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Polymer 44 (2003) 5219–5226
polymer
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Camphorquinone–amines photoinitating systems for the initiation of free radical polymerization

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Received 3 February 2003; received in revised form 10 June 2003; accepted 19 June 2003

Abstract

Results of the camphorquinone/hindered piperidines, visible-light photoinduced polymerization of triethyleneglycol dimethacrylate are presented. The effectiveness of piperidines as a coinitiator is compared with a few aliphatic amines and aromatic amines. The main objective in this research was to study the mechanism of photoinitiation of polymerization. Reactive radicals that initiate the polymerization are formed by a mechanism of hydrogen atom abstraction by the triplet state of camphorquinone, mediated by photoinduced electron transfer. The different efficiencies of the aliphatic amines and of the aromatic amines affecting photopolymerization are explained on the basis of the different quenching reactivities of the excited states of camphorquinone.

Keywords: Camphorquinone–amine; Electron–proton transfer; Photoinitiated polymerization

1. Introduction

The photocuring of dental restorative resin precursors must meet several clinical criteria:

- For each increment (layer) the rate of polymerization must be sufficiently rapid (max.30–40 s) so that the patient does not become uncomfortable.
- The spectrum and intensity of light source used for irradiation must not harm (burn) the oral tissues. The commercially available light sources used for photocuring produce visible radiation in the blue region of spectrum ($\lambda_{max} = 480$ nm).
- The heat of polymerization must be low to avoid damage of the pulp tissue via heat conversion in thin layers.
- Incomplete polymerization of the inner part of the restoration may result in retention of unreacted monomers, which can have an adverse effect on the pulp tissue.
- There must be a minimal volume shrinkage of photocured resin precursor composite. Otherwise, the desired surface contacts between tooth and composite will be not maintained.
- The contents of the composite should not cause any toxic, inflammatory, allergic, carcinogenic or mutagenic reactions in the patient.

In order to meet these criteria it is necessary to develop the most effective, safe photoinitiating system. There is only one commercially available photoinitiating system for dental applications. This is based on camphorquinone (CQ) and different amines (AH) such as *N*,*N*-dimethyl-*p*-toluidine, 2-ethyl-dimethylbenzoate, *N*-phenylglycine, and many others [1–13]. Camphorquinone itself can photoinitiate polymerization, however, only at a low rate. In order to accelerate the polymerization, amines are used as

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doi:10.1016/S0032-3861(03)00568-8

coinitiators. The aminoalkyl radicals that are formed initiate the polymerization. The efficiency of this process depends on the steric structure of the amine-derived radicals, which must approach the reactive unsaturated bond in a monomer [14]. It is generally accepted that formation of aminoalkyl radicals occurs via photoinduced electron transfer (PET). In this paper, we focus on the mechanistic aspects of the quenching reactivities of the singlet excited states and of the triplet excited states of camphorquinone by amines.

2. Experimental

Camphorquinone (CQ) (bornanedione, 1,7,7-trimethyl bicyclo [2.2.1] heptane-2,3-dione] (Aldrich), was twice recrystalized from cyclohexane. Amines (AH) presented in Table 1 (Aldrich, Ciba-Geigy, Kodak) and triethyleneglycol dimethacrylate (TEGDMA) (Fluka) were used as received. Acetonitrile (ACN) (Aldrich) was spectroscopically pure. CQ and AH concentrations used in experiments were 10^{-2} and 10^{-4} M, respectively.

Spectroscopic measurements: UV/vis (Beckman DU 640), steady-state fluorescence and phosphorescence (FluoroMax-2 Jobin Yvon)

Laser flash photolysis: Q-switched nanosecond YAG-laser (with an optical parametric oscillator) generating 9 ns pulses at 466 nm with 6–8 mJ energy; analyzing system equipped with pulsed XBO 450 W lamp, monochromator, fast photomultiplier and a transient digitizer. All measurements were made in an oxygen free atmosphere.

Photoinitiated polymerization was carried under nitrogen using a Philips 500 W lamp (type PF 318 E/49), which produced visible radiations above 400 nm with a total light intensity of 60 mW cm^{-2}. Rates of polymerization were measured using a Perkin Elmer 2 DSC, which was arranged for photocalorimetric data.

