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Role of the Medium on the Reactivity of Cleavable Photoinitiators in Photopolymerization Reactions

Jacques Lalevée, Xavier Allonas,* Safi Jradi, and Jean-Pierre Fouassier

Département de Photochimie Générale, UMR 7525 CNRS, Université de Haute Alsace,
3 rue Alfred Werner, 68093 Mulhouse, France

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ABSTRACT: The efficiency of 11 cleavable photoinitiators in polymerization reactions was determined in various media, such as oligomer, acrylate, and methacrylate monomers in solution or in poly(methyl methacrylate). It was found that the efficiency of the photoinitiator strongly depends on the polymerized medium. The results are explained and discussed on the basis of the viscosity effect on the rate constants of the processes involved, resulting in good efficiency/reactivity relationships. Quantum yields of initiation were calculated for an acrylate photopolymerization in solution. The efficiency in viscous bulk media is quite well reflected in the dissociation quantum yields of the photoinitiators measured in solution. The role of the other low-viscosity media is also explained. Kinetic treatments were used to examine the influence of the monomer structure on the propagation and termination rate constants of the reaction. These results allowed to shed some light on the influence of the medium on the initiation efficiency and to provide a better knowledge of the key parameters for practical applications.

Introduction

A free radical polymerization is the most important reaction encountered in UV radiation curing, and a lot of papers have dealt with the role of the photoinitiator (PI).[1−4] However, the investigation of the photophysical processes involved and the study of the photochemical reactivity are mainly carried out in fluid solution, in contrast to the practical efficiency in polymerization experiments that are obviously carried out in polymeric formulations. Three questions emerge from the literature concerning (i) the possibility of extrapolating the behavior of PI from solution to bulk, (ii) the efficiency for a set of PI depending on the nature of the media, and (iii) the reactivity of the initiating radicals toward monomers. We report here a thorough investigation of these problems by combining measurements of polymerization rates in various fluid and viscous media and taking into account the available kinetic data on the PI excited-state processes in solution. This study will lead to a general discussion of the properties vs efficiency relationships for a series of photoinitiators in various (meth)acrylate media.

Experiments and Methodology

Eleven cleavable photoinitiators obtained from Ciba (**a** to **g** and **i**), Lamberti (**h**), Akzo (**j**), or Merck (**k**) were selected (Scheme 1). Laser spectroscopy experiments were carried out with a Q-switched nanosecond Nd:YAG laser (9 ns pulses at 355 nm; energy reduced down to 10 mJ; Powerlite 9010 Continuum), the analyzing system consisting of a pulsed xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer.[5]

The viscosity of some formulations was measured using a Brookfield DV-II viscometer at controlled temperature.

For film polymerization experiments, a given PI was dissolved in different polymerizable media: (i) a bulk oligomer/monomer 75/25 w/w epoxy acrylate/tripropylene glycol diacrylate (Ebecryl 605 from UCB Chemicals), (ii) monomers in solution of toluene or in bulk: 1,6-hexanediol diacrylate (HDDA, Aldrich), butyl acrylate (BA, Aldrich), methyl acrylate (MA, Aldrich), methyl methacrylate (MMA, Aldrich), butyl methacrylate (BMA, Aldrich), (iii) a monomer (HDDA or BA) dissolved in poly(methyl methacrylate) (PMMA; MW = 120 000 from Aldrich) at a concentration of 75/25 w/w. Ebecryl 605 and PMMA were used as received. Stabilizers were removed from BA, MA, MMA, BMA, and HDDA by column purification (Aldrich AL-154), and the absence of stabilizers from the purified monomer was checked by quenching of 2-chlorothioxanthone.[17]

For the experiments in toluene the solution containing the PI and the monomer was degassed by Ar bubbling for 15 min. To get a good reproducibility of the experiments, thin samples with low PI optical densities (<0.15 at 366 nm) were used. These experimental conditions allow a good dissipation of the heat produced during the polymerization reaction and avoid any internal filter effects. The laminated films (50 μm thick) deposited on a BaF_2 pellet or the liquid cell (100 μm thick) were irradiated with the filtered light (366 nm; incident light intensity: $I_0 = 10$ mW cm^{-2}) of 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 originally proposed in ref 6. Assuming that the termination of the polymerization occurs through a bimolecular process, the rates of polymerization R_p were calculated from the linear part of the conversion vs time curves (Figure 1) and then were corrected to take into account the light absorbed:[1−4]

$$R_p = k_p\left(\frac{R_i}{k_t}\right)^{1/2}[M] \tag{1}$$

where k_p is the rate constant of propagation, k_t the rate constant of termination, and R_i the rate of initiation defined as

$$R_i = \phi_i I_{abs} \tag{2}$$

In this expression, I_{abs} is the amount of light absorbed and ϕ_i represents the initiation quantum yield that corresponds to the number of starting polymer chains per photon absorbed. Under monochromatic light exposure, I_{abs} is given by

$$I_{abs} = I_0(1 - 10^{-OD}) \tag{3}$$

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* Corresponding author: e-mail x.allonas@uha.fr; Tel 33 (0)389336874; Fax 33 (0)389336895.

