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Kinetic studies of a new photoinitiator hybrid system based on camphorquinone-*N*-phenylglicyne derivatives for laser polymerization of dental restorative and stereolithographic (3D) formulations

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The new photoinitiating system based on camphorquinone–*N*-phenylglycine and its derivatives is proposed for replacing widely used photoinitiator camphorquinone–amines for photocuring of polymeric dental formulations. The most important advantage of this new system is that these amino acids should be biologically less harmful than amines. However, it is hard to differentiate between the two for dental purposes without detailed studies. The kinetics of photoinitiated polymerization shows that the electron–proton transfer occurs via formation 'collision' and 'excited charge–transfer complexes', and can be described either by the classical Marcus equation or by the reactivity of free radicals formed. This new photoinitiating system can also be used for the photocuring of stereolithographic (3D) formulations. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Photocuring is a principal method for dental and stereographical applications. However, dental applications of photocuring are seriously limited by a number of factors[1-4] such as: (1) Absorption of a photoinitiating system. The application of visible light for photocuring in the oral cavity is required for health and safety reasons, since ultra-violet (u.v.) radiation may cause tissue burns and allergic reactions, in addition to posing risk of cancerogeic transformations. (2) Photoinitiator efficiency, which influences the speed of polymerization, (i.e. has an effect on the kinetics of polymerization). (3) Toxic considerations. Photocuring processes are performed inside the human oral cavity. Toxic, allergic or mutagenic reactions may be caused by photoinitiators and photoinitiators and products of their photolysis released from dental polymers.

Photoinitiator hybrid systems used in commercially available dental restorative materials consist of camphorquinone (CQ bornanedione, 1,7,7-trimethylbicyclo(2,2,1)-heptane-2,3-dione), which has absorption in the visible region with a λ_{max} at 472 nm (n, π^* transition) (*Figure 1*) and coinitiators which are different types of amines, e.g. *p*-*N*,*N*-dimethylaminobenzoic acid ethyl ester[5], 2(*N*,*N*-dimethylamino)ethyl methacrylate[6,7], *N*,*N*-dimethyltoluidine[8], *N*-methyl-*N*-phenyl-3-aminopropionitrile[9], *N*,*N*-3,5-tetramethylaniline[10], 4,4′-bis(*N*,*N*-dimethylamino) benzophenone[8,11] and many others[8,10]. The great disadvantage of all amines is their high toxicity[12-16] and mutagenicity[17,18].

The visible light used for photocuring is produced by commercially available lamps with fibre optics. These produce visible light by means of a halogen lamp filtered by an edge filter to the blue region of the spectrum[1,19]. Recently, lasers have been used as effective light sources for photocuring of dental materials[20-24]. Lasers best suited to dental applications are nitrogen or argon which produce radiation in the range 457–514 nm at an intensity of 2 W.

In stereolithography, especially when used for a medical purpose[25,26], photoinitiator systems used should have absorption in a visible range, and high photoefficiency which allows high speed polymerization in the range of seconds. The only light source used for stereolithography is laser irradiation.

The reason for this work was to study the new photoinitiating system based on camphorquinone–*N*-phenylglycine derivatives. Glycine derivatives are amino acids, biologically less-toxic[27-29], non-allergic, and

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probably non-mutagenic compounds, which can replace harmful amines as coinitiators.

EXPERIMENTAL

CQ, *N*-phenylglycine (NPG), 2-ethyl-2-(hydroxymethyl)-1,3-propanedil triacylate (TMPTA) (all from Aldrich, Germany) and ethylated bisphenol-A-dimethacrylate (Bis-EMA) (Sartomer-Cray Valley, USA) were used as delivered. Other NPG derivatives were synthesized according to literature[30–33].

Photopolymerization was initiated by 488 nm line emitted from the Omnichrome argon-ion laser Model 543-500 MA (USA). The average power of radiation was 30 mW 0.785 cm^{-2} (measured by Coherent Power Meter Type 543-500 mA). All irradiation procedures were made on the one type of formulation which consists of the mixture of TMPTA and Bis-EMA in the system CQ/NPGs at CQ concentration of 1 wt% and NPGs concentration of 0.1 M. All irradiations were performed in the presence of air (a condition required for dental application).