Cyclic voltametry was performed with an Electrochemical Cypress System (Model Cl-1090), with Ag–AgCl electrodes in solution of 0.1 M tetrabutylammonium perchlorate (supporting electrolyte) in anhydrous ACN.

The detailed procedure of experiments, measurements and for photoisothermal polymerization have been published in our previous publications [6,7,9–11,13].

3. Results and discussion

3.1. Formation of reactive radicals

Camphorquinone (CQ) absorbs UV radiation in the region of 200–300 nm due to the π,π^* transition. It absorbs visible light (400–500 nm) (responsible for its yellow color) due to the n,π^* transition of the α-dicarbonyl chromophore [15–17]. There is a significant difference between ε_{max} for the two transitions, with $\varepsilon_{250\ nm} \approx 10,000\ M^{-1}\ cm^{-1}$ (π,π^*) and $\varepsilon_{468\ nm} = 40\ M^{-1}\ cm^{-1}$ (n,π^*). Irradiation of CQ with visible light causes the formation of singlet CQ (S_1) and by intersystem crossing (ISC, with Φ_{ISC} about 1). It also causes the formation of the triplet CQ (T_1) states [18]. CQ (T_1) has a characteristic transient spectrum with a lifetime ≈20 μs [19,20].

Photoinitiated polymerization occurs by a chain reaction between the free radicals formed by the photoinitiating system and the monomer (MH). Considering the (CQ)-amine (AH) or (CQ)-hydrogen donor (DH) systems, the free reactive radicals (M· and A·) formed, which initiate the polymerization, may arise simultaneously from different reactions such as:

- Hydrogen abstraction from the monomer (MH) by the triplet state CQ (T_1):

$$CQ(T_1) + MH \rightarrow CQH\cdot + M\cdot \quad k_{H(MH)} \tag{1}$$

  CQ itself can photoinitiate the polymerization of TEGDMA in the absence of AH; however, this reaction is not efficient [1].
- Hydrogen abstraction from a hydrogen donor (DH) by the triplet state $CQ(T_1)$:

$$CQ(T_1) + DH \rightarrow CQH\cdot + D\cdot \quad k_{H(DH)} \tag{2}$$

  the evidence for the camphorquinone ketyl radical (CQH·) is a strong ESR signal consisting of four main multiplets [1,21].
- Photoinduced electron transfer (PET) between the singlet CQ (S_1) or the CQ (T_1) triplet state and an amine (AH) by a mechanism that involves the formation of a charge-transfer singlet (CTC_S) or triplet (CTC_T) encounter complex [22]:

$$Q(S_1) + AH \rightarrow [>C-O\cdot^{-}\cdots{}^{+}\cdot NH<] \quad k_{elS} \quad CTC_S \tag{3}$$

$$Q(T_1) + AH \rightarrow [<C-O\cdot^{-}\cdots{}^{+}\cdot NH>] \quad k_{elT} \quad CTC_T \tag{4}$$

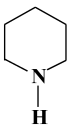
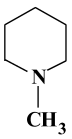
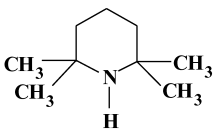
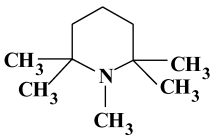
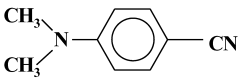
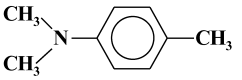
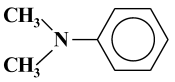
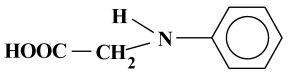
  followed by a proton transfer with the formation of CQH· and A· :

$$CTC \rightarrow CQH\cdot + A\cdot \qquad k_{H+} \tag{5}$$

The CQ (T_1) transient spectrum disappears in the presence of AH [19], which can be additional evidence for the formation of the CQH· radical. The CQH· does not initiate the polymerization because of steric hindrance effects [23], whereas the aminoalkyl radical (A·) is an effective radical that initiates the polymerization through an addition reaction onto the monomer double bond.

