A New Efficient Photoiniferter for *Living* Radical Photopolymerization

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1. Introduction. The radical generation in conventional radical polymerization is irreversible without any possibility to control the final properties of the polymer formed such as the number-average molecular weight (M_n) and the polydispersity PDI. In controlled or living radical polymerization reactions, the radicals are reversibly generated,[1,2] this idea is already largely used in thermal polymerizations.[1]

It is of great interest to apply this approach to light induced polymerization reactions as shown, e.g., in refs 3−8 because of the large possibilities of selected applications in photografting reactions, production of block copolymers, manufacture of multilayer photomaterials, photolithography, and spatial photomodification of polymer networks through the development of 2D and 3D patterned and surface modified polymers with end functional groups. In these reactions, a photoiniferter can be used at once as a photoinitiating system, a transfer agent, and a terminating radical.

Very few structures however have been proposed, the most efficient of them leading to relatively broad M_n distributions.[7−9] There is still a need for new photoiniferter structures providing high rates of polymerization, high M_n, and narrow PDI and allowing one to initiate the polymerization of a large range of monomers for copolymers synthesis.

The new photoiniferter structure proposed in this paper (Scheme 1) is an asymmetric disulfide based on thio-1-phenyl-1*H*-tetrazole and dithiocarbamate moieties (**I**) where the thiotetrazole (TZ•) and the dithiocarbamate (DC•) derived radicals correspond to the initiating and terminating radicals, respectively. Its ability to control a (meth)acrylate photopolymerization will be compared to those of benzyl dimethyldithiocarbamate (**II**) and two other symmetric derivatives: 5,5′-dithiobis (1-phenyl-1*H*-tetrazole) (**III**) and tetramethyl thiuramdisulfide (**IV**). Compounds **II** and **IV** are already known as photoiniferters.[7−9]

2. Experimental Part. Samples. Compounds II, **III**, and **IV** (Aldrich) were used without further purification (purity higher than 98%). **I** was prepared by a classical method developed by Alam et al.: **IV** was added to a solution of **III** in benzene and photolyzed for 1 h with a UV lamp (Hamamatsu L2852) leading to **I** formation. The final purity of **I** was higher than 95%.

For the monomers studied, methyl methacrylate (MMA) was obtained from Aldrich and 1,6-hexanediol diacrylate (HDDA) from Cray Valley.

Laser Flash Photolysis (LFP) Experiments. For nanosecond laser flash photolysis LFP, the setup is based on a pulsed Nd :Yag laser (Powerlite 9010, Continuum) and a transient absorption analysis system (LP900, Edinburgh Instruments). The instrument response was equal to about 10 ns.[11]

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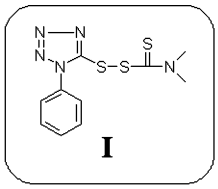
Scheme 1. The New Photoiniferter Proposed (I) and the Mechanism Associated with the Photopolymerization Process



I

$$\text{R-DC} \xrightarrow{h\nu} \text{R}^{\bullet} + \text{DC}^{\bullet}$$

$$\text{R}^{\bullet} + \text{M} \longrightarrow \text{RM}^{\bullet}$$

$$\text{RM}^{\bullet} + \text{M} \longrightarrow \text{RM}_n^{\bullet}$$

$$\text{RM}_n^{\bullet} + \text{DC}^{\bullet} \underset{h\nu}{\rightleftharpoons} \text{RM}_n\text{-DC}$$

Photopolymerization Procedure. The photopolymerization of MMA 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, L2852, 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}).[12]

For cross-linking experiments, the laminated films of HDDA deposited on a BaF_2 pellet (25 μm thick; optical density < 0.15 at 366 nm) were irradiated with the same Xe−Hg lamp. The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (with a Nicolet, Nexus 870). Rates of polymerization (R_p) were calculated from the linear part of the % conversion vs time curves. The compounds studied were compared to 2,2-dimethoxy-2-phenylacetophenone (DMPA), this compound being a classical UV photoinitiator.[1]

Molecular Weight Determination. The number-average molecular weights M_n and PDI were determined by gel permeation chromatography (GPC) using a Waters 2690 apparatus equipped with Styragel columns (HR0.5, HR1, HR4) and a refractive index detector (Waters 410). The molecular weight resolving range of the columns is between 500 and 600 000 g mol^{-1}. Polystyrene standards were used in order to generate a universal calibration curve. Tetrahydrofuran (THF) was used as an eluant.

