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Comparison of the photopolymerization kinetics of triethyleneglycol dimethacrylate initiated by camphorquinone/ *N*-phenylglycine and camphorquinone/D,L-α-phenylglycine

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Summary

This work describes the kinetics of triethyleneglycol dimethacrylate (TEGDM) polymerization, photoinitiated by camphorquinone (CQ) / N-phenylglycine (NPG) and CQ /D,L α-phenylglycine (α-PG), in air and/or in N_2. The rates of polymerization (R_p), double bond conversion (p), monomer conversion (p_{max}), at different concentration of NPG and α-PG were measured and analysed. It was found that CQ/NPG is much more effective photoinitiator system than CQ/α-PG, regarding to the different their chemical structure and H-atom donor ability.

Introduction

Recently several academic and commercial research laboratories try to develop new photocurable dental restorative resins (based on new resin monomer components), or introduce new photoinitiators. Monomers used in dentistry are generally liquids, and during the process of polymerization they become converted to solids (1-10). Thus, to this day the majority of commercial resin composites contain as a photoinitiating system camphorquinone (CQ)/amine (AMH) pairs (9,10). The photoinitiated polymerization is caused by visible light over 400 nm in order to avoid photocancirogenic and photoallergic effects (due to UV irradiation) and the risk of tissue burning (11). The whole procedure is performed *in vivo* in the presence of air, water and saliva (the last two can be technically limited to some extent). The effectiveness of the CQ/AMH systems depends on the H-atom donor ability of amines used as coinitiators. In this paper we have studied a new photoinitiating system based on the CQ/D,L α-phenylglycine (α-PG) and compared it with CQ/N-phenylglycine (NPG). The paper is mainly focused on the kinetics of photopolymerization of triethyleneglycol dimethacrylate (TEGDM) (in air, and nitrogen), and on mechanism of initiation. The TEGDM is a model monomer for the study kinetics of photocuring in the presence of different photoinitiating systems, employed in our labs (11-14).

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Experimental

Camphorquinone (bornanedione, 1,7,7-trimethyl bicyclo(2,2,1)heptane-2,3-dione) (CQ), Aldrich), N-phenylglycine ($C_6H_5NHCH_2COOH$, (NPG)), Aldrich), DL-α-phenylglycine ($C_5H_5CH(NH_2)COOH$, (α-PG), Fluka), and triethyleneglycol dimetacrylate (TEGDM, Fluka) ($CH_2=C-(CH_3)COO[CH_2CH_2O]_3COC(CH_3)=CH_2$) were used as received. The photopolymerization kinetics was monitored by photo-differential scanning calorimetry, using Perkin-Elmer DSC-4 adapted for photochemical measurements. The DSC data obtained were corrected for changes in the base line. A Perkin-Elmer 3600 Data Station was used to read and store data on floppy disks. The polymerization was carried out at a temperature of 40°C (close to the human body temperature of 37°C), in the presence of air or nitrogen. Analytically weighed samples (~20 mg) of the photocurable composition were polymerized in 6.5 mm diameter open aluminium DSC pans. The Philips 500 W lamp (type PF 318 E/49) emitting a visible light from 400 nm wavelength was used for initiation of the polymerization. This type of lamp is equipped with a spherical reflector which gives emitted light at the same intensity over a large surface area. The light intensity measured at the level of the surface of cured samples was 60 mW cm^{-2}.

The polymerization rates (R_p) vs. time were calculated by dividing the peak height dH/dt (expressed in kJ/mol s), at each polymerization point, by the theoretical heat of the reaction, $\Delta H = 56$ kJ/mol per one double bond (calculated for methacrylates (15)). The highest rate of polymerization (R_p^{max}), which corresponds to the reciprocal value of the time it would need to go from 0 to 100 % conversion, at the maximum rate. The double bond conversions (p) were found by integration of the area under the curve of the polymerization rate. Conversion at the time at which the polymerization rate decreased to 0 was taken as the final conversion (p_{max}). Plots R_p *vs* p, give a valuable information on the dependence of R_p^{max} *vs* p.