In the encounter the reactants complex must reorient themselves until a favorable geometry is reached. Calculations on simplified systems shows that the mutual orientation of the reactants can affect the rate constant of the reaction by order of magnitude or more [24,25].

Table 1
List of amines (AH) used

	Amine name	Code (AH)	Amine structure
Aliphatic amines	Propylamine	1	$CH_3-CH_2-CH_2-NH_2$
	Butylamine	2	$CH_3-CH_2-CH_2-CH_2-NH_2$
	Pentylamine	3	$CH_3-CH_2-CH_2-CH_2-CH_2-NH_2$
	N,*N*′-Dimethylethylamine	4	$CH_3-CH_2-N(CH_3)_2$
	N,*N*,*N*′,*N*′,-Tetra-methylethylenediamine	5	$(CH_3)_2N-CH_2-CH_2-N(CH_3)_2$
Piperidines	Piperidine	6	
	1-Methylpiperidine	7	
	2,2,6,6,-Tetramethyl piperidine	8	
	1,2,2,6,6- Penta methylpiperidine	9	
Aromatic amines	4-(Dimethylamino) benzonitrile	10	
	N,*N*-Dimethyl-*p*-toluidine	11	
	N,*N*-Dimethyl-aniline	12	
	N-Phenylglycine	13	

3.2. *Efficiency of formation of radicals (*M· *and A·)*

This efficiency depends on a number of reactions such as:

- Non-radiative physical deactivation of excited states CQ (S_1) and/or CQ (T_1):

$$CQ(S_1) \rightarrow CQ(S_0) + \text{heat} \qquad k_{dS} \qquad (6)$$

$$CQ(T_1) \rightarrow CQ(S_0) + \text{heat} \qquad k_{dT} \qquad (7)$$

- Quenching of the CQ (S_1) and/or CQ (T_1) states by physical processes followed by emission of fluorescence (fl) and/or phosphorescence (ph):

$$CQ(S_1) \rightarrow CQ(S_0) + \text{fluorescence} \qquad k_{fl} \qquad (8)$$

$$CQ(T_1) \rightarrow CQ(S_0) + \text{phosphorescence} \qquad k_{ph} \qquad (9)$$

Fluorescence emission (maximum at 518 nm) from the CQ (S_1) is observed both in oxygen free monomer and in oxygen saturated monomer (TEGDMA) solutions. However, phosphorescence emission (max at 560 nm) from the CQ (T_1) is observed only in oxygen free monomer (TEGDMA) solutions and is quenched by oxygen (reaction (9)) [7].

- Physical quenching of the CQ (T_1) by the monomer (MH):

$$CQ(T_1) + MH \rightarrow CQ(S_0) + MH \qquad k_{qT(MH)} \qquad (10)$$

Appearance of phosphorescence in liquid, oxygen-free TGDMA indicates that the reaction (8) is negligible. The low quantum yield ($\Phi = 0.07 \pm 0.01$) for CQ (T_1) disappearance upon irradiation at 436 nm in carefully degassed solutions suggests the absence of a radical chain process [26]. Low photoactivity of CQ (T_1) in hydrogen atom abstraction from MH, in oxygen free solutions (reaction (1)) is probably due to a steric hindrance of the biradical formed from the CQ carbonyl groups.

- Quenching of the CQ (T_1) by oxygen:
  $CQ(T_1) + O_2 \rightarrow$ oxidation products of CQ and physical quenching $\quad k_{ox}$ (11)

In most organic media, $[O_2] \approx 2 \times 10^{-3}$ M. The quantum yield for the photooxidation of CQ (T_1) at 436 nm is $\Phi = 0.16 \pm 0.01$ [26]. Oxygen quenches the CQ triplet state with a second order rate constant of 2×10^8 M^{-1} s^{-1} [19].

