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Depth of Cure in the UV Photopolymerization of Dimethacrylate-Based Dental Filling Materials*

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ABSTRACT

The photopolymerization of dimethacrylate-based resins, employed as dental filling materials, is often limited in practice to a depth of 1 or 2 mm. Microhardness studies of these materials indicate that the degree of cure below the surface is relatively constant until a depth is reached at which the extent of polymerization rapidly decreases. Based on the kinetics of photopolymerization, two simple models were derived which appear to be qualitatively consistent with this behavior. One of these models was also in general agreement with the dependence of the depth of cure on the exposure time, radiation intensity, absorption coefficient of the material, and the inhibitor concentration in the resin.

INTRODUCTION

In the last decade, photo-initiation of free radical polymerizations has become increasingly important–its applications ranging from photochemically cured inks and surface coatings [1, 2] to the UV

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cured composites used as dental filling materials [3, 4]. The latter materials basically consist of a photosensitizer (usually a benzoin derivative), inhibitor, viscous dimethacrylate monomers, and an inorganic filler (up to 50% by volume), and are activated in situ by high pressure mercury lamps, which emit UV spectral lines at 365 and 400 nm [5, 6], to form a glassy network. For use in the restoration of an enamel cavity or a fractured anterior tooth, the composite material should cure to an adequate depth to minimize the need for the application of successive layers. Thus the successful use of these materials is critically dependent on the depth of cure. It was therefore of interest to investigate some of the factors which control the depth of cure and to compare these results with theoretical models.

EXPERIMENTAL

Six commercially available, UV curable dental composite materials (Kulzer & Co., West Germany; L. D. Caulk & Co., U.S.A.; Espe Dental Products, U.S.A.), coded DMA1 to DMA6, were used in the study and were activated by three UV sources intended for this purpose (denoted by UV1, UV2, and UV3).

A cylinder of the dimethacrylate composite paste (4 mm in diameter 8 mm in length) was formed in an open-ended, split stainless steel mold, and the exit window of the UV source placed directly over the top surface of the material. After irradiation at 22 ± 2°C for a specified time, the mold and sample were transferred to an oven at 37°C for 24 h.

In a number of cases the extent and depth of cure of the material was evaluated by measuring the Knoop microhardness [7] according to the Australian Standard [8]. The cured section of the cylindrical specimen was removed from the mold and cut in half along the cylinder axis with a slow-speed diamond wheel. After mounting the specimen in epoxy resin, the cut surface was given a final polish on a metallographic polishing cloth with 7 μm diamond abrasive. By suitable alignment of the Knoop diamond indentor with the specimen, up to 10 microhardness measurements were made across the specimen diameter, giving a coefficient of variation generally between 5 and 10% at each depth. The depth of cure (D) was taken as the extrapolated depth of the sample at zero hardness (see Fig. 1). Excellent agreement was obtained between the value of D thus obtained and the thickness of cured material remaining after gently removing the uncured material with a plastic spatula.

The absorption coefficients of the dimethacrylate composite pastes were measured with a Blak-Ray Long-Wave UV meter (UV Products Inc., U.S.A.), which has a peak sensitivity around 365 nm, using a technique similar to that of Young et al. [9] (see Fig. 2). Due to the proximity of the UV detector to the specimen, this technique measures

