4464 *Macromolecules* **2009**, *42*, 4464–4469
DOI: 10.1021/ma900452x

Macromolecules
ARTICLE

Coinitiators Based on Group 14 Elements in Photoinitiating Systems for Radical and Cationic Polymerization.

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Received March 3, 2009; Revised Manuscript Received April 29, 2009

ABSTRACT: New co-initiators based on group 14 elements (disilanes, polysilanes, digermanes, distannanes) are proposed. Under their photosensitized excitation, in the presence of benzophenone BP or a thiopyrylium salt TP, a metal−metal bond cleavage is observed. The generated radicals are excellent initiating species for free radical photopolymerization, FRP, and free radical promoted cationic photopolymerization, FRPCP. In FRP, when working both in laminate and under air, the new combinations are found highly reactive and, in most cases, better than the BP/ethyl dimethylaminobenzoate or Eosin/methyldiethanolamine reference systems. Their ability in FRPCP under air is also found excellent. The associated mechanisms are questioned on the basis of laser flash photolysis and ESR experiments.

Introduction

In the last decades, radical photopolymerization reactions have attracted special attention due to their potential applications. For a part, researches have been focused on the design and the investigation of new molecules which are able to generate efficient species for free radical polymerization (FRP).[1−4] However, one of the major issues remain the oxygen inhibition as the initiating radicals derived from the photoinitiator (PI) and the propagating polymer radicals are efficiently scavenged by O_2 and converted to peroxyl radicals. These latter species being unreactive toward the addition process to monomer double bonds, an efficiency decrease is noted for the photopolymerization processes in aerated media. Recently, new photoinitiators generating silyl ($Si^{\bullet}$) or germyl ($Ge^{\bullet}$) radicals in type I or type II PI systems were proposed by us;[5] $Ge^{\bullet}$ radicals were also very recently generated in type I PI systems containing a C−Ge bond.[6] The high inherent reactivity of $Si^{\bullet}$ and $Ge^{\bullet}$ toward acrylate double bonds and their good behavior in aerated conditions were underlined. Free radical promoted cationic photopolymerization FRPCP was also recognized as an efficient and convenient procedure for the design of UV and visible light initiating cationic systems (refs 7 and 8 and references therein) where the produced radical is oxidized by an iodonium salt. The search for new radicals or new production routes in FRP and FRPCP still presents a fascinating challenge.

In organic synthesis, it is well-known that metal (or metalloids for Si and Ge) centered radicals can be generated by a bond cleavage of group 14 elements after an electron transfer with an oxidizing agent Ox (eq 1 with M = Si; Ge; Sn), the low oxidation potential of such a covalent bond rendering the process efficient. Albeit different synthetic applications were found, the mechanistic investigations are very scarce[9,10] and the use of such systems (eq 1) in the photopolymer area has never been reported yet.

$$R_3M{-}MR_3 + Ox \rightarrow Red + R_3M{-}MR_3^{\bullet+} \rightarrow Red + R_3M^{\bullet} + R_3M^{+} \qquad (1)$$

In the present paper, new photoinitiating systems will be designed: they are based on the induced cleavage of M−M bonds, the oxidizing agent working as a photosensitizer. The photoinduced bond cleavage via electron transfer in photoinitiating systems has been seldom mentioned (e.g., ref 11). In fact, the direct homolytic cleavage is usually only encountered (except a few examples where the cleavage can occur through energy transfer), e.g. in C−C, C−P, N−O, C−S bonds for conventional type I photoinitiators[1−3] or in other potentially interesting Si−Si, polysilane, Si−C, Si−S bonds.[5e,12] We will check the ability of selected compounds (Scheme 1), playing the role of a co-initiator CoI as part of a photoinitiating system (containing benzophenone, isopropylthioxanthone, camphorquinone or a thiopyrylium salt as PI), for FRP and FRPCP. The formation of the metal centered radical by a direct bond cleavage and by photosensitization will be investigated by laser flash photolysis (LFP) and electron spin resonance (ESR) experiments. The combinations of both techniques will provide a coherent picture of the radical chemistry associated with these compounds.

Experimental Section

(i). Compounds. The new compounds used in FRP as co-initiators (Scheme 1)—hexaphenyldigermane (**a**), hexaethyldigermane (**b**), hexaphenylditin (**c**), 1,2 diethyl- 1,1,2,2 tetraphenylsilane (**d**), poly(methylphenyl)silane (**e**) and 1,1,1,4,4,4-hexamethyl-2,2,3,3-tetrakis(trimethylsilyl)tetrasilane (**f**)—were obtained from Aldrich. Benzophenone (BP), isopropylthioxanthone (ITX), camphorquinone (CQ) and 2,4,6(4-methoxyphenyl)thiopyrylium tetrafluoroborate (TP) presented in ref 13 were used as photoinitiators/photosensitizers (Aldrich). Ethyldimethylaminobenzoate (EDB, Esacure EDB from Lamberti) was used as a reference amine co-initiator. BP/EDB and Eosin(Eo)/MDEA (methyldiethanolamine) were selected as the reference system in UV and visible light induced FRP, respectively. Diphenyliodonium hexafluorophosphate Ph_2I^+ (Aldrich) was used for FRPCP processes.