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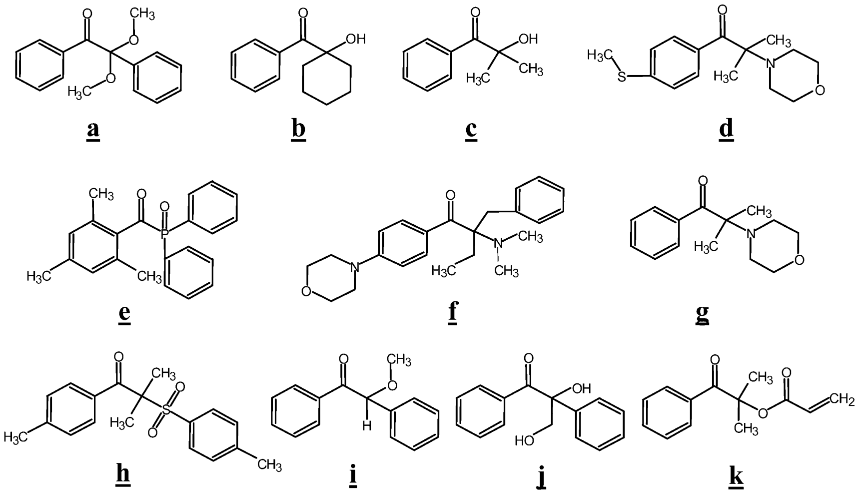
Scheme 1



with OD the optical density of the PI at the irradiation wavelength and I_0 the incident light intensity.

This is usually considered as true in film photopolymerization experiments and at low conversion. Equation 1 was successfully checked with **a** for the polymerization of MA in toluene and in bulk using Ebecryl 605. In this paper, R_p will refer to the maximum rate of the polymerization reaction and was determined from the maximum of the first derivative of the conversion curve. This corresponds to the early time of the polymerization. Accordingly, the concentration of monomer is taken as the initial bulk concentration of the monomer $[M]_0$.

Photoinitiator Properties

A general picture of the primary processes that occur in the excited states of the studied photoinitiators is shown in Scheme 2.

Most of the studied photoinitiators are known to undergo an α cleavage process from their lowest triplet state,[1−4] except for **h** that was reported to yield a *β* cleavage.[7] In the case of **f**, a *β* cleavage can concomitantly occur with the α cleavage,[4] although this process has a low probability. Table 1 gathers the most pertinent values for the triplet state lifetimes and the dissociation quantum yields obtained from the literature or measured in this work using established procedures. Triplet state lifetimes measured by direct observation in the picosecond or nanosecond time scale were preferably selected. Short triplet state lifetimes are generally observed for the compounds.

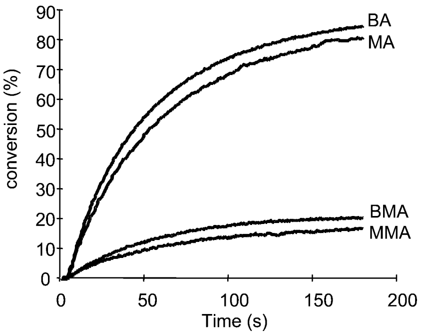


Figure 1. Typical conversion curves for the photopolymerization of BA, MA, BMA, and MMA at 1 M in toluene in the presence of **a**.

Scheme 2

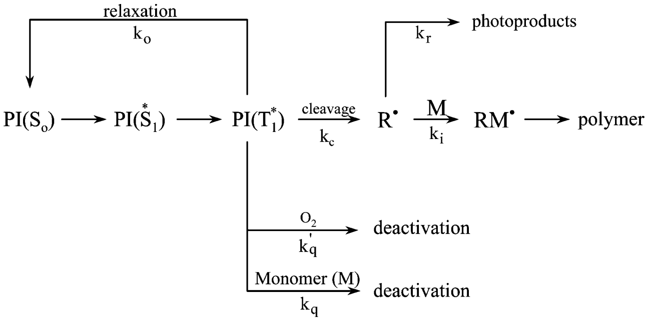


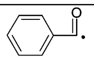
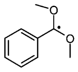
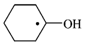
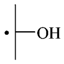
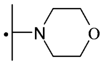
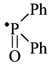
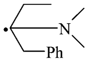
Table 1. Triplet State Lifetimes τ_T^0 and Quantum Yields of Dissociation ϕ_{diss} in Solution and in the Absence of Monomer and Rate Constants k_q for the Quenching of the Triplet States by Monomers

compd	τ_T^0	ϕ_{diss}	k_q ($M^{-1}\,s^{-1}$)
a	0.25 ns[a] <0.1 ns[b]	0.95[c]	
b	0.16−0.38 ns[d]	0.8[c]	
c	0.055−0.45 ns[e] 0.37 ns[f]	0.8[c]	8 × 10^6 (MMA)[g] 2.5 × 10^8 (MMA)[j] 3.3 × 10^8 (MA)[k]
d	10 ns[h]	0.3[c] 0.15[i]	2 × 10^6 (MMA)[h]
e	0.08−0.1 ns[b]	0.7[c]	
f	1.7 *μ*s[j]	0.24[b] 0.9[i]	3.5 × 10^6 (MMA)[k] 2.2 × 10^5 (MA)[k]
g	1 ns[h]	0.3[c]	
h	175 ns[l] 75 ns[m]		4 × 10^7 (MMA)[l]
i	0.02 ns[d]	0.5[n]	
j		0.5[n]	
k	≤ 3ns[j]	0.0[c]	

[a] From ref 8 in benzene. [b] From ref 4. [c] From ref 9. [d] From ref 10. [e] From ref 11. [f] From ref 12. [g] From ref 13. [h] From ref 14. [i] This work, from photolysis measurement. [j] From ref 15. [k] This work, from laser flash photolysis experiments. [l] From ref 7. [m] From ref 16. [n] From photoacoustic calorimetry measurements by using a bond dissociation energy of 54.1 and 53.3 kcal/mol for **i** and **j,** respectively (same procedure as in ref 9). The error on ϕ_{diss} is estimated to be lower than ±0.1.