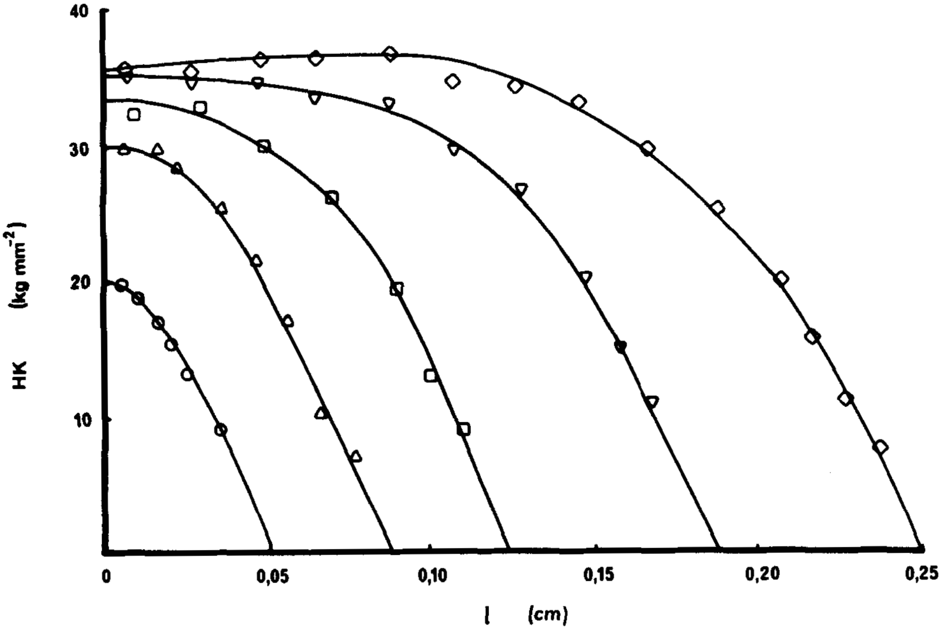

FIG. 1. Variation of Knoop hardness (HK) with depth (ℓ) for the system DMA1/UV1 after 5 s (○), 10 s (△), 20 s (□), 120 s (▽) and 600 s (◇) irradiation.

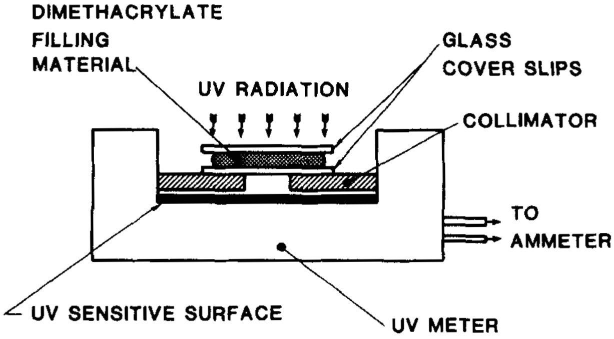

FIG. 2. Schematic illustration of the measurement of the coefficient of absorption for the dimethacrylate composite pastes.

both the unscattered and forward scattered radiation. Both forms of radiation are important in determining the depth of cure. All of the composite pastes exhibited an initial time-dependent increase in absorbance during irradiation by the UV source. Since this variation occurred mainly during the first 10 s and resulted in a variation of less than 10% in the absorption coefficient, a constant measuring time of 10 s after application of the irradiation was employed.

The incident UV intensity was varied by introducing various types of exposed and processed photographic film into the UV radiation path. The absorption coefficients of these films were measured as described above.

Using a Varian 634 UV-visible spectrophotometer the absorptivity of benzoin methyl ether in methyl methacrylate at 365 nm was found to be 8.5×10^4 cm^2/mol. Since the absorptivity at 400 nm was less than 10^3 cm^2/mol, it may be assumed that the 365 nm spectral line emitted by the radiation sources UV1 to UV3 was the predominant photo-initiating radiation.

Inhibition studies were performed by diluting the dimethacrylate composite paste with a small amount (5 ± 1 wt%) of a methyl methacrylate/ethanol mixture containing from 0 to 2 wt% benzoquinone.

THEORY

Neglecting chain transfer, the five principal steps involved in photochemically induced free radical polymerization can be written [10, 11]:

Photosensitization:

$$S \xrightarrow{h\nu} S\cdot \tag{1}$$

Initiation:

$$S\cdot + M \xrightarrow{k_i} SM\cdot \tag{2}$$

Propagation:

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \tag{3}$$

Termination:

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} M_{n+m} \tag{4}$$

Inhibition or retardation:

$$M_n\cdot + X \xrightarrow{k_x} M_nX\cdot \text{ (inactive)} \tag{5}$$

where S, M, and X are the photosensitizer, monomer unsaturation, and inhibitor, respectively, and k_i, k_p, k_t, and k_x are the rate constants.

