Excited-State Properties of Camphorquinone Based Monomeric and Polymeric Photoinitiators

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Dedicated to Prof. *André M. Braun* on the occasion of his 60th birthday

The excited-state properties of a new polymeric photoinitiator-bearing camphorquinone or/and amine moieties were studied and compared to the behaviour of the precursor molecules. The triplet state of the polymeric system was extremely short-lived, due to the close vicinity of the amino group. In addition, the singlet state also reacted with the amino group. A study on camphorquinone and methyldiethanolamine (=2,2′-(methylimino)bis[ethanol]) revealed that both these pathways led to the formation of a ketyl radical and an amine-derived radical. Therefore, high efficiency of the radical generation was expected. However, the radical photopolymerization of a polyfunctional mixture of acrylic monomers with various combinations of monomeric and polymeric photoinitiators gave evidence that the polymeric structure of the photoinitiating system may differently affect the overall cure rate of the formulation.

1. Introduction. – Excited-state properties of photoinitiators are the subject of intense research studies aiming at the increase of their practical efficiency in the photopolymerization reactions of monomer/oligomer formulations [1]. One of the main problems to be solved when incorporating photoinitiators in acrylate multifunctional resins is to increase their solubility, to get a low odour and toxicity, and to reduce the migratable residues so as to enhance the stability to light and reduce yellowing of the cross-linked material. In addition, an improvement of the photoinitiation activity may be of benefit in terms of reduction of exposure time and increase of process productivity [1–5]. This can be achieved by chemical modification of existing structures. For example, successful results have been obtained by the introduction of alkyl chains at usual backbones [6–8], the development of oligomeric compounds [9], and the design of polymeric structures containing photoinitiators [10–22].

Moreover, in the case of two-component photoinitiating systems based, *e.g.*, on a photosensitizer and a photoinitiator or on a ketone and an amine, the primary step of the photochemical processes involves an interaction between the two partners which is strongly affected by the viscosity of the medium. This detrimental effect as well as the effect of the monomer quenching are expected to be reduced when one or both partners are grafted onto the same polymer chain. This has been previously explored by us, *e.g.* in polymeric thioxanthone/morpholino ketone [23] and thioxanthone/amine [24] and in polymeric benzoin ethers [25].

Attractive developments of camphorquinone-based photoinitiating systems sensitive under visible light are observed today for the photocuring of restorative dental composite resins (see, *e.g.*, [26]). In particular, recently reported [27] polymeric radical initiators bearing in the side chain the camphorquinone moiety, exhibited a behaviour clearly related to the structural features of the photoinitiating system, with an overall photoinitiation activity dependent on the polymeric or monomeric nature of both the camphorquinone and the tertiary amine partner in the photoactive combination.

In the present paper, the results concerning the excited-states properties and photoreactivity of polymethacrylic derivatives bearing in the side chain the camphorquinone moiety, or a tertiary-amino group, or both, as well as the combinations with corresponding low-molecular-mass model compounds are reported.

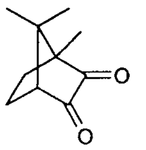
2. Experimental. – 2.1. *Low-Molecular-Mass and Polymeric Photoactive Compounds.* Camphorquinone (CQ) and 2-(*N*-methyl)diethanolamine (=2,2′-(methylimino)bis[ethanol]; MDEA; *Aldrich*) were used as received. The 2-(dimethylamino)ethyl pivalate (AA1) was prepared from 2-(dimethylamino)ethanol (*Aldrich*) according to the reported procedure [27]. The copolymer of 10-(methacryloyloxy)camphorquinone with butyl methacrylate (CQA1) and the terpolymer of 10-(methacryloyloxy)camphorquinone with butyl methacrylate and 2-(dimethylamino)ethyl methacrylate (CQA2), having molar composition 43 : 57 and 19 : 53 : 28, respectively, as well as the homopolymer AA2, were obtained by radical polymerization of the corresponding monomers [27].

2.2. *Laser Flash Photolysis.* The laser flash photolysis system used for the excited state absorption experiments is based on a nanosecond optical parametric oscillator (*Sunlite*, *Continuum*) pumped by a Nd : Yag laser (*Powerlite 9010*, *Continuum*) that generates narrow-band radiation in the VIS and the near-IR spectral region. After frequency doubling, the wavelength is tunable continuously from 225 up to 1800 nm with an energy of *ca.* 50 mJ at 550 nm. The analyzing system (*LP900*, *Edinburgh Instruments*) is equipped with a 450-W pulsed Xe arc lamp, a *Czerny-Turner* monochromator, and a fast photomultiplier. Quenching experiments are done in degassed benzene (spectroscopic grade; *Fluka*) with an optical density of 0.2 at the excitation wavelength (470 nm). The same setup (monochromator/photomultiplier without the Xe lamp) can be used for fluorescence measurements.