Kinetics of polymerization were carried out by measuring the polymerization heat evolution of a sample irradiated with laser through an optical system, in a home-made micro-calorimeter. A semiconducting diode type immersed in the 2 mm thick layer (0.25 ml) of a cured sample was used as a temperature sensor. The amplified signal was transformed with a high-speed analog/digital data acquisition board DAS-1401 (Keithley MetraByte, USA) to a computer, equipped with TestPoint software.

The oxidation potential for electron donors (NPGs) and the reduction potential for CQ were measured in a mixture of a dry acetonitrile and 0.1 M tetrabutylammonium perchlorate (TBAP, which is supporting electrolyte), using a cyclovoltameter type Electrochemical Cypress System Model Cl-1090 (with Ag–AgCl reference electrode).

RESULTS AND DISCUSSION

CQ absorbs light in the region of 200–300 nm due to the $\pi \rightarrow \pi^*$ transition, and 400–550 nm (responsible for its yellow colour) due to the $n \rightarrow \pi^*$ transition of dicarbonyl groups (*Figure 1*)[34–37]. There is a significant difference between intensities for these two transitions. For the $\pi \rightarrow \pi^*$ transition ϵ_{max}^{λ} is about 10 000 compared to 40 for the $n \rightarrow \pi^*$ transition (measured in cyclohexane). This reflects the fact that the $n \rightarrow \pi^*$ transition is symmetry forbidden, while the $\pi \rightarrow \pi^*$ transition is allowed.

Irradiation of CQ at 253.7 nm in methanol or isopropyl alcohol (in N_2 atmosphere) gives a mixture of structurally different endo-hydrocamphors[38,39], whereas in the presence of oxygen it leads to a variety of oxidation (camphoric anhydride) and reduction (mixture of acyloins) products[40]. Irradiation of CQ with light at 470 nm does not cause any visible change in its absorption spectrum (either in N_2 or in the presence of air).

The *N*-phenylglycine (NPG) absorbs light in the region of 200–320 nm due to the $\pi \rightarrow \pi^*$ transition (*Figure 1*). All NPGs are completely transparent at the region of argon-ion laser irradiation. During irradiation of a mixture of CQ–NPG (10/1) in solution with laser radiation at 488 nm, the NPG spectrum decreases, whereas the CQ spectrum remains almost unchanged (*Figure 2*), indicating the occurrence of intermolecular electron transfer following by a proton transfer, (EPT) process.

The EPT processes in the quenching of aromatic carbonyl triplets by amines (AMs) have been the subject of many photochemical investigations[41]. The hybrid system based on benzophenone–AMs is a well known photoinitiator for polymerization as well as for photodegradation (chain scission and/or crosslinking) of polymers[31,42]. The mechanism of the CQ–AM photoinitiator system also occurs by the EPT process[8,11]. Free radicals formed from AM are responsible for the initiation of polymerization. There have also been several studies concerning photochemical generation of radicals in amino acids[43–46], peptides[47] and proteins[48,49] used as coinitiators with different aromatic ketones.

It is generally considered that in the EPT mechanism two types of complexes participate:

(1) The 'collision complex' between the triplet excited state of a light absorbing molecule (A*) (e.g. CQ) and proton (hydrogen) donor molecule (HD) (e.g. AM[50–52] or NPG)

$$A \xrightarrow[I_a]{h\nu} A^* \text{ (singlet)} \xrightarrow{\text{ISC}} A^* \text{ (triplet)} \qquad (1)$$

$$A^* \text{ (triplet)} + HD \underset{k_{-\text{dif}}}{\overset{k_{\text{dif}}}{\longleftrightarrow}} [A^* \cdots HD] \longleftrightarrow [A \cdots HD]^* \qquad (2)$$

(Collision complex)