Since the resin is viscous and forms a gel structure at low degrees of conversion, it may be assumed that the photosensitizer and resultant free radicals do not rapidly diffuse [12]. Under steady-state conditions [10, 11] the rate of initiation is equal to the rate of production of primary free radicals from the photosensitizer. Extending the theory for nonuniform light absorption, derived by Burns and Dainton [12], to a system composed of filler and other absorbing species, in addition to the photosensitizer, the number of quanta absorbed by the photosensitizer per cm^3 per second at a distance ℓ (cm) below the surface may be written:

$$Ia = 2.303\epsilon_s SI_0 \times 10^{-\epsilon\ell} \tag{6}$$

Here ϵ_s is the absorptivity (in cm^2/mol) of the photosensitizer with initial concentration S (in mol/cm^3 based on the resin), ϵ (in cm^{-1}) is the absorption coefficient of the composite material as a whole (including scattering effects [13]), and I_0 is the radiation intensity (einstein/$cm^2 \cdot s$) incident on the surface of the specimen. The rate of initiation is given [10] by the product of quantum yield of the photosensitizer (ϕ) times the amount of radiation absorbed by the photosensitizer:

$$\begin{aligned} R_i &= \phi Ia \\ &= 2.303\phi\epsilon_s SI_0 \times 10^{-\epsilon\ell} \end{aligned} \tag{7}$$

Since we are primarily concerned with the depth of cure—that is, the depth at which little or no decomposition of the photosensitizer (in the absence of excessive bimolecular termination or inhibition) has occurred—we assume that S is constant. Invoking the steady-state hypothesis for the concentration of chain radicals [10], the rate equations (1) to (5) can be solved for two important conditions.

Condition 1: Normal Termination

In this case, assuming S to be constant, the variation in monomer unsaturation with time is given by [10]:

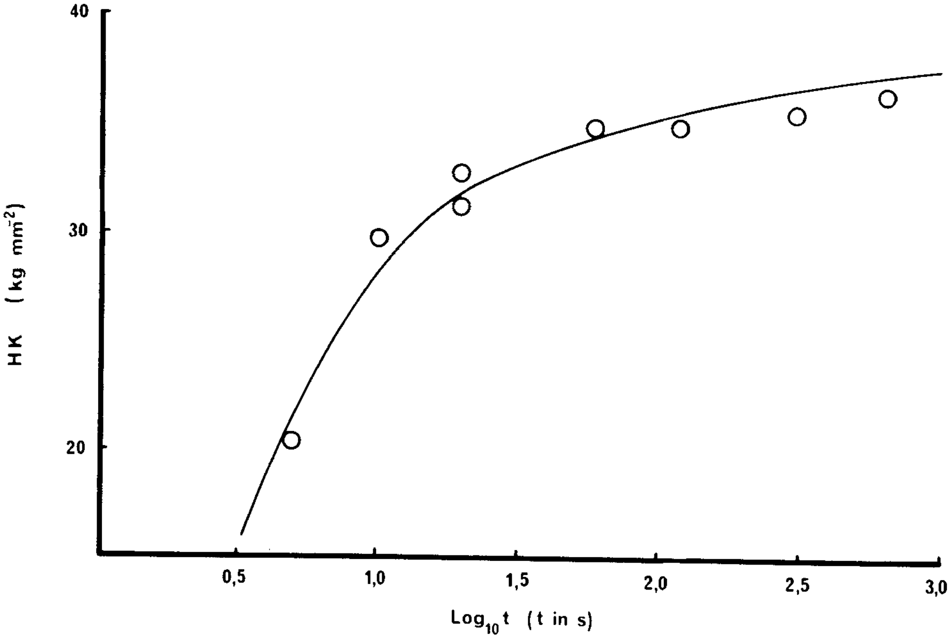

FIG. 3. Variation of maximum Knoop hardness (HK) with exposure time (t) for the system DMA1/UV1.

$$\ln \frac{M_0}{M} = \frac{k_p}{k_t^{0.5}} (2.303\phi\epsilon_s S I_0 \times 10^{-\epsilon \ell})^{0.5} t \tag{8}$$

where M_0 and M are the concentrations of unsaturated units initially and at time t, respectively. Equation (8) predicts that at a constant degree of conversion, ℓ is directly related to both $\log_{10} I_0$ and $\log_{10} t$, with slopes of $1/\epsilon$ and $2/\epsilon$, respectively.

