Photopolymerization kinetics of dimethacrylates using the camphorquinone/amine initiator system

Wayne D. Cook
Therapeutic Devices Branch, Department of Health, 240 Langridge Street, Abbotsford, Victoria, Australia 3067
(Received 14 December 1990; revised 21 February 1991; accepted 28 February 1991)

The kinetics of photopolymerization of dimethacrylates with the camphorquinone (CQ)/amine pair has been studied by isothermal d.s.c. and u.v.-vis. spectroscopy. In accordance with the proposed initiation mechanism of electron and proton transfer from the amine to the triplet CQ ketone, only amines with an abstractable proton on the α-carbon undergo significant rates of polymerization. However, in contrast to other studies of exciplex formation from triplet state ketones and quenchers, only a poor correlation was observed between the rate of radical formation (measured in terms of the maximum polymerization rate) and ionization potential. In general, the efficiency of amines in enhancing initiation was: tertiary > secondary > primary amine. A kinetic scheme for CQ consumption and radical formation was in satisfactory agreement with the experimentally observed rate dependence on the radiation intensity and on the CQ and amine concentrations. For low amine concentrations, the polymerization rate had a half order dependence on concentration, but at intermediate levels, the rate was independent of amine concentration. The polymerization was slightly retarded at high amine concentrations. The influence of CQ concentration and radiation intensity on the polymerization rate generally fitted the theoretical half power relationship, however evidence for primary radical termination and pseudo first-order termination was found at high and low initiation rates, respectively.

(Keywords: photopolymerization; camphorquinone; d.s.c.; dimethacrylates; kinetics; exciplex formation; dental materials)

INTRODUCTION

The technique of photopolymerization has become increasingly common in the last two decades[1,2]. This mode of initiation has found applications in a wide range of areas such as microlithography techniques applied to integrated chip design or to the technique of stereolithography used to fabricate complex three-dimensional shapes. Since the 1960s, the photopolymerization of dimethacrylate resins has found wide application in the dental field, including dental composite resins, adhesives, dentures and impression materials. The initiator system is invariably the camphorquinone (CQ)/amine couple which produces free radicals on exposure to 450–500 nm radiation. The efficiency of this system affects clinically important properties such as the overall rate of polymerization, the depth of cure and the thickness of the oxygen-inhibited layer. Despite the technological importance of this photoinitiator system, there have been few studies of the kinetics of the process.

In this work, the mechanism of the photoinitiation step is investigated by spectroscopic studies of the CQ consumption and by studies of the dependence of the maximum polymerization rate on amine chemistry and concentration. The influence of photoinitiator concentration and radiation intensity on the rate of polymerization of diethoxylated bisphenol-A-dimethacrylate (DEBPADMA) was then examined over the whole conversion range by isothermal d.s.c.

EXPERIMENTAL

The dimethacrylate resins studied (*Table 1*) were triethylene glycol dimethacrylate (TEGDMA, supplied by Esschem Co., USA), bisphenol-A-bis(glycidylmethacrylate) (bisGMA, supplied under the name Nupol by Freeman Chemical Corporation, USA), DEBPADMA (supplied under the name of Alcocure EBDMA by Alcolac Inc., USA) and tridecaethylene glycol dimethacrylate (TDEGDMA, supplied as SR-252 by Santomer Co., USA). Analysis of the concentration of methacrylate groups in the resins by the morpholine method[3] yielded the following molecular weights for the resins: TEGDMA, 285 (cf. theoretical 286), bisGMA, 530 (cf. 512 theoretical) and DEBPADMA, 471 (cf. 452). For some studies, these resins were purified by double extraction of a $CHCl_3$ solution with 10% Na_2CO_3 solution, with 0.5 N HCl and with water, followed by column chromatography through activated Al_2O_3, drying and solvent stripping under vacuum. All other

Table 1 Structure of the dimethacrylate resins

Code	Structure
TEGDMA	$CH_2{=}C(CH_3)COO(CH_2CH_2O)_3COC(CH_3){=}CH_2$
BisGMA	$[CH_2{=}C(CH_3)COOCH_2CH(OH)CH_2OC_6H_4]_2C(CH_3)_2$
DEBPADMA	$[CH_2{=}C(CH_3)COOCH_2CH_2OC_6H_4]_2C(CH_3)_2$
TDEGDMA	$CH_2{=}C(CH_3)COO(CH_2CH_2O)_{13}COC(CH_3){=}CH_2$

0032-3861/92/030600-10

materials were reagent grade materials. For standard formulations, the resins contained 0.25 wt% CQ and 0.30 wt% amine—in other studies the concentrations of CQ and amine were varied in the range 0–2 and 0–6 wt%, respectively.

For most studies, photopolymerization was initiated with a Visilux-2 dental photocuring source (3M, USA). This source consisted of a 75 W tungsten halogen lamp, a series of optical filters and lenses and a fused fibre optic light-guide with a 7 mm exit window. The spectral characteristics of the source are similar to those described elsewhere[4]. The unit emitted radiation predominantly in the 450–500 nm range and had a spectral radiant emittance of 7.3 mW cm^{-2} nm^{-1} at 470 nm (the wavelength of maximum absorbance for CQ). For spectroscopic studies, an alternative source was used; the 150 W Luxor photocuring source (ICI, UK) produced radiation predominantly in the 450–500 nm range[4] and had a spectral radiant emittance of 6.0 mW cm^{-2} nm^{-1} at 470 nm.

Photopolymerization kinetics were monitored with a DSC7 differential scanning calorimeter (Perkin Elmer, USA). As discussed elsewhere[5], this instrument was modified to allow for irradiation of the sample and reference pans by use of a bifurcated fibre optic lead, thus minimizing the thermal heating effect of the source. At high radiation intensities, this technique did not fully eliminate the thermal effect of the source—in these cases, the isothermal run was repeated on the 'fully cured' sample and the data subtracted from the first run.

The output of the Visilux-2 photocuring source was found to decrease by 16% during operation. Since the majority of this variation (11%) occurred within the first 30 s, a shutter was used to delay the irradiation of the d.s.c. pans until 30 s after the source had been activated. Neutral density filters were used to vary the intensity of the radiation at the base of the d.s.c. pan from its unattenuated value of 1.88 mW cm^{-2} nm^{-1} at 470 nm. For simplicity, the radiation intensities quoted are expressed as a relative intensity (I_{rel}), which is the ratio of the irradiance at 470 nm to that delivered by the unattenuated source at the base of the pan.

Approximately 10 mg (± 1 mg) of material was spread as a thin layer (≈ 0.6 mm) over the base of the 4.5 mm diameter aluminium d.s.c. pan. Since the decadic molar absorption coefficient[6] of CQ is $\sim 3.8 \times 10^4$ cm^2 mol^{-1}, films of this thickness with the standard concentration of CQ resulted in $<8\%$ variation in radiation intensity across the film. However, for the maximum CQ level of 2.0 wt%, the radiation was attenuated by up to 47% across the film thickness.

To minimize the effect of dissolved oxygen on the polymerization kinetics, all samples were equilibrated in the d.s.c. under a flow of N_2. On the basis of experiments using longer purge times, a 10 min N_2 purge was sufficient for the studies presented here. All d.s.c. photopolymerizations were performed at 50°C.

The kinetics of CQ consumption were studied at 23°C with u.v.-vis. spectroscopy. To minimize the effect of thickness on the radiation homogeneity, cells were fabricated from glass slides and polysiloxane rubber spacers, and had pathlengths varying from 0.8 to 2 mm. The solution of CQ in resin or solvent was placed in the sealed cell and was evenly irradiated with a photocuring source. The relative radiation intensity (relative to the unattenuated intensity of the Visilux-2 source at the base of the d.s.c. pan) was 0.74. Due to the difficulties in purging oxygen from viscous resins, no attempt was made to degas the samples in these studies. However, shortly after the irradiation had commenced, any dissolved oxygen should have been consumed in side reactions[7], leaving the subsequent kinetics unaffected. U.v.-vis. spectra were collected at varying time intervals and were later analysed by measuring the absorbance at 470 nm above the baseline.