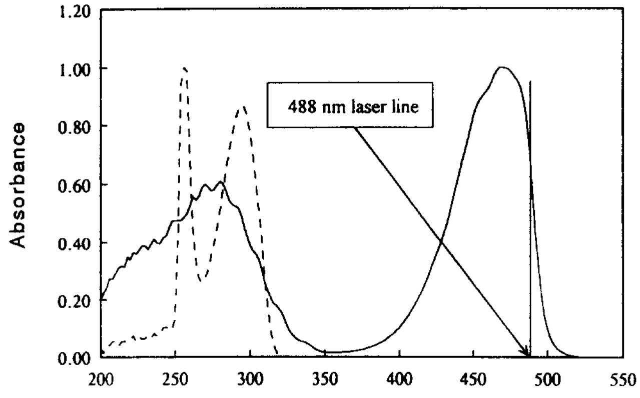


Figure 1 U.v./v is absorption spectra. ——, CQ 2.7 × 10^{-2} M in ethyl acetate; - - - - -, NPG 4.1 × 10^{-4} M in ethyl acetate

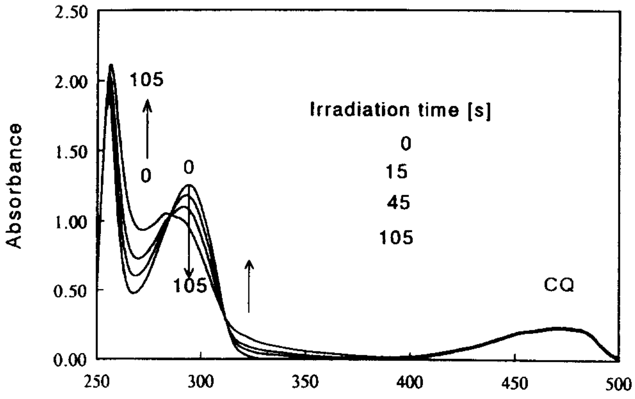


Figure 2 Change of u.v./v is absorption spectra of CQ–NPG: 10/1 in ethyl acetate during argon-ion laser irradiation

Here k_{dif} is the rate constant representing the rate of diffusive encounters between reactants, which can dissociate apart with the rate constant k_{-dif}. In the collision complex between the triplet state of CQ (n, π^*) and HD (in its ground state) the energy transfer from A^* to HD is forbidden, because of the lower E_T AM $= 62\,\mathrm{kcal\,mol^{-1}}$ $(259.5\,\mathrm{kJ\,mol^{-1}})$[53]. The lifetime of the collision complex is very short, and cannot be detected by the nanosecond spectroscopy.

(2) The 'excited charge-transfer complex' is a complex which is formed from a collision complex after intermolecular electron transfer

$$[A\cdots HD]^* \underset{k_{-el}}{\overset{k_{el}}{\rightleftarrows}} [A^{\cdot -}\cdots HD^{+\cdot}] \tag{3}$$

k_{el} is the first order rate constant of electron transfer with reverse step denotes by the rate constant k_{-el}. The triplet energy of A^* is used for an intermolecular electron transfer (IET) process. The difference between the donor (HD) ionization energy and the acceptor (A) electron affinity is a decisive criterion for the excited charge-transfer complex formation. The IET process is followed by the intermolecular proton transfer (IPT) process resulting in the formation of two radicals: CQ ketyl radical $(AH^{\cdot})$ and AM (or NPG) donor radical $(D^{\cdot})$

$$[A^{\cdot -}\cdots HD^{+\cdot}] \xrightarrow{k_H} AH^{\cdot} + D^{\cdot} \tag{4}$$

The $[AH^{\cdot}]$ radicals are not capable of initiating polymerization, whereas $[D^{\cdot}]$ radicals are well known as reacting species[31-33]

$$D^{\cdot} + M(\text{monomer}) \xrightarrow{k_i} DM^{\cdot} \xrightarrow{+nM} \text{propagation reaction} \tag{5}$$

The propagation reaction is in competition with the termination reaction in which inert polymer is formed

$$DM_n^{\cdot} + DM_m^{\cdot} \xrightarrow{k_t} \text{inert products} \tag{6}$$

In the EPT processes the observable rate constant (k_{obs}) is the sum of k_{el} and k_H, i.e.