Results and discussion

The CQ can itself photoinitiate polymerization of different mono- and multi-functional monomers both in air and N2, however, efficiency of this process is low (12-14). The CQ is photoinitiated, under visible light irradiation, to the reactive triplet state CQ^* (11,16). The CQ^* can directly abstract H-atom from a monomer molecule (MH), producing a monomer radical (M•), which may initiate polymerization (11).

$$CQ\ (+h\nu) \rightarrow CQ^* \qquad (1)$$
$$CQ^* + MH \rightarrow CQH\bullet + M\bullet \qquad (2)$$
$$M\bullet + nMH \rightarrow \text{polymerization} \qquad (3)$$

CQ^* with amines (AMH) form much more effective photoinitiating systems, due to the formation of reactive amine radicals (AM•), which initiate polymerization reaction.

$$CQ^* + AMH \rightarrow CQH\bullet + AM\bullet \qquad (4)$$
$$AM\bullet + nMH \rightarrow \text{polymerization} \qquad (5)$$

One of the most effective photoinitiating system is based on the CQ/NPG (17). In this work we have studied another photoinitiating system CQ/α-PG and compared it with CQ/NPG.

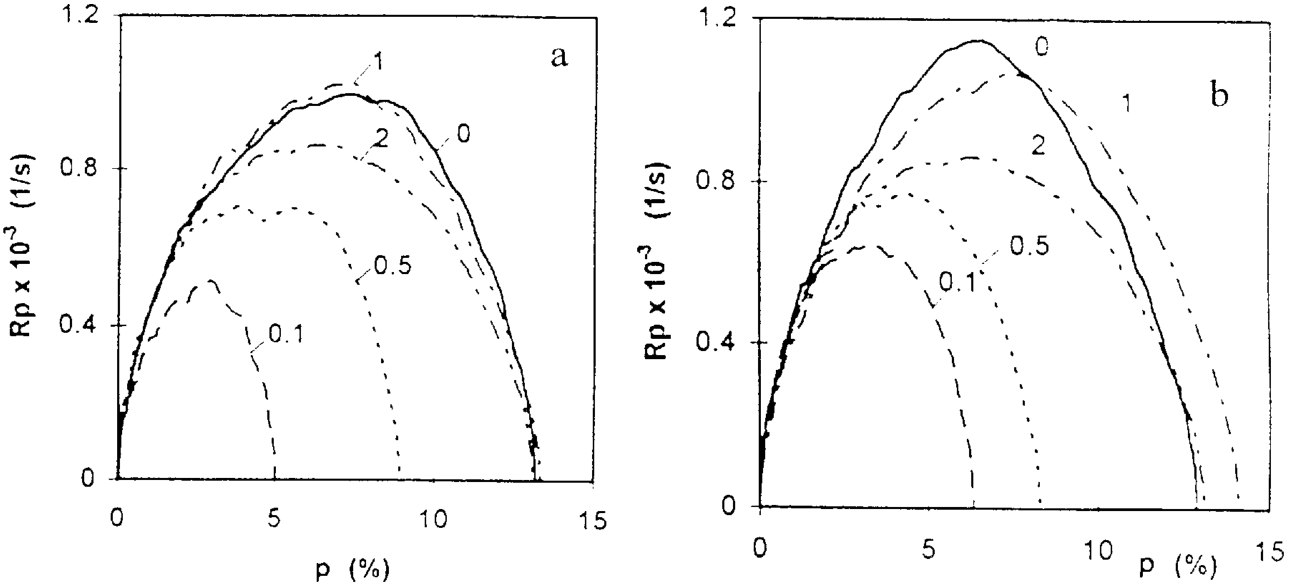

Fig.1. Rate of polymerization (R_p) and double bond conversion (p) of TEGDM photopolymerized at constant CQ concentration (1 wt-%) and different α-PG concentration (0, 0.1, 0.5, 1 and 2 wt-%) in air (a) and in N_2 (b).