RESULTS AND DISCUSSION

The photochemistry of ketones[8,9] and their use as photo-initiators has been extensively studied[10,11]. As discussed by Ledwith[10,11], initiation of the polymerization may result from hydrogen atom abstraction from a substrate (typically monomer) by the excited ketone or may be due to an electron transfer reaction from a donor molecule to the excited ketone (in an excited complex or exciplex), followed by a proton transfer. The formation of an excited complex from a ground-state complex of the ketone with the amine has also been suggested[12]. In the present work, the u.v.-vis. spectra of CQ, *N*,*N*,3,5-tetramethyl aniline (TMA, one of the most effective amine co-initiators) and their mixtures were found to be additive, thus discounting this latter mechanism for the CQ/amine system. Although the photoreduction of CQ with alcohols and alkyl substrates has been described[8,13], little has been published on the photochemistry of CQ in the presence of amines. However, it seems reasonable to expect that the mechanism would be similar to that occurring in the reaction of amines with excited aromatic[10,11,14] and aliphatic[15] ketones. In these systems, the absorption of one quantum of radiation promotes the carbonyl group to an excited singlet state. This excited state may return to the ground state by fluorescence or a radiationless transition (such as internal or external conversion) or it may decompose to another species. The excited singlet may also undergo intersystem crossing to the triplet state. The excited triplet (acting as the electron acceptor) then forms an exciplex with the readily reduced amine (acting as the electron donor) by charge transfer from the nitrogen lone pair to the carbonyl, thus producing two radical ions. In some cases, this charge transfer complex may be deactivated to the starting species or may form a degradation product. However, if proton abstraction at the position α to the nitrogen occurs, then two free radicals are formed. It is generally considered that the amine radical is responsible for initiating the polymerization and that the radical formed from the ketone is not an efficient initiator[2] and dimerizes[11].

Based on the above mechanism, a simple kinetic scheme for the photo-induced reaction the CQ ketone (CQ–C=O) with an amine possessing abstractable α hydrogen atoms (RR′NCHR″R‴) is given as:

$$\mathrm{CQ{-}C{=}O} \underset{k_1}{\overset{h\nu}{\rightleftharpoons}} \mathrm{CQ{-}C{=}O^*(S)} \tag{1}$$

$$\mathrm{CQ{-}C{=}O^*(S)} \xrightarrow{k_2} \mathrm{CQ{-}C{=}O^*(T)} \tag{2}$$

$$\mathrm{CQ{-}C{=}O^*(T)} \xrightarrow{(1-\alpha)k_3} \mathrm{CQ{-}C{=}O} \tag{3a}$$

$$\mathrm{CQ{-}C{=}O^*(T)} \xrightarrow{\alpha k_3} \text{degradation products} \tag{3b}$$

$$\mathrm{CQ{-}C{=}O^*(T) + RR'NCHR''R'''} \xrightarrow{k_a} [\mathrm{CQ{-}\dot{C}{-}O^-\cdot N^+(CHR''R''')RR'}] \xrightarrow{\beta} \mathrm{CQ{-}\dot{C}{-}OH + RR'N\dot{C}R''R'''} \tag{4a}$$

$$\mathrm{CQ{-}C{=}O^*(T) + RR'NCHR''R'''} \xrightarrow{k_a} [\mathrm{CQ{-}\dot{C}{-}O^-\cdot N^+(CHR''R''')RR'}] \xrightarrow{(1-\beta-\gamma)} \text{degradation products} \tag{4b}$$

$$\mathrm{CQ{-}C{=}O^*(T) + RR'NCHR''R'''} \xrightarrow{k_a} [\mathrm{CQ{-}\dot{C}{-}O^-\cdot N^+(CHR''R''')RR'}] \xrightarrow{\gamma} \mathrm{CQ{-}C{=}O + RR'NCHR''R'''} \tag{4c}$$

where k_1 is the rate constant for deactivation of the excited singlet, k_2 is the rate constant for intersystem crossing of the excited singlet to triplet state, k_3 is the rate constant for deactivation or degradation of the triplet and k_a is the rate constant for exciplex formation. The term α is related to the fraction of the CQ triplet state molecules which form degradation products via equation (3a), while β and γ are the fractions of the exciplex species which form free radicals or are deactivated to the ground state, respectively. Thus in the above equations, the fluorescence and radiationless deactivation of the excited CQ singlet are shown in equation (1), the phosphorescence of the triplet state and quenching of the triplet to the ground state are represented in equation (3a) and the loss of the triplet state CQ to degradation products is shown in equation (3b). The deactivation of the exciplex to the ground state is shown in equation (4c), while the formation of radicals or degradation products from the exciplex are shown in equations (4a) and (4b), respectively.

The lifetimes of excited singlet states are normally very short[9] so that the concentration of CQ–C=O*(S) should be low. Since the transition from the singlet to the triplet state is spin forbidden, k_2 should be small and so the concentration of the excited triplet should also be low. If one assumes that the concentrations of the excited singlet and triplet states are low and unchanging (the steady state assumption) then we have:

$$\begin{aligned} &\mathrm{d[CQ{-}C{=}O^*(S)]/d}t \\ &\quad = 2.303 I_0 \varepsilon_{\mathrm{CQ}}[\mathrm{CQ}] - (k_1 + k_2)[\mathrm{CQ{-}C{=}O^*(S)}] \\ &\quad = 0 \end{aligned} \tag{5}$$

$$\begin{aligned} &\mathrm{d[CQ{-}C{=}O^*(T)]/d}t \\ &\quad = k_2[\mathrm{CQ{-}C{=}O^*(S)}] \\ &\qquad - (k_3 + k_a[\mathrm{A}])[\mathrm{CQ{-}C{=}O^*(T)}] \\ &\quad = 0 \end{aligned} \tag{6}$$

where I_0 is the radiation intensity (assumed to be unattenuated by the resin), $\varepsilon_{\mathrm{CQ}}$ is the decadic molar absorption coefficient of CQ and [A] is the amine concentration. The rate of radical formation can then be written as:

$$\begin{aligned} \mathrm{R_i} &= \beta k_a[\mathrm{A}][\mathrm{CQ{-}C{=}O^*(T)}] \\ &= 2.303\beta k_a k_2[\mathrm{A}] I_0 \varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]/\{(k_1 + k_2)(k_3 + k_a[\mathrm{A}])\} \\ &= 2.303\beta k_a k_2[\mathrm{A}] I_0 \varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]/\{k'k_3 + k'k_a[\mathrm{A}]\} \end{aligned} \tag{7}$$

where k' is $(k_1 + k_2)$. The term, $2.303 I_0 \varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]$, in this equation represents the rate at which the radiation is absorbed by the CQ. The ratio of rate constants k_2/k' is the yield of triplet species from the excited singlet state. The efficiency of intersystem crossing from the excited singlet to the triplet state of CQ is believed[13] to be near unity, implying that $k_2 \gg k_1$. Since the term $\beta k_a[\mathrm{A}]/(k_3 + k_a[\mathrm{A}])$ is the yield of radicals formed from the CQ excited triplet state, $\beta k_a k_2[\mathrm{A}]/\{k'(k_3 + k_a[\mathrm{A}])\}$ is the fraction of radicals formed from the excited singlet molecules. Equation (7) has two limiting cases. At low [A], the rate of radical formation is $2.303\beta k_a k_2[\mathrm{A}] I_0 \varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]/k_3 k'$ and so is dependent on the amine concentration and reactivity (through the factors β and k_a). However, at high concentrations of amine, the rate of radical formation approaches $2.303\beta k_2 I_0 \varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]/k'$ which is independent of amine concentration and only depends on the amine reactivity through the term β.

