Macromolecules **2007,** *40,* 8527−8530 **8527**

New Highly Efficient Radical Photoinitiators Based on Si−Si Bond Cleavage

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Received July 6, 2007
Revised Manuscript Received October 10, 2007

Introduction. Free radical photopolymerization is the most important reaction encountered in the UV radiation curing area. A lot of papers have dealt with the role of the photoinitiator PI.[1−4] However, the search for PIs having new properties and/or an enhanced reactivity remains of great interest. One way is concerned with the design of new PIs based on heteroatom centered radicals.[3] Recently, we found that specific and new sulfur centered radicals can lead to an efficient polymerization reaction together with some interesting properties, among them: a reduced oxygen sensitivity and a low selectivity allowing a potential access to a large range of monomers.[5−7] Our recent interest for Si centered radicals[7] prompted us to search for cleavable Si−Si bond based photoinitiators. Up to now, the available addition rate constants of silyl radicals to double bonds are rather scant, the main values being gathered in ref.[8] Twenty years ago, the photodegradation of polysilane polymers or oligomers occurring from a Si−Si cleavage has been reported to be efficient. On the opposite, the photoinitiation ability of these silyl radicals is low as exemplified by the determined low initiation quantum yields Φ_i ($\Phi_i \sim 0.001$ compared to 0.25 for a benzoin ether);[9−10] recently new polysilane structures exhibiting higher photoinitiation efficiencies were proposed.[10d]

In the present paper, we have carefully selected two Si−Si based structures—never proposed as PIs—that mainly differ by their methyl vs phenyl substituents (Scheme 1). Through steady-state experiments, laser flash photolysis and quantum mechanical calculations, we will evaluate the photopolymerization ability of these photoinitiators, investigate the reactivity of the silyl radicals and propose a mechanism for the initiation step.

Experimental Section. The new photoinitiators (10,10′-bis-(10-phenyl-10*H*-phenoxasilin) **PI-1** and 9,9′-dimethyl-9,9′-bis-(9*H*-9-silafluorene) **PI-2**), methyl acrylate (MA), 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO) and 2,2′-dimethoxyphenyl acetophenone (DMPA) used as a reference photoinitiator were obtained from Aldrich. The stabilizer of MA was removed by column purification (Aldrich AL-154).

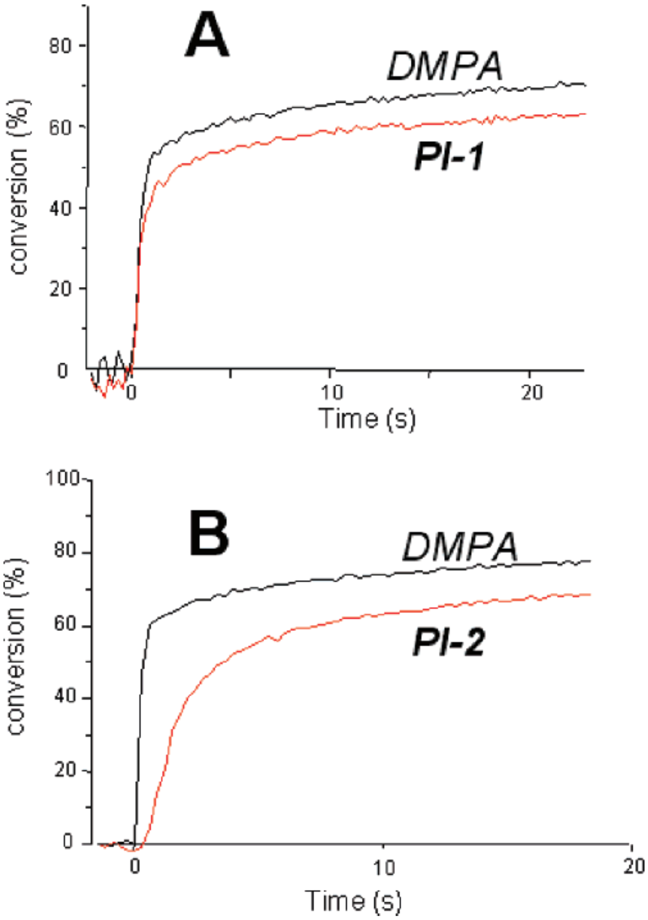
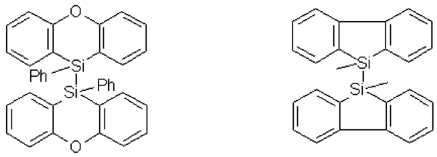


Figure 1. Photopolymerization profiles of Ebecryl 605/HDDA (70/30% w/w) in the presence of the different photoinitiating systems: (A) DMPA and **PI-1** systems (0.1% by weight); (B) DMPA and **PI-2** (1% by weight) (in laminate).