- Quenching of the CQ (S_1) and/or CQ (T_1) by the amines (AH) in the oxygen free solutions:

$$CQ(S_1) + AH \rightarrow CQH\cdot + A\cdot \qquad k_{qS(AH)} \qquad (12)$$

$$CQ(T_1) + AH \rightarrow CQH\cdot + A\cdot \qquad k_{qT(AH)} \qquad (13)$$

Quenching rate constants for the singlet state (singlet state lifetime: 18 ns [19]) can be obtained from the usual Stern–Volmer plots, (Fig. 1). A similar kinetic treatment can be made for the quenching of $CQ(T_1)$ by AH; k_{qT} values can be derived (Table 2). There is an experimental difficulty in obtaining information concerned with values of k_{qS} and k_{qT} in TEGDMA, because the monomer polymerizes in the cuvets during the measurements.

- Back electron transfer from the singlet complex (CTC_S) or the triplet (CTC_T) complex:

$$CTC_S \rightarrow CQ(S_0) + AH \qquad k_{-elS} \qquad (14)$$

Table 2
Data of: ionizing potential IP [4], oxidation potential E_{ox}, (AH/AH^+), free energy (ΔG°), log k_{qS} and log k_{qT} for different amines AH1–AH13

	AH	IP (eV)	E_{ox} (V/SCE)	ΔG^* (eV)	log k_{qS}	log k_{qT}
Aliphatic amines	1	8.78	1.94	0.979	8.7	7.0
	2	8.71	1.88	0.919	8.7	6.6
	3	8.67	1.85	0.889	8.7	7.0
	4	7.74	0.95	−0.011	9.2	8.0
	5	7.59	0.95	−0.011	9.4	8.0
	6	8.05	1.34	0.379	9.0	8.3
Piperidines	7	7.74	1.08	0.119	9.2	8.3
	8	7.59	0.95	−0.011	8.9	8.0
	9	7.23	0.66	−0.301	9.6	8.7
	10	7.6	1.312	0.351	9.4	7.3
Aromatic amines	11	6.9	0.72	−0.241	10.1	9.6
	12	7.12	0.77	−0.191	10.0	9.3
	13	8.41	0.476	−0.485	9.5	8.5

$$CTC_T \rightarrow CQ(S_0) + AH \qquad k_{-elT} \qquad (15)$$

- Scavenging of the free radicals M· and A· by oxygen and formation of peroxy radicals [27]:

$$M\cdot + O_2 \rightarrow MOO\cdot \qquad (16)$$

$$A\cdot + O_2 \rightarrow AOO\cdot \qquad (17)$$

Peroxy radicals (MOO· and AOO·) do not initiate the polymerization because of the steric hindrance effects; however, they can abstract a hydrogen atom from the monomer molecule, producing a new generation of monomer radicals (M·) :

$$MOO\cdot + MH \rightarrow MOOH + M\cdot \qquad (18)$$

$$AOO\cdot + MH \rightarrow AOOH + M\cdot \qquad (19)$$

Peroxy radicals may also undergo many other reactions, e.g.

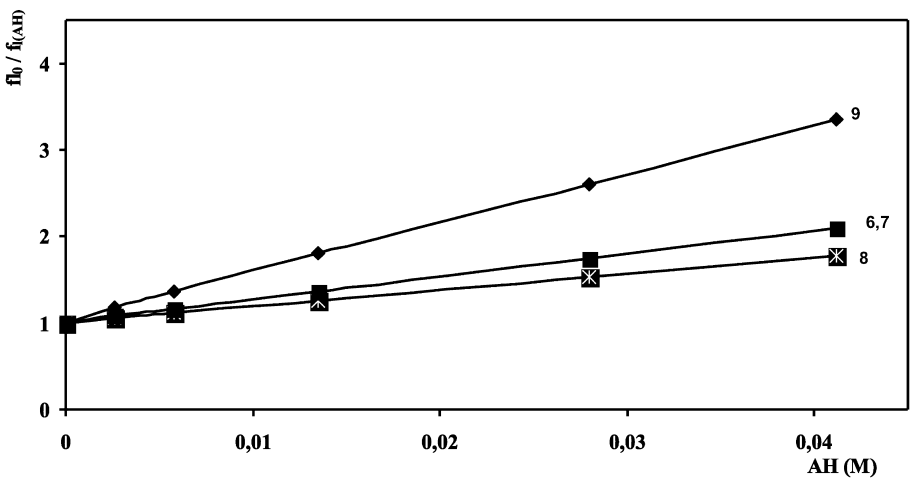


Fig. 1. Stern–Volmer plot (1×10^{-2}) for the quenching of $CQ(S_1)$ by different amines: AH6, AH7, AH8 AH9 in ACN oxygen free solutions.

termination reactions, with radicals M·, A·, $(MH)_n$· and themselves.

