Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 2892

www.rsc.org/obc

PAPER

Structural effects on the photodissociation of alkoxyamines†‡

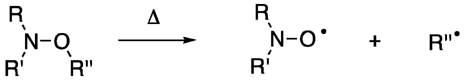
Davy-Louis Versace,[a] Yohann Guillaneuf,[b] Denis Bertin,[b] Jean Pierre Fouassier,[a] Jacques Lalevée*[a] and Didier Gigmes*[b]

Received 19th December 2010, Accepted 2nd February 2011
DOI: 10.1039/c0ob01207f

The search for photosensitive alkoxyamines represents a huge challenge. The key parameters governing the cleavage process remain unknown. The dissociation process of light sensitive alkoxyamines is studied as a function of their chemical structures. The photochemical properties of 6 selected compounds are investigated by ESR and laser flash photolysis. It is found that (i) the selectivity of the cleavable N–O *vs.* C–O bond and (ii) the efficiency of the nitroxide formation are strongly related to the alkoxyamine structure. The distance between the chromophore and the aminoxy group is a key parameter for an efficient pathway of the radical generation as displayed by the photopolymerization ability of these alkoxyamines.

Introduction

Alkoxyamines are characterized by a widespread use in different fields *i.e.* in organic synthesis, ref. 1 and references therein, the design of fluorescence probes[2] or in the development of controlled polymerization processes such as the Nitroxide Mediated Polymerization (NMP)[3] and more recently in Nitroxide Mediated Photopolymerization (NMP^2).[4–10] Usually, nitroxides can be generated by thermolysis of alkoxyamines (at temperature typically ~ 80–130 °C) through a O–C bond cleavage process (Scheme 1). The BDE(O–C) is typically in the 80–130 kJ mol^{-1} range depending on both the alkyl and nitroxide fragments.



Scheme 1 Decomposition of alkoxyamines.

Photosensitive alkoxyamines can be highly worthwhile (being able to decompose under light irradiation at RT) *i.e.* for NMP^2 or organic synthesis applications. Such photosensitive compounds, however, have been the subject of relatively few studies.[4–6] A chromophore with good light absorption properties must be obviously introduced on the alkoxyamine structure as classical alkoxyamines used in thermal processes usually exhibit light absorption at short wavelengths ($\lambda < 250$ nm) which are also absorbed by the solvent or the vessel.[7]

Albeit that the thermolysis process of alkoxyamines has been the subject of numerous studies in the literature,[3] few photosensitive alkoxyamines are known.[4–10] The key parameters governing the cleavage process remain unknown: improved knowledge of the factors governing this reaction and nitroxide production still remains highly desirable. New light sensitive alkoxyamines were recently proposed, as mediators in the NMP^2 process.[8–10] The first step corresponds to the photodecomposition of the alkoxyamine with formation of an initiating radical and a nitroxide (Scheme 1). As in NMP, the reversible reaction between the polymeric radical and the nitroxide allows control of the polymerization reaction through a significant decrease in the proportion of irreversible self-terminating reactions. Typically, the chromophore group must be located on the nitroxide moiety to ensure reversible cleavage of the macroalkoxyamine during the photopolymerization process. It has to be mentioned that, the use of non-absorbing alkoxyamines in conjunction with a thermal initiator (azobisisobutylonitrile) and an iodonium salt was recently reported in photoliving polymerization processes[11a,11b] however the mechanism still remains unclear.[11c]