It should be noted that equation (7) strictly applies to monochromatic radiation, and that for polychromatic sources the term $I_0\varepsilon_{\mathrm{CQ}}$ should be replaced by the integral term[4] $\int_{400}^{550} I_0(\lambda)\varepsilon_{\mathrm{CQ}}(\lambda)\,\mathrm{d}\lambda$, where $I_0(\lambda)$ is expressed in Einstein $\mathrm{s^{-1}\,cm^{-2}\,nm^{-1}}$. If the radiation intensity, $I_0(\lambda)$, is expressed in $\mathrm{W\,cm^{-2}\,nm^{-1}}$ then this term is $(N_{\mathrm{Av}}ch)\int_{400}^{550} I_0(\lambda)\lambda\varepsilon_{\mathrm{CQ}}(\lambda)\,\mathrm{d}\lambda$ where N_{Av} is Avogadro's number, c is the speed of light and h is Planck's constant (this expression corrects a typographical error in reference 4). Since it is assumed that the d.s.c. sample is sufficiently thin that the radiation is not significantly attenuated by the sample, the term $\int_{400}^{550} I_0(\lambda)\lambda\varepsilon_{\mathrm{CQ}}(\lambda)\,\mathrm{d}\lambda$ is directly proportional to the radiation intensity at 470 nm. For the unattenuated Visilux-2 source, the rate of absorption of radiation at the base of the d.s.c. pan $(2.303[\mathrm{CQ}]\int_{400}^{550} I_0(\lambda)\varepsilon_{\mathrm{CQ}}(\lambda)\,\mathrm{d}\lambda)$ was calculated to be 0.034[CQ] Einstein $\mathrm{cm^{-3}\,s^{-1}}$ (when [CQ] is expressed in $\mathrm{mol\,cm^{-3}}$). For the present work, the relative measure of radiation intensity, I_{rel}, was used in place of I_0 in equation (7) and in the related equations.

Using the same kinetic approach, the rate of loss of CQ is:

$$\begin{aligned} -\mathrm{d[CQ]/d}t &= 2.303 k_2(k_a[\mathrm{A}](1-\gamma) + \alpha k_3) \\ &\quad \times I_0\varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]/\{k'k_3 + k'k_a[\mathrm{A}]\} \end{aligned} \tag{8}$$

Spectroscopic studies of the consumption of CQ during irradiation showed that for intermediate to high concentrations of TMA ($\geqslant$0.3 wt%), the kinetics were reasonably well fitted to this first-order expression (equation (8)) and that the rate constant was proportional to the radiation intensity but was independent of [CQ] (*Table 2*). This agreement with first-order behaviour is perhaps unexpected, because in typical runs, the molar concentration of amine was only slightly greater than that of CQ so that the reaction of the triplet CQ with amine (equation (4)) might be expected to lead to depletion of amine and therefore deviation from first-order kinetics. One potential explanation for this anomaly is that the TMA molecule can reduce several CQ molecules because each of the methyl hydrogen atoms in TMA is active. However *Table 2* shows that quadrupling of the TMA concentration has little effect on the rate. A more likely reason for the lack of deviation from first-order kinetics is that at normal amine concentrations, $k_3 \ll k_a[\mathrm{A}]$ (and hence $\alpha k_a \ll k_a[\mathrm{A}]$), resulting in a simplification of equation (8) to a kinetic expression which is independent of the amine concentration. This is equivalent to the assumption that

Table 2 Dependence of the apparent first-order rate constant (k) for CQ consumption (at 23°C) on experimental conditions. Radiation source: Luxor

Reaction medium	CQ (wt%)	Amine[a] (wt%)	I_{rel}	k (min^{-1})[b]
BisGMA/TEGDMA (70/30 w/w)	0.25	0.30 TMA	0.74	0.29 ± 0.05, 0.32 ± 0.02
BisGMA/TEGDMA (70/30 w/w)	0.25	0	0.74	0.20 ± 0.03
DEGDMA	0.25	0.30 TMA	0.74	0.37 ± 0.01, 0.41 ± 0.02
DEGDMA	1.00	0.30 TMA	0.74	0.30 ± 0.01
DEGDMA	0.25	0	0.74	0.18 ± 0.03[c]
DEGDMA	0.25	1.20 TMA	0.74	0.30 ± 0.02
DEGDMA	0.25	0.30 TMA	0.085	0.039 ± 0.004
DEGDMA cured[d]	0.25	0.30 TMA	0.74	0.31 ± 0.02
DEGDMA cured[d]	0.25	0	0.74	0.20 ± 0.02
TDEGDMA[e]	0.25	0.30 TMA	0.74	0.32 ± 0.02
Paraffin[f]	0.25	0	0.74	0.04 ± 0.01[c]
Paraffin[f]	0.25	0.30 An	0.74	0.015 ± 0.003[c]
Paraffin[f]	0.25	0.30 NMA	0.74	0.014 ± 0.004[c]
Paraffin[f]	0.25	0.30 TMA	0.74	0.21 ± 0.01, 0.24 ± 0.02
Paraffin[f]	0.25	0.30 BA	0.74	0.03 ± 0.02
Paraffin[f]	0.25	0.30 Morp	0.74	0.14 ± 0.01
Paraffin[f]	0.25	0.30 TBA	0.74	0.50 ± 0.04
Paraffin[f]	0.25	0.30 DMAE	0.74	0.80 ± 0.02

[a] See *Table 3* for amine abbreviations

[b] Error limits in k are least square errors from the first-order fit to the data

[c] Data showed poor fit ($R^2 < 0.94$) to first-order fit

[d] Glass formed by polymerizing with 0.5 wt% azobisisobutyronitrile at 60°C/24 h prior to irradiation at 23°C

[e] Elastomer forming system

[f] Non-polymerizing liquid

equation (2) is the rate-determining step. In the absence of added amine, the rate was substantially reduced (less so for the bisGMA/TEGDMA system which appears to contain high levels of an impurity reducing agent), showing that equation (3b) represents a minor reaction pathway. In addition, the data were not well fitted to the first-order expression, perhaps because the rate of reduction of CQ (by adventitious amine impurities or other reducers) approached the rate of degradation of deactivation of the CQ triplet state (equations (3a) and (3b)).

It is surprising that the rate of reduction of CQ is not very sensitive to the mobility of the medium (*Table 2*). For the resin systems DEBPADMA and bisGMA/TEGDMA, the reduction of CQ occurs in a relatively viscous medium which ultimately becomes glassy, while for the TDEGDMA resin the matrix is transformed from a relatively fluid liquid to an elastomer. In addition, for the two extreme environments of paraffin and of the pre-cured DEBPADMA glass, the rate constant of CQ oxidation in the presence of TMA varies by only 50%. These results indicate that diffusion does not play an important role in the kinetics. An estimate of the time taken for a CQ molecule to diffuse into the vicinity of the amine can be obtained from the definition[16] of the diffusion constant (D):

$$D = \delta^2/6\tau \qquad (9)$$

Here τ is the time between molecular jumps and δ is the jump distance which is closely related to the effective size of the molecule. Neglecting the difference in molecular size of CQ and the amine, concentrations of 0.25 and 0.3 wt% CQ and TMA correspond to a volume fraction of 0.003 of the molecular sites. Thus on a cubic lattice each of the species would occupy one in every seven molecular sites along each lattice axis, and the average distance between neighbouring CQ and TMA molecules would be about four molecular sites (4δ). After n jumps over a period of $n\tau$, the average CQ molecule will have traversed a distance of $n\delta$ before reaching the neighbouring amine molecule. Because the jumps form a random walk[16], the distance between the origin and finishing points will be $(n\delta^2)^{1/2}$, but since this distance is 4δ, the value of n is 16. During photopolymerization, the diffusion constant for CQ may decrease from $\sim 10^{-6}$ in the uncured resin to 4×10^{-14} cm^2 s^{-1} [for diffusion in poly(methyl methacrylate) at the glass transition[17]] and even less. Thus if the diameter of the site (δ) is estimated as 1 nm, the average time for CQ to diffuse to a TMA molecule would vary from $\sim$2 ns to 40 ms or longer as the material cured. Since the half-life[18] of the CQ triplet is $\sim$0.05 ms, the production of radicals in the transition and glassy states must only occur when the ketone is excited in close proximity to the amine. Both the reduction step (equation (4a)) and the deactivation step (equations (3a) and (3b), neglecting phosphorescence) involve the collision of CQ with another species, so it is reasonable to assume that k_3 and k_a would be similarly affected by changes in the mobility of the environment. As a result, identical variations in k_3 and k_a due to reductions in the diffusion constants cancel out in equations (7) and (8), and no dependency of rate on medium mobility is predicted. It should be noted, however, that equations (7) and (8) are based on the steady state assumption, which will fail when k_3 and k_a are much less than k_2.