- Scavenging of free radicals M· and A· by traces of inhibitor (INH). Commercial TEGDMA contains hydroquinone 75 ppm, as INH:

$$M\cdot + INH \rightarrow \text{inactive products} \quad (20)$$

$$A\cdot + INH \rightarrow \text{inactive products} \quad (21)$$

The scavenging of the free radicals M· and A· by oxygen and traces of INH causes an increase in the inhibition time (t_{inh}) during which the polymerization reaction does not occur.

3.3. Factors affecting the photoinduced electron transfer (PET) reaction between CQ and AH

PET reaction of the $CQ(S_1)$ and/or $CQ(T_1)$ with AH in high viscosity solution of TEGDMA depends on the rate constants of diffusion (k_{diff}) of the reactants and the rate constant of dissociation ($-k_{diff}$) of the encounter complex, which limit the efficiency of electron transfer:

$$CQ(S_1) + AH \underset{k_{diff}}{\overset{k_{diff}}{\rightleftarrows}} (CQ\cdots AH)^* \underset{k_{-el}}{\overset{k_{el}}{\rightleftarrows}} [CQ\cdot^- \cdots AH\cdot^+] \quad (22)$$

$$CQ(T_1) + AH \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftarrows}} (CQ\cdots AH)^* \underset{k_{-el}}{\overset{k_{el}}{\rightleftarrows}} CQ\cdot^- \cdots AH\cdot^+] \quad (23)$$

and proton transfer:

$$[CQ\cdot^- \cdots AH\cdot^+] \rightarrow CQH\cdot + A\cdot \quad (24)$$

If PET is to be efficient, the following inequalities must obtain:

$$k_{diff}[AH] \gg k_{dS} \text{ or } k_{dT} \quad (25)$$

$$k_{et} \gg k_{qS(AH)} \text{ or } k_{qT(AH)} \quad (26)$$

$$k_{-diff} \gg -k_{el} \quad (27)$$

In other words, the rates of forward process must be greater, at each stage, than the rates of competing process.

The relationship between the observed rate constant for PET ($k_{el(obs)}$) and the rate constant for PET (k_{el}) is:

$$k_{el(ob)} = k_{diff}[k_{el}/(k_{el} + k_{-diff})] = \alpha\, k_{diff} \quad (28)$$

The $k_{el(obs)}$ for PET depends on the diffusion of the reactants and the probability of PET (α). For two extreme situations:

(i) The diffusion is very efficient relative to PET ($k_{-diff} \gg k_{el}$)

$$k_{el(ob)} = (k_{diff}/k_{-diff})k_{el} \text{ if } k_{-diff} \gg k_{el} \quad (29)$$

(ii) The diffusion is slow compared to PET ($k_{el} \gg k_{-diff}$)

$$k_{el(obs)} = k_{diff} \text{ if } k_{el} \gg k_{-diff} \quad (30)$$

In case (1), the $k_{el(obs)}$ is a composite of the k_{el} and the pseudo equilibrium constant (k_{diff}/k_{-diff}) for CTC formation. In case (2), the k_{el} is a measure of the rate constant of diffusion of $CQ(S_1)$ or $CQ(T_1)$ to AH.

The relationship between k_{diff} and the temperature and the viscosity becomes [28–30]:

$$k_{diff}(M^{-1}\,s^{-1}) = 2\times 10^5\, T/\eta \quad (31)$$

where T is in K and η is in Pa·s. The k_{diff} values for CQ and AH in acetonitrile are in the range of $10^{10}\,M^{-1}\,s^{-1}$ and for TEGDMA are 0.0004×10^{10}–$0.002\times 10^{10}\,M^{-1}\,s^{-1}$ at 25 °C. If PET is truly diffusion-controlled, then measured values of k_{el} should behave exactly as k_{diff}.