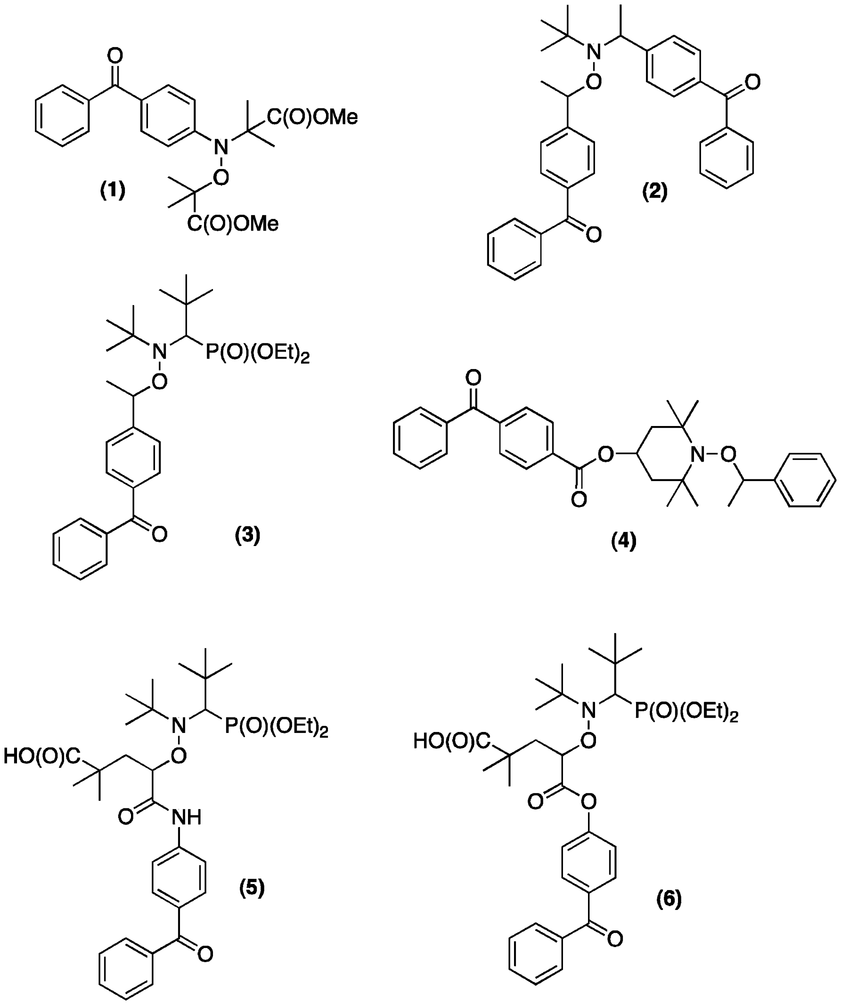
To get new insights into these crucial points, our first NMP^2 experiments were promising and encouraging,[8,10] the photochemical behavior of six alkoxyamines is investigated here (Scheme 2). Two new alkoxyamines (**5** and **6**) are synthesized and compared to three previously presented compounds **1–3**.[8–10] These two new compounds are not expected to show NMP^2 behavior because the chromophore resides in a different moiety to the nitroxide and so would separate as the polymerization takes place. These compounds are designed here for a better understanding of the cleavage process and more particularly to investigate the

---

[a] *Département de Photochimie, CNRS, Université de Haute Alsace, ENSCMu, 3 rue Alfred Werner, 68093, Mulhouse, Cedex, France*
[b] *Laboratoire Chimie Provence, Faculté des Sciences et Techniques, Universités Aix-Marseille I, II, III-CNRS UMR 6264, Equipe CROPS, campus Saint Jérôme Case 542, 13397, Marseille, Cedex 20, France. E-mail: didier.gigmes@univ-provence.fr, j.lalevee@uha.fr*

† This work is dedicated to the memory of Athel Beckwith, a teacher and scientist from whom we learned how to study chemistry by example. His pioneering advances in radical chemistry laid the foundation for much of the current radical clock methodology.

‡ Electronic supplementary information (ESI) available: The different optimized geometries are given for the representative structures **4–6**. See DOI: 10.1039/c0ob01207f



Scheme 2 Investigated alkoxyamines.

behavior of alkoxyamines exhibiting separated chromophore–aminoxy functions. Compound **4** was selected for sake of comparison (its photochemical properties have already been investigated by laser flash photolysis without ESR investigation[5]). All the alkoxyamines have a benzophenone chromophore; the structure of the leaving nitroxide as well as its position on the alkoxyamine varies. In the present paper, we investigate and discuss the effects of the alkoxyamine structure on the efficiency of nitroxide generation, by means of laser flash photolysis, ESR and molecular orbital (MO) calculations.

Experimental part and computational procedure

Materials

Ebecryl 605, an oligomer/monomer formulation based on 75/25 w/w epoxyacrylate/tripropyleneglycoldiacrylate was purchased from Cytec at the highest purity level available and used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (I651 or Irgacure 651 or Esacure KB1 or DMPA) which behaves as a free-radical photoinitiator of acrylate polymerization was provided by Ciba Specialty Chemicals. The alkoxyamine **4** was prepared as described in [ref. 5]. The *N*-acrylamidobenzophenone and the 4-acryloylbenzophenone were prepared as described in refs. 12a and 12b, respectively.

Synthesis of alkoxyamine 5

A solution of BlocBuilder MA or MAMA-SG1 (from Arkema) (4.03 g, 10.58 mmol) and *N*-acrylamidobenzophenone (2.47 g, 9.83 mmol) in THF was introduced in a Schlenk tube equipped with a rotaflo, deoxygenated by nitrogen bubbling and heated at 100 °C for 1 h under stirring. The reaction mixture was then concentrated under reduced pressure. The yellowish oil was dissolved in dichloromethane and extracted with sodium hydroxide solution (5 wt%). The aqueous phase was then acidified with concentrated aqueous hydrochloride until pH 1, and extracted with dichloromethane. After drying on magnesium sulfate, filtration and evaporation of dichloromethane, the mixture was precipitated in cold pentane to obtain the alkoxyamine as a white powder.