Based on the rate of consumption of CQ and the relative radiation intensity in the u.v.-vis. experiments, calculations reveal that <30% of the CQ was consumed in d.s.c. samples after 1 min of unattenuated radiation ($I_{rel} = 1.0$). Under these conditions, the polymerization reaction had almost ceased. Similarly, under more typical d.s.c. irradiation conditions such as $I_{rel} = 0.1$, only 10% of the CQ is consumed during the first 2.5 min of irradiation. Thus the neglect of CQ depletion during the d.s.c. experiments should not introduce significant errors.

Figure 1 illustrates the influence of the chemical nature of the amine co-initiator on the polymerization of a 70/30 w/w blend of bisGMA and TEGDMA. The tertiary amines, TMA and tributylamine (triBA) are the most efficient photoreducers resulting in high polymerization rates whereas the primary amines, aniline (An) and n-butylamine (BA), resulted in very sluggish polymerization. Photopolymerization is also observed in the absence of added amine. This appears to be due to the presence of a reducer impurity in the 'as-received' bisGMA product, because purified bisGMA resin did not readily photopolymerize in the absence of tertiary amine. Although the polymerization rates were influenced by the amine species, the enthalpy of reaction was similar in all cases [206.2 ± 5.7 J g^{-1}, corresponding to ~75% conversion, based on 57.8 kJ mol^{-1} for the polymerization enthalpy of methyl methacrylate (MMA)[19]] suggesting that the limiting conversion is diffusion controlled. The influence of amine co-initiator on the maximum rate is shown in *Table 3* for the DEBPADMA resin. In the absence of amine, polymerization only proceeded to a limited extent (but sufficient to cause gelation). The polymerization was also extremely slow for primary amines and for amines with no α-hydrogens. For those systems which polymerized at a measurable rate, the enthalpy of reaction was independent of amine (146.2 ± 7.8 J g^{-1}, corresponding to 60% conversion).

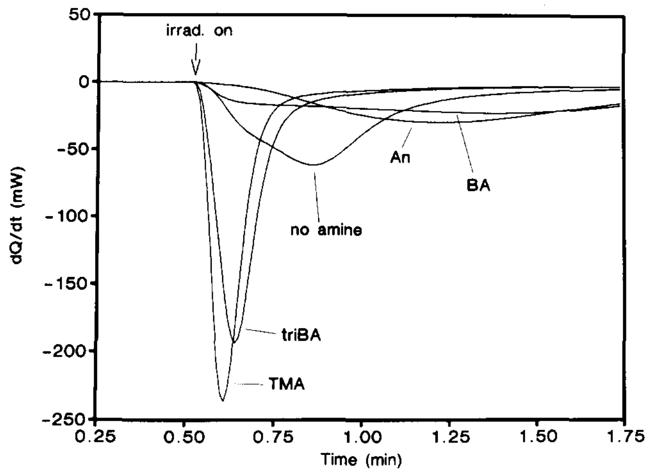

Figure 1 Heat flow (dQ/dt) *versus* time for the photopolymerization at 50°C of 10 mg samples of bisGMA/TEGDMA (70/30 wt%) containing 0.25 wt% CQ and 0.3 wt% amine. The relative irradiation intensity (I_{rel}) was 1.0

According to the steady-state assumption for free radical polymerization, the rate of polymerization is given by[20]:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = (k_p^2/k_t)^{1/2}\mathrm{R}_i^{1/2}[\mathrm{M}] \qquad (10)$$

where [M] is the methacrylate group concentration, k_p and k_t are the propagation and termination rate constants. Combining equations (7) and (10) gives:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = (k_p^2/k_t)^{1/2}\{2.303\beta k_2 k_a[\mathrm{A}] \times I_0\varepsilon_{\mathrm{CQ}}[\mathrm{CQ}]/(k'k_3 + k'k_a[\mathrm{A}])\}^{1/2}[\mathrm{M}] \qquad (11)$$

Table 3 Effect of amine reactivity on maximum normalized rate[a] for DEBPADMA at 50°C

Amine[b]	Amine code	$10^3 \times (\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_{max}/[M]_0$ $I_{rel} = 0.15$	$I_{rel} = 1.5$	I.P.[c] (eV)
Aromatic				
N,*N*-dimethylaniline	DMA		46.9	7.38
N,*N*,3,5-tetramethylaniline	TMA	18.6	46.0	7.30[d]
N,*N*-dimethyl-*p*-toluidine	DMT		44.4	7.24[d]
N,*N*-dimethylamino-*p*-benzladehyde	DMABz	17.1	40.7	7.33
N-methylaniline	NMA	1.4	4.3	7.32
Aniline	An	<0.08	0.7	7.89
Diphenylamine	DPA		0.5	7.25
Aliphatic				
Dimethylaminoethylmethacrylate	DMAEMA	14.4	37.9	
N,*N*-dimethylbenzylamine	DMBA	14.1	34.0	7.69
Tri-n-butylamine	triBA	11.1	31.5	6.98
Dimethylamino-ethan-2-ol	DMAE	8.6	20.9	8.83
Morpholine	Morp	1.9	4.8	8.89
Diethylamine	DEA	1.9	4.0	8.37
Hexamethylenetetramine	HMTA	<0.4	1.4	8.53
n-Butylamine	BA	<0.3	0.4	9.40
No amine		0.5	1.2	

[a] Calculated from the maximum heat flow, the polymerization enthalpy of MMA and the molecular weight of DEBPADMA
[b] Amine concentration 0.30 wt%
[c] Ionization potential—mean values[22]
[d] Values for ring isomers

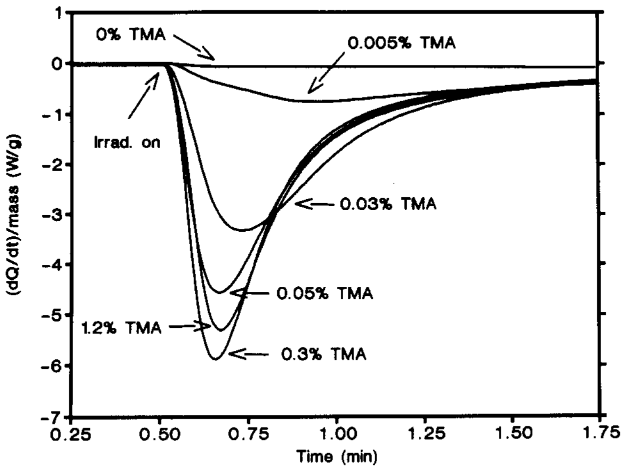

Figure 2 Normalized heat flow [$(\mathrm{d}Q/\mathrm{d}t)$/mass] as a function of time for the photopolymerization at 50°C of DEBPADMA containing 0.25 wt% CQ and various amounts of TMA. The relative radiation intensity (I_{rel}) was 0.10