(ii). Photopolymerization Experiments. For film radical polymerization experiments, 50 μm thick films of an oligomer/monomer formulation based on 75/25 w/w epoxyacrylate/tripropyleneglycoldiacrylate (Ebecryl 605 from Cytec) were exposed to a UV irradiation carried out with the polychromatic light of a Xe−Hg lamp (Hamamatsu, L8252, 150 W). In FRP,

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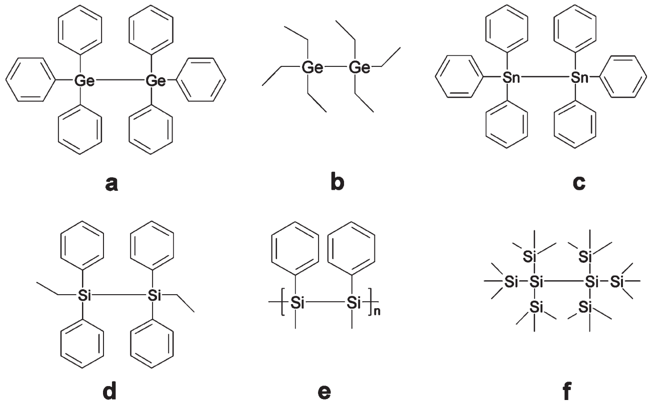
Scheme 1



weight concentrations of 1% for both the PI (except 0.1% for TP) and the co-initiators were used (in order to improve the solubility of CoI, a very small amount of solvent can be added and removed by evaporation before the polymerization experiments; a weak turbidity is observed for some samples). For the visible light polymerization, an irradiation with a filtered xenon lamp (Hamamatsu L8253, 150W) was selected. In film cationic polymerization, weight concentrations of 1% for Ph_2I^+ and 1% for the M−M were used to polymerize a 50 μm thick di(cycloaliphatic epoxide) monomer (Cyracure 6110 from Dow); concentrations of 3% CQ or 0.1% in TP were used.

The evolution of the monomer content was continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) at about 1640 and 800 cm^{-1} in FRP and FRPCP, respectively.[14] The R_p quantity refers to the maximum rate of polymerization and was calculated from the maximum of the first derivative of the conversion vs time curves.

(iii). Laser Flash Photolysis Experiments. Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser (λ_{exc} = 266 or 355 nm, 9 ns fwhm 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 (see detail in ref 15).

(iv). ESR Experiments. ESR experiments were carried out using a X-Band spectrometer (MS 200 Magnettech). The radicals generated under exposure to the Xe−Hg lamp at $\lambda > 310$ nm were observed at room temperature. The procedures for the spin trapping (ESR-ST; the generated radicals were trapped by phenyl-*N*-*tert*-butylnitrone (PBN)) and kinetic ESR (KESR) experiments have been described in detail in ref 16.

(v). Redox Properties. The redox potentials were measured (as described in ref 14b) in acetonitrile by cyclic voltammetry with tetra-*n*-butylammonium hexafluorophosphate 0.1 M as supporting electrolyte (Voltalab 6 Radiometer); the working electrode was a platinium disk and the reference a saturated calomel electrode-SCE in methanol. The free energy change (ΔG_{et}) for the photoinduced electron transfer process is evaluated from the classical Rehm−Weller equation ($\Delta G_{et} = E_{ox} - E_{red} - E_0 + C$; where E_{ox}, E_{red}, E_T, and C are the oxidation potential of the donor, the reduction potential of the acceptor, the excited (triplet or singlet) state energy and the Coulombic term for the formed initial ion pair, respectively).[17]

(vi). DFT Calculations. All the calculations were performed using the hybrid functional B3LYP from the Gaussian 03 suite of program.[18] Reactants and products were fully optimized at the B3LYP/LANL2DZ level (and frequency checked). The bond dissociation energies (BDE) were calculated as the energetic difference between the dimetals and the radicals ($R_3M{-}MR_3 \rightarrow 2\ R_3M^\bullet$).