Yield: 60%. ^{1}H NMR (300.13 MHz, $CDCl_3$): 7.92–7.39 (m, 9H), 5.54 (dd, 1H), 4.30–3.93 (m, 4H), 3.45 (d, *J* = 27.6 Hz, 1H), 2.39–2.17 (m, 2H), 1.44–0.90 (m, 30H). ^{31}P NMR (121.49 MHz, $CDCl_3$): 25.43. ESI-HRMS: calcd for $C_{33}H_{49}N_2O_8P$ $[M+H]^+$ 633.3299, found 633.3283.

Synthesis of alkoxyamine 6

A solution of BlocBuilder MA (5.66 g, 14.85 mmol) and 4-acryloylbenzophenone (3.12 g, 12.37 mmol) in THF was introduced into a Schlenk tube equipped with a rotaflo, deoxygenated by nitrogen bubbling and heated at 100 °C for 1 h under stirring. The reaction mixture was then concentrated under reduced pressure. The yellowish oil was dissolved in dichloromethane and extracted with sodium hydroxide solution (5 wt%). The aqueous phase was then acidified with concentrated aqueous hydrochloride until pH 1, and extracted with dichloromethane. After drying on magnesium sulfate, filtration and evaporation of dichloromethane, the mixture was precipitated in cold pentane to obtain the alkoxyamine as a white powder.

Yield: 55%. ^{1}H NMR (300.13 MHz, $CDCl_3$): 7.91–7.38 (m, 9H), 4.90 (dd, 1H), 4.37–3.98 (m, 4H), 3.50 (d, J = 26.2 Hz, 1H), 2.64–2.45 (m, 2H), 1.54–0.95 (m, 30H). ^{31}P NMR (121.49 MHz, $CDCl_3$): 23.27. ESI-HRMS: calcd for $C_{33}H_{48}NO_9P$ $[M+H]^+$ 634.3139, found 634.3143.

Laser Flash Photolysis (LFP)

The nanosecond laser flash photolysis set up working at 355 nm is based on a nanosecond Nd:YAG laser (Powerlite 9010, Continuum) operating at 10 Hz with a 7 mJ/pulse energy.[13] The analyzing system (LP900, Edinburgh Instruments) used a 450 W pulsed xenon arc lamp, a Czerny–Turner monochromator, a fast photomultiplier and a transient digitizer (TDS 340, Tektronix). The sample was contained in a 1 cm cell. Measurements were done at room temperature.

Electron Spin Resonance (ESR)

Electron Spin Resonance (ESR) experiments were carried out using a X-Band spectrometer (MS 200 Magnettech). The radicals were generated using a polychromatic light irradiation (Xe–Hg lamp; Hamamatsu, L8252, 150 W; $\lambda > 310$ nm). The ESR spectra simulations were done with the PEST WINSIM program.[14] All of the samples were prepared in a 6 mm quartz cylindrical tube and dissolved in *tert*-butylbenzene as the inert solvent.

Polymerization experiments

The photopolymerization profiles were followed by Real-Time FTIR (Nexus 870, Nicolet). All the experiments were carried out at room temperature in laminate using the polychromatic light emitted by a Xe–Hg lamp (Hamamatsu, L8252, 150 W, light intensity at the sample: 22 mW cm^{-2}). Concentrations of 0.5 wt% in DMPA (the reference standard) or in alkoxyamines were used. The monomer formulation was applied on a BaF_2 pellet with a bar coater to form a 25 µm thick liquid film layer. The progress of the polymerization was continuously monitored through the decrease of the 1630 cm^{-1} band corresponding to the C=C bond of the monomer acrylate group.[15]

Computational procedure

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs.[16] The different alkoxyamine structures were fully optimized in the Density Functional Theory framework (at B3LYP/6-31G* level). The Bond Dissociation Energies (BDE) were calculated as the energetic difference between the radicals and the starting molecules.