The polymerization rate ($\mathrm{d}[\mathrm{M}]/\mathrm{d}t$) can be readily calculated from the heat flow ($\mathrm{d}Q/\mathrm{d}t$) and the heat of polymerization of the methacrylate group[19]. For convenience, the maximum normalized polymerization rate, $(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_{\max}/[\mathrm{M}]_0$, which corresponds to the peak exotherm (occurring at 5–20% conversion for the present systems), was used to test the predictions of equation (11). On the basis of the above reaction mechanism (equations (1)–(4)), equation (11) predicts that the polymerization rate should be enhanced for amines which readily undergo electron transfer and which are capable of transferring a proton (equation (4a)). One measure of electron donating ability is the ionization potential (IP). The influence of the IP of aliphatic and aromatic species on the rate of quenching of the benzophenone triplet has been examined[15,21] and separate correlations for these two quenching groups have been established[21]. Although a linear correlation[22] between IP and maximum rate is not observed for the data in *Table 3*, some general trends are found. With the exception of hexamethylene tetramine (HMTA), the tertiary aliphatic amines accelerate the polymerization to a greater extent than the secondary or primary amines as expected from their lower IP. However, the reaction rates of diethylamine (DEA) and dimethylaminoethanol (DMAE) are not consistent with their IP values. The reaction rate for systems containing a primary amine is so slow that it appears to retard the polymerization by triplet state quenching to the ground state, as was also observed in *Figure 1*. The failure of HMTA to follow the general trend may be associated with its rigid tetracyclic structure which does not allow orbital overlap in the transition state and thus fails to gain stabilization during the proton transfer step. The tertiary aromatic amines listed in *Table 3* are all efficient co-initiators of the photopolymerization, as would be expected of their low IP, while the secondary amine *N*-methylaniline (NMA) is less effective even though its IP is of the same order. Despite their relatively low IP values, neither aniline (An) nor diphenylamine (DPA) act as co-initiators because they do not have a transferable proton attached to the carbon next to the amine's nitrogen. The relative ranking of the aniline derivatives shown in *Table 3* is consistent with the data of Ghosh and Ghosh[23] for the benzophenone/ amine-initiated photopolymerization of MMA, however in this work, dimethylaniline was found to be only three times more effective than An. Clarke and Shanks[24] have studied the influence of a variety of amines on the benzophenone-initiated photopolymerization of butyl acrylate. These workers[24] found that in general, the rate of polymerization was greatest for tertiary amines followed by secondary amines and then primary amines as found here.

Table 2 reveals that the rate of CQ consumption is largest when a tertiary amine is present, in agreement with the polymerization rate data (*Table 3*). The rate constants for the systems with primary and secondary amines are of the same magnitude as that found in the absence of amine and no trend can be discerned, presumably due to variations in the rate of degradation of the excited states (equations (3b) and (4b)) and reformation of the ground state (equations (1), (3a) and (4c)). These factors are also probably responsible for the lack of correlation of the polymerization rate with the corresponding rate of CQ depletion for the various tertiary amine co-initiators.

To further elucidate the role of the amine species in the initiation step, photopolymerization studies were performed with varying levels of TMA but with a constant CQ concentration. At low concentrations (<0.6 wt%), the polymerization rate increases and then approaches a maximum (*Figure 2*). Similarly, the time at which the maximum rate occurs decreases and then approaches a minimum as the TMA level is raised. This behaviour (up to 0.6% TMA) is predicted by equation (11) and may be interpreted as a change-over in the rate determining step from equation (4a) to the intersystem crossing step (equation (2)) at higher amine concentrations. *Figure 3* shows the fit of equation (11) to the maximum polymerization rate for I_{rel} of 0.1 and 1.0. According to equation (11), a 10-fold increase in I_{rel} should raise the numerator by $10^{1/2}$ (3.16) and leave the denominator unchanged. In partial agreement, the fitted numerator values differed by a factor of 2.0 and, in the denominator, the term k_3/k_{a} only varied from 6.8×10^{-4} to 4.2×10^{-4} g g^{-1} (where [CQ] is measured in g g^{-1}) for I_{rel} values of 0.1 and 1.0, respectively.

Similar behaviour was also observed at high and low CQ concentrations, as shown in *Figure 4*. According to equation (11), a 20-fold increase in [CQ] should raise the numerator by $20^{1/2}$ (4.47) but leave the numerator unchanged. The fitted data in *Figure 4* show that the numerator was raised by 2.46 and the term k_3/k_{a} varied from 7.3×10^{-4} to 6.03×10^{-4} g g^{-1} for CQ concentrations of 0.05 and 1.0 wt%, respectively, in reasonable agreement with predictions. When NMA was used as the photoreducer, the polymerization rate also appeared to rise to a maximum and then decrease as the amine concentration was increased (*Figure 4*). Similar behaviour was observed for the morpholine system although the maximum polymerization rate did not approach a plateau until the morpholine concentration was $\sim 1\%$. However, these latter data are questionable because the magnitude of the d.s.c. curves depended on the age of the resin sample—samples aged for 2 days at 23°C polymerized $\sim 50\%$ faster than the freshly prepared material. This behaviour may be caused by nucleophilic addition of morpholine to the methacrylate group[3], forming a tertiary amine which is a more efficient photo-reducer.

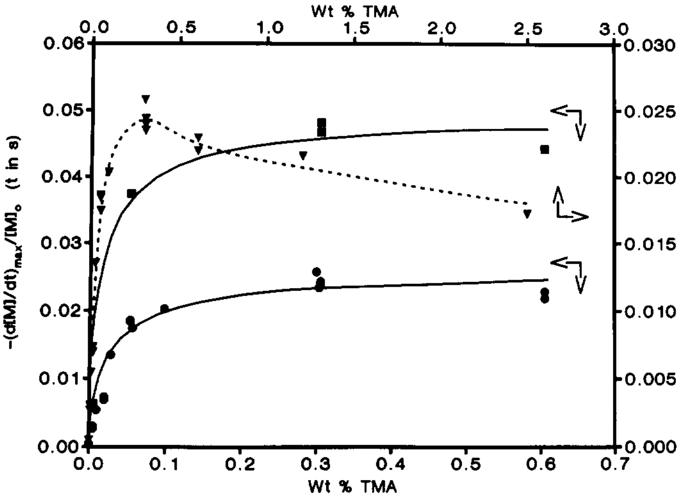

Figure 3 Maximum normalized polymerization rate ($-(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_{\max}/[\mathrm{M}]_0$) as a function of [TMA] in the photopolymerization of DEBPADMA at 50°C with 0.25 wt% CQ and $I_{\mathrm{rel}} = 1.0$ (■) and 0.1 (●). The solid lines are theoretical fits of equation (11) to the data up to 0.6% TMA. The dotted line is the line of sight over the full [TMA] range for the data with $I_{\mathrm{rel}} = 0.1$ (▼)

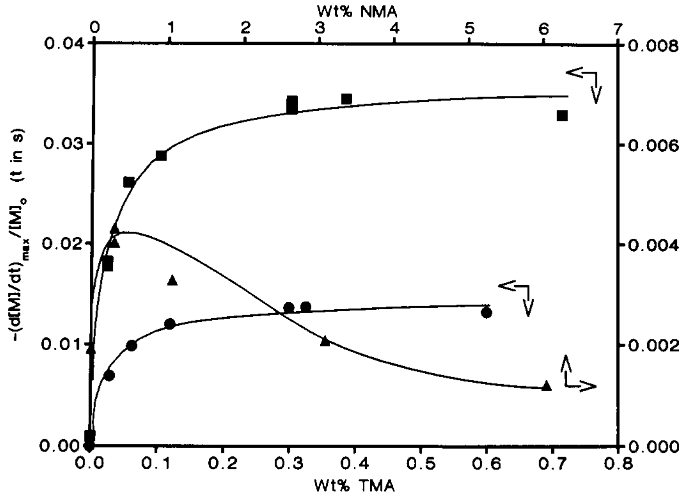

Figure 4 Maximum normalized polymerization rate ($-(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_{\max}/[\mathrm{M}]_0$) as a function of amine concentration in the photopolymerization of DEBPADMA at 50°C. For the photopolymerizations using TMA, I_{rel} was 0.1 and [CQ] was 0.05 (●) or 1.0 wt% (■). In the experiments with NMA (▲), I_{rel} was 0.87 and [CQ] was 0.25 wt%. The solid lines are theoretical fits of equation (11) to the data

As shown in *Figure 3*, the rate approaches a maximum and then decreases as the TMA concentration is raised above 0.04 M ($>$0.6 wt%). The polymerization rate of MMA initiated by fluorenone/indole-3-yl acetic acid also approaches a plateau at high concentrations ($>$0.003 M) of amine[25]. For the fluorenone/DMAE-initiated system, the rate has been found[10,25] to rise to a maximum (at ~0.1 M), decrease and finally attain a constant value, while for the fluorenone/triethylamine system[25] the rate passed through a broad maximum and then descended steeply as the amine concentration was further raised. These data suggest that excess amine acts as a retarder. Imoto *et al.*[26] found that in the AIBN-initiated polymerization of MMA, dimethyl aniline reduced the polymerization rate and suggested that this effect was due to radical transfer to the amine which was incapable of reinitiating the polymerization. At first sight, this conclusion appears to be at odds with evidence[2,11] that the amine radical is responsible for the initiation of the polymerization in the ketone/amine system. However, the data of Imoto *et al.*[26] and others[27] may be interpreted as showing that the amine radical reinitiates the polymerization at a much slower rate than the benzoyloxy radical. If this is the case, then in the absence of a more reactive radical, the amine radical could be responsible for the initiation in the CQ/amine system. In addition, the amine's dual action of accelerating polymerization at low levels and of retarding polymerization at high concentrations may be explained in terms of chain transfer. Retardation of the polymerization by excess amine will result from chain transfer to amine if the rate of addition of the amine radical to monomer is much slower than the propagation reaction.