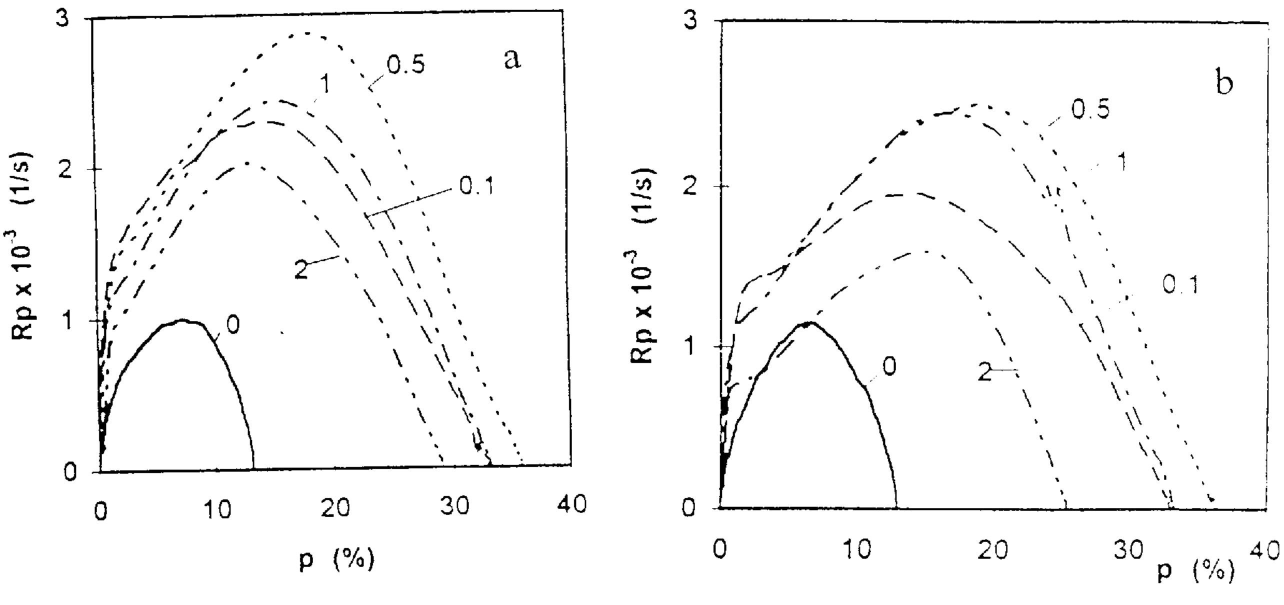

Fig.2. Rate of polymerization (R_p) and double bond conversion (p) of TEGDM photopolymerized at constant CQ concentration (1 wt-%) and different NPG concentration (0, 0.1, 0.5, 1 and 2 wt-%) in air (a) and in N_2 (b).

The TEGDM polymerization was carried out at constant CQ concentration (1 wt-%) and with different concentrations of: α-PG (in air (Fig.1a), and in N_2 (Fig.1b)) and NPG (in air (Fig.2a) and N_2 (Fig.2b)). Increasing of AMH content cause first increasing of rate of polymerization (R_p) and double bond conversion (p), however, later their decreasing. The highest rate of polymerization (R_p^{max}) (Fig.3) and final double bond conversions (p_{max}) (Fig.4) are much higher for the CQ/NPG system (Fig.2) than for CQ/α-PG (Fig.1) and are dependent on the concentration of AMH.

