Photopolymerization Kinetics of Dimethacrylate-Based Light-Cured Dental Resins

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ABSTRACT: The influence of certain factors [structure and concentration of tertiary amines as coinitiators, monomer composition, presence of inorganic pigments, and incident light intensity (I_0)] on the polymerization rates (R_p), polymerization quantum yields, and conversions of bisphenol A–bis(glycidyl methacrylate) (Bis-GMA)/triethylene glycol dimethacrylate based resins was studied. The initial rate of bulk polymerization increased and the final conversion decreased with the content of Bis-GMA in the mixture. In contrast, it was established that, for all monomer compositions, the R_p grew when increasing the I_0, the R_p being directly proportional to the square root of I_0. Such behavior is in agreement with the well-known kinetic expression for the ideal radical photoinitiated polymerization in solution of monofunctional monomers, in spite of the complexity of the dimethacrylate mixtures that were studied. Both the structure and the concentration of reducing amine affected the efficiency of the initiator system and therefore the kinetic behavior of polymerization of these formulations under irradiation. The rate of polymerization increased with the increase of coinitiator concentration over the interval of 0–1%, but later it diminished when increasing the amine content, suggesting that the excess coinitiator retards the polymerization process. The study of the photoreduction of camphorquinone in the presence of different amines showed that the efficiency of the coinitiator depends not only on its ability to photoreduce camphorquinone, forming amine-derived radicals, but also on the reactivity of these radicals toward the initiation of acrylic monomer polymerization. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1016–1023, 2005

Key words: photopolymerization; visible light-cured dental resin; monomer concentration; photoinitiator system

INTRODUCTION

Since the 1960s, the photopolymerization of dimethacrylate resins has found wide application in the dental field,[1–5] because these structures play an important part in different dental materials such as pit and fissure sealants, bonding agents, orthodontic adhesives, and composite resins, among others. Most resins are based mainly on bisphenol A–bis(glycidyl methacrylate) (Bis-GMA)/triethylene glycol dimethacrylate (TEGDM) type monomers,[4] the proportion of which is critical to guarantee such relevant properties as the optimal curing time, suitable viscosity, high conversion efficiency, low concentration of unreacted monomer, and so forth.

The most common photoinitiating system used in dental applications consists of a camphorquinone (CQ)–tertiary amine couple that produces free radicals on exposure to radiation at 450–500 nm.[1,5] Thus, the efficiency of this system should depend on the concentration of both CQ and amine, as well as on the nature of the coinitiator and on the intensity of the curing light. All these factors directly affect several clinically important properties of the cured formulation such as the overall rate of polymerization, the depth of the cured layer, the degree of conversion, and so forth.[1,5,6] At low degrees of double bond conversion, for example, the final cured product contains unreacted monomer and other low molecular weight components (e.g., unreacted photoinitiators and products of photolysis). These components distribute into the polymer crosslinked network and, because of their incompatibility with the cured polymer matrix, can diffuse out and cause toxic, allergic, or mutagenic reactions[7–10] as well as a decrease of the physical and mechanical properties of the resulting materials.[2,6,11]

Because of the practical importance of the described systems, numerous kinetic photopolymerization studies have been carried out on di- and multifunctional acrylic monomers initiated by the CQ/amine pair.[12–18]

For example, Cook[15,16] and Bowman et al.[17,18] studied homopolymerization rate profiles and volume relaxation values of multiethylene glycol dimethacrylates. The effects of the monomer structure (number of ethylene glycol units), reaction temperature, and light intensity on the polymerization kinetics were established. Another work[3] elucidated the effect of the concentration and ratio of the CQ/amine couple on the degree of conversion of TEGDM/urethane dimethacrylate based unfilled light-cured resins.

The aim of this work was to study the dependence of the double bond conversion and polymerization rates of Bis-GMA/TEGDM-based resins (ranging from 40 to 60 wt % of each monomer in the feed) on the incident light intensity, structure and concentration of reducing amine, and presence of inorganic pigments (titanium dioxide) in the light-cured mixtures in order to determine the influence of these parameters on the overall kinetic behavior of the studied systems under visible light irradiation.

