PHOTOINITIATORS : AN OVERVIEW OF MECHANISMS AND APPLICATIONS

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Light-curable monomer and resin formulations are increasingly developed, due to the rapid growth of the industrial applications in various areas, such as coatings and varnishes (optical fibers, wood, plastics, papers ...), adhesives, dental and medical equipment, inks, metal decoration, flooring, imaging, microelectronics [1][2]. One of the most widely used reaction is a light-induced polymerization [3] which readily transforms a liquid resin into a solid film. Improvement of the systems requires further investigation [4] on the (photo)-physical and (photo)-chemical processes involved (in particular, the photoreactivity of sensitizers used to start the reaction) and new ideas concerned with the use of powerful irradiation devices such as lasers in the case of specific applications : direct writing of microcircuits, 3D machining, information storage, manufacture of holographic optical elements [5].

1. PRINCIPLE

The photoinitiation step of such a reaction usually requires the presence of a molecule (called photoinitiator) which absorbs the exciting light and leads to radical or cationic species onto the monomer, through processes which occur in its excited states (scheme 1). For example, it is apparent that the quantum yield of radical initiation (*i.e.* the number of starting chains per photon absorbed) is closely related to the efficiency of the radical generation routes in comparison with the other deactivation pathways (radiative and non radiative processes ; O_2 , monomer and additive quenching reactions). Several approaches have already shown that a direct investigation on the excited state processes involved may lead to a deeper insight into the practical efficiency. In the present paper, recent and relevant outlines concerning the reactivity of radical and cationic photoinitiators, photosensitizers and photoinitiators under laser lights for printing or holographic recording will be discussed.

2. RADICAL PHOTOINITIATORS

Usual and well-known photoinitiators work through α -cleavage, electron transfer or H-abstraction (scheme 2).

The most representative systems of the first generation [7] (scheme 3) are : benzoin ethers, hydroxyalkylketones, dialkoxyacetophenones, benzoyl phosphine oxides (which work through a Norrish type I photolysis process), benzoyloxime esters (that cleave according to a N—O bond scission), benzophenones, benzils, thioxanthenes (which undergo very easily electron transfer and proton transfer, thus leading to the formation of the amine derived initiating radical).

New photoinitiating systems have been recently developed (scheme 4) such as morpholino ketones, sulfoxides (these photoinitiators are built on the benzophenone and thioxanthone skeleton), sulfonyl ketones (they undergo a fast β -cleavage process, leading to efficient radicals), UV-deblockable acid releasing systems (different structures have been recently proposed, *e.g.* sulfonyloxy ketones, sulfonyl ketones, sulfonyloxy ester of benzoin derivatives), photoinitiators carrying long alkyl chains (introduction of C_{10} to C_{13} alkyl chains LC onto the usual backbones of the photoinitiators does not change significantly the photochemical reactivity during the light exposure, but increases the compatibility in the film, polymeric or copolymerizable photoinitiators (the behavior of the primary processes is very similar to that of the parent compound), water-soluble photoinitiators (efficient ionic or hydrophilic compounds based on benzils, benzophenones, thioxanthenes, hydroxy alkyl ketones are suitable photoinitiators for acrylamide polymerization, micelle polymerization and grafting onto cellulosic materials in water), effect of the introduction of a thioether group, α -amino-ketones (a new α cleavable photoinitiator was very recently shown to be much more reactive than the usual morpholino ketone/ thioxanthone combination for the photopolymerization of white pigmented lacquers), ketocoumarines (these structures are very attractive because of their tendency to exhibit a red shifted ground state absorption as a function of the substituents. The electron

transfer is particularly efficient). Full diagrams of the excited state processes have been published [4, 5, 8, 9], *e.g.* scheme 5 [10].

Typical rate constants (k_c , k_e) and quantum yields of cleavage (ϕ_c) or electron transfer (ϕ_{CT}) for photoinitiators under practical conditions of bulk polymerization are listed in Table 1 [4][9]. It is apparent that most systems exhibit high quantum yields which makes these molecules very active as photoinitiators, both in solution and in film polymerization. However, the side reactions of the radicals formed, the quenching of the radicals by the monomer, the interaction of O_2 with the excited species, the deactivation of the radical pairs without any release of radicals, should be considered as detrimental pathways for the photopolymerization efficiency, even if ϕ_c or ϕ_{CT} approaches unity.