Condition 2: Inhibition

Setting X_0 as the initial inhibitor concentration, $b = k_x/k_p$, and assuming S is constant, Eqs. (1) to (5) can be solved [14] to give the expression

$$v_0 - v + (v_0^2 + c^2)^{0.5} - (v^2 + c^2)^{0.5} + c \ln \left\{ \frac{v_0(c + (v^2 + c^2)^{0.5})}{v(c + (v_0^2 + c^2)^{0.5})} \right\} = bet \tag{9}$$

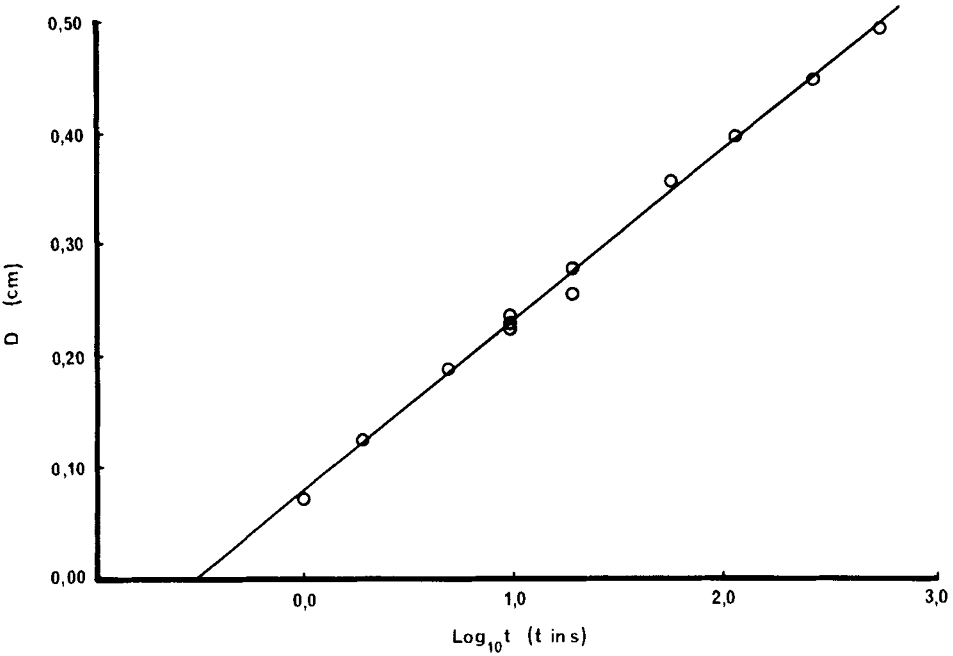

FIG. 4. Variation of depth of cure (D) with exposure time (t) for the system DMA3/UV1.

where $v_0 = k_x X_0$, $v = v_0(M/M_0)^b$, $c^2 = 4k_t R_i$, and $e = 2k_p R_i$.

In the initial stages of the reaction, most of the chains are stopped by the inhibitor so that [15]

$$X_0 - X \simeq R_i t \tag{10}$$

where X is concentration of inhibitor (in mole/cm^3 based on the resin) at time t. Now, X approaches zero at the depth of cure D, so that Eqs. (7) and (10) can be combined to give

$$D = \frac{1}{\epsilon} \log_{10} \left\{ \frac{2.303\phi\epsilon_s S I_0 t}{X_0} \right\} \tag{11}$$

Equation (11) predicts that D is linearly related to both $\log_{10} I_0$ and $\log_{10} t$ with a slope of $1/\epsilon$.

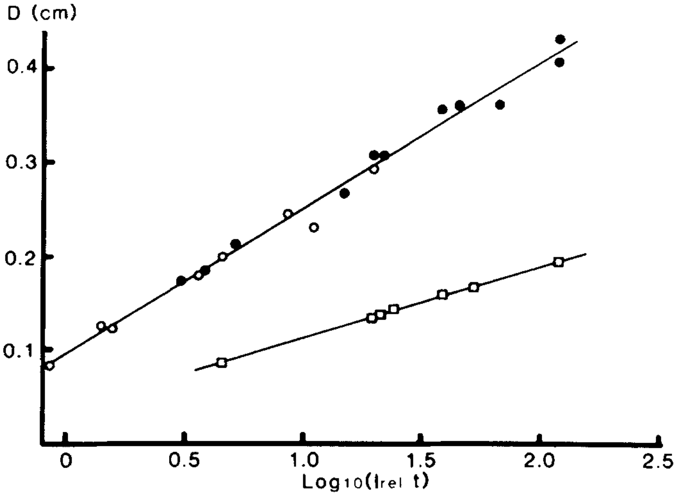

FIG. 5. Variation of depth of cure (D) with $\log_{10}(I_{rel}\ t)$: DMA1/UV1 irradiated for 120 s (□), and DMA3/UV1 irradiated for 20 s (○) and 120 s (●). In this figure I_{rel} is the intensity of the incident radiation (filtered through photographic film) relative to that of the unfiltered beam.