The relationship between k_{qS} and the standard free energy change for PET (ΔG°) has been given by Rehm and Weller [30]. The $\Delta G°$ is expressed as follows:

$$\Delta G° = E_{ox}(AH/AH\cdot^+) - E_{red}(CQ\cdot^-/CQ) - E_{0-0} + C \quad (32)$$

Here, $E_{ox}(AH/AH\cdot^+)$ is the oxidation potential of the electron donor AH and $E_{red}(CQ\cdot^-/CQ)$ is the reduction potential of the electron acceptor (CQ). E_{0-0} is the energy of excitation of CQ(S1) or CQ(T1) and C is the electrostatic interaction energy within ion pairs. When $\Delta G°$ is moderately exorgonic (Table 2), k_{qS} increases according to a logarithmic law as $E_{ox}(AH/AH\cdot^+)$ decreases [30]. It is clear that k_{qS} should depend only on the oxidation potential of the electron donor AH and its chemical structure. Plots of log k_{qS} and log k_{qT} (see reactions (12) and (13)) versus E_{ox}, are shown in Figs. 2 and 3, respectively.

In general, k_{qS} and k_{qT} increase as $\Delta G°$ decreases (i.e. is more negative, Table 2) until a limit depending on the CQ/AH systems is reached. However, it should be noted that the aliphatic amines behave differently from aromatic amines both in the singlet state and in the triplet state. Indeed, two distinct Rehm Weller like plots are observed for these two kinds of amine. One plot, corresponding to the aromatic amines AH10 to AH13, is slightly shifted along the E_{ox} axis. It qualitatively obeys the Rehm Weller behaviour. The reaction is diffusion-controlled when the reaction is exorgonic and the quenching rate constant decreases when

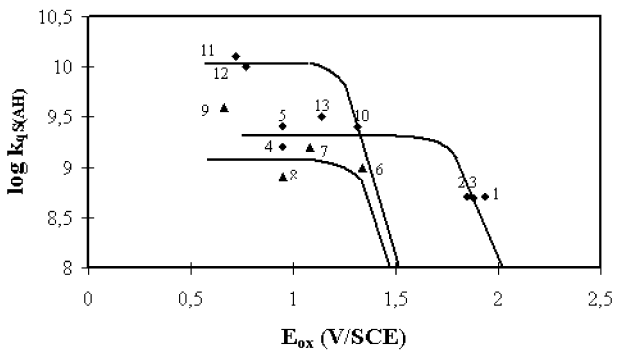


Fig. 2. Logarithm of the rate constants of quenching k_{qS} of $CQ(S_1)$ versus E_{ox}. for different amines AH: aliphatic AH1, AH2, AH3, AH4, AH5; piperidines AH6, AH7, AH8, AH9 and aromatic AH10, AH11, AH12, AH13.

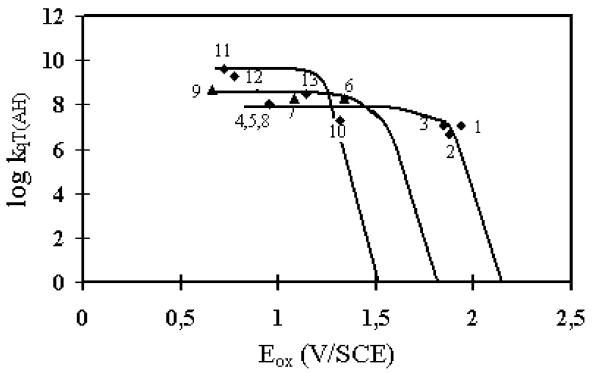


Fig. 3. Logarithm of the rate constants of quenching k_{qT} of CQ(T_1) versus E_{ox}, for different amines AH: aliphatic AH1, AH2, AH3, AH4, AH5; piperidines AH6, AH7, AH8, AH9 and aromatic AH10, AH11, AH12, AH13.

