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ISOTHERMAL PHOTO DIFFERENTIAL SCANNING CALORIMETRY
Crosslinking polymerization of multifunctional monomers in presence of visible light photoinitiators

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Abstract

The effect of photoinitating (camphorquinone/amines) system concentration and sample thickness on the photopolymerization of triethyleneglycol dimethacrylate/2-hydroxypropyl methacrylate has been investigated. The rate of photopolymerization reaches a maximum and then decreases as the concentration of photoinitiating system increases. This effect has been intepreted as inner filter effect.

Keywords: photo-DSC, photoinitiating systems, photopolymerization

Introduction

Photocalorimetry (photo-DSC) has been popular because of the simplicity of the technique and the very short run times used, allowing the study of kinetics and reactivity of photoinitiated polymerization in a short space-time. The kinetic DSC profiles make it possible to compare the rate of polymerization (R_P) of a given monomer in the presence of a photoinitiation system (photoinitiator/coinitiator). The flexibility of photo-DSC allows the investigation of different variables on the photopolymerization such as; structure of monomers and photoinitiators, composition of formulations, irradiation intensity, temperature and effect of atmosphere (inert gases or air (oxygen)). Photo-DSC is a valuable experimental tool that, if used correctly, gives valuable results. However, this technique is very sensitive to a number of experimental variables and sample preparation. Photo-DSC has been widely promoted over the years [1], and has been used for studying kinetics and reactivity of photoinitiated polymerization for dental purposes in our lab [2–10], and by many others [11–16].

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An important consideration in the analysis of the photo-DSC results is the effect of sample thickness on the observed polymerization rate (R_p). This can lead to potentially misleading interpretation of kinetic results from photo-DSC obtained for thin films (μm) if they are applied for thicker layers (mm).

The subject of this work was to use photo-DSC to study kinetics of photopolymerization of difunctional monomer triethyleneglycol dimethacrylate (TEGDMA) as a function of concentration of different photoinitiation systems, absorption of light and light intensity.

Experimental

Camphorquinone (bornanedione, 1,7,7-trimethyl bicyclo [2.2.1] heptane-2,3-dione) (photoinitiator) (CQ, Aldrich) with different amines (coinitiators) such as: N,N-dimethyl-*p*-toluidine (AH1, Aldrich), ethyl 4-dimethylamino benzoate (AH2, Aldrich), 4-dimethylamino benzophenone (AH3, Aldrich) and 4,4′-bis(diethylamino) benzophenone (AH4, Aldrich) have been chosen as photoinitiating systems. Selection of these most effective coinitiator-amines (AH1-AH4) was made from investigation of more than twenty other aromatic amines in a separate study [17]. Photopolymerization kinetics was studied with difunctional triethyleneglycol dimethacrylate monomer (TEGDMA, Fluka) as model system. The main problem in this investigation was low solubility of powdered amines (AH2, AH3 and AH4) in TEGDMA at higher concentrations. CQ and amine AH1 (liquid) are, however, well dissolved in TEGDMA. In order to increase solubility of solid amines, monofunctional monomer 2-hydroxypropyl methacrylate (HPMA, Aldrich) has been used, which is a good solvent for these amines. All photopolymerization kinetics has been studied using a mixture of TEGDMA with HPMA in the mass ratio 9:1. This allows the preparation of CQ+AH mixtures with monomers in a wide range of different concentrations.

For practical reasons and for application of these results in dental restorative materials: 1. All components have been used as delivered, 2. All kinetic measurements were carried out in air, 3. The concentration of components in a given formulation has been given in mass%.

In order to study the polymerization kinetics the rate of polymerization (R_p), maximum rate of polymerization (R_p^{max}), time to reach the maximum rate of polymerization (t_{max}), were monitored by a differential scanning calorimeter (Perkin-Elmer DSC-4) adapted for photochemical measurements.