3. Results and Discussion. The Living Polymerization Mechanism. Scheme 1 recalls the mechanism of a classical living radical photopolymerization process as originally proposed by Otsu et al.[9] The fourth reaction is photochemically reversible (through a photodissociation of the dithiocarbamate end groups) leading to the living character of the polymerization, which is achieved provided that the exchange between the reactive and the dormant species is fast in comparison with the propagation.

The Photodissociation Process of the Iniferters. Laser excitation of **I**, **II**, and **IV** at 355 nm leads to a strong absorption at 600 nm of the DC• radicals (already characterized by Ito et al.) which rises within the resolution time of the experimental setup (<10 ns) (see Supporting Information). Interestingly, this ultrafast cleavage process in **II** can also mimic the photodissociation of the C−S single bond for the dormant species

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Table 1. Polymerization Rates of Methyl Methacrylate (bulk) and $RM_n^•$ Concentrations in the Presence of the Different Photoiniferters (1% w/w) and Photopolymerization Rates of a 1,6-Hexanediol Diacrylate Film (50μM), Where DMPA (2,2-Dimethoxy-2-phenylacetophenone) Is Used as a Reference UV Photoinitiator

monomer	photoiniferters	R_p (M s^{-1})	$[RM_n^•]$ 10^{-6} mol/L
MMA	**I**	0.0027	1.9
MMA	**II**	0.0031	2.2
MMA	**III**	0.018	13.2
MMA	**IV**	<0.00045	<0.33
MMA	**I** + **IV** (1%/1%)	0.0017	1.2
HDDA	**DMPA**	3.8	
HDDA	**I**	0.13	
HDDA	**II**	0.14	
HDDA	**III**	0.89	
HDDA	**IV**	<0.01	

(Scheme 1) demonstrating the fast reversibility of the termination reaction under light irradiation.

For **I**, in addition to the absorption band ascribed to DC•, a second absorption centered at 430 nm is also noted; as the same band is observed for **III** (in a time scale lower than 10 ns) in agreement with a previous report,[14] it can be safely ascribed to the TZ• radical generated after the S−S bond dissociation.

The Reactivity of the New TZ• Radical. The polymerization abilities of the different structures, expressed by the corresponding rates of polymerization R_p of MMA, are gathered in Table 1. Compound **III** is highly efficient. Therefore, TZ• is presumably an excellent initiating radical. This is also supported by the very high addition rate constants of TZ• to methyl acrylate (k_a is 5×10^7 M^{-1} s^{-1} for TZ•[15] and only 4×10^3 M^{-1} $s^{-1}$for the benzyl radical[16]).

The two basic photoiniferter structures **I** and **II**, used at a fixed concentration, exhibit almost the same efficiency. The higher reactivity of TZ• (compared to the benzyl radical) toward the initiation process is probably counterbalanced by (i) the lower absorption of **I** (at 366 nm, the molar extinction coefficients are 35 and 40 M^{-1} cm^{-1} for **I** and **II**, respectively) and (ii) the possibility of an in-cage recombination of the thiyl radicals for **I**, a process already encountered in other disulfides.[17] As expected, **IV** is unefficient (it contains two terminating DC• radicals).