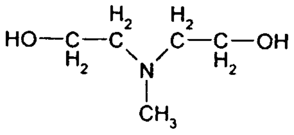
2.3. *Photopolymerization Experiments.* The photoinduced polymerization and cross-linking experiments were performed at 25°, under inert atmosphere, on a 0.2 mm thick film matrix constituted by an equimolar mixture of hexanediol diacrylate (HDDA) and butyl acrylate (BA) containing 1 mol-% of photoinitiator, in terms of camphorquinone moiety, and an equimolar amount of tertiary-amine moiety, exception made for terpolymer CQA2, where the molar ratio was fixed at 19 : 28 [27]. The time evolution of the curing process was followed for 600 s irradiation time at $\lambda > 400$ nm by microwave dielectrometry at 9.5 GHz, by measuring the imaginary part of the dielectric constant e'' (loss factor) of the reacting system [28]. Method and apparatus are described in detail elsewhere [29].

3. Results and Discussion. – 3.1. *Excited-State Properties of Camphorquinone* (CQ). As CQ will be used as the model compound in this study, it is useful to review briefly some of the main properties of its excited states. CQ strongly absorbs light in the UV ($\pi \rightarrow \pi^*$ transition) and exhibits a slight absorption at 470 nm with a low absorption coefficient indicating a $n \rightarrow \pi^*$ transition [26]. This latter absorption band gives to CQ the possibility to be used as a visible photoinitiator. Although a slight fluorescence can be observed ($\phi_{\mathrm{fluo}} = 3.3 \cdot 10^{-3}$ in benzene [30]), excitation in the $S_0 \rightarrow S_1$ absorption band leads nearly quantitatively to the triplet state T_1 ($\phi_{\mathrm{ISC}} = 1$ [30]). The triplet energy of CQ is 51.6 kcal/mol [31].

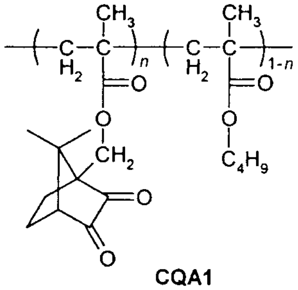
Under our experimental conditions and under condition of low-light-energy excitation, the triplet-triplet annihilation can be avoided so that the decay of the triplet-state absorption can be fitted with a first-order kinetics: the lifetime of the triplet state was *ca.* 20 μs under Ar and was reduced to 2.8 μs under air. Knowing the concentration



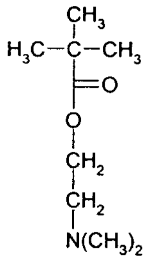
CQ



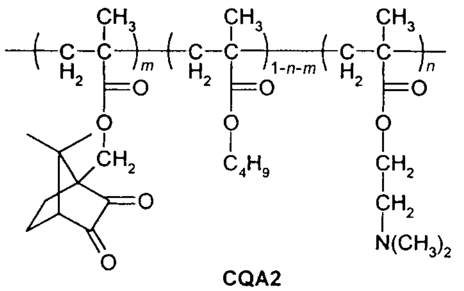
MDEA



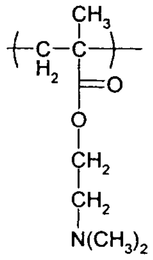
CQA1



AA1



CQA2



AA2

of O_2 in benzene ($1.9 \cdot 10^{-3}$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$ [32]), this leads to a quenching rate constant by O_2 of *ca.* $2 \cdot 10^{8}$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$, significantly lower than the diffusion rate constant. Such a low quenching efficiency of molecular O_2 towards triplet state has been recently explained in terms of partial charge-transfer reaction [33]. The transient absorption spectrum reported in *Fig. 1*, exhibits absorption maxima at 310, 595, 680, and 770 nm, in agreement with the triplet absorption spectrum reported in [34]. From flash-photolysis experiments, the decays of the transients at different wavelengths are very similar and are essentially due to the triplet state. In contrast, the rise time of the transient kinetics is different depending on the analysing wavelength. Indeed, it can be seen in *Fig. 2* that the rise time $\tau = 21$ ns of the transient observed at 700 nm matches fairly well the fluorescence lifetime $\tau_o = 18$ ns observed at 500 nm, giving confidence to the attribution of this transient to the triplet state. However, the transient absorption at 330 nm under air exhibits a fast rise, within the laser pulse, followed by a two-component decay. The slow part of the decay corresponds to the triplet-state deactivation ($\tau \approx 2.5 - 3$ µs), and the fast component decays as the singlet state does, with a lifetime $\tau = 18$ ns: at this wavelength, the signal is the sum of the singlet-singlet $S_1 \rightarrow S_n$ and triplet-triplet $T_1 \rightarrow T_n$ absorptions. The fast rise is assigned to the building up of the S_1 population (*i.e.*, of the