The rate of polymerization (R_p) has been calculated from the isothermal photo-DSC measurements by dividing the heat of polymerization dH/dt (kJ mol^{-1} s^{-1}), at each polymerization point, by the theoretical heat of the reaction ΔH_o (kJ mol^{-1}) (based on full conversion of the monomer). The reaction rates *vs.* time were calculated by dividing the peak height dH/dt (expressed in kJ mol^{-1} s^{-1}), at each polymerization point, by the theoretical heat of the reaction, ΔH_o=56 kJ mol^{-1} per one double bond (calculated for methacrylates) [18–20], according to the relation:

$$R_p=(\mathrm{d}H/\mathrm{d}t)\ 1/\Delta H_o m \qquad (1)$$

where *m* is the sample mass (mg). The polymerization was carried out at a temperature of 40±0.01°C (close to the human oral temperature 37°C).

A Philips 500 W lamp (type PF 318 E/49) emitting visible light from 400 nm was used for the initiation of the polymerization. This type of lamp is equipped with a spherical reflector, which gives the emitted light the same intensity over a large surface area. The light intensity was measured with EG&G photometer, model 550-1 equipped with a monochromator. Photopolymerization was also performed at various light intensities using neutral-density step filters (Melles Griot).

The absorbance measurements were carried out on a Beckman DU 7500 spectrophotometer.

Results and discussion

The kinetics of photopolymerization depends on many factors such as choice of photoinitiator, its concentration, the composition of the formulation and functionality of monomers used. It is furthermore affected by various physical factors such as light intensity and wavelength, the thickness of the sample, temperature etc. [21, 22]. The photo-DSC allows from the recorded kinetic profiles, rapidly and quantitatively evaluate the influence of those factors on the polymerization rate (R_p), the inhibition time (t_{inh}), and the double bond conversion (p). The R_p at any time of the reaction (t) is given by equation:

$$R_p = -\mathrm{d[M]/dt} \quad (\mathrm{M\ s^{-1}}) \tag{2}$$

where [M] is the monomer concentration. In Fig. 1, R_p is plotted *vs.* time of irradiation and in dependence on the photoinitiator system (CQ+AH) for TEGDMA/HPMA in the mass ratio 9:1. The results shown in Fig. 1 indicate, that the effectiveness of the CQ+AH photoinitiating systems differ in TEGDMA/HPMA in order: AH4>AH3>AH2>AH1. t_{max} at R_p^{max} is the same for all AH studied and it was 23 s from the point of light ON. R_p^{max} is very much dependent on the ratio of CQ:AH. Increasing AH content causes decreasing R_p^{max} (Fig. 2) for two reasons:

- excess of AH quenches the triplet state of CQ,
- excess of AH acts as retarder for polymerization by trapping initiating radicals and by termination reactions.

The highest R_p^{max} were obtained at the concentration of [CQ] 1 mass% and [AH] 0.2 mass%. Increasing [AH] causes decreasing R_p^{max} (Fig. 2). With increasing [AH]>1.0–1.8 mass%, depending on the amine, polymerization reactions do not occur.

It has been found that as the concentration of photoinitiating system (CQ+AH at a given ratio) increases, R_p reaches a maximum and then decreases (Fig. 3). The highest R_p^{max} has been obtained at 1 mass% of CQ+AH (10:1). Further increasing CQ+AH concentration to 3 mass% causes rapid decreasing of R_p^{max}. At CQ+AH concentration 5 mass% polymerization almost does not occur. The time of irradiation (t_{max}) at which