Results and Discussion

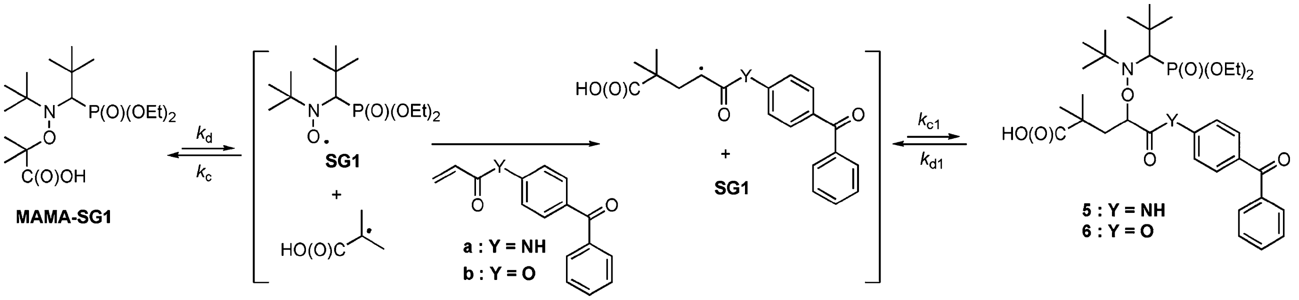
1 Synthesis of alkoxyamines

Functionalized alkoxyamines are usually prepared by multi-step synthesis. Recently, Gigmes *et al.*[12c] proposed a straightforward method to obtain functionalized alkoxyamines in one step. They developed a clean intermolecular radical 1,2 addition of alkoxyamines on activated olefins, which generate a "second generation" functionalized alkoxyamine (Scheme 3). The challenge is to avoid multiple addition and then to circumvent any undesired polymerization, the thermal stability of the obtained alkoxyamines has to be higher than the starting material.

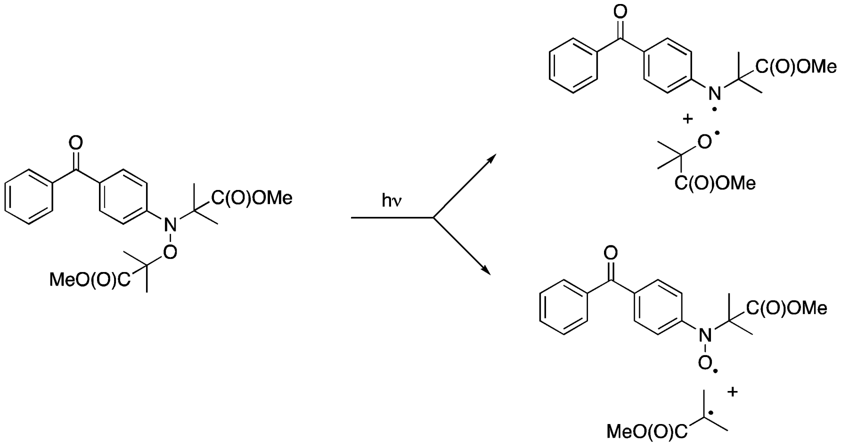
Following this strategy alkoxyamines **5** and **6** were efficiently prepared from the 1,2 radical addition of MAMA-SG1, at 100 °C in deoxygenated THF solutions, onto benzophenone derivatives (Scheme 3). In each case, monomer conversion was above 90% and the corresponding alkoxyamines were obtained with a yield close to 60% after purification. The success of these reactions is strongly related to the lower BDE of the NO–C bond in MAMA-SG1 compared to that in **5** or **6**. Indeed, compared to **5** and **6**, for MAMA-SG1 the 1-carboxy-1-methy ethyl moiety introduces both a destabilization of the ground state of the starting alkoxyamine, and a higher stabilization of the generated alkyl radical, which results in lower NO–C BDE.

2 Light absorption properties of 1–6

The absorption spectra of **4–6** are shown in Fig. 1. The introduction of the benzophenone moiety on the alkoxyamines leads to good absorption properties in the 300–400 nm range. The weak



Scheme 3 Intermolecular radical 1,2 addition of MAMA-SG1 onto benzophenone derivatives.



Scheme 4 Competitive dissociation processes for **1** under light irradiation.

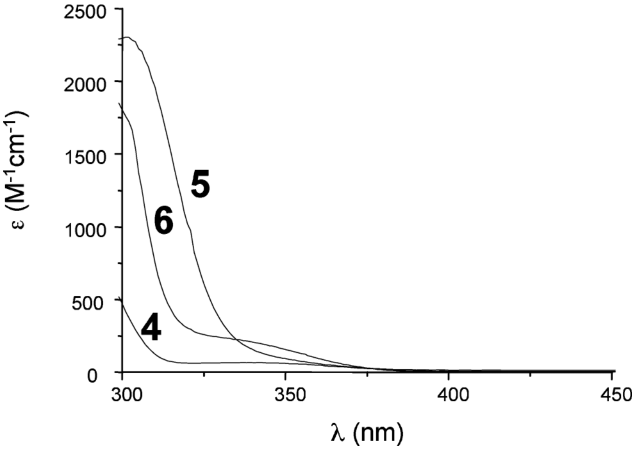


Fig. 1 UV-visible absorption spectra of **4**, **5** and **6** in acetonitrile.

absorption band (or the shoulder for some compounds) usually observed at about 330 nm is ascribed to the nπ* transition of the benzophenone chromophore; the molar extinction coefficients are typically in the 100–500 M^{-1}cm^{-1} range. A $\pi\pi$* transition located between 250 and 310 nm also associated with the benzophenone structure is observed. For **1–3**, the UV absorption properties are reported[8–10] with similar trends for the nπ* and $\pi\pi$* transitions. These good absorption properties of **1–6** are in contrast to those of typical alkoxyamines used for thermal processes which do not exhibit any absorption at $\lambda > 280$ nm.[7]

3 Cleavage process: ESR results

The observation of nitroxides generated under light irradiation requires specific selected conditions to get a rapid conversion of the alkyl radicals into unreactive species and to avoid their recombination with nitroxides. Different trapping agents such as other nitroxides, hydrogen donors or oxygen have already been used to prevent this back-reaction.[17–18] For easy handling and rapid measurements, the use of oxygen is chosen. In this case, the carbon-centered radicals (resulting from C–O bond dissociation) are trapped by oxygen to yield peroxyl radicals, thereby preventing the recombination between the nitroxide and the carbon-centered radical. As a consequence, the intensity increase of the ESR signal is only related to the formation of nitroxides. Peroxyl radicals are not observed in these experiments.