Features of the Living Radical Photopolymerization of MMA. Figure 1 shows the conversion of MMA vs time and M_n vs conversion plots for **I**, **II** and **I** + **IV** as photoiniferters. The increase of the molecular weight with both the conversion and the PDIs represent the best parameters to characterize the living process. For **I** and **II**, the M_n vs conversion plots give linear relationships (this behavior was already known for the reference **II**[7]). This result demonstrates that the photodissociation of the C−S bond at the chain end, the subsequent propagation and recombination of the propagating radical with the DC• radical also occur for **I**. The M_n evolution follows a linear trend. For **I** and **II**, the deviation from the origin usually observed (see Otsu et al.) indicates that a part of the carbon−carbon termination mechanism still remains in the early stage of the reaction, the linear trend being always ascribed to the carbon−dithiocarbamyl radical recombination.

The initial slope of the conversion vs time plots is directly related to the polymerization rate ($R_p/[M_0]100$—where M_0 stands for the initial monomer concentration). Using the classical polymerization relationship (eq 1), the propagating radical concentrations are evaluated in Table 1 (taking a propagation rate constant of 143 M^{-1} s^{-1} for MMA[18]). For the (**I** + **IV**) two- component system, the $RM_n^•$ concentration is decreased

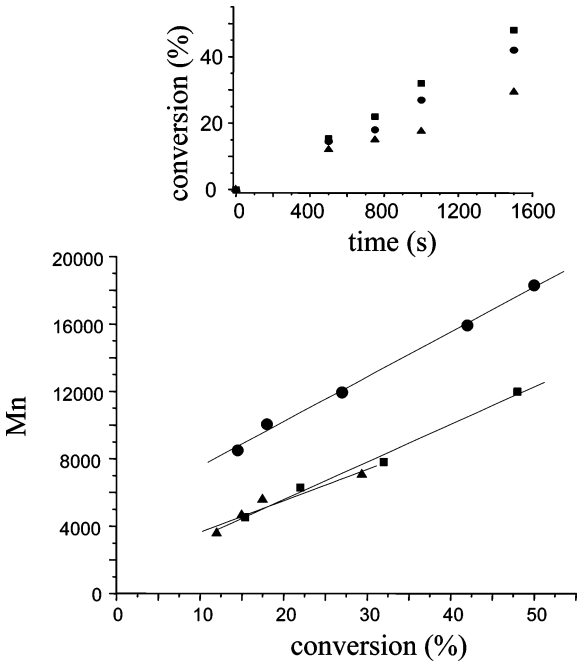

Figure 1. Effect of the photoiniferters. Number-average molecular weight (M_n) vs conversion curves (photopolymerization of MMA in bulk in a sealed glass tube after Ar bubbling and irradiation with the UV light of a Xe−Hg lamp). Inset: Conversion of MMA in bulk vs time. Key: square, **II**, 1%; circle, **I**, 1% and up; triangle, **I** 1% + **IV** 1%.

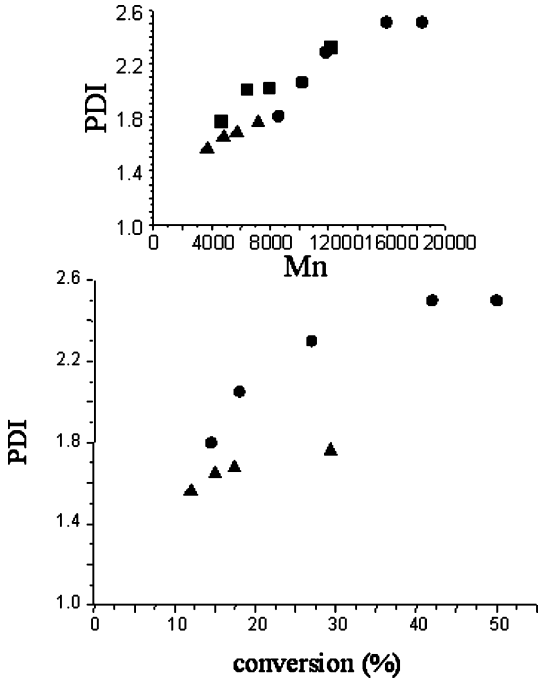

Figure 2. Effect of the photoiniferters. PDIs vs conversion. MMA in bulk. Inset: PDIs vs M_n. Key: **I** (circle); **II** (square) and **I** + **IV** (up triangle).