RESULTS AND DISCUSSION

The dependence of Knoop hardness on depth is illustrated in Fig. 1 for the system DMA1/UV1, irradiated for different periods. With exposures of greater than 10 s, the Knoop hardness exhibits a pseudo-plateau region followed by a rapid decrease with increasing depth. As the exposure time is increased, the iso-hardness region is extended. The maximum hardness in this region also shows an initial increase but appears to reach a plateau at longer exposures (see Fig. 3). Similar results to the above have been found [16] with UV polymerized dental fissure sealants which are closely related to the present materials.

Although hardness is not a fundamental property, it has been often used to monitor curing in network polymers [17]. Furthermore, the indentation hardness has been correlated [18] with the elastic modulus of polymers. For a glass-forming network polymer such as that studied here, the latter property rises during the polymerization due to the transformation of the material from a viscous liquid to a rubber and finally to a glass [19]. Thus the results in Fig. 1 suggest that the degree of cure is relatively constant below the surface until a depth is reached where the extent of conversion rapidly decreases.

TABLE 1. Comparison of Theoretical and Experimental Evaluation of ϵ

UV cured composite code	UV source code	ϵ^{a} (experimental)	ϵ calculated from D vs $\log_{10} t$ data and		ϵ calculated from D vs $\log_{10} I_{rel}$ data and	
			Eq. (8)	Eq. (11)	Eq. (8)	Eq. (11)
DMA1	UV1	11.7	22.8	11.4	13.2	13.2
DMA1	UV2	13.9	25.8	12.9		
DMA2[b]	UV1	14.1	31.4	15.7		
DMA3	UV1	7.6	13.2	6.6	6.5	6.5
DMA4	UV2	13.8	21.2	10.6		
DMA5	UV2	8.5	17.6	8.8		
DMA6	UV3	10.6	18.2	9.1		
DMA6[b]	UV3	11.7	17.8	8.9		

[a] Average values.
[b] Containing 5 ± 1% methyl methacrylate/ethanol mixture.

Figures 4 and 5 reveal that linear relationships exist between the depth of cure D and the logarithm of both the exposure time and the relative radiation intensity (I_{rel}). This behavior is in qualitative agreement with both the normal termination (Eq. 8) and inhibition (Eq. 11) models. In Table 1 the absorption coefficients of the composite pastes are compared with those obtained from the D versus $\log_{10} t$ and D versus $\log_{10} I_{rel}$ plots by application of Eqs. (8) and (11). It appears that the inhibition model is in better quantitative agreement with the results.

Figure 6 shows the variation of hardness with depth for the system DMA2/UV1 containing 0, 0.019 and 0.049 wt% benzoquinone. The influence of additional inhibitor appears to be similar to that of decreasing the exposure time, which is in qualitative agreement with Eq. (11). According to a rearranged form of Eq. (11), $I_0 t \times 10^{-\epsilon D}$ should be linear with X_0. Using a relative measure for the intensity (I_{rel}) in place of I_0, Fig. 7 shows a plot of those variables for the systems DMA2/UV1 and DMA6/UV3 when inhibited with additional amounts of benzoquinone. In this figure, the influence of the additional absorption by the benzoquinone on ϵ has been taken into account. The resulting linear relationships are in qualitative agreement with Eq. (11) and may indicate that DMA2 is more inhibited than DMA6.

