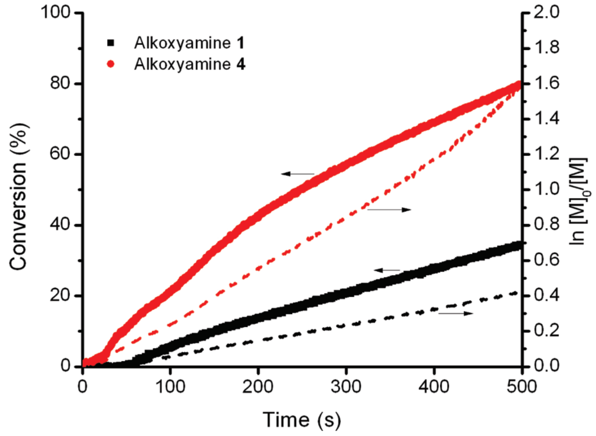


Figure 6. Kinetic plot for the photopolymerization of *n*-butyl acrylate using **1** or **4** (1% w/w).

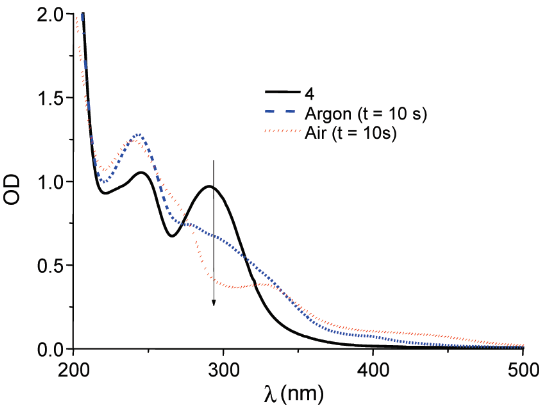


Figure 7. Photolysis of **4** in acetonitrile under air or argon. The irradiation conditions are similar to those of the photopolymerization experiments. A full bleaching of **4** is noted in the presence of scavenger (air) after 10 s of irradiation (280 nm). A shoulder is observed at ~450 nm and can be tentatively ascribed to the nitroxide.

conditions (which allows us to trap the carbon-centered radicals by oxygen to avoid the recombination process and the alkoxyamine regeneration) fully decomposes **4** (disappearance of the absorption band at 280 nm), whereas under inert conditions, only a small amount of **4** was consumed. This result means that the lifetime of macroradicals is drastically prolonged, and this enables a living process.[30] Second, in a real polymerization process, the monomer acts as a scavenger for the initiating radical, which suggests that **4** was totally consumed in 10 s and that the polymerization process for $t > 10$ s is initiated by the decomposition of macroalkoxyamines.

The molecular weight distributions for the *n*-butyl acrylate polymerization performed with **1** are similar, whatever the conversion (Supporting Information), and the M_n values are close to 250 000 g·mol^{-1} with PDI close to 2.5. Such high M_n values compared with the theoretical ones ([**1**] = 1% w/w, i.e., 48 500 g·mol^{-1} at 100% conversion) could be explained by a nonefficient photolysis of **1**, leading to very small amounts of alkyl and nitroxide radicals. The alkyl radicals initiate the polymerization of *n*-butyl acrylate, a monomer with a high propagation rate constant. At the same time, the amount of nitroxide is not sufficient to trap the alkyl macroradicals and stop or moderate the propagation. The combination of these phenomena led to polymers with high M_n, as already observed in NMP.[24] In a similar way, when using Irgacure 651, the reversible recombination obviously does not take place, and almost constant M_n values versus conversion were also found.[31]