by a ∼ 2-fold factor (compared to **I** and **II**) in agreement with the increase of the DC• production.

$$R_p = k_p\,[RM_n^•][M_0] \qquad (1)$$

The PDIs are lower than 2.0 at M_n < 8000 for **I** and **II**, albeit slightly lower in the case of **I** for a given M_n value (Figure 2). However, interestingly, the molecular weight for a given conversion is found higher for **I** than for **II**. This corresponds

to a great advantage exhibited by **I**, compared to **II**, which can be useful for an access to a larger M_n range. In the case of **III**, higher PDIs are obtained (3 to 4): as expected, this compound is not suitable for a photopolymerization control.

As previously noted by Bertin et al. for the benzyl dithiocarbamate derivatives, the PDIs can be greatly improved by an increase of the terminator radicals concentration (DC•). In Figure 2, the PDIs obtained with **I** + **IV** are better with an average value of 1.6 for conversions between 10 and 30%. The addition of **IV** also leads to a decrease of the positive intercept in the M_n vs conversion plots evidencing a decrease of the usual bimolecular carbon−carbon termination reaction due to a better control of the polymerization (in agreement with the lower PDIs observed).

The **III** + **IV** systems also lead to a living character (linear M_n/conversion relationship and lower PDI than with **III** alone). The relative behavior of **I** vs **III** + **IV** is different since the absorption and the photochemical and photophysical properties of the systems are different. A large panel of situations can be of course encountered: **III** alone should lead to a bad control with a high R_p, the addition of **IV** should result in a better control with a concomitant strong decrease of R_p. For applications which do not require such conditions, a two component system (**III** + **IV**) can allow a good polymerization rate/control compromise.

Behavior of the Photoiniferters for Cross-Linking Experiments of HDDA Films. The Role of the DC• Radicals. The polymerization ability of the photoiniferters in a HDDA matrix is quite similar to that noted for MMA in bulk (Table 1—kinetics are given in the Supporting Information). The polymerization rates is about 20 times lower with **I** or **II** than with DMPA). **III** exhibits a high reactivity but one-fourth than DMPA: this lower efficiency of **III** is attributable to the lower UV absorption of this compound compared to DMPA at 366 nm i.e., the absorption coefficient at 366 nm (maximum emission of the light source) is 127 M^{-1} cm^{-1} for DMPA and only 25 M^{-1} cm^{-1} for **III**. A control of the polymerization also occurs. Indeed, the concentration of the DC• radical can be changed by using a two component system (**III** + **IV**) in which the concentration in **IV** is adjusted. A plot of R_p vs 1/[**IV**] yields: $R_p = -0.046 + 0.102(1/[\mathbf{IV}])$ ($r = 0.995$ and $n = 5$; see Supporting Information—Figure 3). This evidences a direct relationship between R_p and 1/[**IV**] and therefore 1/[DC•]. A steady-state analysis of Scheme 1 leads to a polymerization rate described by eq 2 where k_p, k_t, Φ_i, and Φ_r represent the propagation and the termination rate constants, the initiation and dissociation quantum yields of the dormant species, respectively (I_{abs1} and I_{abs2} stand for the light intensity absorbed by the photoiniferter and the dormant species). The agreement between eq 2 and the above relationship supports the fact that the termination process corresponds to the recombination of the propagating radical (RM_n•) with DC•, the usual bimolecular termination (between two propagating radicals) being predominantly avoided.[19]