Two main cleavage processes can be expected in alkoxyamines (Scheme 4). In **1–3**, the formation of nitroxides under light irradiation is clearly demonstrated.[8-10] For **1**, a competitive N–O cleavage process has also been found and is supported by the observation of aminyl radicals. For **2** and **3**, the C–O cleavage is highly selective and quantitative as the final nitroxide concentration, after irradiation and complete photolysis, is equal to the initial alkoxyamine concentration.

In **4**, the nitroxide could also be detected (thanks to the observation of a strong ESR signal: $g \sim 2.0065$ and $a_N = 15.4$ G) as shown in Fig. 2; no other bond cleavage was noted as only nitroxides were observed albeit that the associated signal decreases for long irradiation time ($t > 350$ s). This can be ascribed to the quenching of the triplet state of **4** by the formed nitroxides. Indeed, such a process is efficient for long lived triplet states (see *e.g.* ref. 7). The formation of nitroxides is more difficult in **4** compared with **2–3**. Indeed, for a similar light absorption, the increase in nitroxide concentration is much slower for **4** *i.e.* at a 400 s time scale for **4** compared to 1–10 s for **2–3** (Fig. 2).

In **6**, the starting ESR signal ($a_P = 46.2$ G; $a_N = 13.6$ G) at time $t = 0$ is assigned to the stable and known SG1 radical[19] that may be present in the starting sample due to the known higher thermal lability of the SG1-based alkoxyamines.[7] The ESR signal does not increase with irradiation time which indicates a low nitroxide initiation ability (Fig. 2C). A similar behavior is observed for **5**. As in **4**, no evidence for N–O cleavage can be provided in **5** and **6**.

4 Excited state processes: a LFP investigation

Upon laser excitation of **4**, **5** and **6**, transient absorptions at about 550, 480 and 520 nm are observed (Fig. 3). These species are strongly quenched by camphorquinone ($k > 10^7$ M^{-1}s^{-1}) and oxygen ($k > 10^9$ M^{-1}s^{-1}), which are well known triplet energy acceptors (Fig. 3D). Therefore, these transients can be confidently ascribed in any case to a triplet state located on the benzophenone moiety. The lifetime of this transient (Table 1) is quite short (0.9 μs for **4**) but it increases for **5**, **6** (2.2–2.5 μs). The reduced lifetime of **4** compared to that of the benzophenone triplet state is in agreement with previous data on this compound[5], and is also

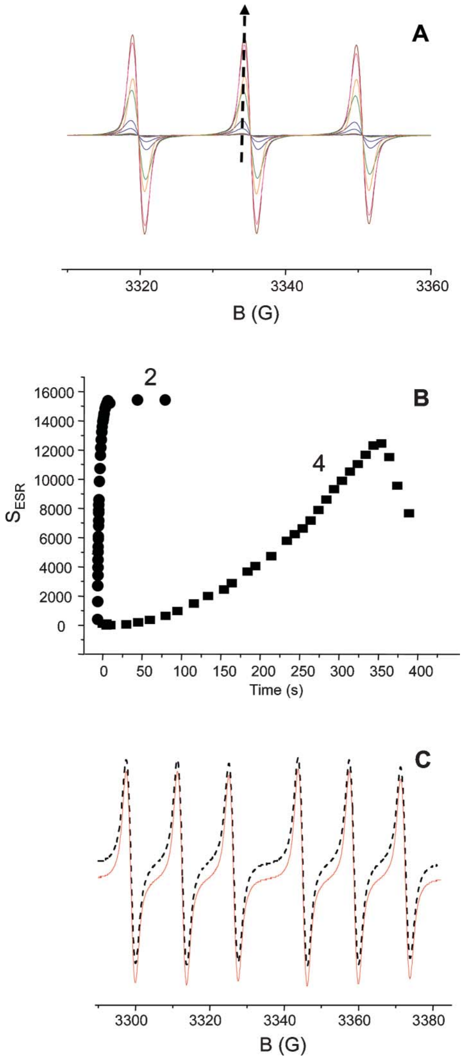


Fig. 2 (**A**) ESR spectra obtained under light irradiation of **4** in *tert*-butylbenzene in aerated conditions. The increase of the ESR spectrum is ascribed to the nitroxide radical. Light intensity = 44 mW cm^{-2}. (**B**) Double integration of the ESR signal ascribed to the nitroxide *vs.* the irradiation time in **2** and **4** for similar light absorptions; light intensity = 44 mW cm^{-2}. (**C**) ESR spectra for **6** in *tert*-butylbenzene: --- (before irradiation) and — (at 60 s of irradiation); light intensity = 220 mW cm^{-2}. In aerated conditions.