Scheme 1



PI-1 **PI-2**

Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser (λ_{exc} = 266 nm, 9 ns HWHM 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.[11] The steady state and time-resolved fluorescence properties were examined with a Fluoromax-4 (Jobin-Yvon-Horiba) apparatus. A Time-correlated single-photon counting (TCSPC) accessory is used for lifetime determinations. The samples were excited using a Nano LED emitting at 266 as an excitation source. The decays were fitted with the iterative reconvolution method on the basis of the Marquardt−Levenberg algorithm. Such a reconvolution process allows an overall time resolution down to 200 ps.

The triplet benzophenone (^{3}BP) was used as an actinometer for the determination of the dissociation quantum yields Φ_{diss}:

$$\Phi_{diss} = \frac{\Delta OD_{Si}}{2\Delta OD_{BP}} \frac{\epsilon_{BP}}{\epsilon_{Si}} \qquad (1)$$

ΔOD_{Si}, ΔOD_{BP}, ϵ_{BP}, and ϵ_{Si} stand for the optical densities (ΔOD) and the extinction coefficients (ϵ) for the silyl radicals and the triplet state of benzophenone, respectively. ΔOD were measured for the same amount of light absorbed.[12a] A factor of 2 must be included since two silyl radicals are generated for each cleavage. In this equation, ϵ_{Si} was calculated by fitting the recombination kinetics with a second-order law (rate constant: k_r/ϵ where k_r is the recombination rate constant); k_r

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10.1021/ma071489k CCC: $37.00

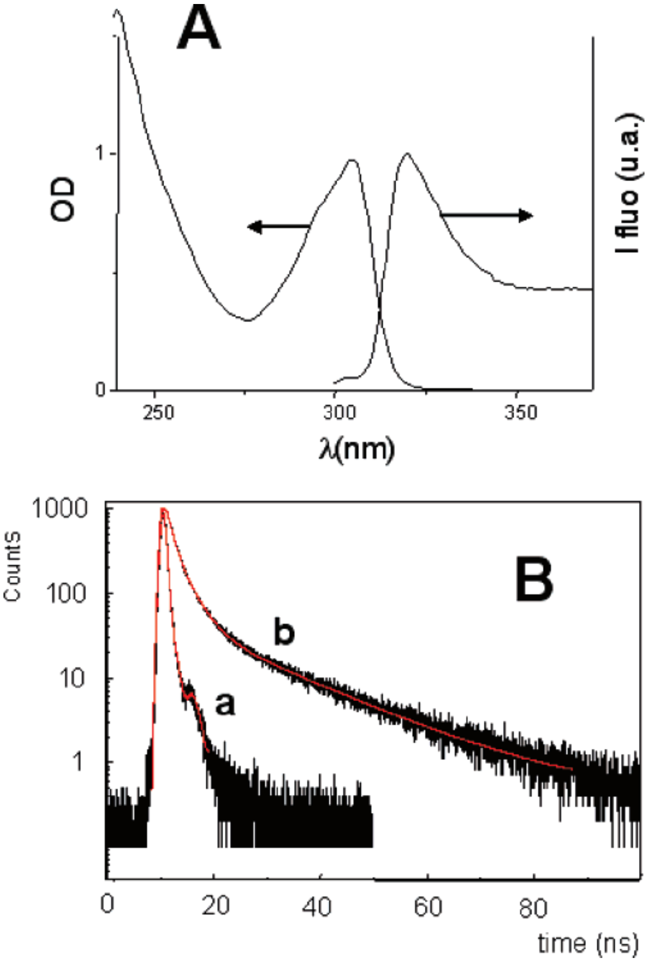


Figure 2. (A) Absorption and fluorescence spectra of **PI-1** in acetonitrile. (B) Time-resolved fluorescence monitored at 346 nm for **PI-2** in acetonitrile solution. Key: (a) nonirradiated sample; (b) sample after photolysis.