EXPERIMENTAL

Materials

The monomers studied in this work were Bis-GMA (Nupol, Freeman Chemical Corporation) and TEGDM (Merck). Both were used as received. CQ (Aldrich Chemical Co.) was >99% pure and was used without further purification. Triethanolamine (TEA, Aldrich), N,N-dimethyl-p-toluidine (DMPT, Fluka), N,N-dimethyl aniline (DMA, Fluka), and 2-(N,N-dimethylamino)ethyl methacrylate (DMAEM, Aldrich) were purified by distillation under reduced pressure and stored in the dark under nitrogen. 4-(Dimethylamino) benzophenone (DMAB) was obtained from commercial suppliers (Aldrich) and recrystallized from ethanol–water mixtures. N,N,3,5-Tetramethyl aniline (TMA, Aldrich) was used without further purification. In addition, ethyl acetate (Merck) and titanium dioxide (TiO$_2$) were used as solvent and pigment, respectively.

Photopolymerization

The photopolymerization kinetic was monitored by differential scanning photocalorimetry. This experimental system consists of a conventional differential calorimeter (Perkin–Elmer DSC-7) suitably modified to permit irradiation of the samples within the calorimeter chamber. The ends of a twin-light conducting fiber were inserted into the cover of the DSC aluminum block by drilling holes directly above the sample and the reference holders so that the exit windows of each optical fiber were located 3 mm above the base of the DSC pan. A detailed description of the modified differential calorimeter (PDSC) is found in previous publications.[19,20] In our current work the twin-branch flexible light guides (each 50 cm long) are terminated with a ferrule connector, which is plugged into the light guide socket of a cold light source (Schott KL-1500). This irradiation source allows the direct regulation of the light intensity in graduated stages by means of a brightness control. Installation of neutral filters in the filter holder or on the focusing attachment of the instrument extends the range of intensity control. In order to avoid the heating effect of the photocuring source and to isolate the 470-nm wavelength, a solid heat filter (Schott KG-1) and a 470 green filter (Schott VG-9) were placed into the filter holder.

The PDSC calibration, data processing, determination of incident and absorbed light intensity, as well as complementary details, are described elsewhere.[19,20] All polymerizations were carried out in bulk at 40°C. Sample quantities of about 20 mg were accurately weighed and spread as a layer over the base of the 6.5-mm diameter aluminum DSC pan.

In all kinetics studies, 0.5 wt % CQ was used to initiate the polymerization. The monomer compositions chosen for the study were 40:60, 50:50, and 60:40 wt % Bis-GMA/TEGDM. These ratios of the base monomer (Bis-GMA) and a reactive monomer diluent (TEGDM) are widely used in chemical- and light-cured dental resins. The incident light intensity was changed from 0.13 to 1.80 mcal/s.

In order to identify the optimal CQ/amine ratio, DMAEM was selected as the coinitiator and 40/60 Bis-GMA/TEGDM as a monomer mixture. The concentrations of DMAEM were 0, 0.25, 0.5, 1, 1.5, 2.5, and 5 wt %. The incident light intensity was maintained constant at ~0.45 mcal/s.

The following experimental conditions were selected for the study of the influence of the structure of the amine on the R_p in the Bis-GMA/TEGDM resin: I_0 = 0.45 mcal/s, Bis-GMA/TEGDM = 40/60 wt %, and CQ/amine = 1/2 mol/mol.

The polymerization conversion (mol/L) was calculated from the heat flow and the sample mass, whereas the enthalpy was assumed to be 13.6 kcal/mol for each methacrylic group.[4] All values reported for the kinetic parameters (Tables I–III) correspond to the average of at least three measurements, with a maximum relative error of 3%.

Photoreduction

The rates and the quantum yields of the photoreduction of CQ were measured under irradiation at 470 nm in ethyl acetate solutions in the presence of fixed quantities of the above-mentioned amines (CQ/amine = 1/2 mol/mol). The decrease in the CQ concentration produces the decrease of its absorption band, which was followed on a Shimadzu UV-265 FS spectrophotometer by taking readings of its absorbance

TABLE I
Kinetic Parameters for Photopolymerization of Different Bis-GMA/TEGDM Mixtures Under Isothermal Conditions (40°C) and Different Incident Light Intensities (0.5/1 wt % CQ/DMAEM)

Bis-GMA/ TEGDM composition (wt %)	I_0 (mcal/s)	$R_p \times 10^2$ (mol/Ls)	Conversion at 15 min (%)	$\phi_m \times 10^{-2}$
40/60	0.15	0.67	45.8	4.2
	0.50	1.35	59.8	2.2
	1.13	2.15	74.2	1.6
	1.80	2.73	82.7	1.3
50/50	0.15	0.81	38.2	4.5
	0.45	1.50	53.4	2.7
	1.03	2.33	67.7	1.9
	1.54	2.93	76.8	1.6
60/40	0.13	1.01	33.7	6.4
	0.49	1.76	47.2	3.0
	1.14	2.66	58.8	2.0
	1.64	2.86	68.2	1.5

values at the maximum, located at 470 nm, over different irradiation periods.