$$k_{obs} = k_{el} + k_H \tag{7}$$

However, the dominant role is played by k_{el}, and at this assumption

$$k_{obs} \approx k_{el} \tag{8}$$

The k_{obs} (in high viscous monomers (TMPTA-*bis*-EMA) which limit diffusion effects, and at high concentrations of HD) is practically a first-order rate constant with such an assumption, the concentration of donor radicals $[D^{\cdot}]$ is given by

$$[D^{\cdot}] = \sqrt{\frac{2I_a\Phi_{ISC}k_{el}}{k_t}} \tag{9}$$

Hence, for the CQ $\Phi_{ISC} = 1$[43], equation (9) is simplified to

$$[D^{\cdot}] = \sqrt{\frac{2I_ak_{el}}{k_t}} \tag{10}$$

The overall rate of polymerization (R_p) for a process proceeding via EPT is finally determined by the nature of the donor and the efficiency of the generated donor radicals $[D^{\cdot}]$, and is given by:

$$R_p = k_i[M][D^{\cdot}] = k_i[M]\sqrt{\frac{2I_ak_{el}}{k_t}} \tag{11}$$

where k_{el} is a limiting factor, and is given by

$$k_{el} = \chi Z \exp - \left(\frac{\Delta G^{\#}}{RT}\right) \tag{12}$$

where χ is the transmission coefficient (negligible), Z is the universal frequency factor (ca. $6 \times 10^{12}\,\mathrm{s^{-1}}$ at 25°C), $\Delta G^{\#}$ is the activation free energy given by the Marcus equation for neutral reactants[54-56] as

$$\Delta G^{\#} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \tag{13}$$

where λ is the reorganization energy (factor dependent on the nature of solvent and reacting molecules) necessary to reach the transition state both of excited molecules (A^*) and of electron donor molecules (DH)[57,58], and ΔG^0 is given by the Rehm–Weller equation[59,60]

$$\Delta G^0 = E_{ox}(HD/HD^{\cdot +}) - E_{red}(A^{\cdot -}/A) - \frac{Ze^2}{\epsilon a} - E_T(A) \tag{14}$$

where $E_{ox}(HD/HD^{\cdot +})$ is the oxidation potential of the electron–hydrogen donor molecule (NPGs), $E_{red}(A^{\cdot -}/A)$ is the reduction potential of the electron acceptor (CQ), $Ze^2/\epsilon a$ is the Coloumbic energy, which is considered negligible to the overall magnitude of ΔG^0, $E_T(A)$ is the triplet energy of CQ ($E_T = 51\,\mathrm{kcal\,mol^{-1}}$, $210.5\,\mathrm{kJ\,mol^{-1}}$). The ΔG^0 can be easily determined from the cyclovoltammetric measurements (CV)[61]. For a reversible, diffusion-controlled, electron transfer reaction at a stationary electrode, the CV contains distinctly peaked anodic and cathodic waves for the electrolysed species since no convective mass transfer is employed and the time interval between forward and reverse potential sweeps is relatively short (*Figure 3*). The calculated data of ΔG^0 for NPGs obtained from the CV measurements are given in *Table 1*.

Combination of equations (12), (13) and (14) gives the following equation for R_p (proceedings via electron transfer from NPG to the excited state of CQ)

$$R_p = k_i[M]\left[\frac{2I_a}{k_t}\chi Z \exp\left(-\frac{\frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2}{RT}\right)\right]^{0.5} \tag{15}$$

Considering that for the initial time of polymerization $[M] =$ a constant, $[HD] =$ a constant, $k_i =$ a constant and $2I_a/k_t =$ a constant assuming termination proceedings via reaction (6), the R_p will be simplified to

$$\ln R_p = C - \frac{\lambda\left(1 + \frac{\Delta G^0}{\lambda}\right)^2}{4RT} \tag{16}$$

where C is the constant dependent on k_i, I_a, k_t, [M] and [HD].