Table 1. Absorption, Fluorescence, and Polymerization Ability of PI-1 and PI-2

	λ_{max} (nm)		photoinitiating properties[c]	
	absorption	fluorescence	Rp_{rel}(laminate)	Rp_{rel}(under air)
PI-1	305 (17700[a])	320 (<200[b])	0.96 (3.37[d])	0.85 (2.99[d])
PI-2	276 (40050[a]) 287 (37 920[a])	345 (<200[b])	0.35 (1.11[d])	0.12 (0.38[d])

[a] The extinction coefficients are given in parentheses (in mol^{-1} L cm^{-1}) in acetonitrile. [b] The fluorescence lifetimes are given in parentheses (in picosecond). [c] The Rps are relative to DMPA. [d] The Rps in parentheses are corrected from the amount of light absorbed (see text).

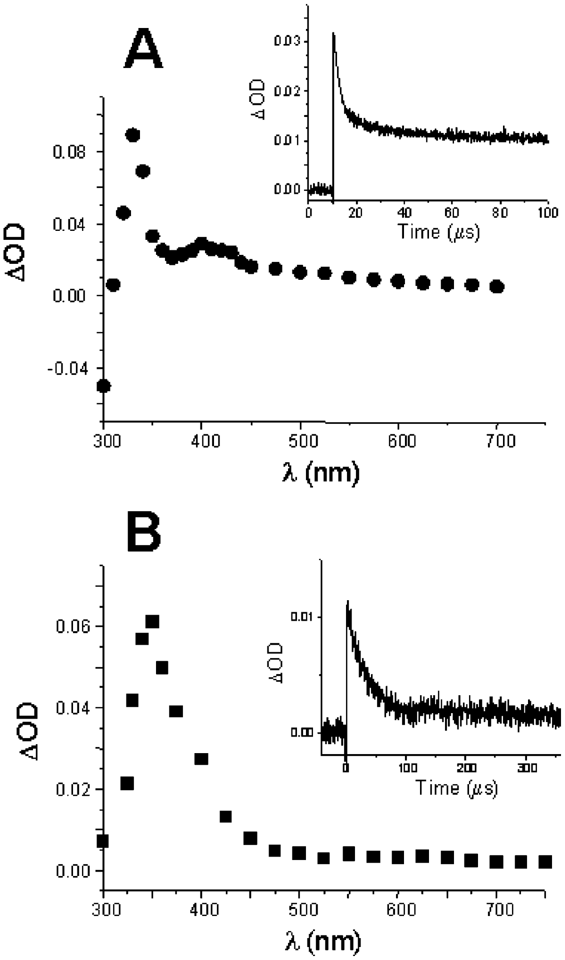


Figure 3. Transient absorption spectra recorded immediately after the laser excitation of **PI-1** (A) and **PI-2** (B) at 266 nm in acetonitrile. Inserts: decay traces observed at 340 nm (**PI-1**) and 350 nm (**PI-2**). A bleaching of the ground state absorption occurs in **PI-1** below 300 nm.

was assumed equal to the diffusion rate constant corrected by the spin multiplicity factor as usually done.[12b] For BP, ϵ was extracted from the literature.[12a]

For film polymerization experiments, a given photoinitiator (weight concentrations of 0.1% for PI-1 and 1% for PI-2 are used in order to obtain a good solubility) was dissolved in the polymerizable medium (Ebecryl 605 (Cytec)/1,6-hexanediol diacrylate 70%/30% w/w). For comparison, DMPA was used in the same conditions. The laminated or aerated films (50 μm thick) deposited on a BaF_2 pellet were irradiated with the glass plate filtered polychromatic light (incident light intensity: $I_0 \approx$ 5 mW cm^{-2}) delivered by a Xe−Hg lamp (Hamamatsu, L8252, 150 W). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (Nexus 870, Nicolet) as reported in.[13] The rates of polymerization Rp were calculated from the linear part of the conversion vs time curves. They could be corrected to take into account the light absorbed[1−4] assuming, as usual, the square root dependence of Rp on the amount of light absorbed I_{abs}. In the 300−500 nm wavelength range, the quantity I_{abs} was calculated according to eq 2 where I_0 andOD (which depend on the wavelength) stand for the light source intensity I_0 at the sample (obtained by an absolute irradiance measurement with the Ocean Optics HR4000) and the absorbance of the photoinitiator (OD).