RESULTS AND DISCUSSION

Influence of monomer composition

All exothermal profiles for the bulk photopolymerization of the selected monomer compositions show a gradual rise in R_p values up to a maximum and then a fast decline. This behavior is characteristic of network-forming dimethacrylate systems and it is associated with the autoacceleration or gel effect,[4,16,21] which arises from a decrease in the rate of the diffusion-controlled termination reaction, resulting from a rapid increase in viscosity that reduces the mobility of growing radical chains. Therefore, the initial increase in the reaction rate is probably caused by a combination of both the increase in the concentration of growing radicals and the relative increase in the propagation in respect to the termination rate. The later decrease in

TABLE II
Kinetic Parameters for Photopolymerization of 40/60 wt % Bis-GMA/TEGDM Blend Under Isothermal Conditions (40°C) in Presence of Different Amine Co-initiators

Amine	$R_p \times 10^2$ (mol/Ls)	$\phi_m \times 10^{-2}$
DMPT	1.47	2.8
TMA	1.73	3.1
DMA	1.81	3.3
DMAB	3.05	7.1
TEA	0.64	1.2
DMAEM	1.20	2.2

$I_0 = 0.45$ mcal/s.

TABLE III
Photoreduction of Camphorquinone (CQ) in Presence of Different Amines, Acting as Reducing Agents, in Ethyl Acetate Solution

Amine	I_0 (mcal/s)	$R_r \times 10^6$ (mol/Ls)	ϕ_r	R_p^2/ϕ_r
DMPT	3.05	1.05	0.089	24.3
TMA	3.00	1.32	0.112	26.7
DMA	3.38	1.70	0.132	24.8
DMAB	2.90	2.24	0.159	58.5
TEA	2.84	5.56	0.535	0.7
DMAEM	2.87	5.05	0.486	3.0

Irradiation wavelength = 470 nm.

the reaction rate may be caused by depletion of monomer in the system and by the fact that the propagation reaction becomes diffusion controlled because of the reduction in the monomer mobility when vitrification is approached.

The kinetic curves obtained for the studied compositions are shown in Figure 1, which shows that at the initial stage of polymerization, the monomer conversion increases with the content of Bis-GMA in the system. However, at higher reaction times the behavior is the opposite and at the end of irradiation the system richer in Bis-GMA becomes the less polymerized one. This behavior can be attributed to a reduction in the mobility of the reacting species in the polymerizing system rich in Bis-GMA because of its high viscosity. When the concentration of the Bis-
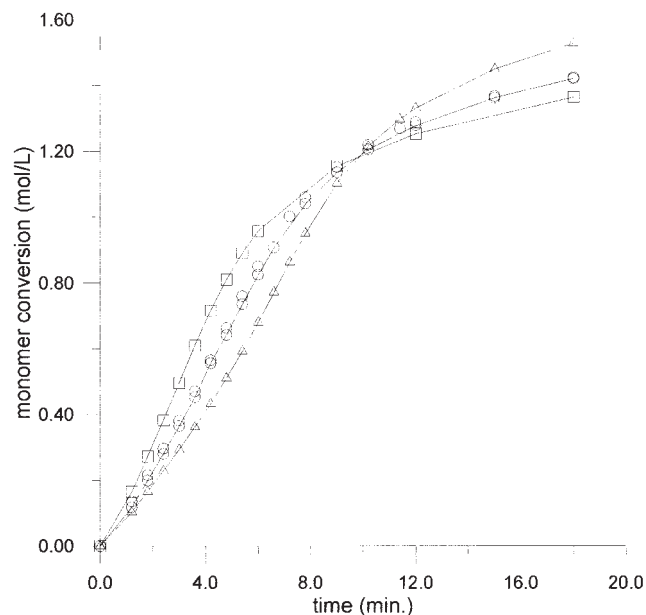