The influence of CQ concentration on the kinetics was also studied. *Figure 5* shows the isothermal d.s.c. traces for varying levels of CQ. Clearly, the rate of polymerization is very sensitive to the CQ concentration over the whole range studied—as the CQ level is lowered,

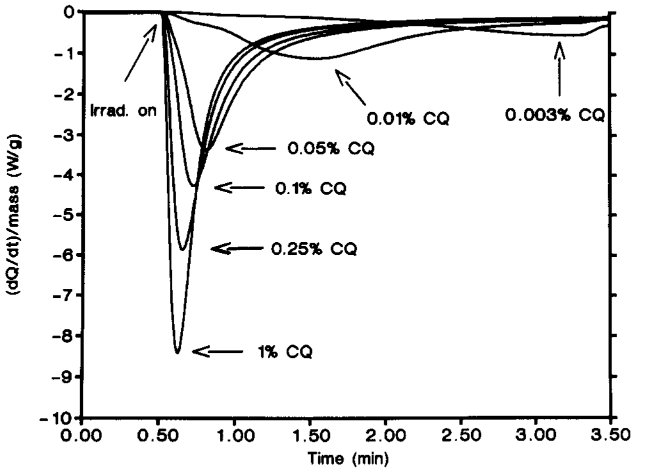

Figure 5 Normalized heat flow [(dQ/dt)/mass] *versus* time for the photopolymerization at 50°C of DEBPADMA containing 0.30 wt% TMA and various amounts of CQ. The relative radiation intensity (I_{rel}) was 0.10

the maximum heat flux is reduced and the time at which this occurs is increased. According to equation (11), the rate of polymerization is proportional to the square root of the initiator concentration. However, *Figure 6* shows that at high radiation intensities ($I_{\mathrm{rel}} = 1.0$) the order of the reaction with respect to [CQ] was only 0.30 ± 0.02 but at lower intensities the fitted orders of 0.46 ± 0.03 (for $I_{\mathrm{rel}} = 0.1$) and 0.48 ± 0.13 (for $I_{\mathrm{rel}} = 0.01$) approached the theoretical value. This latter value is in agreement with the half order dependence of rate on ketone concentration found by Ledwith *et al.*[28] for the anthraquinone photo-initiated polymerization of MMA (which involves a hydrogen atom abstraction mechanism) and for the charge transfer fluorenone/amine systems[25,29]. Other studies of the photopolymerization of MMA by the benzophenone/triethylene-tetramine initiator couple[30], of multifunctional acrylates with benzoin ethyl ether[31] and of diallyl esters with dimethoxydeoxybenzoin[32] have confirmed the half order dependency. For both radiation levels, the data in *Figure 6* appear to curve from the fitted line at low and high [CQ]. It is unlikely that the reduction in slope at high CQ levels is due to CQ depletion during the run, because the effect should be negligible, particularly for the data with $I_{\mathrm{rel}} = 0.1$. Some of the curvature may be caused by an attenuation of the radiation intensity (by up to 47%) through the film by CQ absorption. Another explanation is that at high rates of initiation (occurring at high values of [CQ] and I_{rel}), primary radical termination occurs, as was found in the photopolymerization of MMA, with benzophenone/dimethylaniline[23] or with benzophenone/triethylamine[33]. Deviation of the data from the half-order dependency at low initiator concentrations may be due to the consumption of initiating radicals by adventitious inhibiting impurities.

For a non-accelerating reaction, the d.s.c. curve should show an abrupt rise at the start of the reaction, followed by a slow decline as the monomer is consumed. Instead, the d.s.c. traces in *Figures 1, 2* and *5* reveal a steady increase in the rate to a maximum at ~15% conversion. As noted by Tryson and Schultz[31], this behaviour is associated with the Trommsdorff effect caused by a rapid decrease in the termination rate constant k_t. During the free radical polymerization, the rate controlling step of the termination reaction changes[34,35] from segmental diffusion (k_t independent of molecular weight) to translational diffusion (k_t dependent on chain radical size) and finally to reaction diffusion (where the motion of the radical ends occurs by a series of propagation steps[34]). It may be argued[5] that for network-forming systems, most of the polymerization is in the regime of reaction diffusion termination, with the result[35] that k_t is primarily dependent on $k_p[M]$. In some circumstances, k_p may also vary rapidly with conversion because the propagation step becomes diffusion controlled—this may be caused by vitrification of the matrix or because the vinyl group is pendant to a chain and has reduced mobility. However, provided that initiation, propagation and termination continue by the bimolecular mechanism, and that the steady-state assumption is held, equation (10) remains valid. Although the rate constants, k_p and k_t and possibly R_i may vary with the extent of reaction (and possibly the kinetic chain length), they are independent of time. Thus equation (11) may be integrated to give:

$$-\ln\{[M]/[M]_0\} = \{(k_p^2/k_t) \times 2.303\beta k_2 k_a [A] I_0 \varepsilon_{CQ} [CQ] \div (k'k_3 + k'k_a[A])\}^{1/2} t \qquad (12)$$

where $[M]_0$ is the initial monomer concentration. According to this equation, a plot of monomer concentration or of monomer conversion *versus* $[CQ]^{1/2}t$ should be independent of [CQ]. *Figure 7* shows the extent of reaction (obtained from the integrated d.s.c. curves) plotted against $[CQ]^{1/2}t$ in accordance with equation (12). Considering the 600-fold variation in CQ concentration, the superposition of the data are reasonable. Because the total enthalpy of reaction was virtually independent of the polymerization conditions (for those systems where the polymerization had ceased at the end of the d.s.c. run), the superposition of the data was improved at longer irradiation times (not shown in *Figure 7*).

As expected, the influence of radiation intensity on the d.s.c. curves (*Figure 8*) was similar to that of initiator concentration (*Figure 5*)—as I_{rel} was raised, the location of the maximum heat flow shifted to earlier times and

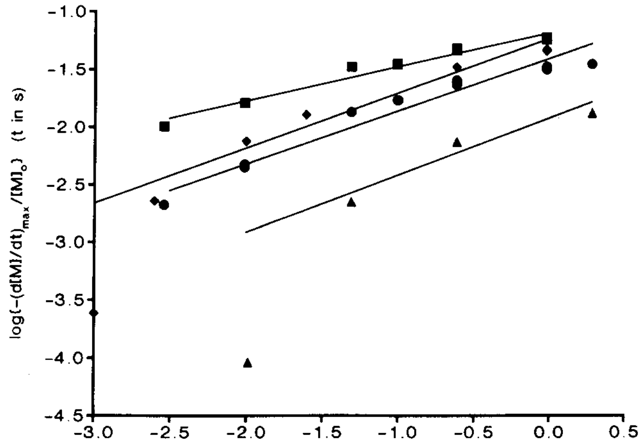

Figure 6 Log-log plot of the maximum normalized polymerization rate $[-(d[M]/dt)_{\mathrm{max}}/[M]_0]$, in the photopolymerization of DEBPADMA at 50°C with 0.30 wt% TMA, as a function of [CQ] at I_{rel} values of 1.0 (■), 0.1 (●) and 0.01 (▲) and as a function of I_{rel} at 0.25 wt% CQ (◆)