$$I_{abs} = \int I_0(1 - 10^{-OD})\, d\lambda \qquad (2)$$

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs.[14] The Si−Si bond dissociation energies (BDE) were calculated with addition of the ZPE correction. The computational procedure used to characterize the addition reaction of the silyl radicals to acrylate has been already discussed in detail for carbon and sulfur centered radicals.[15−16] Reactants, products and transition states TS were fully optimized in the density functional theory framework (at B3LYP/LANL2DZ level—for a good description of the Si atom) allowing the determination of both the reaction enthalpy ΔH_R and the barrier (that corresponds to the energetic difference between the TS and the reactants), taking into account the zero point energy correction.

Results and Discussions. **(a) Photopolymerization Ability.** The photoinitiating abilities of **PI-1** and **PI-2** were investigated and compared to that of the well-known type I photoinitiator

Table 2. Reactivity of the PI-1 and PI-2 Derived Silyl Radicals; Si−Si Bond Cleavage Characteristics (See Text)

	silyl radicals reactivity			Si−Si bond cleavage		
	k_i(MA) ($mol^{-1}\ L\ s^{-1}$)	k_q(TEMPO) ($mol^{-1}\ L\ s^{-1}$)	$k'_q(O_2)$ ($mol^{-1}\ L\ s^{-1}$)	Φ_{diss}	k_{diss} (s^{-1})	BDE[d] (kcal/mol)
PI-1	8.1×10^8 (2.5/−93.5)[a] (3.5×10^8)[b]	1.3×10^9	4.6×10^9	1.0 (2080[c])	$>10^8$	59.9
PI-2	5.1×10^6 (5.2/−100.4)[a]	3.4×10^8	3.2×10^9	0.80 (1510[c])	$>10^8$	63.0

[a] In parentheses: barrier and addition enthalpy to MA (in kJ/mol) calculated at B3LYP/LANL2DZ level. [b] Addition to methyl methacrylate. [c] Extinction coefficient of the silyl radicals ($mol^{-1}\ L\ cm^{-1}$) at 340 and 350 nm for **PI-1** and **PI-2**, respectively. [d] Si−Si bond dissociation energy calculated at UB3LYP/LANL2DZ level with ZPE correction.

DMPA (Figure 1). The relative polymerization rates with respect to DMPA are given in Table 1 as well as the relative rates corrected from the absorbed light intensity. Under a polychromatic light exposure, **PI-1** exhibits a practical efficiency close to that of DMPA. For **PI-1**, however, a significant absorption is only noted for the 313 nm band (Figure 2). Therefore, the overall absorption is obviously lower than for the reference. Considering the same amount of absorbed light, the intrinsic photochemical reactivity appears as about 3 times higher (in laminated conditions or under air) than that of DMPA. **PI-1** is a remarkable photoinitiator. For **PI-2**, a lower reactivity is found (about 1 in laminated condition and 0.35 under air).

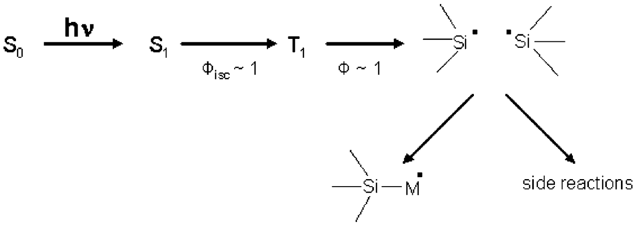
For both compounds **PI-1** and **PI-2**, the final conversions obtained were higher than 75% for polymerization time of 120 s.

(b) Excited States and Radical Properties. The absorption properties of **PI-1** and **PI-2** are gathered in Table 1. The absorption coefficients of the UV transition mainly observed below 330 nm are representative of $\pi-\pi^*$ transitions. The first excited singlet state S_1 is characterized by a weak fluorescence emission (Figure 2, Table 1). As evaluated by the single photon counting technique, the S_1 state lifetimes are found within the time resolution of the experimental setup ($\tau < 200$ ps). A component with a longer decay time appears for both compounds (the fluorescence decay is fitted according to a multi-exponential function): as its contribution increases all through the experiment (1 h), it is safely ascribed to the fluorescence of a photoproduct.