Table 1. Polymerization Rates and Conversions of Ebecryl 605 Using a Benzophenone/$R_3M{-}MR_3$ System (1%/1%, w/w)[a]

	laminate		under air	
	$R_p/[M_0] \times 100$	convn (%)[b]	$R_p/[M_0] \times 100$	convn (%)[b]
EDB	8.8	71	6.7	65
a	18.9	76	11.5	65
b	13.9	73	12.7	75
c	16.7	73	15.4	72
d	15.2	72	13.5	71
e	19.2	72	17	71
f	9.6	69	6.2	71

[a] UV irradiation with the xenon−Hg lamp. In laminate and under air. $R_p/[M_0]$ (s^{-1}). [b] Conversion at t = 120 s.

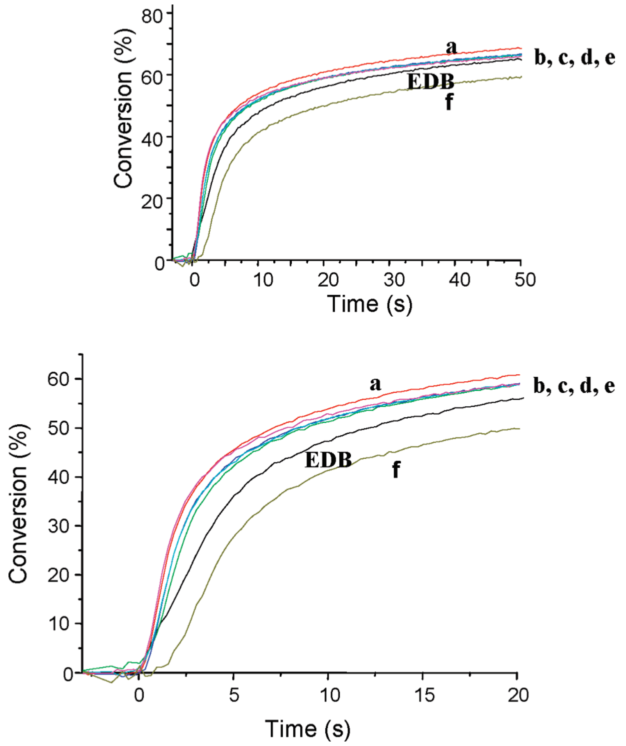


Figure 1. Conversion vs time curves for the laminated photopolymerization of Ebecryl 605 using BP/CoI (1%/1%) as photoinitiating system. UV light irradiation.

Results and Discussions

1. Coinitiators Based on Group 14 Elements for FRP. With the exception of **e**, the use of compounds **a**−**f** as type I photoinitiating systems leads to low rates of polymerization under a polychromatic light exposure. This is obviously ascribed to the low UV absorption properties of these compounds for $\lambda > 320$ nm (for example, **a** and **d** only absorb at 237 and 238 nm in acetonitrile, respectively) as a very high efficiency for the germyl or silyl radical formation is found by LFP (see below). For **e**, the polymerization rate is lower than with BP sensitization.

The polymerization results using BP/EDB and the different BP/$R_3M{-}MR_3$ systems, under a UV light exposure, both in laminated films and under air in the same experimental conditions, are gathered in Table 1; typical polymerization profiles are shown in Figure 1. The first significant result is the general high reactivity of these new CoIs compared to EDB. The polymerization rates R_p are higher than for the reference (for **f**, R_p is slightly higher than EDB despite a higher inhibition period). From these results, the new proposed structures appear as good co-initiators.

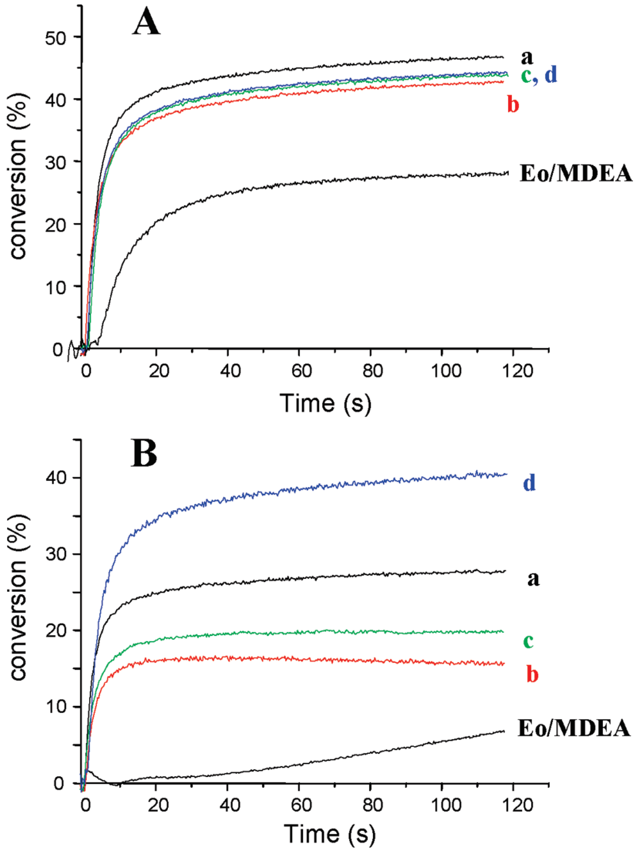


Figure 2. Conversion vs time curves for the photopolymerization of Ebecryl 605 in laminate (A) and under air (B). TP/CoI (0.1%/1% w/w) was used as a photoinitiating system (xenon lamp irradiation).