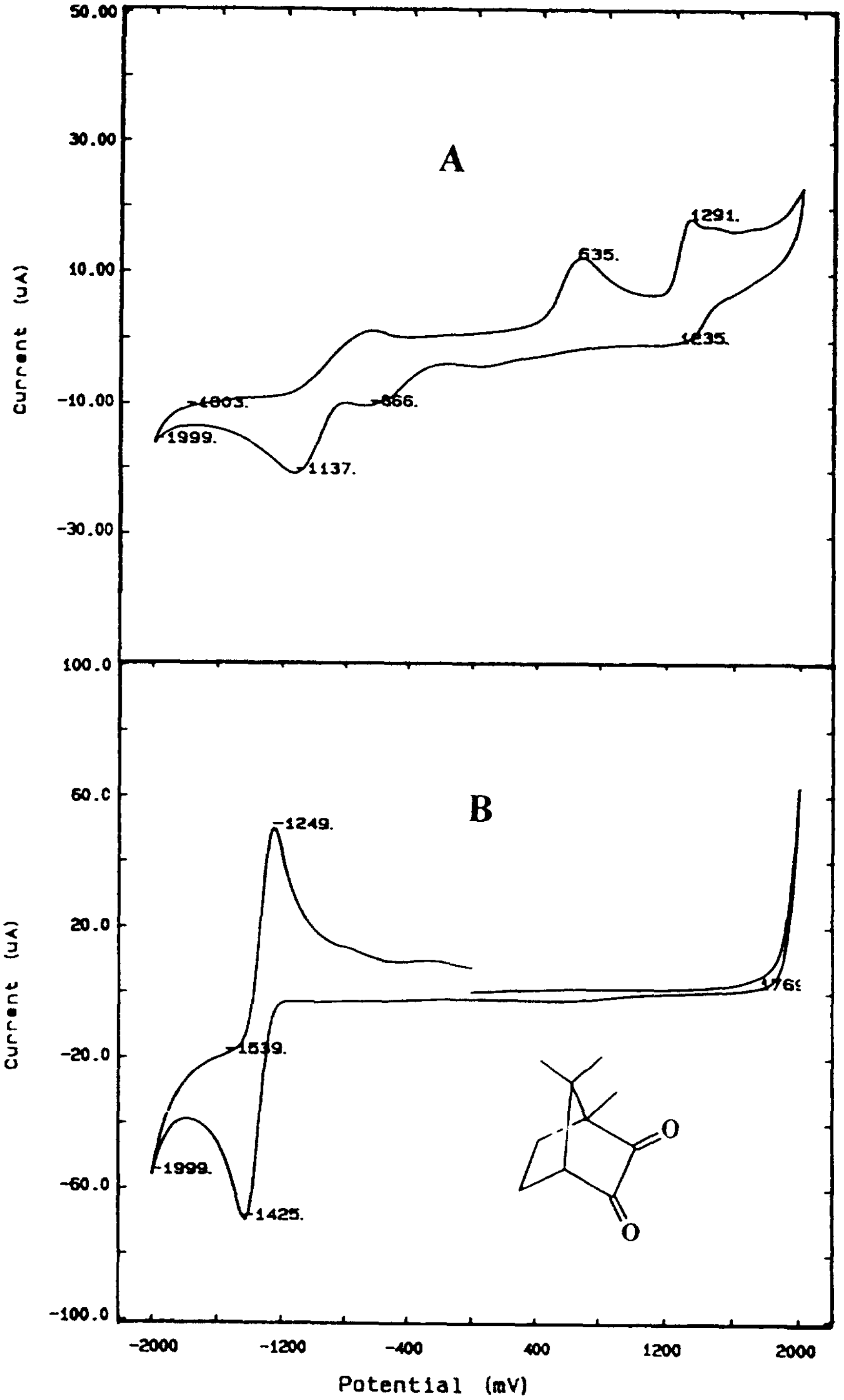


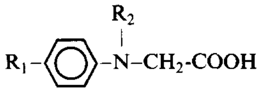
Figure 3 Cyclycvoltammograms. (A) CQ (10^{-3} M); (B) *N*-phenylglycine (NPG) (10^{-4} M) in acetonitrile in the presence of tetrabutyloammonium perchloride (0.1 M) as the supporting electrolyte