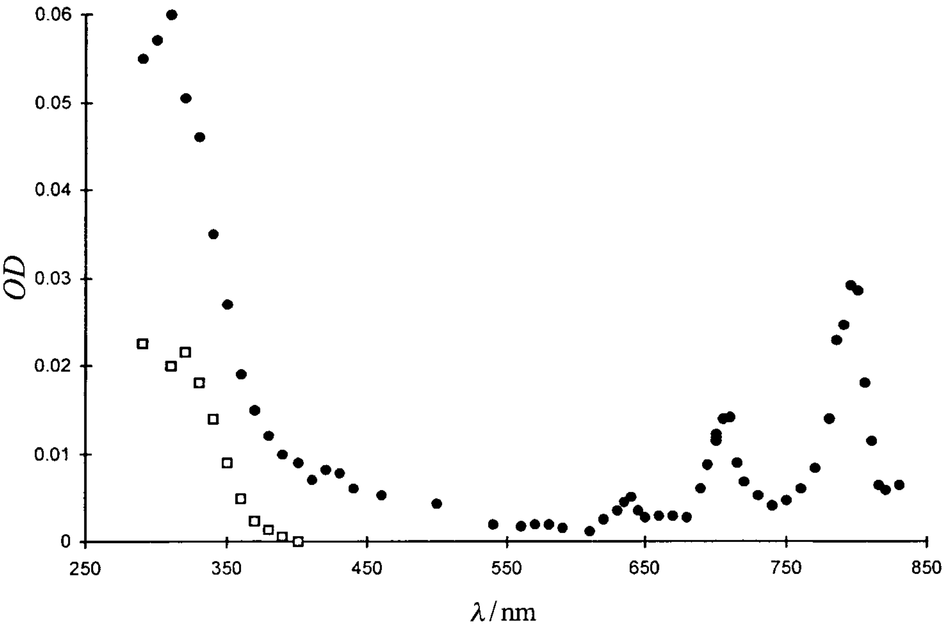


Fig. 1. *Transient spectra of the CQ triplet state in benzene 0.1* μs *after the laser pulse* (●) *and 1* μs *after pulse with* 10^{-3} M *MDEA* (□)

$S_1 \rightarrow S_n$ absorption). From *Fig. 2*, the absorption coefficient of the $S_1 \rightarrow S_n$ transition is found to be 1.25 times that of the triplet at 330 nm.

Camphorquinone is known to give a ketyl radical by photoreaction with hydrogen donor DH (solvent or amine) according to *Eqn. 1* [34][35]. Indeed, upon addition of the amine MDEA, the triplet-state lifetime is shortened (and the transient initial optical density (*OD*) is decreased which demonstrates the occurrence of an excited singlet state quenching), and a new long-lived transient is observed in the UV part of the transient spectrum. This spectrum seems to be similar to that briefly described in the literature for the reaction of propan-2-ol with ^{3}CQ [34] and is ascribed to the ketyl radical CQH$^\bullet$ (*Fig. 1*). The quenching of ^{3}CQ by MDEA and AA1 occurs with high rate constants: $6.1 \cdot 10^8$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$ and $2.0 \cdot 10^8$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$, respectively. Due to the polymeric form of AA2, the quenching rate constant for this amine can not be compared directly. From *Table 1*, it can be seen that the quenching rate constants (expressed as $\mathrm{dm}^3\,\mathrm{g}^{-1}\,\mathrm{s}^{-1}$) slightly decrease from MDEA to AA2. Beyond the effect due to the increase in the molecular mass, AA1 and AA2 appear to be less efficient quenchers than MDEA. This decrease can be attributed to a higher oxidation potential of AA1 compared to MDEA, the latter taking advantage of better electron donating groups.

$$^3\mathrm{CQ} + \mathrm{DH} \rightarrow \mathrm{CQH}^\bullet + \mathrm{D}^\bullet \qquad (1)$$

3.2. *Excited-State Properties of Polymeric Camphorquinones CQA1 and CQA2.* The ground-state absorption spectra of CQA1 and CQA2 are not affected by the presence of the methacryloyloxy group and exhibit a maximum of absorption in the VIS