Table 2. Polymerization Rates and Conversions of Ebecryl 605 Using a TP/R$_3$M−MR$_3$ System (0.1%/1%, w/w)[a]

	laminated		under air	
	$R_p/[M_0] \times 100$	convn (%)[c]	$R_p/[M_0] \times 100$	convn (%)[c]
ref[b]	2	27	< 0.5	< 10
a	12.3	47	9.3	28
b	9.7	42	5.3	16
c	9.6	44	5.2	20
d	9.0	44	8.2	41
e	10.2	47	9.1	37
f	7.6	43	4.5	32

[a] Irradiation with the xenon lamp ($\lambda > 300$ nm). In laminate and under air. $R_p/[M_0]$ (s^{-1}). [b] Reference: Eosin/MDEA (0.05%/1% w/w). Formulations based on TP/amine systems are not stable (for more detail see ref 13b). The polymerization rate for ref is different to that found in ref 13b because of the lower light intensity used here. [c] Conversion at t = 120 s.

For the investigated compounds, the obtained final conversions are higher than 70% for a polymerization time of 120 s. The most striking result is the higher polymerization rates under air when using these BP/R$_3$M−MR$_3$ couples (than BP/EDB) in Ebecryl 605. This observation can be put together with the similar behavior already noted for BP/silanes.[5] On the opposite, the ITX/(**a-f**) combinations do not work well: the R_ps are 4−10 times lower than a reference ITX/EDB system. This observed reactivity trend is quite similar to that previously found for BP/R$_3$M−H and ITX/R$_3$M−H with M = Si or Ge.[5d,5f]

Typical conversion−time profiles are shown in Figure 2 when using the TP/R$_3$M−MR$_3$ and the reference Eosin/MDEA systems under xenon lamp irradiation; the R_ps are gathered in Table 2 (the reported results cannot be directly compared to those of Table 1 as the experimental conditions—in particular, the light source and the light intensity—are changed). The new proposed CoIs exhibit a high reactivity. In the presence of TP, **a** to **f** are clearly characterized by a higher reactivity (as supported by the five to 6-fold increase of R_p compared to the reference Eo/MDEA). Under air, no polymerization was obtained using the reference (Eosin/MDEA) in contrast to the proposed systems that are not found strongly affected by oxygen. For visible light polymerization in the presence of CQ/(**a-f**), a low reactivity is found (the R_ps are 3−10 times lower than for a reference system CQ/EDB).