The dissociation quantum yield ϕ_{diss} that relates the number of radicals produced per photon absorbed is also a relevant information. When possible, direct measurements of dissociation quantum yields in solution were used instead of photolysis quantum yield, for some reasons discussed elsewhere.[9] Although in-cage recombination can formally affect the dissociation process of geminate radical pair, it is expected that the spin correlation between radicals formed from the triplet state makes this effect negligible. From Table 1, it can be seen that all the compounds dissociate under light excitation, except for **k**. According to Scheme 2, the dissociation quantum yield ϕ_{diss} in the absence of monomer should be corrected in bulk by taking into account the triplet state quenching of PI by the monomer.

Table 2. Addition Rate Constants k_i of Some Initiating Radicals to Monomers

Radical	Structure	k_i ($M^{-1}s^{-1}$)
R1		9 10^4 (MMA)[a] 2.7 10^5 (BA)[b] 5 10^5 (BA)[c]
R2		< 10^4 (MA)[d] <5 10^6 (BMA)[e]
R3		2.5 10^7 (BA)[e] 1.1 10^7 (BA)[f]
R4		3.5 10^7 (MA)[g] 1.3 10^7 (BA)[f] 1.6 10^7 (MMA)[c]
R5		4.5 10^7 (MA)[h] 4.0 10^7 (BA)[e,h] 2.9 10^7 (BA)[f]
R6		6 10^7 (MMA)[i] 11 10^7 (MMA)[j] 2.3 10^7 (MA)[i] 3.3 10^7 (MA)[j]
R7		6.1 10^6 (MA)[f]

[a] From ref 23. [b] From ref 24. [c] From ref 4. [d] From ref 25. [e] From ref 26. [f] From ref 27. [g] From ref 18. [h] From ref 19. [i] From ref 28. [j] From ref 29.

Such an effect has been reported for aromatic ketones/(meth)-acrylates,[13−15,17] and it has been found that the quenching rate constant is dependent on the enthalpy of formation of the corresponding 1,4-diradical.[17] However, for short triplet states, the monomer quenching is not a competitive reaction to the α cleavage process. Therefore, ϕ_{diss} can be expressed by

$$\phi_{\mathrm{diss}} = \phi_{\mathrm{ST}} \frac{k_c}{k_c + k_0} = \phi_{\mathrm{ST}} k_c \tau_T^0 \tag{4}$$

where k_c and k_0 are the rate constants of the processes described in Scheme 2, leaving out both the oxygen and monomer quenching. τ_T^0 is the triplet state lifetime in the absence of any additive, and ϕ_{ST} is the intersystem crossing quantum yield. In the following, ϕ_{diss} will be considered as mostly independent of the media.

Therefore, after light excitation the photoinitiators dissociate into two radicals. Although the lack of information prevents the discussion of the reactivity for all the radicals produced, Table 2 shows that the available addition rate constants k_i of the radicals onto double bonds differ strongly depending on the chemical structure of both the radical and the double bond.[18−22] Very recently, it was clearly demonstrated that a partial electron transfer between the two reactants can occur in the transition state, enhancing the rate constant.[19] This effect was quantitatively rationalized,[20,21] explaining the reactivity of some initiating radicals.[22]

For compounds **a** to **c**, **g**, **i**, and **j**, a benzoyl radical R1 was formed for each case. Table 2 shows that this radical reacts at relatively low rate constant with the monomers ($k_i \sim (1-3) \times 10^5$ M^{-1} s^{-1}). Para-substituted benzoyl radicals have a reactivity rather similar to R1. Indeed, the rate constants of addition onto BA in acetonitrile are 6×10^5, 4.1×10^5, and 3.8×10^5 M^{-1} s^{-1} for *p*-methylthio-, *p*-morpholino-, and trimethylbenzoyl radicals, respectively.[4] **a** also yields a dimethoxybenzyl radical R2 that reacts at low rate constant with methyl acrylate ($k_i < 10^4$ M^{-1} s^{-1}).[25] The real reactivity efficiency of this radical with a monomer remains unclear, this compound being known to dissociate into methyl radical and methyl benzoate under light excitation or through thermal reaction.[25] The methyl radical has a low rate constant of addition onto methyl acrylate ($k_i = 3.4 \times 10^5$ M^{-1} s^{-1}).[18] This means that whatever the radical produced by **a**, the rate constant of addition would not be higher than 3×10^5 M^{-1} s^{-1}. **i** produces a substituted benzyl radical for which the addition rate constant is unknown. However, knowing that this radical is structurally related to the benzyl radical ($k_i = 430$ M^{-1} s^{-1} on MA[18]) and to R2, the limiting value for the rate constant of addition of R2 is 10^4 M^{-1} s^{-1}. Therefore, the reactivity of **i** is expected to be comparable to **a**, although in the latter case, the subsequent cleavage leads to the formation of a methyl radical that will increase the reactivity of **a** with respect to **i**. A dissociation into a benzoyl radical R1 and an aliphatic ketyl radical R3 or R4 is operative for both **b** and **c**, respectively. These ketyl radicals react with acrylates and methacrylates with a high rate constant ($k_i \sim (1-4) \times 10^7$ M^{-1} s^{-1}), and therefore, their reactivity is expected to be predominant compared to that of R1. Apart from R1, **d**, **f**, and **g** also produce an aminoalkyl radical R5 or R6. Similarly to R3 and R4, R5 is known to react with a high rate constant ($k_i \sim 3.4 \times 10^7$ M^{-1} s^{-1}) as a consequence of the large amount of charge transferred to the monomer in the transition state.[19] Although R7 has a similar nature, the possible steric hindrance can explain a lower reactivity ($k_i \sim 6.1 \times 10^6$ M^{-1} s^{-1}).[27] In the case of **e**, the phosphinoyl radical R6 reacts with high rate constants ($k_i \sim (3-11) \times 10^7$ M^{-1} s^{-1}) on both acrylates and methacrylates. The reactivity of this radical is expected to be predominant compared to that of the trimethyl-substituted benzoyl radical. **j** produces both a benzoyl radical R1 and an aromatic ketyl radical. The reactivity of the latter is not known but might be compared to that of the diphenylketyl radical for which the rate constant of addition onto methyl acrylate is lower than 9×10^3 M^{-1} s^{-1}.[23] Therefore, the reactivity of **j** is expected to be mainly controlled by the initiating properties of R1. The reactivity of the radicals formed after the *β*-cleavage of **h** is not known.