Equation (16) shows that if the EPT process between the excited (triplet) state of CQ and NPGs is a limiting step for the photoinitiated polymerization of TMPTA–*bis*-EMA system, one should observe a parabolic relationship between the logarithm of the rate of polymerization (R_p) and the thermodynamical parameter (ΔG^0), i.e. Marcus plot. The R_p can be easily determined from measuring the heat of polymerization and can be used by a direct comparison of CQ–NPG's polymerization efficiency. *Figure 4* shows examples of typical curves obtained for two different *para*-substituted *N*-phenylglycines. The obtained results for the series of *para*-substituted *N*-phenylglycines, acting as the electron donors in studied CQ–NPG photoinitiator systems, can be fitted to the shape of a parabola (*Figure 5*), which strongly supports the proposed EPT mechanism.

The overall rate of polymerization (R_p) for a process initiated via EPT is finally determined by the redox properties of the electron acceptor and the electron donor, the quantum yield of photoinitiator bleaching being the result of direct free radicals coupling (direct coupling between HA$^\cdot$ and D$^\cdot$ radicals), photoreduction of the electron acceptor resulting from the hydrogen abstraction from the solvent (monomer), and the

Table 1 The structures, oxidation potentials and method of synthesis of tested electron donors:

General formula:



No.	N-substituent R_2	p-substituent R_1	E_{ox} (mV)	ΔG^0 (eV)
1	H	H	426	−0.485
2	H	NC	707	−0.204
3	H	NO_2	781	−0.130
4	H	$H_3C-\overset{\overset{O}{\|}}{C}-$	635	−0.276
5	H	$Ph-\overset{\overset{O}{\|}}{C}-$	661	−0.250
6	H	$EtO-\overset{\overset{O}{\|}}{C}-$	639	−0.276
7	H	Cl	479	−0.432
8	H	CH_3	437	−0.474
9	H	*tert*-But.	436	−0.475
10	H	PhO	479	−0.432
11	H	MeO	343	−0.568
12	Me	H	—	—
13	$-\overset{\overset{O}{\|}}{C}-CH_3$	H	—	—
14	Ph	H	—	—

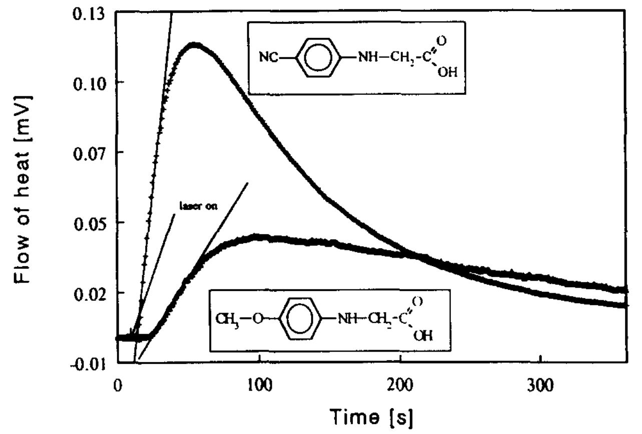


Figure 4 Rate of heat evolution during photoinitiated polymerization of TMPTA-*bis*-EMA mixture in the presence of photoinitiating system CQ–NPG. Type of donor shown in figure

reactivity of the initiating radical [D$^\cdot$][8,62–64]. Substitution of the carboxylic group in NPG by an ester group causes a rapid decreasing polymerization efficiency (*Figure 6*). The Hammett relationship[65,66] for the R_p of the TMPA-*bis*-EMA mixture gives a linear relationship for CQ–NPGs (*Figure 7A*). This observation indicates also that reactivity of the free radicals formed may have an effect on overall rate of polymerization initiated via intermolecular electron transfer process. For CQ–NPG esters there is no observable Marcus parabolic relation for CQ–NPG esters (*Figure 8*) as well as there being no linear Hammett relationship (*Figure 7B*). These results show how the structure of the donor molecule (HD) may influence the polymerization initiating ability of the photoredox pair: CQ–NPGs in the TMPTA-*bis*-EMA mixture.