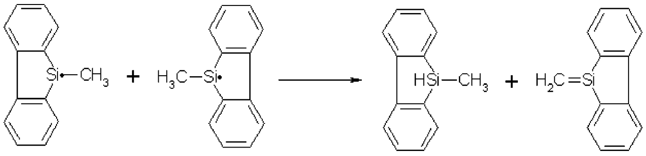
Under laser excitation at 266 nm of **PI-1** and **PI-2**, new transients are observed (Figure 3). The spectra are relatively similar to that found for $Ph_3Si^\bullet$ (maxima at about 330 nm).[8] The transients are strongly quenched by both oxygen and TEMPO (Table 2) which are excellent radical trapping agents. Therefore, the obtained transients can be confidently ascribed to the silyl radicals generated through the homolytic cleavage of the Si−Si bond. The rise time of the silyl radicals is less than the resolution time of the laser setup (<10 ns): for both compounds, the dissociation rate constants are thus higher than $10^8\ s^{-1}$.

For **PI-1** and **PI-2**, the dissociation quantum yields Φ_{diss} are very close to 1 (Table 2) and the quantum yields for the radical production are close to 2, thereby demonstrating the high efficiency of the cleavage process. The calculated Si−Si BDEs are quite weak (Table 2) compared to those of the C−C bonds (roughly 60 vs 85 kcal/mol). This lower value is also in agreement with the fast cleavage observed. The lower Φ_{diss} determined for **PI-2** is likely in line with the higher BDE of this derivative.

Scheme 2



Scheme 3



As revealed by quantum mechanical calculations, the S_1 states of **PI-1** and **PI-2** are not dissociative (a successful optimization is possible): their short lifetimes can probably be explained by high intersystem quantum yields (close to 1). On the opposite, the triplet states T_1 are found dissociative at B3LYP/LANL2DZ level: they directly generate two silyl radicals during the optimization procedure. As a consequence, the cleavage process is assumed as mainly originates from T_1.

The very high reactivity of the silyl radicals for the addition to MA must be outlined (Table 2): it is noticeably higher than that reported for the well-known phosphinoyl, hydroxy isopropyl or benzoyl initiating radicals (for example, the reaction is about 4000 and 20 times more efficient for **PI-1** and **PI-2** than the similar addition of the benzoyl radical[2,3,15]). The barriers calculated for the addition to MA with a DFT procedure (Table 2) are also in good agreement with the high experimental rate constants obtained. The **PI-1** derived silyl radical should be considered as one of the most efficient powerful initiating agent reported so far.[15]

(c) Initiation Mechanism. Scheme 2 accounts for the initiation of the photopolymerization.

The reactivity difference between **PI-1** and **PI-2** can be ascribed to the clearly lower reactivity of the silyl radicals generated from **PI-2** (in the present polymerizable medium, the rate constants are not leveled off by the diffusion)[13] and the slightly lower dissociation quantum yield. Some side reactions of the silyl radicals (recombination with the growing polymer chains, transfer reaction through hydrogen abstraction...) can also be invoked. Among them, the competitive quenching reaction depicted in Scheme 3 should occur, as it was already suspected in other related structures bearing a α-labile hydrogen.[8] Such a reaction holds true for **PI-2** but is not feasible in **PI-1** which contains a phenyl group in place of the methyl substituent. The stability of the formed peroxy radicals and their further reactions are also likely influenced by the methyl vs phenyl substitution: this should explain the relative behavior of **PI-1** and **PI-2** under air.

Conclusion. To the best of our knowledge, this is the first report on such highly efficient Si−Si bond breaking based photoinitiators of radical photopolymerization reactions. The reactivity is noticeably higher than that of DMPA. The detrimental effect of the methyl substitution on the Si atom likely explains why the few examples of polysilanes reported so far did not lead to efficient initiating structures. This new class of photoinitiators has already a promising potential which should still increase thanks to the adequate introduction of red-shifted absorbing chromophores and the enhancement of the solubility in an acrylate matrix.

Acknowledgment. The authors thank the CINES (Centre Informatique National de l'Enseignement Supérieur) for the generous allocation of time on the IBM SP supercomputer.

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MA071489K