The initiation quantum yield ϕ_i for a photoinitiator generating one initiating radical can be written as

$$\phi_i = \phi_{\mathrm{diss}} p_{\mathrm{RM}} \tag{5}$$

where p_{RM} represents the probability for the reaction of the initiating radical with the monomer:

$$p_{\mathrm{RM}} = \frac{k_i[M]}{k_r + k_i[\mathrm{M}]} \tag{6}$$

In this equation, k_i is the addition rate constant of the radical to

Table 3. ϕ_{rel} Values as a Function of the Polymerizable Medium[a]

PI	Eb 605[b]	HDDA/PMMA[c]	BA/PMMA[d]	HDDA[e]	BA[e]	MA[e]	MMA[e]	BMA[e]
a	1	1	1	1	1	1	1	1
b	0.7	1.2	1.5	3.9	3.4	3.6	0.7	1.35
c	0.4	1	1.1		3.5	3.5	0.85	1
d	0.7	0.35	0.8	2.8	2.1	2.3	0.65	1
e	0.7	1.2	1.3		3.2	3.7	3.5	3.5
f	1.5	1.65			3.2	3.5	1.6	2.45
g	0.15	0.25	0.3		1.7			
h	<0.05				0.45			
i	0.4		0.5		0.5			
j	0.2				1.2			
k	<0.05	<0.05			<0.05			

[a] See text. Intensity: 20% of I_0. The error on ϕ_{rel} is typically ± 0.1 except for the experiments in Ebecryl 605 where the error reaches ± 0.2. [b] Ebecryl 605: bulk. [c] HDDA/PMMA (75/25% w/w). [d] BA/PMMA (75/25% w/w). [e] HDDA, BA, MA, MMA, BMA, 1 M of double bond in toluene.

the monomer double bond. The pseudo-rate constant k_r stands for all the possible side reactions of the radicals. If two initiating radicals are formed, the probability of initiation of both radicals should be taken into account in eq 5.

The value of p_{RM} strongly depends on side reactions that can trap the radical before the addition reaction on the double bond. Co-initiators, stabilizers, or monomers can react with the initiating radical yielding to inhibition of the initiation reaction. Recombination of the radicals to form the ground state PI or some photoproducts also affects the efficiency of the initiation reaction. It is generally very difficult to evaluate quantitatively p_{RM} as the value of k_r remains usually unknown and might depend on the presence of additives and, to a lesser extent, on the viscosity of the media. However, for a given radical, k_i can also affect p_{RM}, and this would explain the variation of p_{RM} between two different media.

Results and Discussion

1. Initiation Efficiency of the Photoinitiators in Various Media. A relative initiation efficiency (ϕ_{rel}) of a given photoinitiator (PI) can be expressed as with respect to that of a reference photoinitiator (PIr).

$$\phi_{rel} = \frac{\phi_i(\mathrm{PI})}{\phi_i(\mathrm{PIr})} \tag{7}$$

Taking into account that all the rates of polymerization should be corrected for the amount of energy absorbed by each sample, ϕ_{rel} is calculated from the conversion curves:

$$\phi_{rel} = \left(\frac{R_p(\mathrm{PI})}{R_p(\mathrm{PIr})}\right)^2 \frac{I_{abs}(\mathrm{PIr})}{I_{abs}(\mathrm{PI})} \tag{8}$$

where R_p(PI) and R_p(PIr) are the rates of polymerization for the photoinitiator (PI) and the reference photoinitiator (PIr), respectively. I_{abs}(PI) and I_{abs}(PIr) are the amounts of energy absorbed by PI and PIr calculated from eq 3. In the present work, **a** will be used as the reference.

Relative efficiencies ϕ_{rel} for the polymerization reactions carried out in solution and in several bulk media in the presence of the studied photoinitiators are listed in Table 3. The relative ordering of the PIs efficiency differs from one media to another: for example, in Ebecryl 605 the order is **f** > **a** > **b**, **d**, **e** > **c**, **i** > **g**, **j** > **h**, **k**, although in BA (1 M), the order becomes **b**, **c**, **e**, **f** > **d**, **g** > **a**, **j** > **h**, **i** > **k**. As far as the comparison remains possible, the values obtained in the case of Ebecryl 605 are in line for **f** and **d** with those reported for the photopolymerization of triethylene glycol diacrylate (they differ for **b** and **c**) followed by using fluorescence probe techniques.[30] More interestingly, the ϕ_{rel} values for a given PI change as a function of the polymerizable medium: for **b**, $\phi_{rel} = 0.7$ in Ebecryl 605, 1.2 in HDDA/PMMA, 1.5 in BA/PMMA, 3.9 in HDDA (1 M), 3.4 in BA (1 M), 3.6 in MA (1 M), and 0.7 in MMA (1 M). The whole results qualitatively show that (i) the efficiency order of PISs cannot be obviously extrapolated from solution to bulk and (ii) the photochemical reactivity observed for a given PI during the photoinitiation step is largely dependent on the polymerizable medium properties (nature of the monomer and viscosity). Interestingly, the relative efficiencies of the PIs are very similar in HDDA, MA, and BA and decrease for MMA and BMA, confirming the well-known tendency of methacrylates to be less reactive than acrylates.