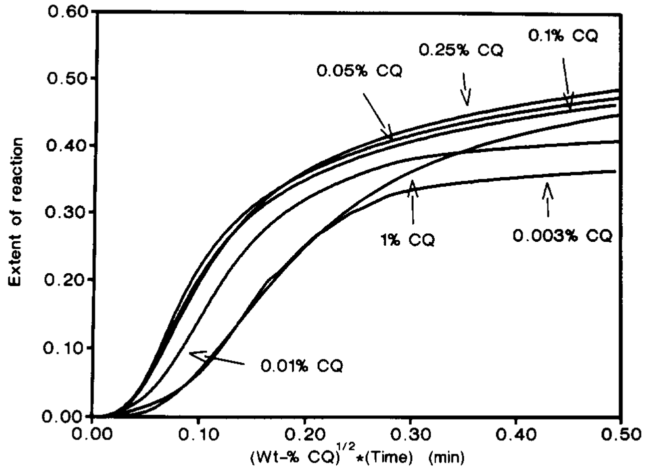

Figure 7 Extent of reaction *versus* $t[\mathrm{CQ}]^{1/2}$ (where [CQ] is expressed as wt%) for the photopolymerization at 50°C of DEBPADMA containing 0.30 wt% TMA and various concentrations of CQ. The relative radiation intensity (I_{rel}) was 0.10

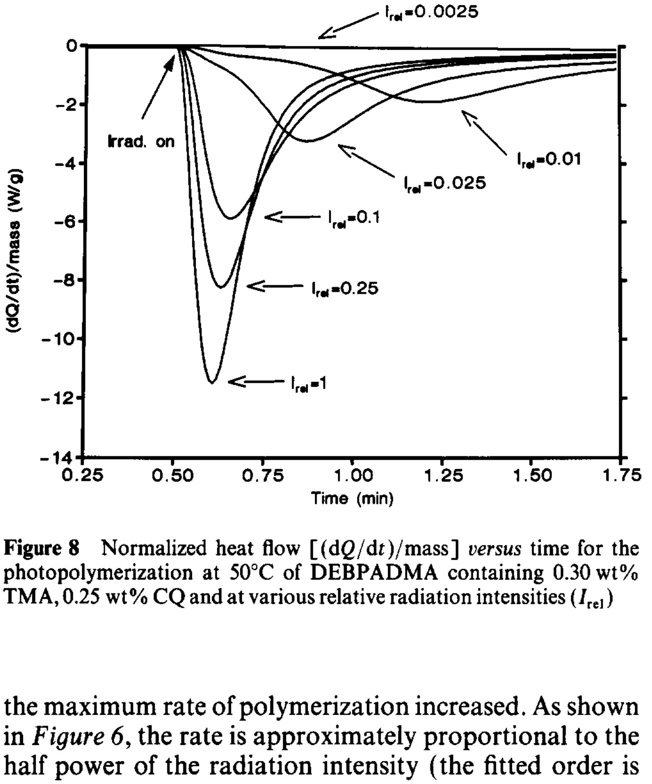

Figure 8 Normalized heat flow [(dQ/dt)/mass] *versus* time for the photopolymerization at 50°C of DEBPADMA containing 0.30 wt% TMA, 0.25 wt% CQ and at various relative radiation intensities (I_{rel})

the maximum rate of polymerization increased. As shown in *Figure 6*, the rate is approximately proportional to the half power of the radiation intensity (the fitted order is 0.47 ± 0.05), which compares with the exponent of 0.54 ± 0.06, obtained previously[5] for an elastomer-forming urethane dimethacrylate. A half order dependence was also found for the low conversion results of the fluorenone/amine photo-initiated polymerization of MMA[29], the solution photopolymerization of trimethylolpropane trimethacrylate by dimethoxyphenylacetophenone[36], and for the initial polymerization of an undiluted diallyl ester by dimethoxydeoxybenzoin[32]. Further studies of the diallyl system[37] showed that the exponent reached 0.75 at 50% conversion and approached unity at 70% reaction. Similarly, Hayden and Mellville[38] found that for the photopolymerization of 22 mol% ethylene glycol dimethacrylate in MMA, the exponent rose from 0.55 in the early stages to 0.75 at 30% conversion in the region of diffusion-controlled propagation. Other workers[31,39–41] have also found that the intensity exponent was between 0.5 and unity for the photopolymerization of undiluted diacrylates. This deviation from ideality is generally interpreted as a tendency towards first-order termination of the chain radical, either caused by its immobilization[37] or by reaction of the radical with trace impurities[31,39]. Such behaviour is expected for very reactive radicals or when the mobility of the radical is severely hindered by the growing network structure. *Figure 6* exhibits some deviation from the fit at low and high radiation intensities, possibly due to pseudo first-order termination and recombination of the primary radicals, respectively.

Since the monomer concentration, [M] on the right-hand side of equation (11), is directly related to the extent of cure, the equation can also be rewritten as:

$$-(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/I_0^{1/2} = \{(k_\mathrm{p}^2/k_\mathrm{t})2.303\beta k_2 k_\mathrm{a}[\mathrm{A}]\varepsilon_{\mathrm{CQ}}[\mathrm{CQ}] \div (k'k_3 + k'k_\mathrm{a}[\mathrm{A}])\}^{1/2} \times \left([\mathrm{M}]_0 + \int_0^t (\mathrm{d}[\mathrm{M}]/\mathrm{d}t)\,\mathrm{d}t\right) \qquad (13)$$

According to this form, a plot of $(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/I_0^{1/2}$ *versus* the residual monomer concentration $([\mathrm{M}]_0 + \int_0^t (\mathrm{d}[\mathrm{M}]/\mathrm{d}t)\,dt)$ or the extent of cure $(-\int_0^t (\mathrm{d}[\mathrm{M}]/\mathrm{d}t)\,\mathrm{d}t)$ should be independent of the radiation intensity. Using I_{rel} in place of I_0, the d.s.c. data are overlaid in *Figure 9* by plotting $I_{\mathrm{rel}}^{-1/2}(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]_0$ *versus* the extent of reaction, in accordance with equation (13). Reasonable superposition over the whole of the conversion range is obtained for the intermediate intensity ranges. The data at low and high radiation intensities do not coincide with the general trend due to the above-mentioned pseudo first-order termination and primary radical termination. The extent of cure at the maximum polymerization rate (*Figure 9*) is systematically reduced as the initiation rate decreases—a similar effect was also observed when the CQ or TMA concentration was lowered. This behaviour is not predicted by equation (11) and suggests that either k_p or k_t are slightly dependent on the radical concentration. Since an increased radical concentration raises the polymerization rate but lowers the kinetic chain length, the termination rate may rise due to the enhanced mobility of the radicals and hence cause a delay of the position of the maximum.