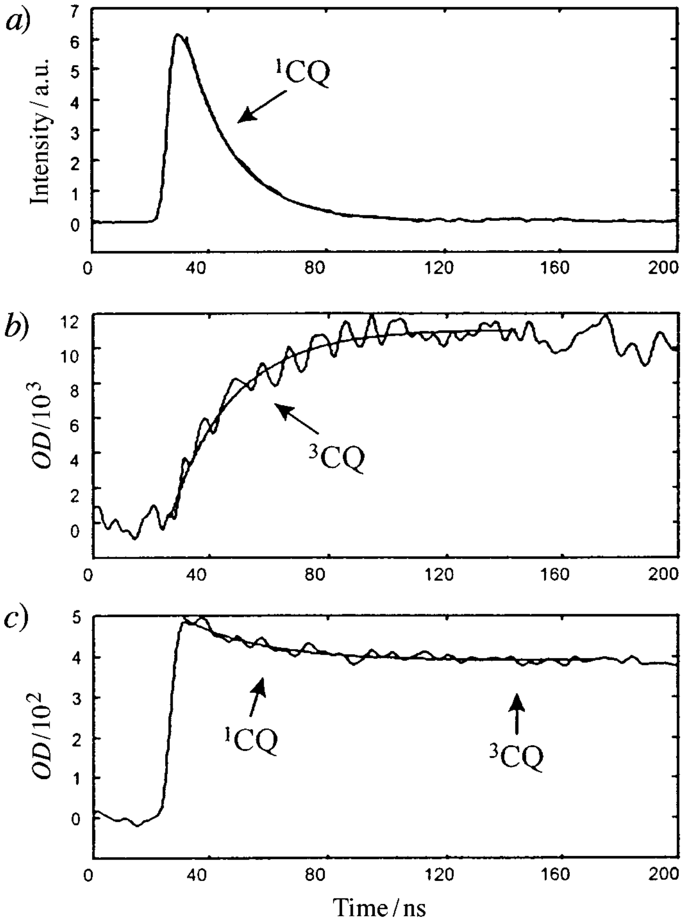


Fig. 2. a) *Fluorescence decay of CQ recorded at 500 nm,* b) *transient absorption of the triplet state recorded at 700 nm, and* c) *transient kinetics observed at 330 nm.* On each kinetic, the corresponding best fit is superimposed.

wavelength range around 470 nm, as previously reported in [27]. Excitation of both CQA1 and CQA2 in the n → π* transition gives rise to some transients just after the laser pulse that are very similar to that observed for CQ. Therefore, anchoring

Table 1. *Quenching Rate Constant of CQ and CQA1 Excited States*[a])

	$k_q/10^8$M^{-1} s^{-1}			$k_q/10^6$ dm^3 g^{-1} s^{-1}		
	O_2	MDEA	AA1	MDEA	AA1	AA2
^{3}CQ	2.0	6.1	2.0	5.1	1.2	0.6
^{3}CQA1	1.3	3.2	1.3	3.1	0.6	0.4

[a]) By taking an equivalent concentration in functional unit ($M = 157$ g · mol^{-1}), one can estimate the quenching rate constant of ^{3}CQ and ^{3}CQA1 by AA2 to $1.0 \cdot 10^8$ M^{-1}s^{-1} and $0.7 \cdot 10^8$ M^{-1} s^{-1}, respectively.

camphorquinone to a polymethacrylic chain does not change significantly the photophysical properties of the molecule. The lifetime of ^{3}CQA1 is *ca.* 20 μs in Ar-saturated benzene, and the quenching by molecular O_2 appears to be less efficient than for CQ ($k_q = 1.3 \cdot 10^8$ $\text{M}^{-1}\text{s}^{-1}$). The same remark is valid for the quenching of ^{3}CQA1 with all the amines studied (*Fig. 3* and *Table 1*), the quenching rate constants being decreased by about a factor of two compared to CQ. This suggests that polymeric crowded camphorquinone is slightly less available for the quenching than free CQ, indicating a lower coupling efficiency between the reactants or a lower reduction potential of CQA1 compared to CQ. Ketyl radical was formed in each case.

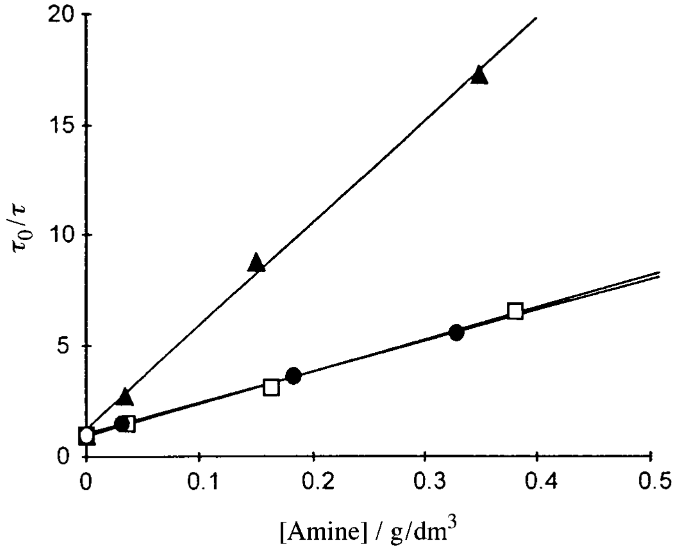


Fig. 3. Stern-Volmer *plot for the quenching of CQA1 by MDEA* (▲), *AA1* (□), *and AA2* (●)