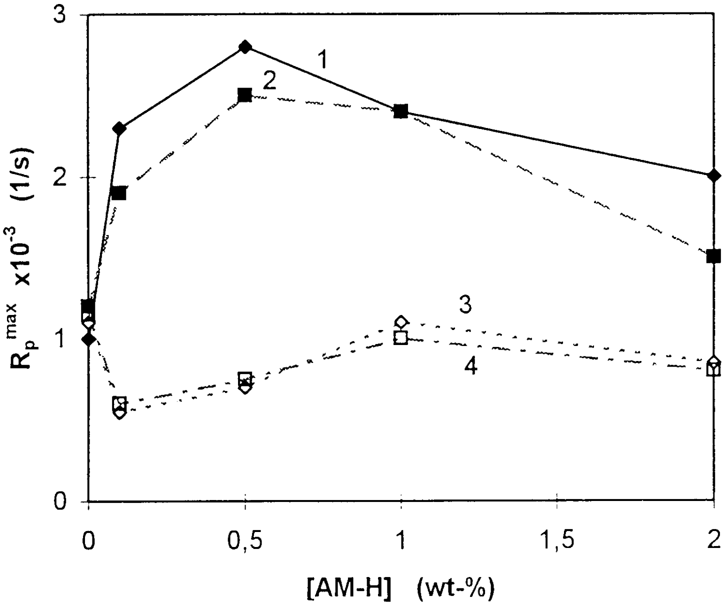

Fig.3. Maximum rate of polymerization (R_p^{max}) of TEGDM *vs.* NPG (1) in air, (2) in N_2, and *vs* α-PG concentration (3) in air, (4) in N_2 at CQ concentration 1 wt-%.

The highest monomer conversions (p_{max}) were obtained : 12-14 % for the CQ (1 wt-%)/α-PG (1 wt-%)(Fig.1 and Fig.4), and 33-35 % for the CQ (1 wt-%)/NPG (0.5 wt-%)(Fig.2 and Fig.4), both in air as well in N_2. Plots R_p *vs* p show that R_p^{max} : for the CQ (1 wt-%)/α-PG (1 wt-%) occurs at 6-8 % of the monomer conversion (p) (Fig. 1), and for the CQ (1 wt-%)/NPG (0.5 wt-%) at 18-20 % p.

Times at which R_p^{max} appears (t_{Rp}^{max}) are much longer for the CQ (1 wt-%)/α-PG (1 wt-%) 450 s, than for the CQ (1 wt-%)/NPG (0.5 wt-%) 120 s (Fig.5). These results indicate that CQ/NPG system is more efficient potoinitiator than CQ/α-PG one.

In spite of oxygen quenching of CQ^* and inhibition effect caused by the reaction of free radicals (R•) formed with O_2, photocuring of TEGDM occurs in the presence of air (12-14). The presence of oxygen may in some cases increase the polymerization rate (13).

The peroxy groups (OOH) formed can undergo CQ-assisted photodecomposition to very reactive oxy radicals (RO•), which may abstract H-atom from a monomer (MH) and increase the observed R_p and p.

$$R\bullet + O_2 \rightarrow RO_2\bullet \text{ (inhibition reaction)} \qquad (6)$$
$$RO_2\bullet + MH \rightarrow ROOH + M\bullet \qquad (7)$$
$$ROOH\ (CQ^*) \rightarrow RO\bullet + \bullet OH \qquad (8)$$
$$R\bullet\ (M\bullet, RO\bullet, etc) + nMH \rightarrow \text{polymerization} \ (9)$$

Probably, all of these competitive reactions cause, that photocuring of TEGDMA by CQ/α-PG and CQ/NPG both in air as well in N_2 occur with a similar kinetics, which is diffusion controlled