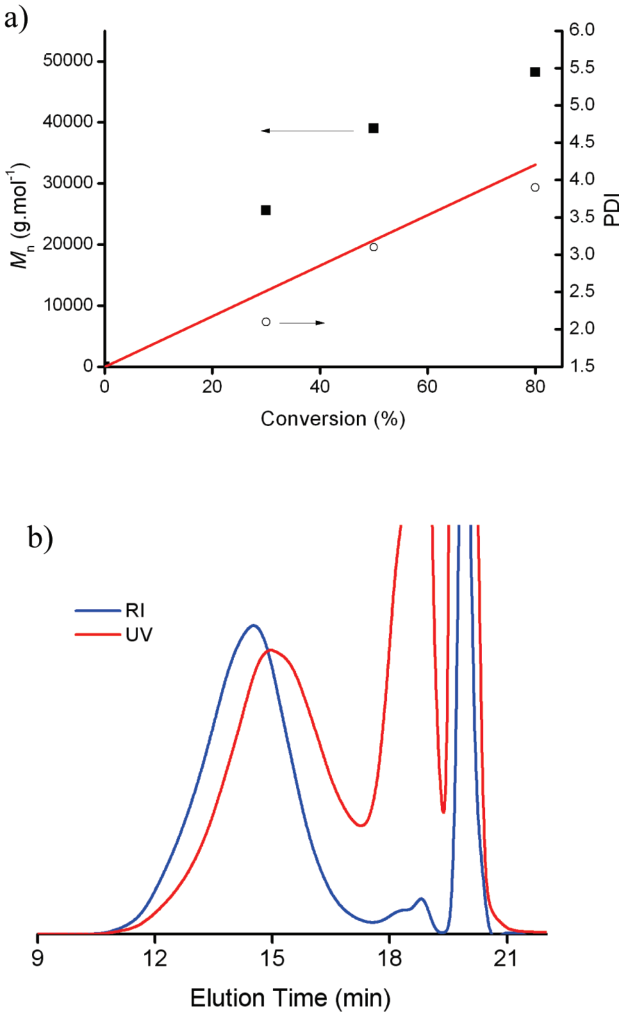


Figure 8. (a) M_n and PDI versus conversion for the photopolymerization of *n*-butyl acrylate with **4** (1% w/w targeted M_n = 41 300 g·mol^{-1} at 100% conversion). (b) Typical SEC curves associated with NMP[2] experiments (48% of conversion) with a detection of the polymer chains by both RI and UV-absorption λ = 280 nm (maximal absorption for the chromophore of **4**).

When **4** is used as initiator instead of **1**, a linear evolution of M_n with the conversion is noted (Figure 8a). Interestingly, the amplitude of the M_n change is quite large (25 000−40 000 g·mol^{-1}). This behavior suggests a partial controlled character for the photopolymerization process. Moreover, the relatively low M_n obtained compared with the one obtained using alkoxyamine **1** is another indirect proof that alkoxyamine **4** strongly moderates the reactivity of the polymerization process and allows the generation of a controlled and living system.

The PDIs are found to be quite large from 2.2 for a conversion of ~30% (irradiation time 100 s) to 3.9 for a conversion of 80% (irradiation time 500 s), demonstrating that the control process is not perfect. It has to be noticed that the experimental conditions, that is the irradiation system (geometry, UV lamp, etc.) can be of importance for both the kinetics and the behavior (control, livingness) of the polymerization. As light from the source penetrates the sample, it is absorbed by the alkoxyamine, causing a decrease in light intensity with depth into the sample. This can cause gradients in polymerization rate and therefore also leads to heat and mass transfer-related effects.[32,27] It also has to be

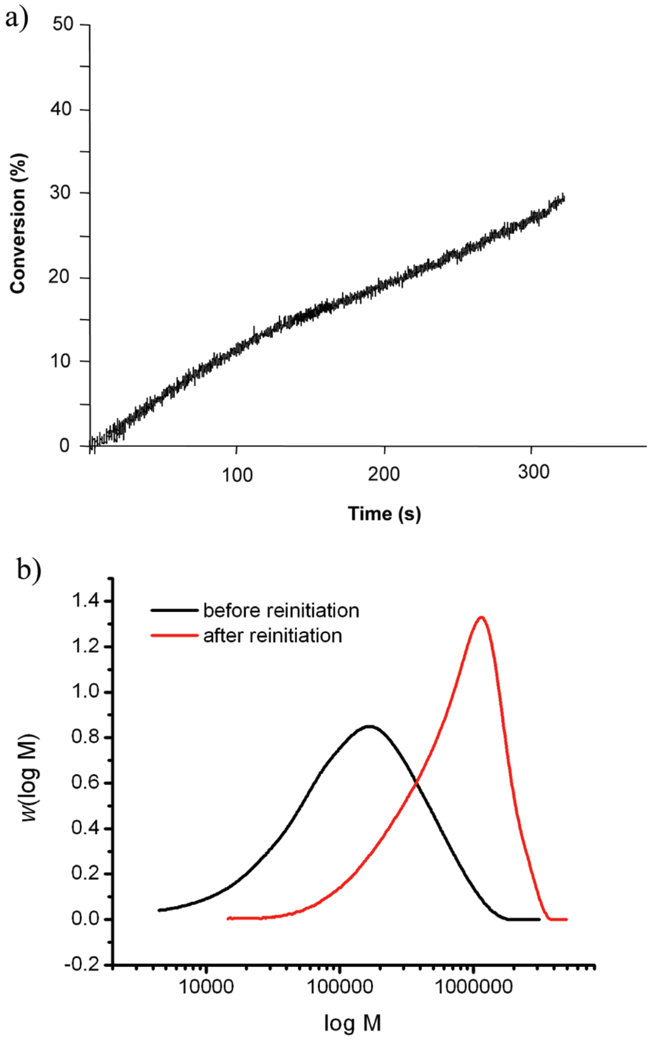


Figure 9. (a) RT-FTIR conversion versus time plot for the reinitiation experiment (macroinitiator: 200 s of irradiation, 39% conversion); the excess of monomer was removed under vacuum, and the polymerization kinetics presented was initiated (nBA) by the macroalkoxyamine formed in the first step. (b) Molecular weight distribution before ($M_n = 64\,000$ g·mol^{-1}, PDI = 3.3) and after reinitiation ($M_n = 425\,000$ g·mol^{-1}, PDI = 2.2).