Polymethacrylic derivative CQA2 bearing in the side chain the CQ moiety and the tertiary amine is expected to exhibit a high reactivity. It can be seen in *Fig. 4* that the fluorescence lifetime of CQA2 is 10 ns (for CQA1, the lifetime is similar to that of CQ itself). Transient absorption reveals a complex kinetics (*Fig. 4*) that clearly exhibits short excited states and a long-lived transient ascribed to the ketyl radical. The fast decay corresponds to both the singlet and the triplet states. A bi-exponential fit of this part of the signal leads to lifetimes of 8.4 ns for the singlet state (in good agreement with that measured by fluorescence) and 62 ns for the triplet state. The latter value (which corresponds to a value expected for CQA1 in the presence of *ca.* 0.05M MDEA or 0.12M AA1) demonstrates how efficient the interaction between the reactive groups is.

However, the strong interaction of the camphorquinone moiety with the nearby amino group raises the question of a possible interaction in the singlet state. Assuming a value τ_0 of 18 ns for the singlet-state lifetime of the camphorquinone moiety in the absence of amine leads to the calculation of the quantum yield ϕ_{RS} of CQA2 molecules that have reacted with the amine from the singlet state (*Eqn. 2*).

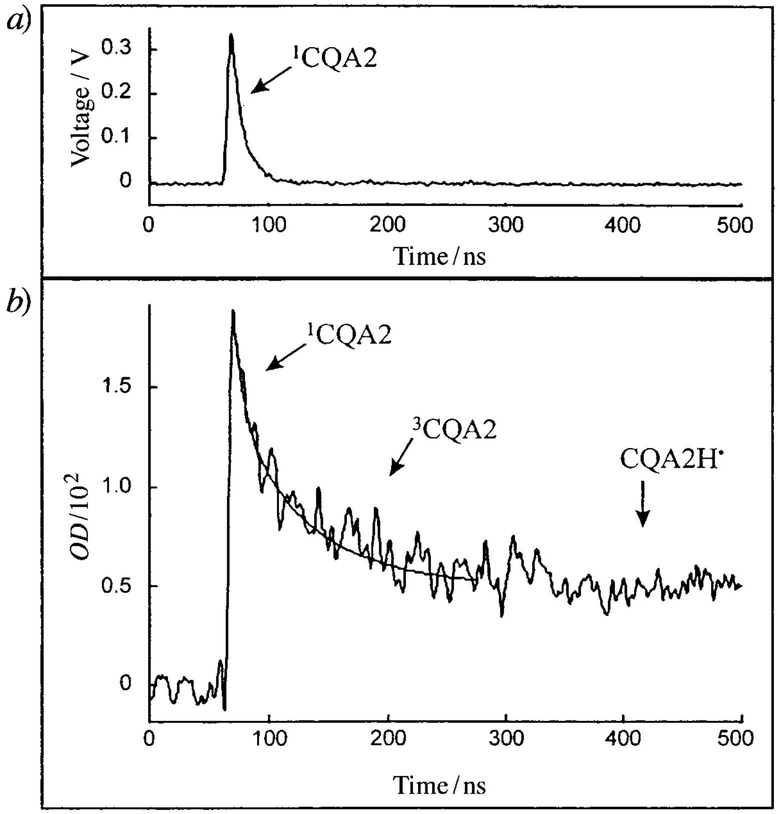


Fig. 4. a) *Fluorescence decay of CQA2 observed at 500 nm and* b) *transient absorption at 330 nm and corresponding bi-exponential best fit* (see text)

Therefore, the singlet-state lifetime is significantly reduced, and the formation of the triplet state is also affected and decreased by a factor of two. This should lead to a decrease in the overall efficiency of the system if the generation of the initiating radicals from the singlet state is not operative. Then, it is necessary to investigate in more details this point.