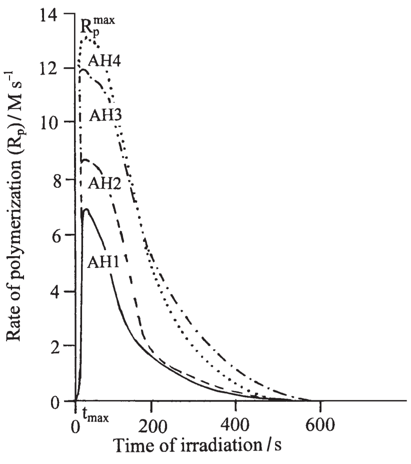

Fig. 1 Rate of polymerization (R_p) of TEGDMA/HPMA (9:1) photopolymerized in the presence of CQ (1 mass%) and different AH (0.2 mass%):
AH1 (R_p^{max}=7.28 M s^{-1}, t_{max}=22.9 s); AH2 (R_p^{max}=8.7 M s^{-1}, t_{max}=21.4 s);
AH3 (R_p^{max}=11.9 M s^{-1}, t_{max}=22.8 s); AH4 (R_p^{max}=13.09 M s^{-1}, t_{max}=23.01 s)

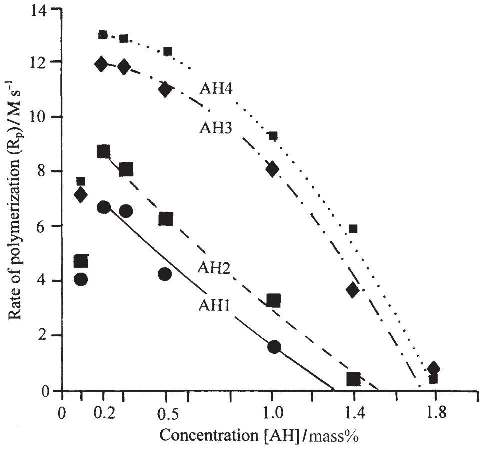

Fig. 2 Maximum rate of polymerization (R_p^{max}) of TEGDMA/HPMA (9:1) photopolymerized at constant CQ concentration (1 mass%) and different AH concentrations (0.1. 0.2, 0.3, 0.5, 1.0, 1.4 and 1.8 mass%)

R_p^{max} appears, gradually shifts with the decreasing concentration of a given photoinitiating system (CQ+AH) content.

Photoinitiating systems with higher extinction coefficients (ε_{CQ}+ε_{AH}) at the principal wavelength of the light have rised to optimum concentrations at lower initiator levels. It should therefore be possible to predict the appropriate initiator concentration for a particular film thickness.

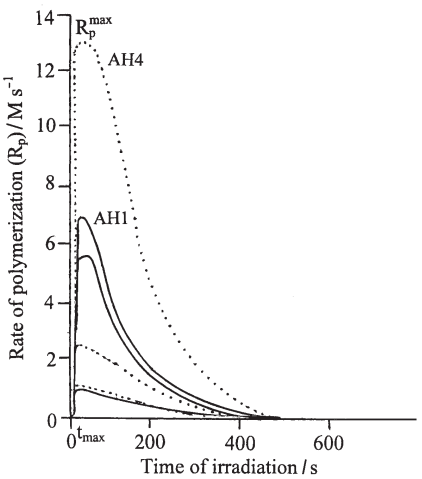

Fig. 3 Rate of polymerization (R_p) of TEGDMA/HPMA (9:1) photopolymerized in the presence photoinitiator system (CQ (1 mass%)+AH (0.2 mass%)), at different mass%: — 1 mass % (CQ+AH1) (R_p^{max}=7.28 M s^{-1}, t_{max}=22.9 s), ···· 3 mass% (CQ+AH1) (R_p^{max}=5.51 M s^{-1}, t_{max}=17.46 s, 5 mass% (CQ+AH1) (R_p^{max}=0.906 M s^{-1}, $t_{max=}$9 s) and 1 mass% (CQ+AH4) (R_p^{max}=13.09 M s^{-1}, t_{max}=23.01 s), 3 mass% (CQ+AH4) (R_p^{max}=2.6 M s^{-1}, t_{max}=24.5 s), 5 mass% (CQ+AH4) (R_p^{max}=1.3 M s^{-1}, t_{max}=23.14 s)

The effect caused by excessive levels of light absorbing photoinitiating system is well known and has been termed 'the inner filter effect' [23–27]. This is where the light of any or all wavelengths fails to reach the base of a sample because the molecules near the surface and/or in deeper layers absorb most of it. The effect of light screening results in a loss of the polymerization rate, and presence of unpolymerized monomer in the photocured sample.