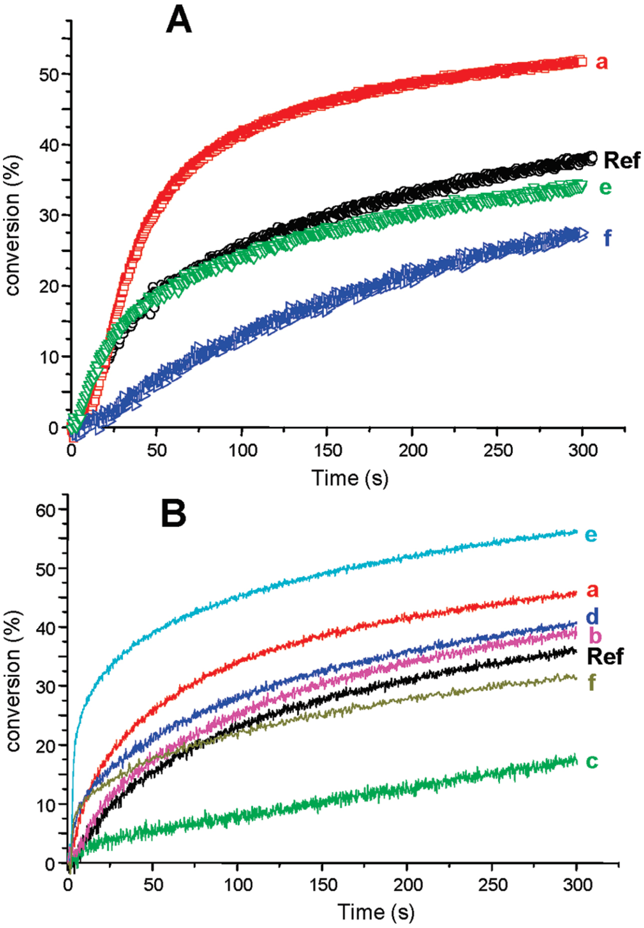


Figure 3. Polymerization profiles of Cyracure 6110 under air using various photoinitiating systems: **(A) Ref**, CQ/**EDB**/Ph$_2$I$^+$ (3%/1%/1%); **a**, CQ/**a**/Ph$_2$I$^+$ (3%/1%/1%); **e**, CQ/**e**/Ph$_2$I$^+$ (3%/1%/1%); **f**, CQ/**f**/Ph$_2$I+ (3%/1%/1%); **(B) Ref**, TP/Ph$_2$I$^+$ (0.1%/1%); **a**, TP/**a**/Ph$_2$I$^+$ (0.1%/1%/1%); **b**, TP/**b**/Ph$_2$I$^+$ (0.1%/1%/1%); **c**, TP/**c**/Ph$_2$I$^+$ (0.1%/1%/1%); **d**, TP/**d**/Ph$_2$I$^+$ (0.1%/1%/1%); **e**, TP/**e**/Ph$_2$I$^+$ (0.1%/1%/1%); **f**, TP/**f**/Ph$_2$I$^+$ (0.1%/0.5%/1%) (xenon lamp irradiation).

2. Coinitiators Based on Group 14 Elements in FRPCP. Results are reported in Figure 3 and Table 3. A higher efficiency for the cationic photopolymerization reaction, upon a xenon lamp exposure and under air, in the presence of the TP/**a**/Ph$_2$I$^+$ system compared to the reference photoinitiating system **Ref1** (CQ/EDB/Ph$_2$I$^+$) is clearly observed (this **Ref1** has been selected as a reference for its better reactivity in aerated media[5f] compared to CQ/Ph$_2$I$^+$ proposed in [8a]). With the exception of **c**, the introduction of **a** to **f** into TP/Ph$_2$I$^+$ (**Ref2**) drastically increases both the polymerization rates and the final conversions (at t = 300 s). A remarkable efficiency is noted for **e** (for this compound which absorbs light for $\lambda > 300$ nm; the system

Table 3. Polymerization Rates of Cyracure 6110 under Air[a]

	$R_p/[M_0] \times 100$	Conv(%) $t = 300$s
Ref1	0.7	38
Ref2	0.4	36
Ref3	<0.2	[b]
a	1.1	46
b	0.5	39
c	0.2	18
d	2.2	41
e	11.6	56
f	4.5	31

[a] **Ref1** is CQ/**EDB**/Ph_2I^+ (3%/1%/1%); **Ref2** is TP/Ph_2I^+ (0.1%/1%); **Ref3** is TP/**a** (0.1%/1%); **a**, TP/**a**/Ph_2I^+ (0.1%/1%/1%); **b**, TP/**b**/Ph_2I^+ (0.1%/1%/1%); **c**, TP/**c**/Ph_2I^+ (0.1%/1%/1%); **d**, TP/**d**/Ph_2I^+ (0.1%/1%/1%); **e**, TP/**e**/Ph_2I^+ (0.1%/1%/1%); **f**, TP/**f**/Ph_2I^+ (0.1%/0.5%/1%). $R_p/[M_0]$ (s^{-1}). Irradiation with the xenon lamp ($\lambda > 300$ nm). [b] A polymerization is observed with a low conversion ~10%.