$$\phi_{\mathrm{RS}} = 1 - \frac{\tau}{\tau_{\mathrm{o}}} = 0.45 \qquad (2)$$

3.3. *Ketyl-Radical Formation from the Singlet State.* The mechanism of ketyl-radical formation from a singlet state is not well-documented [36] and is expected to be inefficient or occurring at low yield. In some systems, avoided crossing preceding H-abstraction does not lead to radicals but is an important pathway for the deactivation of the singlet state [37]. However, on the basis of CIDEP experiments, it has been claimed that singlet excited states are involved in the photoreduction of CQ by propan-2-ol [38]. The *Scheme* depicts the possible mechanisms of interaction of the excited states of

Scheme

$$\begin{tikzcd}
\mathrm{CQ} \arrow[r, shift left, "h\nu"] & {}^{1}\mathrm{CQ} \arrow[l, shift left, "k_o^S"] \arrow[r, "k_{\mathrm{ISC}}"] \arrow[d, "k_q^S\,[\mathrm{MDEA}]"'] & {}^{3}\mathrm{CQ} \arrow[r, "k_q^T\,[\mathrm{MDEA}]"] \arrow[d, "k_o^T"] & {[\mathrm{CTC}]} \arrow[r] & \mathrm{CQH}^{\bullet} + \mathrm{A}^{\bullet} \\
 & {[\mathrm{CTC}]} \arrow[d] & \mathrm{CQ} & & \\
 & \mathrm{CQH}^{\bullet} + \mathrm{A}^{\bullet} & & &
\end{tikzcd}$$

CQ with MDEA where k_{ISC} stands for the rate constant of intersystem crossing, k_q^S for the bimolecular quenching rate constant of singlet state by the amine, k_o^S for other deactivation pathways of the singlet state (including fluorescence), k_q^T for the quenching rate constant of the triplet state by MDEA, and k_o^T for other deactivation pathways.

To get more insights in the mechanisms of ketyl-radical formation in the CQ/amine system, the quenching of excited CQ was monitored at a sufficient concentration of MDEA to quench both the triplet and singlet states (*Fig. 5*). It is obvious that the triplet quantum yield is markedly affected by the singlet-state photoreduction and decreases with increasing amine concentration, whereas the concentration of the $\mathrm{CQH}^{\bullet}$ radicals increases very rapidly and then reaches a plateau (experimental points in *Fig. 5*). The quenching rate constant of ${}^{1}\mathrm{CQ}$ by MDEA is found from the fluorescence decays: $k_q^S = 3.7 \cdot 10^9\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, a value tenfold higher than for the triplet state. Knowing this value, it is possible to calculate the evolution of the triplet quantum yield ϕ_{ISC} as a function of the amine concentration according to *Eqn. 3*.

As mentioned above, in the absence of any quencher, ϕ_{ISC} is unity or very close to unity so that $k_o^S \ll k_{\mathrm{ISC}}$ can be assumed, which leads to a value of $k_{\mathrm{ISC}} \approx 1/\tau_o = 5 \cdot 10^7\ \mathrm{s}^{-1}$. The dependence of the triplet absorbance OD^{T} is accounted for by *Eqn. 4*. *Fig. 5* shows that the calculated dependence of OD^{T} on MDEA concentration fits fairly well the experimental results, thus confirming the validity of the *Scheme*. The quantum yield of the ketyl-radical formation from the triplet state $\phi^{\mathrm{T}}_{\mathrm{CQH}^{\bullet}}$ is given by *Eqn. 5* where ϕ_k^{T} represents the yield of ketyl radicals formed from the charge-transfer complex in the triplet state. The dependence of the ketyl-radical absorbance is then calculated from *Eqn. 6*, with $OD_{\mathrm{max}}^{\mathrm{COH}^{\bullet}} = 0.018$ in the present experiments. If we consider that no $\mathrm{CQH}^{\bullet}$ is formed from the singlet state, it is clear that the amount of ketyl radical formed by this way reaches a maximum when most of the triplet states are quenched, but with a non-significant quenching of the singlet state. At high quencher concentration, both triplet and singlet states are quenched, the triplet pathway for ketyl-radical formation becomes lower, resulting in a decrease of the ketyl-radical absorbance (*Fig. 5*, *c*): this predicted behaviour does not fit the experimental dependence.