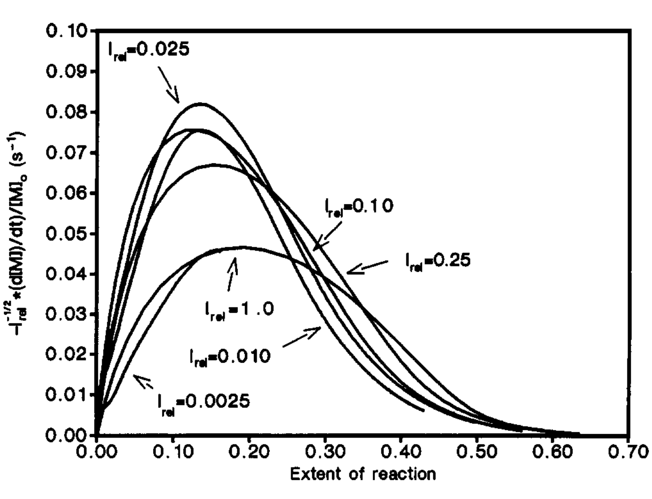

Figure 9 $I_{\mathrm{rel}}^{-1/2}(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}]_0$ *versus* the extent of reaction for the photopolymerization at 50°C of DEBPADMA containing 0.30 wt% TMA, 0.25 wt% CQ and at various relative radiation intensities

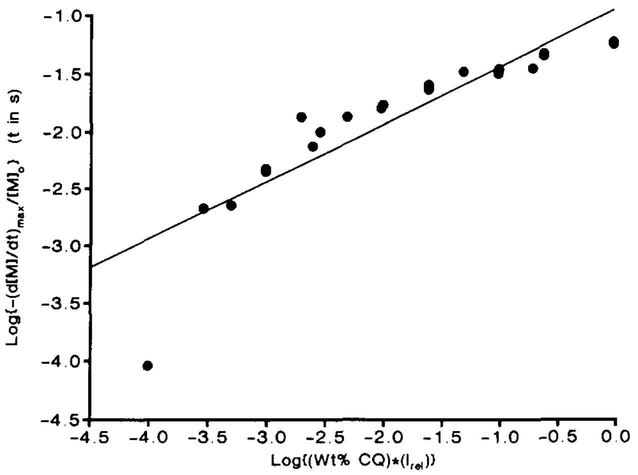

Figure 10 Log–log plot of the normalized maximum polymerization rate $[-(d[M]/dt)_{max}/[M]_0]$ *versus* $[CQ]I_{rel}$, the product of CQ concentration (expressed as wt%) multiplied by the relative radiation intensity

The combined influence of CQ concentration and relative radiation intensity on the maximum polymerization rate is shown in *Figure 10*. The fitted slope of 0.50 ± 0.05 agrees well with the theoretical value but as discussed above, deviation from this value occurs at low and high polymerization rates.

CONCLUSIONS

Studies of the initiation step in the polymerization of DEBPADMA with the CQ/amine couple suggest that the initiating radicals originate from a hydrogen abstraction reaction of the excited triplet state of CQ with the hydrogens α to the amine nitrogen. Based on correlations between the IP of quenching agents and rate of quenching of the ketone triplet state, previous studies[15,21] of the quenching of triplet state ketones suggested that the reaction of an amine with an excited ketone involves electron transfer followed by proton transfer and does not occur by direct hydrogen transfer. In the present study, the correlation of polymerization rate is poor. This may occur because the charge transfer step is faster than proton transfer or because the conversion of the exciplex to free radicals (equation (4a)) is not efficient and depends on amine structure. Alternatively, the reactivity of the initiating radical with the methacrylate group may be less for secondary and primary amine radicals. The dependence of polymerization rate on TMA concentration is consistent with a change in the rate-determining step as a function of amine concentration. This behaviour complicates analysis of the relative efficiencies of various amine co-initiators, because the rate is dependent on the amine concentration only at low amine concentrations.

The polymerization rate of DEBPADMA is approximately proportional to the square root of CQ concentration and radiation intensity, as predicted by simple kinetic theory. There is some evidence that deviations occur at low CQ concentrations and low intensities due to pseudo first-order consumption of CQ, probably as a result of the consumption of radicals by adventitious inhibiting impurities. At high concentrations of CQ, deviation from half order behaviour occurred due to radiation attenuation by CQ as a function of depth through the sample. Recombination of primary radicals at high initiation rates (at elevated [CQ] and high radiation intensities) may also be responsible for deviation of the data from the half order dependence.

ACKNOWLEDGEMENTS

The author is pleased to acknowledge Dr J. M. Charlesworth for reviewing the manuscript and the staff of the Therapeutic Devices Branch for their support.

REFERENCES

1 Kloosterboer, J. G. *Adv. Polym. Sci.* 1988, **84**, 1
2 Green, G. E., Stark, B. P. and Zahir, S. A. *J. Macromol. Sci., Rev. Macromol. Chem.* 1981–1982, **C21**, 187
3 Critchfield, F. E., Funk, G. L. and Johnson, J. B. *Anal. Chem.* 1956, **28**, 76
4 Cook, W. D. *Biomaterials* 1986, **7**, 449
5 Cook, W. D. *J. Appl. Polym. Sci.* 1991, **42**, 2209
6 Cook, W. D. *J. Dent. Res.* 1982, **61**, 1436
7 Meinwald, J. and Klingele, H. O. *J. Am. Chem. Soc.* 1966, **88**, 2071
8 Monroe, B. M. *Adv. Photochem.* 1971, **18**, 77
9 Froehlich, P. and Wehry, E. L. in 'Modern Fluorescence Spectroscopy 2' (Ed. E. L. Wehry), Plenum Press, New York, 1976
10 Hutchison, J. and Ledwith, A. *Adv. Polym. Sci.* 1974, **14**, 49
11 Ledwith, A. in 'Developments in Polymerization' (Ed. R. N. Haward), Applied Science, London, 1982, Ch. 2
12 Smets, G. *J. Macromol. Sci.* 1984, **A21**, 1685
13 Munroe, B. M. and Weiner, S. A. *J. Am. Chem. Soc.* 1969, **91**, 450
14 Cohen, S. G. and Chao, H. M. *J. Am. Chem. Soc.* 1968, **90**, 165
15 Yip, R. W., Loutfy, R. O., Chow, Y. L. and Magdzinski, L. K. *Can. J. Chem.* 1972, **50**, 3426
16 Allen, P. E. M. and Pattrick, C. R. 'Kinetics and Mechanisms of Polymerization Reactions', John Wiley and Sons, New York, 1974
17 Zhang, J. and Wang, C. H. *Macromolecules* 1987, **20**, 2296
18 Charlesworth, J. M. personal communication, 1990
19 Sawada, H. *J. Macromol. Sci.* 1969, **C3**, 313
20 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953
21 Guttenplan, J. B. and Cohen, S. G. *J. Am. Chem. Soc.* 1972, **94**, 4040
22 Levin, R. D. and Lias, S. G. 'Ionization Potential and Appearance Potential Measurements, 1971–1981', US Department of Commerce, National Bureau of Standards, 1982
23 Ghosh, P. and Ghosh, R. *Eur. Polym. J.* 1981, **17**, 817
24 Clarke, S. R. and Shanks, R. A. *J. Macromol. Sci.* 1982, **A17**, 77
25 Ledwith, A., Bosley, J. A. and Purbrick, M. D. *J. Oil Col. Chem. Assoc.* 1978, **61**, 95
26 Imoto, M., Otsu, T., Ota, T., Takatsugi, H. and Matuda, M. *J. Polym. Sci.* 1956, **22**, 137
27 Walling, C. and Indicator, N. *J. Am. Chem. Soc.* 1958, **80**, 5814
28 Ledwith, A., Ndaalio, G. and Taylor, A. R. *Macromolecules* 1975, **8**, 1
29 Ledwith, A. and Purbrick, M. D. *Polymer* 1973, **14**, 521
30 Ghosh, P. and Bandyopadhyay, A. R. *Eur. Polym. J.* 1984, **20**, 1117
31 Tryson, G. R. and Shultz, A. R. *J. Polym. Sci.* 1979, **17**, 2059
32 Bellobono, I. R. and Zeni, M. *Makromol. Chem., Rapid Commun.* 1986, **7**, 733
33 Ghosh, P. and Mukerji, N. *Eur. Polym. Sci.* 1979, **15**, 797
34 Stickler, M. *Makromol. Chem.* 1983, **184**, 2563
35 Soh, S. K. and Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 1315
36 Fizet, M., Decker, C. and Faure, J. *Eur. Polym. J.* 1985, **21**, 427
37 Bellobono, I. R., Selli, E., Righetto, L., Rafellini, P. and Trevisan, L. *Makromol. Chem.* 1989, **190**, 1945
38 Hayden, P. and Mellville, H. *J. Polym. Sci.* 1960, **43**, 215
39 Decker, C. and Bendaikha, T. *Eur. Polym. J.* 1984, **20**, 753
40 Kloosterboer, J. G. and Lijten, G. F. M. *Polym. Commun.* 1987, **28**, 2
41 Muller, U., Strehmel, B. and Neuenfeld, J. *Makromol Chem., Rapid Commun.* 1989, **10**, 539