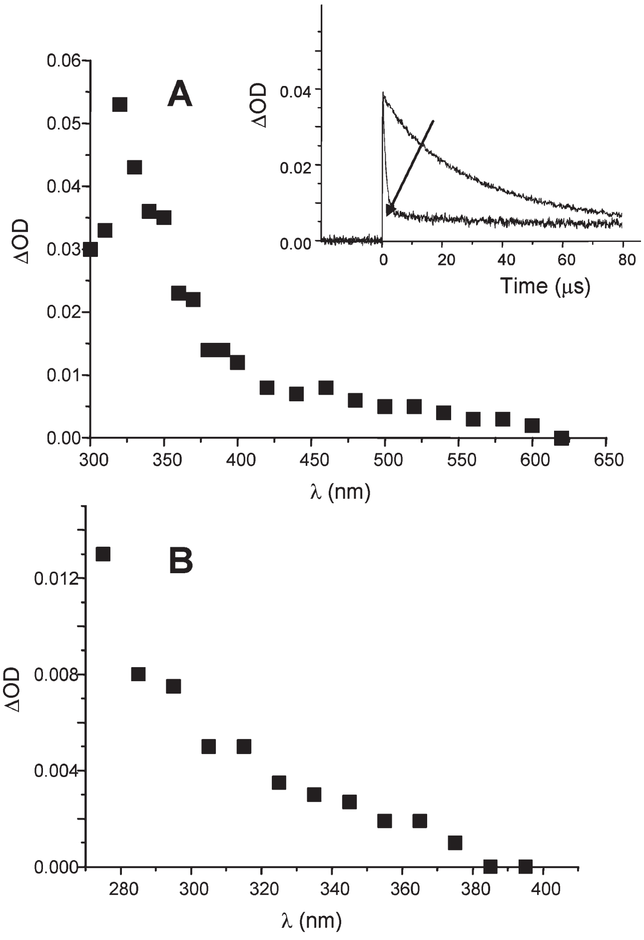


Figure 4. Transient absorption spectra recorded immediately after the laser excitation of **a** (A) and **b** (B) at 266 nm in cyclohexane. Insert: the quenching of $Ph_3Ge^\bullet$ observed at 330 nm by methylacrylate.

Table 4. Rate constants characterizing the formation and the reactivity of the metal centered radicals derived from b and d

		k_q ($M^{-1}s^{-1}$ (in 10^8))		
	E_{ox} (V)	**BP**[a]	**TP**[b]	ESR-ST (BP) HFS (G)
b	1.36	1.5	5 (130[c])	$a_N = 14.8$; $a_H = 5.9$
d	1.74	2.0	8 (< 100[c])	$a_N = 14.7$; $a_H = 5.7$

[a] Solvent: cyclohexane [b] Solvent: acetonitrile. [c] Quenching of the singlet state.

e/Ph_2I^+ leads to polymerization but is improved by addition of TP). A reactivity order **e** ≫ **f** > **d** > **a** > **b** > **(Ref2)** > **c** is found. The high efficiency under air using silyl or germyl radicals has been already evidenced.[5,13b] Albeit slightly less efficient than these TP/(**a**−**f**)/Ph_2I^+ systems, the photoinitiating systems based on CQ/(**a**−**f**)/Ph_2I^+ lead to fast polymerization processes: the R_ps are similar to that of the reference CQ/EDB/Ph_2I^+ (Figure 3).

Upon irradiation with a UV light, the addition of **e** into BP/Ph_2I^+ slightly increases both the polymerization rate and the final conversion. The BP/Ph_2I^+ system being already highly efficient,[5f] the use of $R_3M{-}MR_3$ is less interesting than in the case of a xenon lamp irradiation.

3. Mechanistic Investigation. The laser irradiation at 266 nm of **a**, **b**, **c**, and **d** leads to the formation of transients (Figure 4) ascribed to the metal centered radicals generated through the M−M bond cleavage as the spectra are similar to those reported previously for such species using another way.[5,9b] The corresponding radicals add to an acrylate double bond such as methylacrylate (Figure 4) with very high rate constants (1.8×10^8, 2×10^8, 4.8×10^7, 8.8×10^8 and 2.2×10^7 M^{-1} s^{-1} for radicals generated from **a**, **b**, **c**, **d**, and **f**, respectively).

The interaction of ^{3}BP and ^{3}TP with $R_3M{-}MR_3$ (followed at 525 and 550 nm respectively) is very efficient as reflected by the high reaction rate constants (Table 4). For ^{1}TP, time-resolved fluorescence experiments were carried out (Table 4). The oxidation potentials of the investigated $R_3M{-}MR_3$ are gathered in Table 4 when available (these structures are often not soluble enough in acetonitrile for the determination of E_{ox}). The reactivity of **b** and **d** will be investigated now in more detail as their redox properties are accessible.

(i). Interaction with ^{3}BP. From calculations with the Rehm−Weller equation, it can be concluded that the electron transfer process for BP/**b** (eq 2) is quite permissible ($\Delta G_{et} = +0.17$ eV (using for BP: $E_T = 2.98$ eV and $E_{red} = -1.79$ V)[19]). Since $BP^{\bullet -}$ is not observed in LFP experiments, an oxidation of this species is expected (eq 3). For **d**, the electron transfer process is less favorable ($\Delta G_{et} = +0.55$ eV) and an energy transfer reaction should occur (eq 4). The values of the triplet energy levels of $R_3M{-}MR_3$ are not available. From quantum mechanical calculations, it can be noted that these states are dissociative and lead to radical formation. The M−M bond dissociation energies are quite low: 58.4, 57.9, 49.8, 61.3, and 36.4 kcal/mol (at UB3LYP/LANL2DZ level) for **a**, **b**, **c**, **d**, and **f**, respectively. This is also in agreement with an efficient cleavage process.