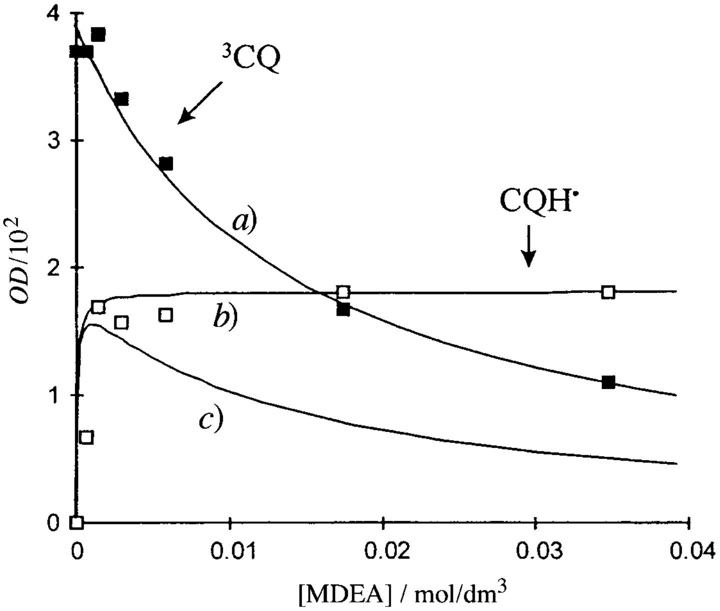


Fig. 5. *Optical density of ³CQ* (■) *and maximum of ketyl radical* (□) *experimentally observed at 330 nm* vs. *concentration of MDEA. a*) Triplet optical-density variation calculated from *Eqn. 4*, and *b*) variation of the optical density of CQH˙ calculated with participation of the singlet pathway and *c*) without participation of the singlet pathway to the formation of ketyl radical (*Eqns. 8* and *6*, resp.).

$$\phi_{\mathrm{ISC}} = \frac{k_{\mathrm{ISC}}}{k_{\mathrm{o}}^{\mathrm{S}} + k_{\mathrm{ISC}} + k_{\mathrm{q}}^{\mathrm{S}}[\mathrm{MDEA}]} \tag{3}$$

$$OD^{\mathrm{T}} = \phi_{\mathrm{ISC}} \cdot OD^{\mathrm{T}}[\mathrm{MDEA}] \rightarrow 0 \tag{4}$$

$$\phi_{\mathrm{CQH\bullet}}^{\mathrm{T}} = \phi_{\mathrm{ISC}} \frac{k_{\mathrm{q}}^{\mathrm{T}}[\mathrm{MDEA}]}{k_{\mathrm{o}}^{\mathrm{T}} + k_{\mathrm{q}}^{\mathrm{T}}[\mathrm{MDEA}]} \phi_{\mathrm{k}}^{\mathrm{T}} \tag{5}$$

$$OD^{\mathrm{CQH\bullet}} = \phi_{\mathrm{CQH\bullet}}^{\mathrm{T}}\, OD_{\mathrm{max}}^{\mathrm{CQH\bullet}} \tag{6}$$

Thus, one has to take into account the possibility to form a ketyl-radical from the excited singlet state. In that case, the quantum yield of ketyl radical formation from the singlet state $\phi_{\mathrm{CQH\bullet}}^{\mathrm{S}}$ is given by *Eqn. 7*, where $\phi_{\mathrm{k}}^{\mathrm{S}}$ is the yield of the ketyl radicals formed from the charge-transfer complex generated in the singlet state. The dependence of the absorbance of the ketyl radicals is now given by *Eqn. 8*.

$$\phi_{\mathrm{CQH\bullet}}^{\mathrm{S}} = \frac{k_{\mathrm{q}}^{\mathrm{S}}[\mathrm{MDEA}]}{k_{\mathrm{o}}^{\mathrm{S}} + k_{\mathrm{q}}^{\mathrm{S}}[\mathrm{MDEA}]} \phi_{\mathrm{k}}^{\mathrm{S}} \tag{7}$$

$$OD^{\mathrm{CQH\bullet}} = (\phi_{\mathrm{CQH\bullet}}^{\mathrm{T}} + \phi_{\mathrm{CQH\bullet}}^{\mathrm{S}})\, OD_{\mathrm{max}}^{\mathrm{CQH\bullet}} \tag{8}$$

Fig. 5,b, shows that *Eqn. 8* is in good agreement with the experimental results confirming the role of the singlet state in the production of ketyl radicals. These experiments give the first direct evidence for such a reaction in the case of the photoreduction of CQ by an amine. Therefore, it can be concluded that the quenching of the singlet state has no detrimental effect upon the radical production, since the decrease in the triplet-state formation is counterbalanced by the radical formation from the singlet state.

The same general behaviour is observed for CQA1 and CQA2, and the yields of ketyl radicals are almost similar. This means that the production of the initiating amine-derived radicals can be settled at the same level either by a low concentration of amine in the monomeric CQ-based system or by a polymeric CQ/amine. No specific enhancement of the photochemical reactivity is observed in the polymeric system compared to low molecular mass compounds.