Table 4. Calculated $\phi_i K^2 I_0$ Values (See Text)

PI	HDDA	MA	BA	MMA	BMA
a	430	21.5	56	0.8	0.8
b	1850	75.5	196	0.6	1.05
c		86.5	191.5	0.75	0.8
d	1350	48	120	0.55	0.8
e		76	175	3	2.9
f		89.5	170	1.5	2.1

2. Global Polymerization Efficiency. Equation 1 can be rewritten as

$$\left(\frac{R_p}{[\mathrm{M}]_0}\frac{1}{1-10^{-\mathrm{OD}}}\right)^2 = K^2\phi_i I_0 \tag{9}$$

where $K^2\phi_i I_0$ represents the driving force of the overall efficiency for the photopolymerization of a given monomer M in the presence of a given photoinitiator PI. In this expression, ϕ_i is related to the relative role of M and PI and K is given by $K^2 = k_p{}^2/k_t$. The results obtained for the photoinitiators **a** to **f** in solution with identical monomer concentration (1 M) are gathered in Table 4. I_0 remains constant in these experiments. It can be seen that the $K^2\phi_i I_0$ term largely depends on the monomer (HDDA $\gg$ BA > MA > BMA > MMA) and on the photoinitiator to a lesser extent.

The parameter K^2 is crucial to characterize the overall efficiency of a polymerizable medium. From the results of Table 4, the evolution of this factor between two monomers can be examined. It is considered that ϕ_i for **a** does not depend on the nature and the viscosity of the medium (see below). From the K^2 parameter values, it appears that the efficiency of the studied monomers toward the propagation/termination reactions decreases in the series HDDA > BA > MA > MMA ~ BMA. As expected, acrylates are more efficient than methacrylates. The termination rate constants being rather close, this fact can be mainly explained by the higher propagation rate constants of the acrylate monomers, as determined by pulsed laser polymerization (PLP) techniques.[31] Another point of interest is the influence of the acrylate structure on the parameter K.

Table 5. Calculated K^2 Ratios for HDDA/BA, BA/MA, BMA/MMA, MA/MMA, and BA/BMA in Solution (See Text)

PI	K^2(HDDA)/ K^2(BA)	K^2(BA)/ K^2(MA)	K^2(BMA)/ K^2(MMA)	K^2(MA)/ K^2(MMA)	K^2(BA)/ K^2(BMA)
a	7.7	2.6	1.0	26.9	70.0
b	8.2	2.8	0.9	24.5	74.1
c		2.2	0.9	28.0	68.4
d	8.4	2.7	0.9	24.7	71.4
e		2.7	1.0	24.0	66.0
f		2.1	0.9	27.3	62.0

Indeed, it is worthwhile to note that the chain length is very important by inducing a steric effect that decreases the k_t value. As a consequence, butyl acrylate is more efficient than methyl acrylate. This conclusion is also in agreement with PLP results which have demonstrated that for both monomers k_p is similar whereas k_t is affected by steric hindrance.

To circumvent the effect of the photoinitiator reactivity, the evolution of $K^2\phi_i I_0$ for a given PI from a monomer M_1 to a monomer M_2 can be expressed as

$$\frac{K^2(M_1)}{K^2(M_2)} = R\left(\frac{\phi_{rel}(M_2)}{\phi_{rel}(M_1)}\right) \tag{10}$$

where R represents the ratio of the $K^2\phi_i I_0$ values for M_1 and M_2. Such K^2 ratios determined in toluene are shown in Table 5. Very interestingly, these results show that the effect of the chemical structure of the photoinitiator is completely suppressed, allowing to focus the discussion on the relative reactivity of the monomers toward their propagation/termination properties. When a comparison is possible, a good agreement with the literature was found: for MA/MMA, the value of 25.9 for R as calculated from Table 4 and eq 10 is very close to that of 28.8 extracted from bulk polymerization at 30 °C.[32] The behavior of HDDA also highlights the special influence of the acrylate structure on the propagation/termination reactions: HDDA is about 8 times more efficient than BA (Table 5). However, a deeper comparison with the literature is not straightforward because of the general different experimental conditions for the available k_p and k_t values. A complete analysis of the influence of the monomer structure on k_p and k_t is beyond the scope of this paper. However, it clearly appears that the method here employed allows good evaluation of the relative k_p^2/k_t values for different monomers.

3. Viscosity Effects. The viscosity of the medium should affect, for a given monomer, the initiation step through the radical addition to the monomer (k_i) which can be dependent on the diffusion of the reactants in the medium. To study this effect, photopolymerization experiments were performed in toluene solution containing different amounts of PMMA. Table 6 reports the rates of polymerization R_p of MA (1 M) in toluene/PMMA as a function of the PMMA content (in wt %) and in the presence of **a** and **c**. The R_p values are almost similar for **a** whatever the viscosity of the sample, demonstrating the good reliability of the R_p measurements. On the contrary, the R_p values decrease for **c** when the amount of PMMA is going from 0 to 13.7%, i.e., when the viscosity increases. For **a** and **c**, the triplet state lifetime is very short, and therefore the quenching by the monomer cannot compete with the cleavage process. Thus, ϕ_i is only dependent on ϕ_{diss} and p_{RM} whatever the viscosity and the chemical nature of the medium.