$$^3BP + R_3M{-}MR_3 \rightarrow BP^{\bullet -} + (R_3M{-}MR_3)^{\bullet +} \rightarrow BP^{\bullet -} + R_3M^\bullet + R_3M^+ \quad (2)$$

$$BP^{\bullet -} + R_3M^+ \rightarrow BP + R_3M^\bullet \quad (3)$$

$$^3BP + R_3M{-}MR_3 \rightarrow BP + {}^3(R_3M{-}MR_3) \rightarrow BP + 2R_3M^\bullet \quad (4)$$

These results are also consistent with the ESR-ST experiments which demonstrate the formation of germyl and silyl radicals in BP/**b** and BP/**d**, respectively: the hyperfine splitting constants (Table 4) are in good agreement with the HFS reported for such kinds of structures.[20]

The fast generation of a metal centered radical explains the high activity of BP/**b** and BP/**d** in FRP. For polymerization in other acrylate (or monomer) matrix, different results can perhaps be obtained due to the competition between the deactivation of the triplet state by the monomer and the sensitization of the M−M cleavage process.

For ITX (or CQ)/**b** (or **d**), the triplet energy levels and/or the redox properties are less favorable for reactions 2 and 4 than for BP: $E_T = 2.74$ eV and $E_{red} = -1.57$ V for ITX and $E_T = 2.2$ eV and $E_{red} = -1.44$ V for CQ.[5f] This can be in line with the low polymerization initiating ability of these systems.

(ii). Interaction with ^{3}TP and ^{1}TP. Using a triplet energy level of 2.3 eV and $E_{red} = -0.39$ V for TP,[21] the ^{3}TP/**b** and ^{3}TP/**d** interaction can be ascribed to an electron transfer sequence as $\Delta G_{et} = -0.55$ and -0.17 eV, respectively. This obviously also holds true in the singlet state as the energy is higher by about 0.2 eV. The following sequence is expected (eq 5); the same holds true for ^{1}TP. This is fully consistent with the very intense ESR spectrum centered at $g = 2.0044$ (see Figure 5 for TP/**e**) and characteristic of the 2,4,6-triphenylthiabenzene radical[22] (formally denoted here as $TP^{\bullet -}$) thereby demonstrating the electron transfer pathway. In ESR-ST, silyl and germyl radicals are also observed (see Figure 5 for TP/**e**). The observation of $TP^{\bullet -}$ demonstrates that the reduction of R_3M^+ ($TP^{\bullet -} + R_3M^+ \rightarrow TP + R_3M^\bullet$) only partly occurs or does not take place.

$$^3TP + R_3M{-}MR_3 \rightarrow TP^{\bullet -} + (R_3M{-}MR_3)^{\bullet +} \rightarrow TP^{\bullet -} + R_3M^\bullet + R_3M^+ \quad (5)$$

The R_3M^+ species which is able to initiate the cationic photopolymerization to some extent is thus directly generated (**Ref3** in Table 3). In the presence of an iodonium salt, as reported previously for M = Si or Ge,[5f] the $R_3M^\bullet$ radical is oxidized leading to the same electrophilic structure (R_3M^+) which should enhance the overall efficiency. The decomposition of Ph_2I^+ after reduction with $TP^{\bullet -}$ can also occur (eq 6). As already observed in other thiopyrylium salt/iodonium salt systems,[13a] a direct ^{3}TP (or ^{1}TP)/Ph_2I^+ interaction should exist in **Ref2** of Table 3 (eq 7), the cation radical $TP^{\bullet +}$ being the initiating species.

$$TP^{\bullet -} + Ph_2I^+ \rightarrow TP + Ph_2I^\bullet \rightarrow TP + PhI + Ph^\bullet \quad (6)$$

$$^3TP\ (\text{or } ^1TP) + Ph_2I^+ \rightarrow TP^{\bullet +} + Ph_2I^\bullet \rightarrow TP^{\bullet +} + PhI + Ph^\bullet \quad (7)$$

(iii). Reactivity of Peroxyl Radicals. For the systems proposed here, a very good efficiency in FRP and FRPCP in aerated conditions is found. In the silyl or germyl radical chemistry such a behavior has been already observed.[5] It involves a complex set of reactions: (i) the generation of the silyl or germyl radicals; (ii) the fast addition of silyl or germyl radicals to O_2; (iii) the reorganization of the formed peroxyl (e.g., $R_3SiOO^\bullet$) to regenerate a silyl radical $RSi^\bullet(OR)_2$;[16a] (iv) the degradation of the formed peroxides (e.g., R_3SiOOR' generated by recombination of silyl with peroxyl radicals)[5] to generate initiating radicals under light irradiation. However, a particular feature of the $R_3M{-}MR_3$ compounds is their involvement in a homolytic substitution reaction SH_2 (as supported in ref 23 for the addition to organometallic species) that is assumed here as shown in eq 8.