3. CATIONIC PHOTOINITIATORS

A promising development of cationic photopolymerization initiated by onium salts or organo metallic compounds seems to take shape. Excellent reviews have been recently published in this field [11][12][13][14]. Information concerned with the processes involved and kinetic measurements through time-resolved laser-spectroscopy, begins to be published in the literature. Scheme 6 summarizes the main photoprocesses encountered in the photochemistry of cationic photoinitiators.

4. SENSITIZATION PROCESSES

Visible photosensitizers have always been considered as attractive systems either for direct initiation through visible light (conventional or laser beams) or to increase the energy dose received by a substrate subjected to polychromatic light. Extension of the spectral sensitivity of a photoinitiator I can be achieved by adding a photosensitizer, S. Such an energy transfer process must be exothermic with the energy level of the excited donor exceeding that of the acceptor by a few $Kcal\ M^{-1}$ (with a difference of $3\ Kcal\ M^{-1}$, the energy transfer is almost diffusion controlled). However, the two terms photoinitiator and photosensitizer are often used in a more general sense to define any process involving either energy transfer (to generate from I the same radicals as those obtained through direct excitation) or an electron transfer followed by a proton transfer (to form new initiating radicals) [15]. A first example concerns (scheme 7) [16], the photopolymerization of pigmented systems that has been a challenge for a long time and led to the search for suitable combinations of photosensitizers and photoinitiators. Due to the spectral window offered by TiO_2 , the former belong generally to the thioxanthenes ; the basic idea to solve this problem was to lower the triplet state energy level E_T of the photoinitiator in order to enhance the energy transfer from the thioxanthone : this would have been achieved by introducing a thioether group. In a general way, this energy transfer process competes with an electron transfer process, the balance of which depends on the nature of the systems used and of the environment.

	k_{cleavage} (s ⁻¹)	k_e (M ⁻¹ s ⁻¹)	k_q (M ⁻¹ s ⁻¹)	ϕ_C	ϕ_{CT}
$\geq 10^{11}$	-	-	1
-	3×10^9	7×10^7	0.3
-	$\sim 10^9$	$\sim 10^6$	0.9
7×10^5	1.6×10^9	0.7×10^8	0.11
10^8		2×10^8	0.8
2×10^7	7×10^8	1.5×10^8	0.05
10^7	2×10^9	$\sim 10^8$
$\leq 10^9$		3×10^8	0.3
7×10^8	5×10^4	1
8.6×10^8	3.7×10^5
2.5×10^9	1.1×10^7		

Table 1. Reactivity of carbonyl triplet states, rate constants of cleavage k_c and electron transfer k_e with methyldiethanolamine and monomer (methyl methacrylate MMA) quenching in toluene. Computed quantum yields of cleavage (ϕ_c) and electron transfer (ϕ_e) (in toluene solution of MMA 7 M. [Amine] = 0.05 M) for the reaction $T_1 \rightarrow R^*$ and $T_1 + \text{Amine} \rightarrow \text{CTC Complex}$.

schema 7

schema 9

Cationic photopolymerization can be sensitized by hydrocarbon [17] and ketones [17][18][19] mostly through an electron transfer process with the sensitizer itself or radicals derived from the photolysis of the sensitizer.

5. LASER LIGHT INDUCED POLYMERIZATION

The use of lasers for inducing photochemical events in monomer film or polymer matrix is a tempting subject not only because of the magic character of the laser but also because of practical and fundamental specific advantages : *e.g.* high energy concentration onto a small surface, high spatial resolution, very short exposure times allowing a scanning of the film surface by the laser spot, easy focalization, spectral selectivity, narrow bandwidth of the emission. This procedure of laser-induced chemical reactions seems to be a very promising method and applications are currently explored or/ and seriously envisaged [5]. This has created a need for testing photoinitiators and resins, understanding the processes involved and for developing new efficient systems under visible or near IR laser lights (under blue laser lights, usual photoinitiators are obviously able to work efficiently [20]). Typical systems are represented in scheme 8. Among them, ketocoumarins appear as very sensitive under Ar⁺ laser exposure at $\lambda = 488$ nm (scheme 9) [21][22].

6. PHOTSENSITIVE SYSTEMS FOR HOLOGRAPHIC RECORDING

Such systems should meet the same requirements as those developed in the above paragraph [23-25]. However, the organic matrix plays a significant role on the hologram characteristics. Monophotonic [25] and biphotonic [26,27] (with two photons of different wavelength) recording media have been recently developed.

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