noted that polyacrylates are prone in both conventional and controlled radical polymerization processes (especially when the conversion is high) to intermolecular polymer chain transfer,[33] which leads to an important increase in the polydispersity index due to the long-chain branches created.[34−36] Nevertheless, in that case, the important increase in PDI versus conversion could be likely ascribed to the N−O bond cleavage in (macro)alkoxyamine inducing a lack of persistent radicals. For classical photoiniferters, such a behavior was also noted; that is, the deviation from the origin of the M_n versus conversion plot corresponds to a usual behavior and indicates that a part of the carbon−carbon termination mechanism still remains in the early stages of the reaction, the linear trend being always ascribed to the polymeric radical/persistent radical recombination reaction.

To fully evidence the living character of the formed polymers, a characterization of the polymer chains was also carried out by SEC experiments using both RI and UV detection.[37] For experiments similar to the one presented in Figures 7 and 8a, the comparison of the UV signal at 280 nm (maximal absorption for the chromophore of **4**) and the refractive index RI signal evidence that a large part of the chains is linked to the chromophoric group; that is, the polymer is able to reinitiate the polymerization (Figure 8b). The nonperfect overlapping is due to the nonperfect living character and also to the fact that mass-sensitive (RI signal) and number-sensitive (UV signal) detectors are used. Nevertheless, these data fully evidence a partial living character for the formed polymers.

To further illustrate the livingness of the polymer, a reinitiation test was performed.[38] A similar experiment to the one displayed in Figures 7 and 8 was performed. The polymerization was carried out for 200 s (39% of conversion; a different light intensity than Figures 7 and 8 is used), and a poly(*n*-butyl acrylate) with a M_n of 64 000 g·mol^{-1} and a PDI of 3.3 was obtained. After evaporation of the residual monomer, the polymer was again diluted by a second addition of *n*-butyl acrylate before a second irradiation. The reinitiation process was observed by RT-FTIR, and 30% of conversion was obtained in < 300 s, confirming the photoinitiation ability of the starting polymer (Figure 9a). The molecular weight distributions MWDs before and after reinitiation (500 s, 42% of conversion) are displayed in Figure 9b.

The clear shift of the MWD distribution before and after reinitiation, that is, from 64 000 to 425 000 g·mol^{-1}, evidenced a good reinitiation, even if one could notice a long tail toward lower molar masses. Because of both the N−O versus O−C competitive dissociation and the fact that high molar masses polymers are obtained, the control of the second bloc is difficult to obtain. It is not possible to check if the polymer after reinitiation still possess the chromophoric end chain because at such a high molecular weight, the too low concentration of the chromophoric group prevents its detection by dual detection RI/UV.

Conclusion

The photolysis of alkoxyamine **4** bearing a chromophoric group directly linked to the aminoxyl function of the nitroxide moiety is investigated. Laser flash photolysis experiments show a singlet state cleavage and (to a minor extent) a possible triplet state cleavage leading to a C−O bond homolysis. An additional N−O cleavage is supported by ESR experiments.

Using this compound as a photoiniferter for the polymerization of *n*-butyl acrylate, a linear growth of the polymer chain combined with a partial living character has been evidenced: to the best of our knowledge, this is the first example of using an efficient photosensitive nitroxide being able to achieve fully an NMP^2 process. The control process could presumably be optimized by using other alkoxyamines exhibiting a better C−O bond cleavage selectivity. This kind of compound also appears to be a promising conventional PI for the free radical photopolymerization of multifunctional monomers. New compounds will be proposed in forthcoming works.

Acknowledgment. This work was supported by the "Agence Nationale de la Recherche" ANR under grant NMP2 07-JCJC0143. We would like to thank Kevin Guillaneuf for his help in Scheme 6.