the reaction becomes endorgonic. In the case of the aliphatic amines AH1–AH4, AH5 and AH6–AH9, the corresponding plots are shifted from about 0.5 eV towards the more positive $\Delta G°$ values and the plateau value does not reach the diffusion value. The first effect has been already observed and ascribed to specific electrostatic terms that are not properly taken into account in the Rehm Weller description [31,32]. The second effect, i.e. a non-diffusion controlled reaction, was ascribed to a low electronic coupling between the acceptor/amine system for the PET reaction [33]. In addition, the plateau value ($k_q \sim 1.5 \times 10^9$ M^{-1} s^{-1}) for the singlet state PET is higher than that for the triplet state reaction ($k_q \sim 2 \times 10^8$ M^{-1} s^{-1}). This means that the electronic coupling between CQ and the aliphatic amines is lower in the triplet state than in the singlet state. This explains, in part, the results reported here and in the literature [2]. At high ionization potential, aliphatic amines are more efficient than aromatic amines, a fact that results from the better quenching efficiency of aliphatic amines in the endorgonic region. On the contrary, aromatic amines are more efficient at low ionization potential, a fact that underscores the higher quenching rate constants in the exorgonic region.

The PET mechanism of formation of reactive aminoalkyl radicals may be only effective at the beginning of the initiation of the polymerization. Because PET is strongly diffusion controlled, its effectiveness decreases as the viscosity of the polymerizing medium increases. At the same time, another simultaneous mechanism of formation of reactive radicals by a direct hydrogen atom abstraction of CQ (T_1) on the monomer (which should not be dependent on the viscosity in the close vicinity of both partners) may occur.

4. Kinetics of polymerization initiated by CQ–AH system

The kinetics of polymerization of multifunctional monomers is complicated by a number of factors [5,34,35]:

- The steady-state assumption that the rate of initiation (R_i) equals the rate of termination (R_t) is only valid at a very low conversion of monomer, not exceeding 1–3%.
- The rate of polymerization (R_p) expressed by Eq:

$$R_p = -\mathrm{d[MH]}/\mathrm{d}t = k_p/k_t^{1/2}[\mathrm{MH}](\Phi_i\, \varepsilon_{CQ}\, I_o[\mathrm{CQ}])^{1/2} \quad (33)$$

(where: k_p and k_t are rate constants of propagation and termination, respectively; Φ_i is the quantum yield of initiation, ε_{CQ} is the extinction coefficient of CQ (40 M^{-1} l cm^{-1} at 468 nm), I_o is the incident light intensity at 468 nm) is valid only for linear polymerization, but not for a crosslinking photopolymerization. Nevertheless, Eq. (33) is often used to describe the photopolymerization of multifunctional monomers of low monomer conversion (<1–2%) [34].

- The Φ_i values are difficult to determine.
- Rates of initiation (R_i), propagation (R_p) and termination (R_t) are time diffusion controlled and change during polymerization [5,36].
- Monomolecular, bimolecular and mixed termination reactions [37,38].
- At high light intensities and high CQ–AH concentrations, the effect of primary radical termination reduces the increase in polymerization rate afforded by auto-acceleration and decreases the final conversion [13].

Rates of photoinitiated polymerization (R_p) are commonly measured by two methods: real-time infrared (RTIR) spectroscopy based on the disappearance of the double bond absorption during the polymerization [39] and photo-DSC [40], which gives the heat of polymerization. Typical R_p curves obtained by photo-DSC for the studied CQ–AH systems are shown in Fig. 4 and data R_p^{max} are collected in Table 3. The most effective photoinitiating CQ–AH systems contain aromatic amines (AH10–AH13) and hindered piperidine (AH9). The later are more effective coinitiators than aromatic amines AH. From Fig. 4 and Table 3, it is clearly seen that the points corresponding to the most efficient amine coinitiators lie in the exorgonic regions of the plots and are associated with the highest values of the quenching rate constants, whereas the amines, which completely avoid the polymerization, are located in the

Table 3
Rate of polymerization (*R*p) of TEGDMA in the presence of CQ (6×10^{-2} M) and different AH1–AH13 (6×10^{-3} M)