Figure 1 Kinetic curves for the photopolymerization of the Bis-GMA/TEGDM mixtures at different monomer compositions under isothermal conditions (40°C); $I_0 = 1.29$ mcal/s, 0.5/1 wt % CQ/DMAEM. Bis-GMA/TEGDM (wt %): (△) 40/60, (○) 50/50, and (□) 60/40.
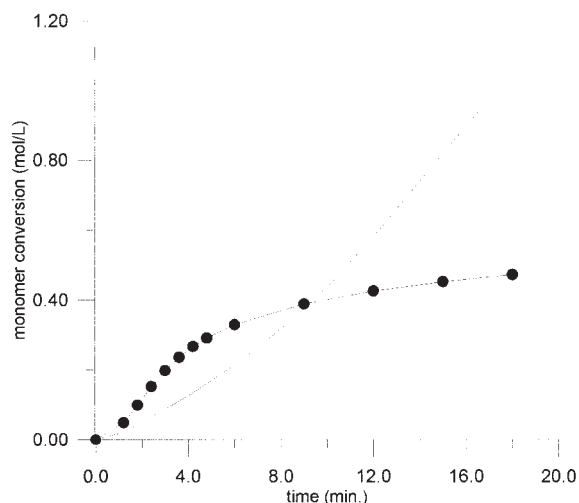
Figure 2 Kinetic curves for the homopolymerization of (●) Bis-GMA and (—) TEGDM at 40°C ($I_0 = 0.15$ mcal/s, 0.5/1 wt % CQ/DMAEM).

GMA monomer is increased, macroscopic gelling occurs at a lower conversion; this severely limits the translational and segmental mobility of polymer growing macroradicals. These results are in good agreement with those obtained for the homopolymerization of both monomers (see Fig. 2) where the initial rate for the Bis-GMA monomer was 12 times greater than TEGDM [(8.2 and 4.1) $\times$ 10^{-3} mol/L s, respectively] at $I_0 = 0.15$ mcal/s. Nevertheless, after 18 min of irradiation only 25% conversion was reached for Bis-GMA, whereas TEGDM achieved 52% at the same time. The low degree of conversion (and consequently the high concentration of residual double bonds) adversely affects important properties of dental materials (such as toxicological, physical and mechanical ones) because, as mentioned above, the unreacted monomer may cause toxic and allergic reactions as well as a decrease in the hardness of the polymer matrix. All these factors should be considered when selecting the monomer formulation for light-cured dental resins.

Influence of incident light intensity

The kinetic curves at different irradiation light intensities show similar behavior for the studied monomer formulations, an example of which is presented in Figure 3. As may be expected, the monomer conversion increases when increasing the incident light intensity (I_0). These conversion versus time plots were used to calculate the polymerization rates (R_p) and the quantum yields (ϕ_m) of polymerization (at initial time). The former parameter was determined by the slope of a linear least squares fit of the initial steady-state region of the curves, whereas the latter was

calculated as the ratio of the monomer conversion degree (mol) and the amount of absorbed energy (einstein) at the same region. The results obtained are summarized in Table I. Note that for all compositions the polymerization rate and the final conversion grow and the quantum yield decreases when increasing the I_0, indicating a decrease in the conversion of monomer into polymer per mole of photons absorbed; therefore, there will be more polymer chains that will be shorter. It also can be observed that the mixture with greater monomer diluent content (60% of TEGDM) displays maximum values of final conversion (82.7% at $I_0 = 1.8$ mcal/s), which guarantees the lowest quantity of the unreacted (residual) monomers in the polymerized matrix. This suggests that the lower the viscosity of this system is, the greater is the mobility of the monomer and macroradicals, thus producing a better extension of curing.

In contrast, it was found that the overall rates of polymerization of the above systems were directly proportional to the square root of the incident light intensity (Fig. 4), indicating that, in spite of the complexity of the present formulation of dimethacrylic monomers, the mechanism of the polymerization fits the well-known general kinetic expression for the ideal radical polymerization of monofunctional vinyl monomers in solution.