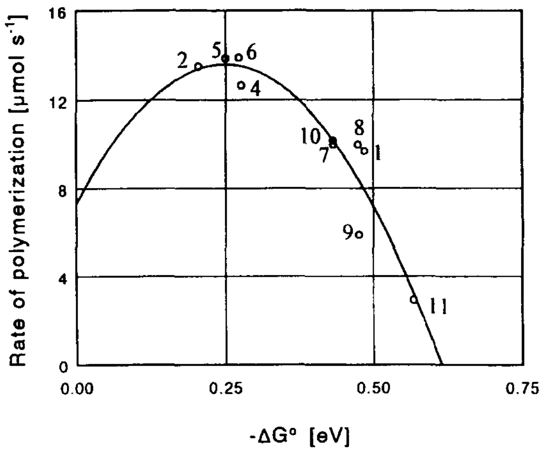


Figure 5 Rate of polymerization as a function of the free energy of activation (ΔG^0) for photoinitiated system: CQ–NPGs (1/1) (results give the Marcus parabolic relation). Polymerization of TMPTA-*bis*-EMA (1/1) in the presence of photoinitiator: CQ–NPGs (1/1). Numbers indicate the type of donor (*Table 1*)

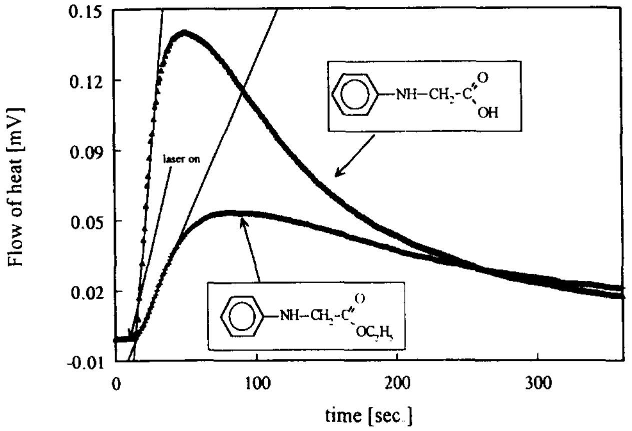


Figure 6 Rate of heat evolution (flow) during photoinitiated polymerization of TMPTA-*bis*-EMA (1/1) in the presence of photoinitiator system: CQ–NPGs. Type of electron donor shown in figure

Interesting properties of CQ–NPGs are observed for one more series of NPGs, N-phenyl-N(H, alkyl, phenyl, acetyl)glycines. The effect of NPG structure on their photoinitiation ability is demonstrated in *Figure 9*. The data clearly show that the structures of NPG derivatives distinctly changes their efficiency as a coinitiator in CQ–NPG initiating systems.

CONCLUSIONS

The new photoinitiating system based on CQ–NPG and its derivatives (especially p-nitro-N-phenylglycine) can be used for replacing widely used photoinitiator CQ–AMs for photocuring of polymeric dental formulations. The most important advantage of this new system is that these amino acids should be biologically less harmful in comparison to amines. However, it is hard to differentiate between the two for dental purposes without detailed studies. The kinetics of photoinitiated polymerization show for the electron–proton transfer occurring via formation 'collision' and 'excited charge-transfer complexes'. The efficiency of polymerization depends on the structure of the hydrogen-donor molecule, and the reactivity of the radicals formed. This new