However, the singlet- and triplet-state quenching of the camphorquinone derivatives by acrylate monomers occurs to some extent and can compete with the amine quenching. In viscous media, such as in photocurable monomer/oligomer formulations, where the diffusion of the reactants is restricted, one can expect that monomer quenching will compete efficiently when free CQ and amines are used since both rate constants (for monomer interaction and electron transfer with the amine) are reduced in the same way by the viscosity effect. When a CQ/AH polymeric system is used, one can expect that the interaction between CQ and AH is less affected by the viscosity than that between CQ and the monomer. As a consequence, the overall photochemical reactivity of the polymeric photoinitiating systems in the presence of monomer is expected to be better. However, on the opposite side, the difficulty to exit from the radical pair or/and the radical coupling of the two radicals formed (because of the medium) as well as the difficulty for the amine-derived polymeric radical to move towards the monomer units can decrease the efficiency of the initiation process.

3.4. *Photopolymerization Results.* The data of photoinitiating activity obtained in the photopolymerization of the HDDA/BA mixture (*Table 2*) indicate that different efficiencies in the curing process are displayed when different CQ/AH combinations are used. In particular, although the quenching rate of ^{3}CQ by AA1 is remarkably higher than that given by the same amine with ^{3}CQA1 (*Table 1*), the combination of polymeric CQ/monomeric amine (CQA1/AA1) provides the highest maximum polymerization rate of monomer formulation, appreciably larger than those given by the CQ/AA2 and CQ/AA1 systems. By contrast, the terpolymeric system CQA2, as well as the combination of both polymeric CQ and amine (CQA1/AA2), give the lowest values of R_{pmax}. It, therefore, appears that the presence of one polymeric component in the CQ/AH combination favorably affects the photoinitiating activity, the system CQA1/AA1 exhibiting the highest efficiency, probably because of the

Table 2. *Photoinitiation Activity, in Terms of Maximum Polymerization Rate (R_{pmax}), of Polymeric and Low Molecular Mass Systems in the Photocuring of the HDDA/BA Mixture*

	CQ/AA1	CQ/AA2	CQA1/AA1	CQA1/AA2	CQA2
$R_{\text{pmax}}/10^3\ \text{s}^{-1}$	11.5	12.5	15.7[a])	6.7[a])	6.3[a])

[a]) Values taken from [27].

reduced reactivity of the hindered macromolecular ketyl radicals, formed from the CQA1 interaction with the amine, for termination reactions with the propagating species. Accordingly, the combination between CQ and polymeric amine (CQ/AA2) gives a somewhat lower activity, with a maximum rate value close to that given by the all-low-molecular-mass system CQ/AA1, as a consequence of the increased mobility of the terminating ketyl radicals, accompanied by the reduced possibility of movement of the polymeric amine initiating radicals in the reaction medium. When both the photoactive components are polymeric (CQA1/AA2), the steric hindrance to exciplex formation and diffusion process, as confirmed by the low k_q value found for the quenching of ^{3}CQA1 by AA2 (*Table 1*), accounts for the low value of polymerization rate observed. The terpolymeric system CQA2, bearing both the CQ and amine groups linked in the side chain, is expected to favor the interaction between the CQ and AH moieties due to their close vicinity along the macromolecular chain, and, indeed, its fluorescence lifetime is very short. However, it actually displays the lowest activity with respect to all the other combinations, thus suggesting that cage recombination between the amine-derived radicals and ketyl radicals, as well as low mobility of the macromolecular initiating radicals, play a detrimental role as regards the efficiency of this type of photoinitiator.

4. Conclusion. – Excited states of polymethacrylic derivatives bearing in the side chain a camphorquinone moiety and/or a tertiary-amine moiety were studied by laser flash photolysis and time-resolved fluorescence spectroscopy. It was found that the methacryloyloxy group does not affect strongly the photophysical properties of CQ nor the aliphatic amino group, when one of these molecules is polymer-bound. Intermolecular quenching of the triplet state by aliphatic amine occurs at moderately high rate and leads to ketyl-radical formation. In systems containing CQ and amine, both the singlet and the triplet states react and lead to ketyl radicals.

Photopolymerization experiments with the acrylic formulation HDDA/BA indicate that the chemical structure of the CQ/amine system appreciably affects the photoinitiating activity, although the photophysical properties of these systems do not appear significantly influenced by the macromolecular nature of the photosensitive groups. Therefore, it can be concluded that the different photoinitiating activities observed by combining systems of different structure are mainly due to the hindering effect of the macromolecular chain bearing the side chain photoactive group, which may favor or disfavour, with respect to the monomeric CQ/amine combination, the overall rate of polymerization and curing of the acrylic formulation, depending on the presence of one or both the components, respectively, in the polymeric form.

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