Increasing the photoinitiating system concentration over 1 mass% may lead to self-screening. Self-screening that occurs in the samples also shows itself as an exotherm distortion. Here, the normally symmetrical exotherm is distorted to show a steep leading edge (indicative for very fast polymerization on the sample surface), and a long tailing back edge (indicating a low probability of a light absorption by the photoinitiator near the bottom of the sample).

The rate of photoinitation of polymerization (R_i) depends on: the number of photons absorbed by the photoinitiator (CQ), the quantum yield (Φ_i) of reactive aminyl radicals (A•) produced in the reaction (4), and the reactivity of the radicals A• with the monomer (M) molecule [10]:

$$CQ \xrightarrow{hv} CQ^* \tag{3}$$

$$CQ^*+AH \rightarrow CQH+A\bullet \tag{4}$$

$$A\bullet+M \rightarrow \text{polymerization} \tag{5}$$

The intensity of light reaching a depth (x) decreases exponentially and is given by the equation:

$$I_x=I_o(1-\exp(-2.303\varepsilon[\mathrm{CQ}]x) \qquad (6)$$

where I_o is the intensity of incident light and ε is the molar extinction of CQ. The difference in I_x/I_o is not extreme for lower photoinitiating system concentrations and/or thinner samples (1–10 μ). The R_p observed by photo-DSC, however, is the average rate for the entire sample, limiting the comparison of rates to approximately equal sample sizes and reduces effects introduced by the size of the sample. The rate of polymerization (R_p) is given by equation [28]:

$$R_p=k_p/k_t^{0.5}[\mathrm{M}](\Phi I_o(1-\exp(-2.303\varepsilon[\mathrm{CQ}]x))^{0..5} \qquad (7)$$

where k_p and k_t are rate constants of propagation and termination of polymerization. In Fig. 4, $R_p^{\max}$ taken from Fig. 3 has been plotted *vs.* the square root of the fraction of the absorbed light $(1-\exp(-2.303\varepsilon[\mathrm{CQ}]d)^{0..5})$ at an average $d\approx10$ μm. According to Eq. (7) the plots in Fig. 4 show a reasonable linear relationship as expected.

The change in light intensity through a layer at depth x, $-\mathrm{d}I_x/\mathrm{d}x$, gives the rate of light absorption in the layer according to the relations [28]:

$$R_x=-\mathrm{d}I_x/\mathrm{d}x=I_x 2.303\varepsilon[\mathrm{CQ}] \qquad (8)$$

or

$$R_x=I_o(1-\exp(-2.303\varepsilon_I[\mathrm{CQ}]x)2.303\varepsilon_I[\mathrm{CQ}] \qquad (9)$$

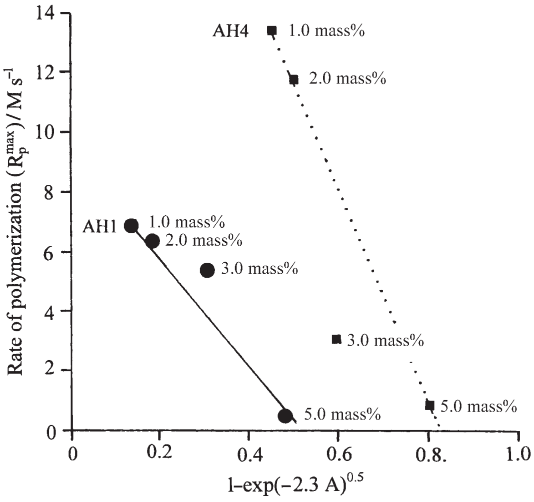

Fig. 4 Maximum rate of polymerization ($R_p^{\max}$) of TEGDMA/HPMA (9:1) photopolymerized in the presence photoinitiator system (CQ (1 mass%)+AH (0.2 mass%)), at different mass%: AH1 and AH4 *vs.* the fraction of incident light absorbed ($R_p^{\max}$ data taken from Fig. 3)

Since R_p depends on the light intensity (I_o) the thickness of the sample (x) will obviously affect the observed rate of polymerization (R_p). Increase in light intensity causes an increase in the rate of initiator decomposition, radical formation, chain initiation and the maximum of the double bonds conversion (p_{max}), respectively.