The evolution of R_p in the case of **a** suggests that both ϕ_i and p_{RM} are constant in these different media. This is attributed to the fact that the rate constant of addition of the different radicals formed from **a** ($k_i \sim 3 \times 10^5$ M^{-1} s^{-1} as discussed above) are lower or close to the diffusion in the three different media. Indeed, the diffusion rate constant decreases from 1.1×10^{10} M^{-1} s^{-1} in toluene to 8.4×10^6 M^{-1} s^{-1} in toluene containing 13.7% of PMMA.

The dimethylketyl radical R4 formed from **c** exhibits an addition rate constant of about 3×10^7 M^{-1} s^{-1}. Therefore, in toluene the initiation rate constant is not controlled by the diffusion ($k_i \ll k_d$). In solution containing 7.4% or 13.7% of PMMA, the diffusion rate constant, as roughly estimated from the Stokes−Einstein equation and the viscosity values, is close to or lower than the addition rate constant. Therefore, the apparent initiation rate constant k_i' must be corrected for the diffusion by

$$k_i' = \frac{k_i k_d}{k_i + k_d} \tag{11}$$

This would yield to corrected values k_i' of 1.4×10^7 and 6.5×10^6 M^{-1} s^{-1} in toluene containing 7.4% and 13.7% of PMMA, respectively. Assuming that k_r remains constant, the increase of the viscosity will induce a decrease of p_{RM} that could explain the decrease of R_p observed for **c**.

The ϕ_{rel} values for a photoinitiator (PI) and the reference (PIr) can be expressed as

$$\phi_{rel} = \frac{\phi_{diss}(PI)p_{RM}(PI)}{\phi_{diss}(PIr)p_{RM}(PIr)} \tag{12}$$

Figure 2 shows that a linear relationship relates the relative efficiency ϕ_{rel} of **c** and the corrected initiation rate constant of the dimethylketyl radical formed from **c**. Assuming that the dissociation quantum yield of both **a** and **c** are not dependent on the media, this clearly demonstrates the validity of the conclusion drawn above.

Unfortunately, because of the well-known difficulties encountered in optical detection of the initiating radicals corresponding to the PIs studied here, the direct investigation of the viscosity effect on k_i by laser flash photolysis is difficult. Some experiments were performed using the phosphinoyl radical of BAPO (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide) which is easily observed through transient laser absorption spectroscopy. In that case, k_i values for the reaction with Ebecryl 605 in toluene solution and in bulk are 6×10^7 and 8.2×10^4 M^{-1} s^{-1}, respectively, as measured by us. The viscosity of Eb 605 being 14×10^3 cP, the corresponding diffusion rate constant can be roughly estimated to be 4.2×10^5 M^{-1} s^{-1}, in relatively good agreement with the initiation rate constant measured in this media. The phosphinoyl radical formed from the BAPO dissociation has a similar reactivity than R6. Both these radicals are known to be highly reactive toward the addition reaction to acrylate (Table 2), clearly demonstrating that the initiation rate constant is limited by the diffusion in bulk. Therefore, in Eb 605, all the radicals studied will be characterized by a k_i value close to the rate constant of diffusion ($k_i \sim 10^5$ M^{-1} s^{-1}) whatever their chemical structures and the monomer nature. As a consequence, the reactivity of photoinitiators leading to very reactive radicals will decrease from solution to bulk, as shown for **c**: p_{RM} decreases with the viscosity, and accordingly the R_p values decrease.

These experiments confirm the validity of the assumption made previously for p_{RM}. This clearly demonstrates that the media can differently affect the efficiency of a PI depending on the viscosity.

Table 6. Rates of Polymerization R_p of MA (1 M) in Toluene/PMMA as a Function of the PMMA Content in the Presence of a and c[a]

			R_p (M s^{-1})			
PMMA (wt %)	viscosity (cP)	k_d (M^{-1} s^{-1})	**a**	**c**	ϕ_{rel}	k_i' [b] (M^{-1} s^{-1})
0	0.587	1.1×10^{10}	4.93	8.42	3.5	3×10^7
7.4	210	2.8×10^7	4.81	6.73	2.27	1.4×10^7
13.7	705	8.4×10^6	4.75	5.02	1.32	6.5×10^6

[a] Viscosity of the media and corresponding diffusion rate constants k_d. Diffusion corrected rate constant of initiation k_i'. [b] Calculated from eq 11 for the dimethylketyl radical.

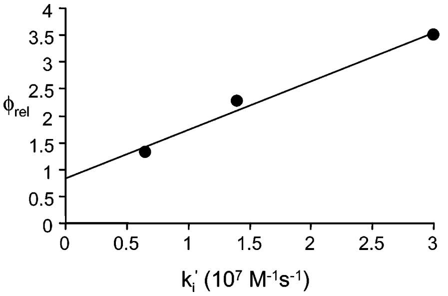


Figure 2. Change of the relative initiation efficiency ϕ_{rel} of **c** with the apparent initiation rate constant k_i' of the dimethylketyl radical.

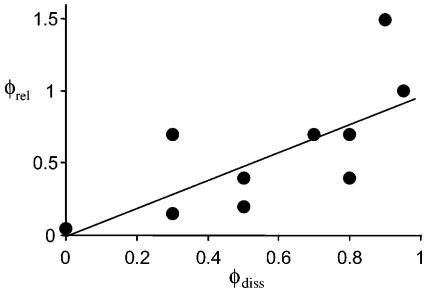


Figure 3. Plot of ϕ_{rel} vs ϕ_{diss} for the photopolymerization of Ebecryl 605 in a film matrix.

4. ϕ_{diss} vs ϕ_{rel} Correlations. From the previous results, one expect that in a viscous monomer, ϕ_{rel} will correlate with ϕ_{diss} since p_{RM} should be rather similar for the different photoinitiators. On the other hand, in solution, the rate constants for the addition reaction are not limited by the diffusion, and there will be a large difference of p_{RM} for the **b**, **c**, **d**, **e**, **f**, **g**, and **k** compounds (k_i in the range of 10^7 M^{-1} s^{-1}) and **a** ($k_i \sim 10^5$ M^{-1} s^{-1}).