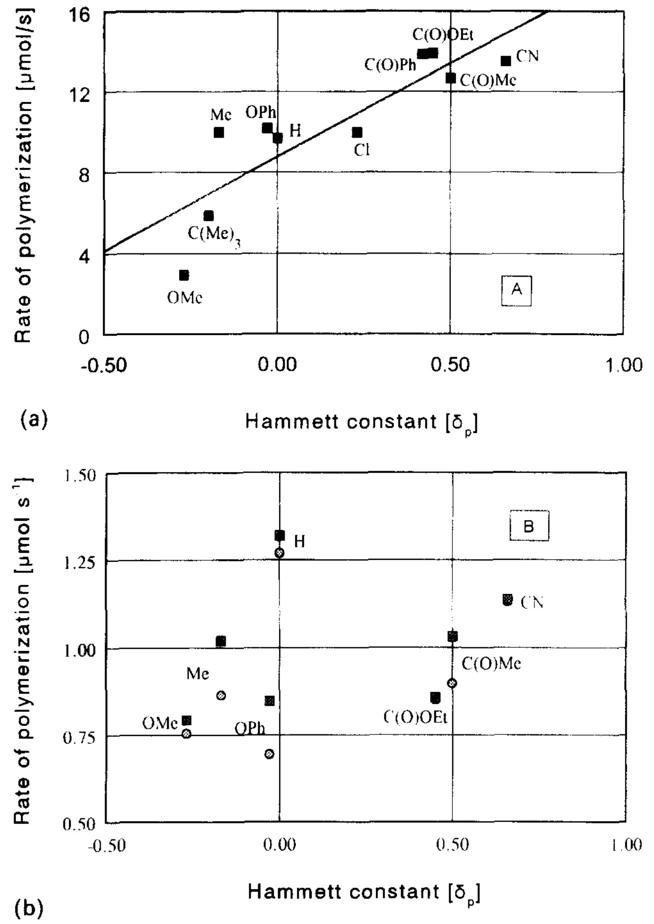


Figure 7 The Hammett relationship for the rates of polymerization of TMPTA-*bis*-EMA (1/1) in the presence of photoinitiator: CQ–NPGs (A) and (B) CQ-esters of NPGs

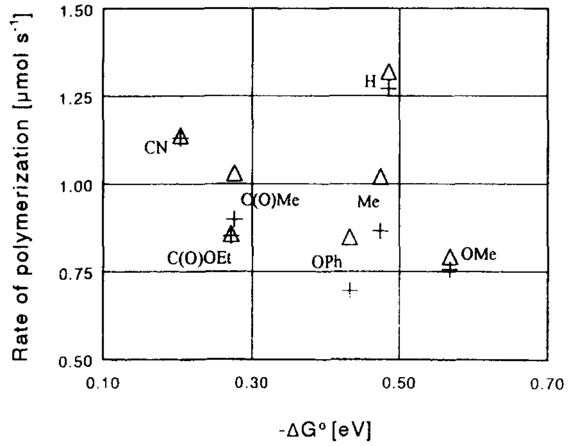


Figure 8 Rate of polymerization of TMPTA-*bis*-EMA (1/1) as a function of the free energy of activation (ΔG^0) for the photoinitiator system: camphorquinone (CQ)–NPG esters

photoinitiating system can also be used for photocuring of stereolithographic (3D) formulations.

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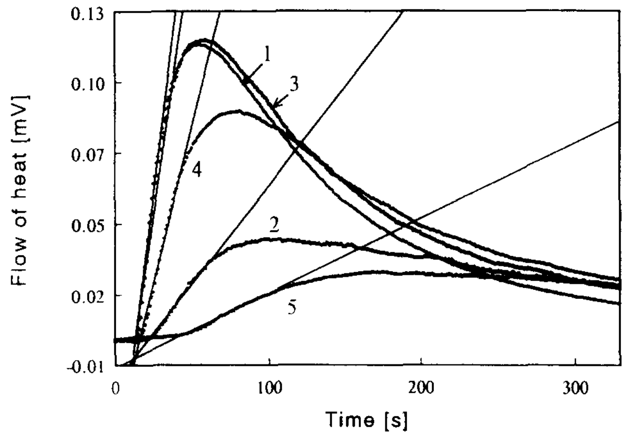

Figure 9 Rate of heat evolution observed during argon-ion laser initiated polymerization of TMPTA-*bis*-EMA mixture (1/1). Absorbing chromophore: CQ, electron donors: (1) NPG, (2) *N*-methyl-*N*-phenylglycine, (3) *N,N*-diphenylglycine, (4) *N*-phenylglycine ester, (5) *N*-acetyl-*N*-phenylglycine

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