If the photoinitiation of polymerization is theoretically proportional to the square root of the light intensity (I_o), the rate of polymerization (R_p) in a layer at depth x is proportional to $R_x^{1/2}$. The observed rate of polymerization R_x^{obs} is then proportional to this quantity averaged over the total depth of photocuring (x) according to [28]:

$$R_p^{obs}=x^{-1}\int_0^x R_x^{0.5}dx \tag{10}$$

R_x^{obs} values calculated show higher rates for thinner samples, e.g. for x=4 μ (CQ+AH1), R_x^{obs}=6.8 M s^{-1} in comparison to R_x^{max}=4.8 M s^{-1}.

It is obvious from Eq. A, that R_p is proportional to the square root of the intensity of the incident light. A low photoinitiating system (CQ+AH1) concentration (1 mass%) was chosen in order to keep the optical absorbance of CQ, which is a necessary condition to apply Eq. (7). The plot R_x^{max} *vs.* light intensity in Fig. 5 shows a linear relationship.

The influence of air oxygen (in air) on the kinetics of photopolymerization of TEGDMA has been thoroughly investigated by our group elsewhere [3, 5, 7]. The presence of oxygen leads to an induction period before polymerization takes place, because oxygen biradical (•O–O•) reacts very rapidly with photogenerated free radicals.

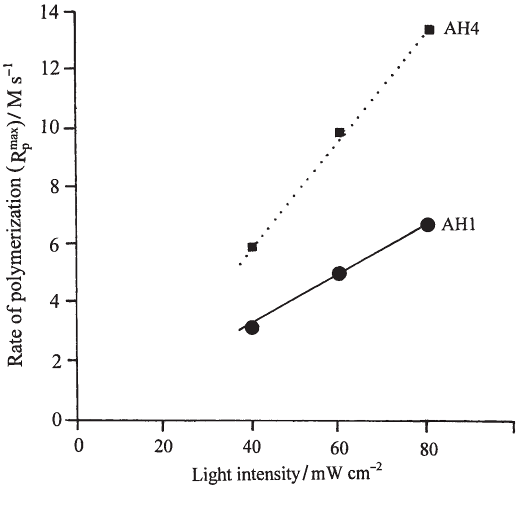

Fig. 5 Rate of polymerization (R_P) of TEGDMA/HPMA (9:1) photopolymerized in the presence photoinitiator system (CQ (1 mass%)+AH (0.2 mass%)) at 1 mass% *vs.* square root of the intensity of the incident light

Conclusions

An optimum of the photoinitiating system (CQ+AH) content and concentration corresponding to a maximum extent of the rate of polymerization (R_x^{max}) can be experimentally determined. From such studies it should be possible to predict the most appropriate level of photoinitiating system for a particular film thickness of a given dental polymer restorative resin.

The depth of photocuring is a very important problem in the dental clinical situation [29]. At thicker layers, the photopolymerization cannot be completed and after the curing procedure presence of unpolymerized monomer in the photocured filling may occur. The thickness of a dental resin restorative used for clinical photocuring depends on the dentist standpoint. However, photocuring in a tooth cavity occurs under non-isothermal conditions and depends on many factors, which are almost impossible to be controlled by the dentist. If the restoration shape and thickness vary greatly in the tooth cavity, and the photopolymerization is not made correctly, several serious problems may appear. The most troublesome are; unreacted monomers in cured restoration layer, strong differences in the mechanical properties, and problems with as shrinkage and stress [30]. Nevertheless, correct photocuring conditions can hardly be obtained easily and are difficultly controlled even by the experienced dentists.

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