$$R_p = k_p[\Phi_i I_{abs1} + \Phi_r I_{abs2}][M]/(k_t[DC^\bullet]) \qquad (2)$$

Conclusion

The new asymmetric disulfide photoiniferter **I** proposed here appears as powerful to control the final properties of the formed polymer. It leads to high M_n whereas a combination of **I** with a tetramethyl thiuramdisulfide **IV** is better for obtaining both low M_n and narrower PDI. Moreover, the control of the polymerization of multifunctional monomers usable in the UV Curing area also appears as feasible. Compound **I** can also create a large variety of dormant species (R−M_n−DC) in a polymer matrix: the formation of a PMMA−polystyrene copolymer through a sequential approach was easily achieved (see Supporting Information). Other copolymers can be probably formed using the outstanding low selectivity property of TZ• toward monomers (mentioned above). In fact, preliminary results have underlined the high reactivity of TZ• radical i.e., the addition rate constants are found higher than 10^7 M^{-1} s^{-1} for the addition to electron deficient (methyl acrylate...) or electron rich (vinyl acetate...) monomers.

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Supporting Information Available: Figure 1, polymerization kinetics of HDDA film (50 μm) in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA), **I**, **II**, **III**, or **IV**, Figure 2, decay of the dimethyldithiocarbamyl radicals observed at 600 nm by LFP, Figure 3, plot of R_p vs 1/[**IV**] for HDDA films, and text giving a discussion of the copolymer synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Matyjaszewski, K. *Advances in Controlled/Living Radical Polymerization*; ACS Symposium Series; American Chemical Society: Washington, DC, 2002.
(2) Otsu, T. J. *Polym. Sci. Part. A.; Polym. Chem.* **2000**, *38*, 2121−2136.
(3) Luo, N.; Metters, A. T.; Hutchinson, J. B.; Bowman, C. N.; Anseth, K. S. *Macromolecules* **2003**, *36*, 6739−6745.
(4) Reddy, S. K.; Sebra, R. P.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci. Part. A.; Polym. Chem.* **2005**, *43*, 2134−2144.
(5) Otsu, T.; Matsunaga, T.; Doi, T.; Matsumoto, A. *Eur. Polym. J.* **1995**, *31*, 67−78.
(6) Kuriyama, A.; Otsu, T. *Polym. J.* **1984**, *16*, 511−516.
(7) Otsu, T.; Taraki, T. *Polym. Bull. (Berlin)* **1986**, *16*, 277−282.
(8) Bertin, D.; Boutevin, B.; Gramain, P.; Fabre, J. M.; Montginoul, C. *Eur. Polym. J.* **1998**, *34*, 85−90.
(9) Otsu, T.; Yoshida, M. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127−132.
(10) Alam, M. M.; Watanabe, A.; Ito, O. *J. Org. Chem.* **1995**, *60*, 3440−3444.
(11) Lalevée, J.; Allonas, X.; Fouassier, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 9613−9621.
(12) Stansbury, J. W.; Dickens, S. H. *Dental Mater.* **2001**, *17*, 71−86.
(13) Ito, O.; Matsuda, M. *J. Phys. Chem.* **1981**, *85*, 1365−1368.
(14) Alam, M. M.; Watanabe, A.; Ito, O. *Int. J. Chem. Kinet.* **1996**, *28*, 405−411.
(15) Lalevée, J.; Allonas, X.; Fouassier, J. P. To be published.
(16) Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340−1371.
(17) Lochschmidt, A.; Eilers-Konig, N.; Heineking, N.; Ernsting, N. P. *J. Phys. Chem. A* **1999**, *103*, 1776−1784.
(18) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley and Sons: New York, 1989.
(19) A previously published study by Kannurpatti et al. (*Macromolecules* **1996**, *29*, 7310) on the use of a disulfide as both a photoinitiator and an iniferter agent has indicated a square root dependence between R_p and the disulfide concentration (tetraethylthiuram disulfide). This current difference of behavior with **III** + **IV** can be ascribed to the termination mechanism. A direct comparison with this previous work is not straightforward.

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