Supporting Information Available: Typical SEC curves associated with NMP^2 experiments (*n*-butyl acrylate) with a detection of the polymer chains by RI detection, conversion versus time plot for the photopolymerization of *n*-butyl acrylate without initiator, and molecular weight distributions for the *n*-butyl acrylate polymerizations initiated by **1** at different conversions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Fouassier, J. P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamental and Applications*; Hanser Publishers: New York, 1995. (b) *Photochemistry and UV Curing: New Trends*; Fouassier, J. P., Ed.; Research Signpost: Trivandrum, India, 2006.
(2) Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121–2136.
(3) Manga, J. D.; Polton, A.; Tardi, M.; Sigwalt, P. *Polym. Int.* **1998**, *45*, 14–21.
(4) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
(5) Scaiano, J. C.; Connolly, T. J.; Mohtat, N.; Pliva, C. N. *Can. J. Chem.* **1997**, *75*, 92–97.
(6) Yoshida, E. *Colloid Polym. Sci.* **2010**, *288*, 7–13.
(7) Yoshida, E. *Colloid Polym. Sci.* **2010**, *288*, 73–78.
(8) Yoshida, E. *Colloid Polym. Sci.* **2009**, *287*, 1417–1424.
(9) Yoshida, E. *Colloid Polym. Sci.* **2009**, *287*, 767–772.
(10) Yoshida, E. *Colloid Polym. Sci.* **2008**, *286*, 1663–1666.
(11) Hu, S.; Malpert, J. H.; Yang, X.; Neckers, D. C. *Polymer* **2000**, *41*, 445–452.
(12) Goto, A.; Scaiano, J. C.; Maretti, L. *Photochem. Photobiol. Sci.* **2007**, *6*, 833–835.
(13) Defoin, A. *Synthesis* **2004**, 706–710.
(14) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206–4215.
(15) Lalevee, J.; Allonas, X.; Jradi, S.; Fouassier, J. P. *Macromolecules* **2006**, *39*, 1872–1879.
(16) Lalevee, J.; Allonas, X.; Fouassier, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 9613–9621.
(17) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; , Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh PA, 2001. (b) Foresman J. B.; Frisch A. In *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian. Inc.: Pittsburgh, PA, 1996.
(18) Das, K.; Pink, M.; Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **2006**, *128*, 5334–5335.
(19) Spagnol, G.; Shiraishi, K.; Rajca, S.; Rajca, A. *Chem. Commun.* **2005**, 5047–5049.
(20) Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Free Radicals*; Academic Press: New York, 1968.
(21) Calder, A.; Forrester, A. R. *Chem. Commun.* **1967**, 682–&.
(22) Grubbs, R. B.; Wegrzyn, J. K.; Xia, Q. *Chem. Commun.* **2005**, 80–82.
(23) Greene, A. C.; Grubbs, R. B. *Macromolecules* **2009**, *42*, 4388–4390.
(24) Chauvin, F.; Dufils, P. E.; Gigmes, D.; Guillaneuf, Y.; Marque, S. R. A.; Tordo, P.; Bertin, D. *Macromolecules* **2006**, *39*, 5238–5250.
(25) Bertin, D.; Gigmes, D.; Marque, S. R. A.; Tordo, P. *Macromolecules* **2005**, *38*, 2638–2650.
(26) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.
(27) Rosen, G. M.; Britigan, B. E.; Halpern, H. J.; Pou, S. *Free Radicals: Biology and Detection by Spin Trapping*; Oxford University Press: New York, 1999.
(28) Manga, J. D.; Tardi, M.; Polton, A.; Sigwalt, P. *Polym. Int.* **1998**, *45*, 243–254.
(29) Kilambi, H.; Reddy, S. K.; Bowman, C. N. *Macromolecules* **2007**, *40*, 6131–6135.
(30) Kothe, T.; Marque, S.; Martschke, R.; Popov, M.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1553–1559.
(31) Lalevee, J.; Blanchard, N.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2008**, *41*, 2347–2352.
(32) Goodner, M. D.; Bowman, C. N. *Chem. Eng. Sci.* **2002**, *57*, 887–900.
(33) Junkers, T.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7585–7605.
(34) Castignolles, P.; Graf, R.; Parkinson, M.; Wilhelm, M.; Gaborieau, M. *Polymer* **2009**, *50*, 2373–2383.
(35) Gaborieau, M.; Nicolas, J.; Save, M.; Charleux, B.; Vairon, J. P.; Gilbert, R. G.; Castignolles, P. *J. Chromatogr., A* **2008**, *1190*, 215–223.
(36) Castignolles, P. *Macromol. Rapid Commun.* **2009**, *30*, 1995–2001.
(37) Hosseini Nejad, E.; Castignolles, P.; Gilbert, R. G.; Guillaneuf, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2277–2289.
(38) Guillaneuf, Y.; Gigmes, D.; Marque, S. R. A.; Astolfi, P.; Greci, L.; Tordo, P.; Bertin, D. *Macromolecules* **2007**, *40*, 3108–3114.