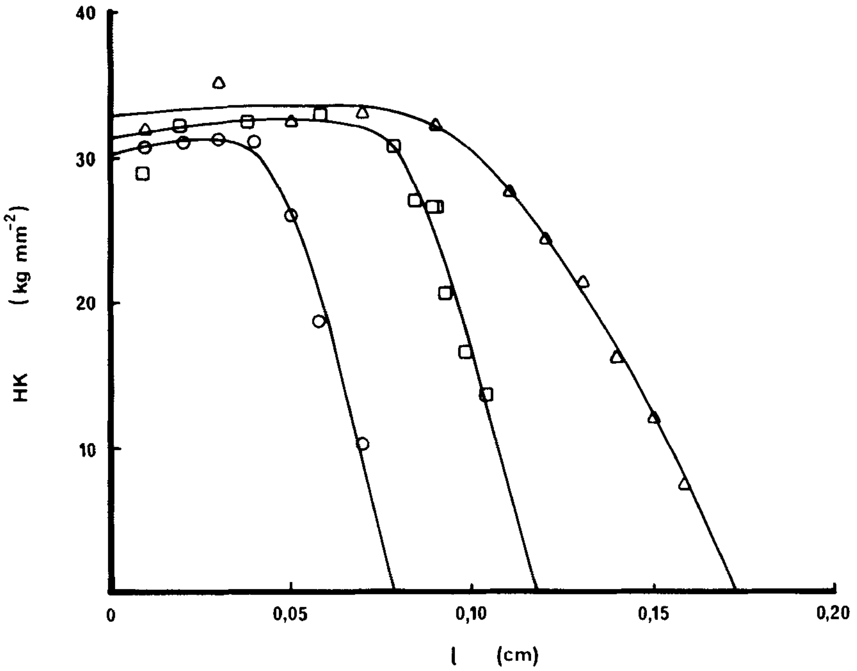

FIG. 6. Variation of Knoop hardness (HK) with depth for DMA2 containing 0 (△), 0.019 (□) and 0.049 (○) wt% benzoquinone, and irradiated with UV1 for 300 s.

In Fig. 8, Eqs. (8) and (9) have been used to provide an estimate of the variation of conversion with depth and the influence of exposure time, radiation intensity, and inhibitor concentration on this variation. The values of the parameters in these equations were chosen as follows. I_0 and ϵ were assigned values of 7×10^{-7} einstein/cm^2·s and 10 cm^{-1}, respectively, which are typical of those measured in the study. Since for benzoin methyl ether ϵ_s (at 365 nm) is 8.5×10^4 cm^2/mol and ϕ in methyl methacrylate is 1.48 [2], these values were employed, although it must be recognized that the high viscosity of the dimethacrylate resin may result in a much lower quantum yield due to recombination of the primary radicals in the cage [10]. A typical [3, 4] photosensitizer concentration of 7×10^{-5} mol/cm^3 was also used. For the inhibitor, k_x was chosen as 4×10^6 cm^3/mol·s which is that of benzoquinone in methyl methacrylate at 35.9°C [11], while X_0 is typically [3, 4] of the order of 2×10^{-6} mol/cm^3. The value of k_p used was that of methyl methacrylate [20] (3.84×10^5 cm^3/mol·s at

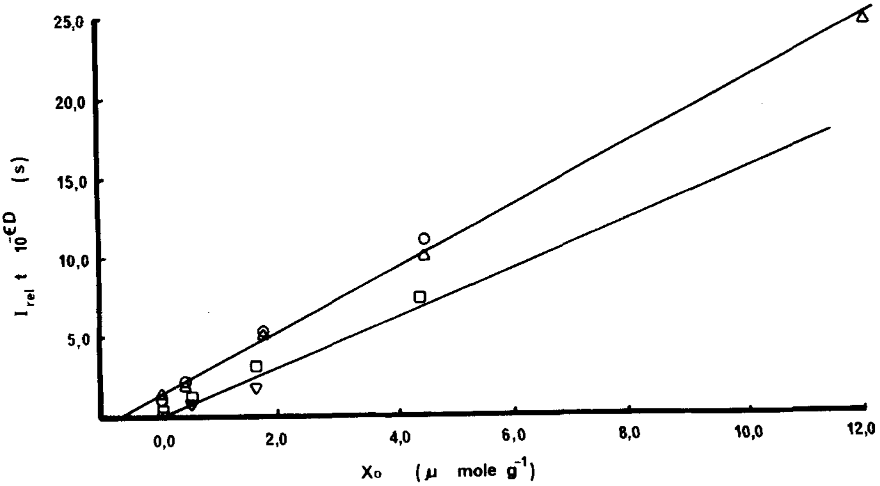

FIG. 7. Plot of I_{rel} t $10^{-\epsilon D}$ versus the concentration of benzoquinone (X_0) added to the systems: DMA2/UV1 after irradiation for 60 s (○) and 300 s (△); and DMA6/UV3 after irradiation for 5 s (▽) and 120 s (□).