Viscous Media. The relative efficiency of the photoinitiators ϕ_{rel} is plotted against the quantum yield of dissociation ϕ_{diss} in Figure 3 for the photopolymerization of Ebecryl 605. A clear trend tends to show that these two properties are strongly related and that in viscous media the polymerization efficiency is mainly governed by primary photophysical processes occurring from the photoinitiator excited states. Discrepancies likely originate from the p_{RM} values which can be affected by the presence of stabilizers that cannot be removed from Ebecryl 605. The complexity of this medium unfortunately prevents any deep discussion, but it supports the statement that the reactivity of the initiating radicals is leveled off in viscous media.

Compared to Ebecryl 605, the HDDA/PMMA matrix (75/25 w/w) would correspond to a better model system for which a quantitative comparison can be made. The correlation between ϕ_{rel} and ϕ_{diss} for the polymerization of the viscous matrix HDDA/PMMA shown in Figure 4 is quite good. As previously, it can be expected that there are no important changes of the p_{RM} values as a function of the photoinitiator.

The correlation remains good in the case of the photopolymerization of BA in a PMMA matrix (Figure 4), showing that the viscosity plays a significant role of the leveling off of the rate constant values.

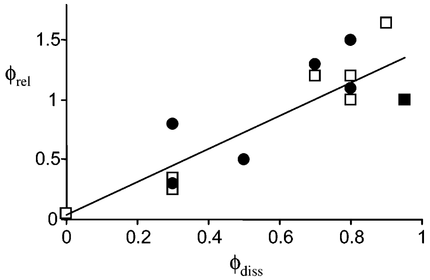


Figure 4. Plot of ϕ_{rel} vs ϕ_{diss} for the photopolymerization of BA/PMMA (open square) and HDDA/PMMA (plain circles) in a film matrix.

Photopolymerization in Solution. As discussed above, the values of k_i in solution (Table 2) are strongly affected by the radical structure and are not affected by the viscosity ($k_d > k_i$). Consequently, p_{RM} is now expected to strongly vary from one PI to another.

In the case of the polymerization of BA (1 M) in toluene solutions, the plot of ϕ_{rel} as a function of ϕ_{diss} for compounds **b**, **c**, **d**, **e**, and **g** gives a straight line, suggesting that no other PI parameter than the dissociation quantum yield contributes to the reactivity. This could be explained by the fact that (i) the short-lived triplet state is not quenched by the monomer and therefore the cleavage process is not affected by the presence of a monomer and (ii) the high values of k_i of the corresponding radicals (Table 1) yield values of p_{RM} that are close to unity. **b** and **c** lead to a very similar ϕ_{rel} values, demonstrating that similar dissociation quantum yields and similar addition rate constants lead to very similar reactivity in solution. The same remark applies to **d** and **g**. In the case of these PIs, the reactivity is still controlled by the cleavage efficiency, as in bulk media.

The monomer quenching strongly occurs for **f** (Table 1), and the value of the dissociation quantum yield should be corrected in the presence of a monomer according to

$$\phi_{diss}^{c} = \phi_{diss} \frac{1/\tau_0}{1/\tau_0 + k_q[\mathrm{BA}]} \tag{13}$$

Assuming that the quenching rate constants of the triplet are similar for BA and MA, this gives a corrected quantum yield $\phi_{diss}^{c} = 0.65$ for **f** in the presence of 1 M BA.

Compounds **a**, **i**, and **j** are clearly out of the correlation. For these PIs, the values of k_i are quite low, and consequently the p_{RM} values can be lower than 1. The experiments in MA solution yield to similar observations.

These experiments in solution allow to shed some light on the evolution of p_{RM} with the radical structure. By taking into account the behavior of the other PIs, one can calculate a p_{RM} value for **a**, **i**, and **j**. Indeed, by using the ϕ_{rel} value of **c**, and assuming that p_{RM} of **c** is unity, eq 12 leads to a value of 0.24 for p_{RM} of **a**. Close estimates of 0.25, 0.15, 0.23, 0.21, and 0.19 were found using the results of **b**, **d**, **e**, **f**, and **g**, respectively. It can be seen that these values are quite close, although the

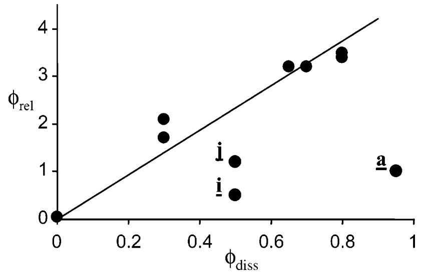


Figure 5. Plot of ϕ_{rel} vs ϕ_{diss} for the photopolymerization of BA (1 M in toluene). For **f**, $\phi_{diss}^{\mathbf{c}} = 0.65$ was used (see text).

two structurally related PI **d** and **g** lead to slightly lower values. An average value of $p_{RM} = 0.21$ for **a** demonstrates that the side reactions occur with a rate constant of about 3.8 higher than the addition reaction. This may correspond to radical recombination reactions that are diffusion-controlled in solution. By using the p_{RM} value estimated for **a**, similar calculations lead to p_{RM} of 0.22 and 0.55 for **i** and **j**, respectively. Finally, despite the fact that ϕ_{diss} is unknown for **h**, Figure 5 allows an evaluation of 0.1 for $\phi_{diss}p_{RM}$. These $\phi_{diss}p_{RM}$ values represent the initiation quantum yields ϕ_i in BA (1 M).