AH	R_p (10^{-4} s^{-1})	AH	R_p (10^{-4} s^{-1})
1	0	8	0
2	0	9	12,1
3	0	10	21,3
4	1,4	11	23,2
5	5	12	11,5
6	0	13	20
7	0	No amine	10

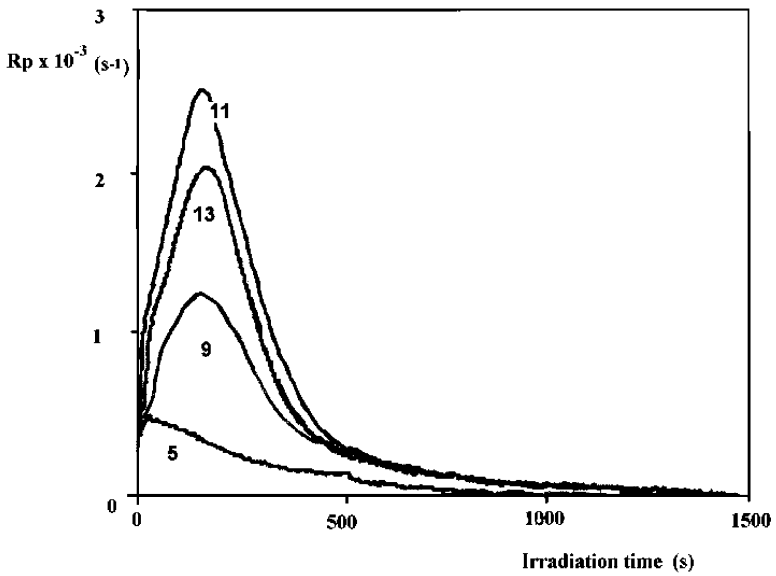


Fig. 4. Rate of polymerization (R_p) of TEGDMA as a function of the irradiation time in the presence of CQ (6×10^{-2} M) and different amines AH5, AH9, AH11, AH13 (6×10^{-3} M) in oxygen free solutions.

endorgonic region. Thus, one may conclude that the efficient hydrogen abstraction from amines by CQ(T_1) occurs via electron transfer (reaction (5)). However, if the reaction occurs from the CQ(T_1), direct hydrogen abstraction from monomer (reaction (1)) may also take place (see amine AH10, $\Delta G^\circ > 0$).

Retardation of polymerization may be a result of both physical quenching of the CQ(T_1), which prevents radical formation, as well as a result of side reactions (like chain-transfer reaction). Generally, the polymerization is either not observed or it proceeds with a very low rate in the presence of amines containing primary or secondary amino groups (with the exception of the aromatic amine AH13). It was found, that systems in which an amine participates in hydrogen bonding may be less reactive due to the increase of the bonding energy required to ionize the lone pair [40]. This is in agreement with the data shown in Table 2. Moreover, it is important that the amine-derived radicals that are formed become available for the initiation of polymerization.

5. Conclusions

Photoinitiated CQ–AH polymerization occurs through electron/proton transfer. The efficiency of the polymerization depends not only on the efficiency of the quenching of CQ(T_1) by amines, but also on the relative importance of processes that lead to the formation of radicals being able to initiate the polymerization and processes to lead to a physical quenching preventing radical formation. The reactivity of the aromatic amine- derived radicals seems to be a function of the number of methyl groups that are attached to the N atom. Exception of this rule is *N*-phenylglycine which is very effective coinitiator. Hindered amines are also effective electron donors through the PET reaction to CQ. However, their activity as coinitiators depends on their structure; they can strongly accelerate or completely suppress the polymerization. Radicals formed from the hindered methyl piperidine are the most effective species for the initiation of polymerization of TEGDMA.

Acknowledgements

The authors gratefully acknowledge the support of the Foundation pour l'Ecole Nationale Superieure de Chimie de Mulhouse which generously provided a post-doc fellowship for Dr Julita Jakubiak, and of the Swedish Institute which provided post-doc fellowships for Dr Alina Sionkowska, Dr Julita Jakubiak and Dr Ewa Andrzejewska.

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