$$R'OO^\bullet + R_3M{-}MR_3 \rightarrow R'OO{-}MR_3 + R_3M^\bullet \quad (8)$$

Through (eq 8), the conversion of a peroxyl to an efficient metal centered radical is achieved and appears as fast. In fact, a rate constant of about 800 $M^{-1}\,s^{-1}$ is found for a Si−Si unit in **e** (the solubility of these compounds in t-butylbenzene not being excellent for the determination of the rate constants of (eq 8) by the KESR technique, only the $R'OO^\bullet$/**e** interaction where R′ stands for tBu was investigated). This high value, compared to the hydrogen abstraction rate constant (6 $M^{-1}\,s^{-1}$) in $R'OO^\bullet$/EDB,[16b] demonstrates the interest of (eq 8) to overcome the oxygen inhibition in FRP.

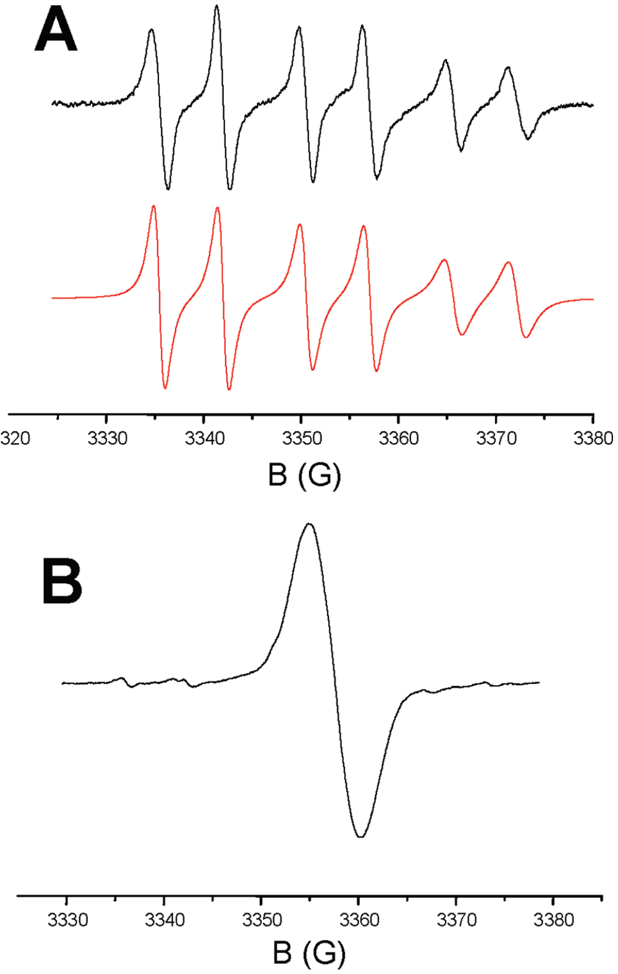


Figure 5. (A) ESR-ST experiments for TP/**e** in acetonitrile using PBN: experimental (up) and simulated (down) spectra. A silyl radical is observed (see text). (B) ESR spectrum of TP/**e** in acetonitrile. Xe−Hg irradiation.

For FRPCP in aerated media, the role of oxygen in the sequence of reactions is crucial and decisive. Reaction 8 allows the formation of a metal centered radical $R_3M^\bullet$ which (i) can be oxidized by Ph_2I^+ to generate R_3M^+ or (ii) reacts with oxygen to yield a peroxyl radical $R_3MOO^\bullet$, which is further oxidized by Ph_2I^+ and forms a R_3MOO^+ cation (this structure was already shown to be very efficient in the case of silyl or germyl peroxyls).[5f] These contributions explain quite well both the efficiency difference between $TP/R_3M{-}MR_3/Ph_2I^+$ and TP/Ph_2I^+ and the high reactivity of the new proposed structures for the FRPCP processes under air.

Conclusion

In this paper, efficient $R_3M{-}MR_3$ bond cleavable compounds usable in radical or cationic (sensitized) photopolymerization reactions, even under air, are presented. The FRP in the presence of $BP/R_3M{-}MR_3$ and/or $TP/R_3M{-}MR_3$ is excellent under air. The new photoinitiating systems proposed here for FRPCP also exhibit a high performance in aerated media with an enhanced rate of polymerization and percent conversion. A general comparison of systems based on either the hydrogen abstraction from $R_3M{-}H$ or the $R_3M{-}MR_3$ bond cleavage in other photoinitiating systems will be proposed in forthcoming works.

References and Notes

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