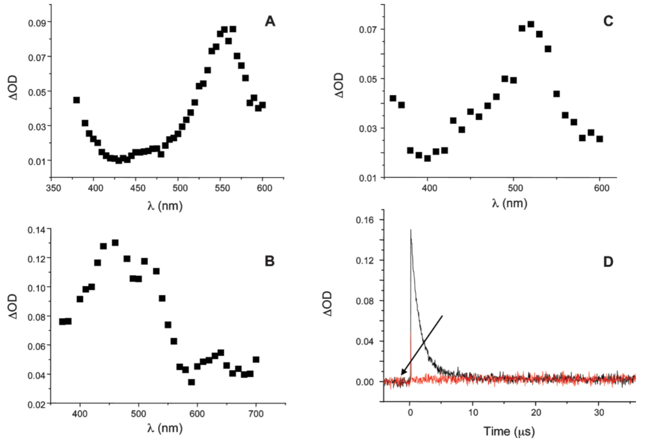


Fig. 3 Transient absorption spectra of (A) **4**, (B) **5**, (C) **6** in acetonitrile at time $t = 0$ after laser excitation at 355 nm. (D) Transient decay at 460 nm upon addition of camphorquinone to **5** under argon.

consistent with the cleavage from the triplet state, which is in line with the nitroxides observed by ESR experiments. For **5–6**, the triplet state lifetimes are higher than those found for **4**, which confirms the lack of formation of nitroxides in ESR experiments. The dissociation process for this reaction is probably rather hard.

The same holds true in **1–3** where triplet states have been already observed in LFP experiments (maximum absorption at 525 nm). The lifetimes were further reduced (200 ns – 1.5 μs)[8–10] than for the benzophenone triplet state (~5 μs under similar experimental conditions), supporting the cleavage processes observed by ESR.

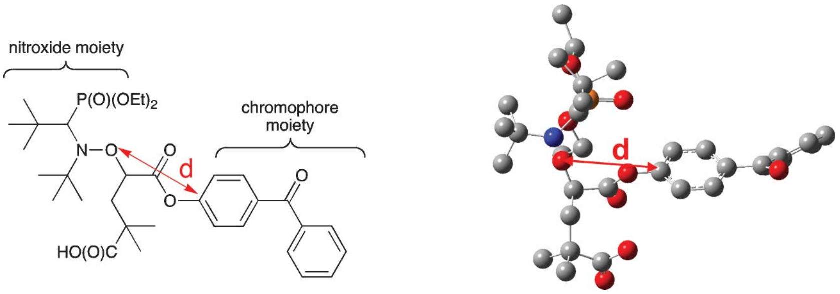
5 Molecular orbital calculations

At a first sight, the radical production efficiency is connected with (i) the amount of light absorbed by the chromophore and (ii) the cleavage quantum yield which is governed by the intersystem crossing quantum yield, the energy transfer to the bond being broken and the bond breaking ability. As stated in[4] for photosensitized decomposition of TEMPO-based alkoxyamines (R-TEMPO when R is a benzyl group), the cleavage of the C–O bond in **1–6**, is seen to result from an intramolecular energy transfer from the chromophore triplet state to the dissociative triplet surface associated with the C–O bond: the more reduced the distance, the more efficient the transfer. Considering the bond dissociation energies BDE (for N–O and C–O) and the triplet energy levels (E_T) calculated for **1–6** (Table 1), the dissociation process is found highly exothermic (ΔH_{diss} = BDE − E_T ~ −80 to −160 kJ mol^{-1}) for all the investigated compounds. As a consequence, in a qualitative approach, the production efficiency of the nitroxides in **1–3** can be related to the energy transfer efficiency *i.e.* to the close vicinity between the chromophore and the aminoxy function. In fact, only one (for **1**) or two

Table 1 Parameters characterizing the cleavage processes for the investigated alkoxyamines (molecular orbital calculations at B3LYP/6-31G* level)

Alkoxyamines	BDE (C–O) (kJ mol^{-1})	BDE (N–O) (kJ mol^{-1})	E_T (kJ mol^{-1})	d (Å)[a]	τ (triplet state) in μs
1	122	143	265	1.44	1.5
2	118	187	265	2.49	0.39
3	80	143	266	2.36	0.02
4	115	146	258	6.51	0.9
5	87	134	264	3.47	2.2
6	105	155	267	4.17	2.5

[a] distance determined by molecular orbital calculations (see also Scheme 5).