The factor of 7 in ϕ_{rel} values between **c** and **i** (Table 3) is related to

$$\frac{\phi_{diss}^{\mathbf{c}} p_{RM}^{\mathbf{c}}}{\phi_{diss}^{\mathbf{i}} p_{RM}^{\mathbf{i}}} = 7 \tag{14}$$

and consequently

$$\frac{p_{RM}^{\mathbf{c}}}{p_{RM}^{\mathbf{i}}} = 4.4 \tag{15}$$

Assuming that k_r is independent of the media, the relative increase of the p_{RM} of **c** when going from bulk ($p_{RM}^{\mathbf{c}} = p_{RM}^{\mathbf{i}}$) to solution ($p_{RM}^{\mathbf{c}} > p_{RM}^{\mathbf{i}}$) is explained by the change of the relative efficiency of the radicals formed from **c** and the other photoinitiators as a function of the medium.

As stated above, the addition rate constant of the methyl radical formed from the dimethoxybenzyl radical R2 is about 3.1×10^5 M^{-1} s^{-1}. Assuming that the reactivity of the two radicals formed from **a** both behave similarly as the benzoyl radical R1, and by taking into account the probability of reaction of two radicals for the PI **a** and **c**, one can write from eq 12:

$$\frac{p_{RM}^{R1} + p_{RM}^{R4}}{2p_{RM}^{R1}} = 4.15 \tag{16}$$

This leads to $p_{RM}^{R4} = 7.3p_{RM}^{R1}$, demonstrating the high reactivity of the isopropyl radical compared to the benzoyl one in solution polymerization (as already reported[4]), whereas in bulk experiments their efficiency is similar because of a leveling effect due to the viscosity.

A similar correlation of ϕ_{rel} with ϕ_{diss} for the polymerization of MMA in solution cannot be observed. The dissociation quantum yields are drastically affected by the fact that the bimolecular quenching rate constant of the triplet state by MMA are usually higher than those obtained for acrylates (Table 1): for example, for **f**, $k_q = 3.25 \times 10^6$ M^{-1} s^{-1} for MMA and $k_q = 2.2 \times 10^5$ M^{-1} s^{-1} for MA. Similar trends have been already observed.[15,17,23] Attempts were made to calculate the corrected dissociation quantum yields, but the large error associated with each parameter required prevent any reliable calculation. This is mostly due to the high reactivity of the MMA with triplet states and to the assumption made on addition rate constants. In such a case, the determination of the photophysical properties of the PI in the media would be the only way to investigate this medium.

From a general point of view, all the reported data and the derived calculations appear as quite consistent: the small discrepancies in the ϕ_{rel} vs ϕ_{diss} correlations, although acceptable, could originate from the assumption that ϕ_{diss} is not dependent on the viscosity. In fact, the exit yield of the radicals from the primary spin-correlated and spin-decorrelated radical pairs formed after the cleavage process might be affected by the viscosity. However, measurements of ϕ_{diss} in viscous or bulk media are up to now experimentally hardly possible.

Conclusion

Radical photopolymerization experiments using cleavable photoinitiators were performed in deaerated media and corrected for the amount of light absorbed. This study clearly shows the huge effect of the viscosity of an oxygen-free photopolymerizable medium on the relative efficiency of various photoinitiators and provides a good explanation for the different behaviors observed. The most striking difference is observed with compounds **b** to **f** which yield radicals among the highest reactive ones toward the double bond compared to the other PI such as **a**, **g**, **h**, **i**, or **j**: a 3-fold increase of the efficiency ϕ_{rel} is noted when going from bulk to solution. This effect is mainly attributed to the fact that the rate constants of initiation are very high in solution but are diffusion-controlled in bulk decreasing the corresponding values by orders of magnitude.

For practical applications in aerated media, the role of the oxygen must be taken into account. In addition, the differences in the absorption properties of the photoinitiators have an important effect on the whole efficiency of the system. This is particularly true in usual industrial polymerization conditions under polychromatic light with a fixed photoinitiator concentration. The relative practical efficiency will be obviously different from ϕ_{rel} because of a change of the amount of light absorbed.

An interesting point is the evidence of a quite acceptable correlation of the relative efficiency ϕ_{rel} with the quantum yield of dissociation ϕ_{diss} in viscous media such as Ebecryl 605 and HDDA/PMMA. This correlation remains valid in a BA/PMMA mixture or in fluid media (BA or MA solutions), providing that the monomer quenching of the PI triplet state is weak and the radical addition to the monomer is efficient. This is the case for (i) most of the PI used in this study since they have rather short-lived triplet states and (ii) most of the usual photoinitiating radicals toward acrylates and methacrylates, except for the benzoyl radical. The dependence is more complicated in the case of methacrylates because of the high values for the quenching rate constants.

This study shows that a deep knowledge of the photophysics and photochemistry of the photoinitiators in solution can thus serve as a good basis for the prediction of the polymerization efficiency in film experiments.

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Appendix

One reviewer has suggested that a chain transfer process to the acrylate backbone could be partly responsible for the highest reactivity of acrylates with respect to methacrylates. This interesting hypothesis has deserved additional photopolymerization experiments in our lab. Briefly, when benzophenone was used as photoinitiator, the corresponding initiation can be only attributed to hydrogen abstraction from the acrylate backbone, and the subsequent reaction can represent a chain transfer process. Although some polymerization occurs under these conditions, the rate of polymerization was found clearly lower than the ones obtained with cleavable photoinitiators. Therefore, the chain transfer process occurring in the acrylate backbone should not affect the data obtained at early time of the photopolymerization process. These results will be presented in a forthcoming paper.

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