22.5°C). For k_t a value of 10^9 cm^3/mol·s was selected (cf. 4.42 × 10^{10} cm^3/mol·s for methyl methacrylate [20] at 22.5°C and low degrees of conversion) to simulate the effect of the higher viscosity of the dimethacrylate resin on k_t [20]. Since the conversion curve for the normal termination model (Eq. 8) has the same shape but is merely shifted horizontally when S, I_0, or t is altered, only one curve is presented.

It should be noted that in the derivation of Eqs. (8) and (9), S was assumed to be constant. Thus these equations cannot model the "dead-end polymerization" [10] which results in a limiting value of conversion due to the depletion of photosensitizer, even if steric restrictions to the polymerization were not important. Furthermore, the parameters ϕ, k_x, k_p, and particularly k_t will decrease throughout the course of the polymerization [10, 20] due to changes in the viscosity and its influence on diffusion rates. These variations may tend to cancel one another in both Eqs. (8) and (9), due to the manner in which they are combined. Despite the above-mentioned limitations of the equations, the curves shown in Fig. 8 appear to be generally consistent with the Knoop hardness curves of Figs. 1 and 6, although in all cases the curves only intercept the zero conversion axis at infinite depth. Gelation, however, is not expected below a few percent

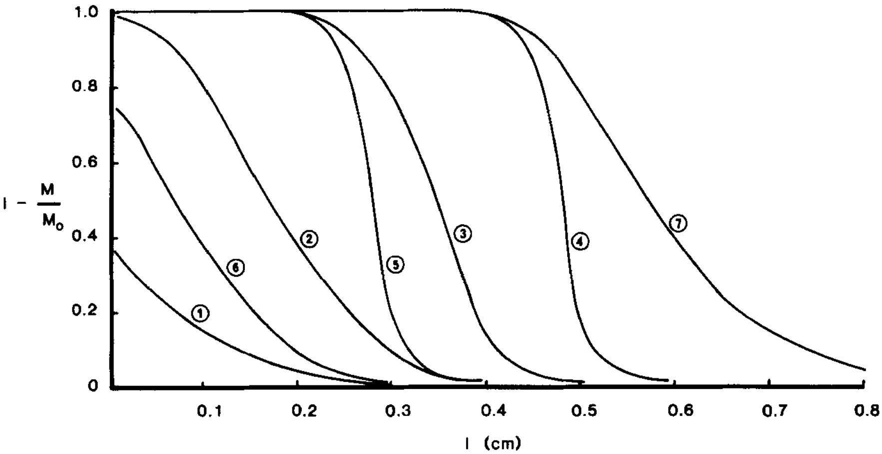

FIG. 8. Plot of conversion $(1 - \frac{M}{M_0})$ versus depth (ℓ) as calculated from Eq. (9) and the parameters listed in the text, with the following irradiation times (t): Curve ①, t = 10 s; Curve ②, t = 10^2 s; Curve ③, t = 10^3 s; Curve ④, t = 10^4 s; Curve ⑤, t = 10^3 s but X_0 increased by a factor of 10; Curve ⑥, t = 10^2 s but with I_0 decreased by a factor of 10. For comparison, Curve ⑦ represents the conversion versus depth calculated from Eq. (8) and the values listed in the text with t = 10^4 s.

conversion of the unsaturation, so that the Knoop hardness is likely to be insensitive to conversion in this region. It is also interesting to note that in Fig. 8 the conversion curves calculated from Eq. (9) become sharper when the exposure time is increased. This behavior is not experimentally observed in the Knoop hardness curves of Fig. 1, possibly due to the above-mentioned limitations of Eq. (9) or because of the varying sensitivity of the Knoop hardness on conversion.

CONCLUSIONS

The photopolymerization of dimethacrylate-based resins used as dental restoratives has been investigated using microhardness techniques. The results suggest that the degree of cure below the surface is relatively constant until a depth is reached after which the extent of polymerization decreases rapidly.

Two theoretical models based on the kinetic steps of free radical photopolymerization were derived to explain these results. The inhibition model appears to be in quantitative agreement with the dependence of depth of cure on the exposure time, radiation intensity, and inhibitor level.

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