Scheme 5 Representation of the distance between the chromophore and the aminoxy groups (left) and geometry for **6** optimized at UB3LYP/6-31G* level (right) (d, determined by molecular orbital calculations are shown in Table 1).

(for **2–3**) bonds are located between these two moieties. For **4–6**, six (for **4**) or four (for **5–6**) bonds separate the two fragments which is in agreement with their lower nitroxide production. For **5–6**, the cleavage process is difficult. The nature of the spacer used also affects the cleavage process *i.e.* **4** exhibits a higher nitroxide formation than **5–6** despite the longer distance. For a more refined analysis of the structure effect on the dissociation process, an analogous series of compounds must be investigated as has been done for other photoinitiators.[20]

To take into account the real structure of the molecules and not only the number of bonds, the distance between the chromophore and the aminoxy function was evaluated from the relaxed geometries determined by molecular orbital calculations (Scheme 5). The results provided in Table 1 show that a trend similar to that found above for the number of bonds is obtained. The flexibility of the linking group is probably also an important factor as thermal activation can change the distance between the two functions. The linking groups in (**4–6**) can also slightly affect the chromophore properties depending on their chemical nature (ester, amide): the investigation of an analogous series is still needed for more in depth studies.

For these very large structures, the obtained BDEs can be probably slightly affected by the configuration *i.e.* different local dips will coexist and can be thermally populated. The calculated BDEs resulting from full optimization procedures will be used for sake of comparison. For **2–4**, the C–O bond is weaker than N–O with the difference in respective BDEs higher than 50 kJ mol^{-1}. This is in agreement with the selective C–O cleavage process for these compounds. For **5–6**, the same difference is noted but the energy transfer is less favorable (longer d values compared to **1–3**) so that the yield in nitroxide is low. For **1**, BDE(N–O) is quite close to BDE(C–O) in agreement with the formation of stabilized aromatic aminyl radicals: this results in the observed competitive N–O and C–O bond cleavages.[8]

6 Photoinitaitor ability

The investigated alkoxyamines generated both carbon centered radicals and nitroxides, the photoinitiating abilities were investigated in an acrylate matrix. The results obtained using **4–6** are shown in Fig. 4. For all these compounds, the polymerization rate R_p is lower than that of the reference photoinitiator (DMPA). With **1–3**, the R_ps were found to be significantly higher than those determined here for **4–6**.[8–10] This is related to the higher cleavage efficiency for these structures (**1–3**) (see above) leading to the formation of the initiating carbon centered radicals. R_p is better when **4** is used instead of **5–6** (Fig. 4), this is in agreement with the enhanced dissociation process found for this structure. For **5–6**, the poorest R_ps are noted, as expected, from the rather difficult cleavage process described above. These R_p values roughly correlate with the radical production in **1–6**.

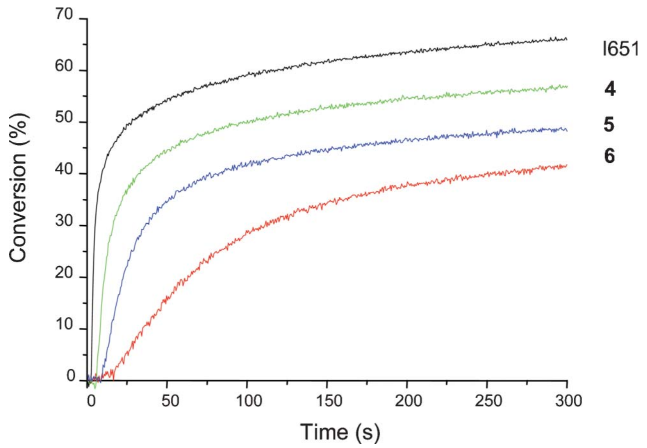


Fig. 4 Conversion *vs.* irradiation time curves for the photopolymerization of Ebecryl 605 in laminated conditions. Photoinitiating system (0.5 wt%): DMPA; **4**, **5** and **6**. Polychromatic light intensity: 22 mW cm^{-2}.

Conclusions

In the present paper, the effect of the alkoxyamine structure on the photodissociation process was investigated. It is found that (i) when the π system of the chromophore is directly linked to the aminoxy function, both N–O and C–O cleavage occurs, which is in agreement with the formation of stabilized aminyl radicals in **1** (ii) when the chromophore and the N–O containing moiety are separated, distance becomes an important parameter: a 2 bond separation length appears the best compromise between efficient nitroxide formation (**2–3** *vs.* **4–6**) and selective C–O cleavage reaction (**2–3** *vs.* **1**). The synthesis of new alkoxyamines based on other high energy chromophores exhibited good to excellent absorption in the UV-near visible wavelength range, the use of other spacers for the benzophenone chromophore will be examined in forthcoming studies.