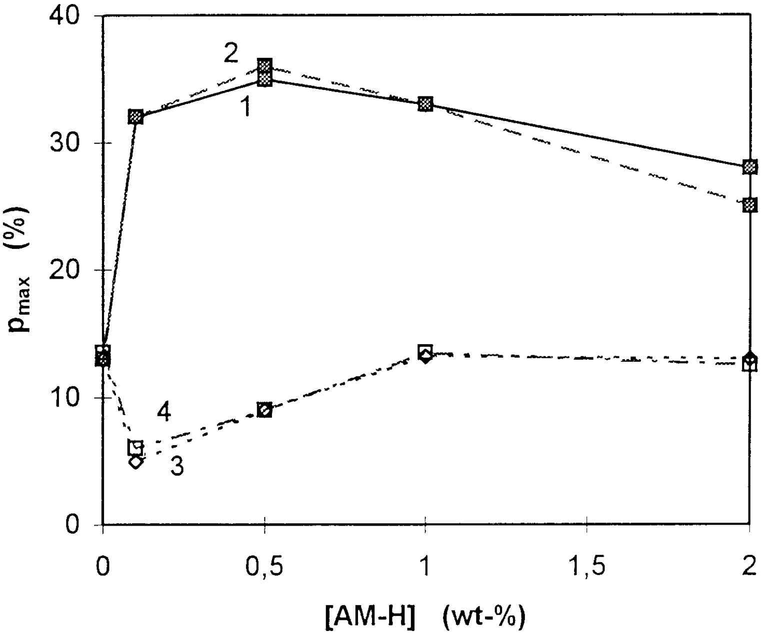

Fig.4. Maximum double bond conversion (p_{max}) of TEGDM *vs.* NPG (1) in air, (2) in N_2, and *vs* α-PG concentration (3) in air, (4) in N_2 at CQ concentration 1 wt-%.

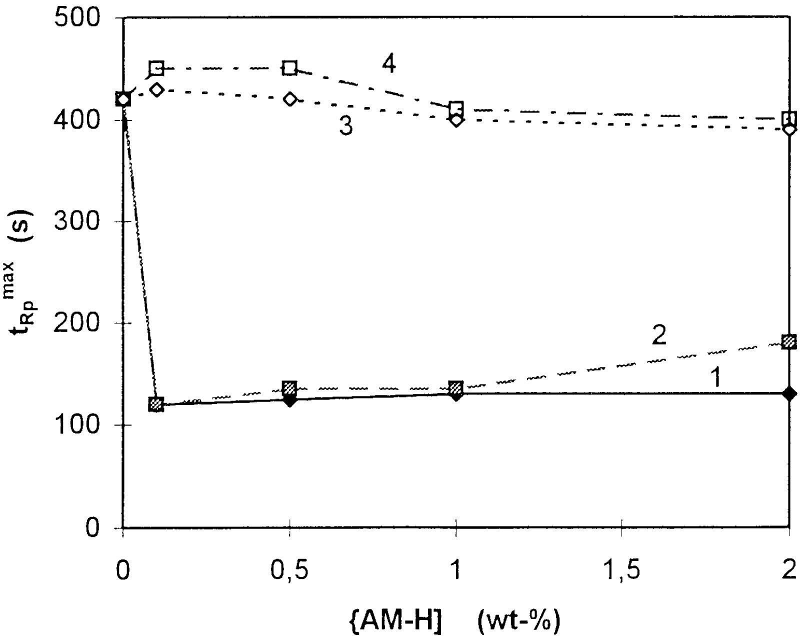

Fig.5. Time at which R_p^{max} appears (t_{Rp}^{max}) of TEGDM vs. NPG (1) in air, (2) in N_2, and *vs* α-PG concentration (3) in air, (4) in N_2 at CQ concentration 1 wt-%.

Effect of AMH concentration on the kinetic of photopolymerization is much complex and has been discussed elsewhere (12). Amines react with CQ^* giving a short lived charge-transfer complex (CTC) (9,10,12).

$$CQ^* + AMH \rightarrow \underset{(CTC)}{[CQ...AMH]^*} \qquad (10)$$

In the CTC state an electron/proton transfer occurs and free radicals (AM•) are formed.

$$CTC \rightarrow CQH\bullet + AM\bullet \qquad (11)$$

Efficiency of this process depends on the AMH structures (geometrical restrictions), ion-pair interactions and delocalization of charge (CTC), donor H-atom ability, and radical (AM•) character. The weaker N-H bond in NPG ($C_6H_5\mathbf{NH}CH_2COOH$) leads to easier proton transfer than in α-PG ($C_5H_5CH(\mathbf{NH_2})COOH$).

The AMH concentration effect on the decreasing R_p and p (Figs 1-4) appears to arise from a higher AMH contribution in the quenching CQ^* (12). This quenching proceeds by charge transfer, perhaps, accompanied by some reversible N-H proton transfer, which decrease amount of the AM• radicals.

Conclusions

It was found that CQ/NPG is much more effective photoinitiator system than CQ/α-PG, regarding to the different their chemical structure. The marked difference in reactivity of CQ^* towards amines, would also arise from the lower ionisation potential NPG than α-PG, and ease of charge transfer from N, followed by proton transfer (18).

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