Acknowledgements

This work was supported by the “Agence Nationale de la Recherche” ANR under Grant NMP2 07-JCJC0143.

References

1 (*a*) *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, R. G. Hicks, Ed., 2010, John Wiley & Sons, West Sussex, 2010; (*b*) A. Studer and T. Schulte, *Chem. Rec.*, 2005, **5**, 27; (*c*) C. B. Wagner and A. Studer, *Eur. J. Org. Chem.*, 2010, **30**, 5782.

2 (*a*) J. C. Scaiano, C. Aliaga, M. N. Chrétien, M. Frenette, K. S. Focsaneanu and L. Mikelsons, *Pure Appl. Chem.*, 2005, **77**, 1009; (*b*) Š. Chmela and L. Hrčková, *Eur. Polym. J.*, 2009, **45**, 2580; (*c*) J. P. Blinco, K. E. Fairfull-Smith, A. S. Micallef and S. E. Bottle,, *Polym. Chem.*, 2010, **1**, 1009.

3 (*a*) K. Matyjaszewski, in ACS symposium series, *Advances in Controlled/Living Radical Polymerization*, 2002, American Chemical Society, Washington D.C; (*b*) K. Matyjaszewski, in ACS symposium series, *Controlled Radical Polymerization*, 1998, American Chemical Society, Washington D.C.

4 J. C. Scaiano, T. J. Connolly, N. Mohtat and C. N. Pliva, *Can. J. Chem.*, 1997, **75**, 92.

5 S. Hu, J. H. Malpert, X. Yang and D. C. Neckers, *Polymer*, 2000, **41**, 445.

6 A. Goto, J. C. Scaiano and L. Maretti, *Photochem. Photobiol. Sci.*, 2007, **6**, 833.

7 D.-L. Versace, J. Lalevée, J.-P. Fouassier, Y. Guillaneuf, D. Bertin and D. Gigmes, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2910.

8 Y. Guillaneuf, D. Bertin, D. Gigmes, D.-L. Versace, J. Lalevée and J.-P. Fouassier, *Macromolecules*, 2010, **43**, 2204.

9 D.-L. Versace, J. Lalevée, J.-P. Fouassier, Y. Guillaneuf, D. Bertin and D. Gigmes, *Macromol. Rapid Commun.*, 2010, **31**, 383.

10 Y. Guillaneuf, D.-L. Versace, D. Bertin, J. Lalevée, D. Gigmes and J.-P. Fouassier, *Macromol. Rapid Commun.*, 2010, **31**, 1909.

11 (*a*) E. Yoshida, *Colloid Polym. Sci.*, 2009, **287**, 767; (*b*) E. Yoshida, *Colloid Polym. Sci.*, 2010, **288**, 341; (*c*) Y. Yagci, S. Jockusch and N. J. Turro, *Macromolecules*, 2010, **43**, 6245.

12 (*a*) N. S. Allen, D. Mallon, A. Timms, A. W. Green and F. Catalina, *Eur. Polym. J.*, 1993, **29**, 533; (*b*) C. Carlini, F. Ciardelli, D. Donati and F. Gurzoni, *Polymer*, 1983, **24**, 599; (*c*) P. E. Dufils, N. Chagneux, D. Gigmes, T. Trimaille, R. S. A. Marque, D. Bertin and P. Tordo, *Polymer*, 2007, **48**, 5219.

13 J. Lalevée, X. Allonas and J. P. Fouassier, *J. Am. Chem. Soc.*, 2002, **124**, 9613.

14 D. R. Duling, *J. Magn. Reson., Ser. B*, 1994, **104**, 105.

15 (*a*) M. A. Tehfe, J. Lalevée, D. Gigmes and J. P. Fouassier, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1830; (*b*) M. A. Tehfe, M. A. J. Lalevée, D. Gigmes and J. P. Fouassier, *Macromolecules*, 2010, **43**, 1364; (*c*) J. Lalevée, M. A. Tehfe, D. Gigmes and J. P. Fouassier, *Macromolecules*, 2010, **43**, 6608.

16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, A. Montgomery, R. E. S. Jr., J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 03, Revision B2*, Pittsburgh PA., 2003.

17 D. Bertin, D. Gigmes, S. Marque and P. Tordo, *E-Polymers*, 2003, **2**, 1.

18 S. Marque, C. Le Mercier, P. Tordo and H. Fischer, *Macromolecules*, 2000, **33**, 4403.

19 C. L. Mercier, S. Acerbis, D. Bertin, F. Chauvin, D. Gigmes, O. Guerret, M. Lansalot, S. Marque, F. Moigne, H. Fischer and P. Tordo, *Macromol. Symp.*, 2002, **182**, 225.

20 X. Allonas, J. Lalevée and J.-P. Fouassier, *J. Photochem. Photobiol., A*, 2003, **159**, 127.