Influence of amine structure

According to the well-established behavior of the CQ/amine system,[5,6,12–14,22] substituted dialkylamine rad-
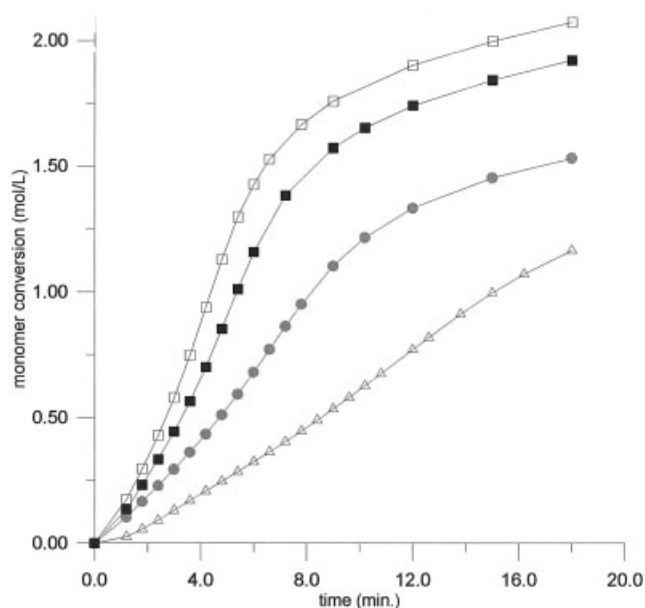

Figure 3 Kinetic curves for the photopolymerization of 40/60 wt % Bis-GMA/TEGDM under isothermal conditions (40°C) for different incident light intensities (I_0): (△) 0.15, (●) 0.50, (■) 1.13, and (□) 1.80 mcal/s (0.5/1 wt % CQ/DMAEM).
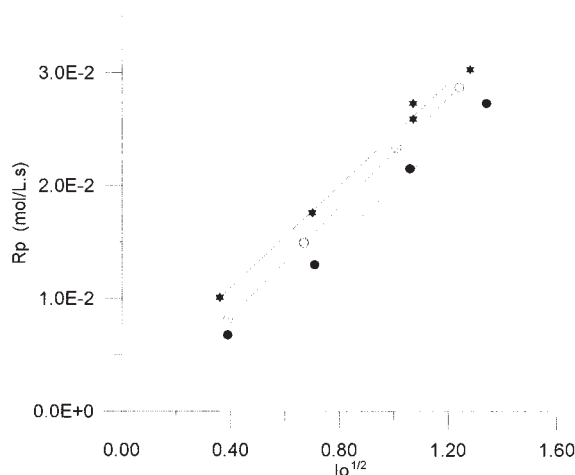
Figure 4 The dependence of the rate of polymerization (R_p) on the square root of the incident light intensity (I_0) for different compositions of Bis-GMA/TEGDM: (●) 40/60, (○) 50/50, and (★) 60/40 wt % (40°C, 0.5/1 wt % CQ/DMAEM).

icals must be produced via formation of an exciplex by an electron transfer plus proton transfer mechanism when these systems are irradiated at a wavelength only absorbed by CQ (absorption maximum at a 470-nm wavelength).

All the substituted N,N-dialkylamine structures used in this work are shown in Scheme 1. The experimental conditions and obtained results are shown in Table II where it can be observed that the R_p and ϕ_m depend on the structure of each specific amine. These differences can be explained mainly on the basis of the following considerations:

1. the different efficiencies of each amine in the photoreduction of CQ under irradiation, which leads to differences in the radical production rate and therefore in the rate of the polymerization process; and
2. the different reactivities of the corresponding amine-derived radicals toward the initiation of the acrylic monomer polymerization, and thus the efficiency of this process.

In order to establish the contribution of these two factors, a study of the photoreduction kinetics of CQ in the presence of the different amines was performed. The experimental conditions and the calculated parameters, such as the photoreduction rate (R_r) and the photoreduction quantum yield (ϕ_r) of CQ, are shown in Table III. A comparison of the above results with the values obtained for the R_p in the presence of these amines (Table II) is shown in Figure 5. Note that for the aromatic N,N-dimethyl amine derivatives (DMA, DMAB, TMA, and DMPT) a good correlation exists between the ϕ_r of CQ, proportional to the amine radicals production rate, and the R_p, thus indicating that

the efficiency in radical generation has a direct influence upon the R_p. However, the lack of correlation between the values of R_r and R_p obtained for both aliphatic amines (TEA and DMAEM) suggests that higher rates of radical production in the presence of these amines seems to be compensated by the low reactivity of their corresponding alkyl amino radical toward acrylic moiety.

According to the general equation for radical photoinitiated polymerization,

$$R_p = k_p/k_t^{1/2} \cdot [M] \cdot (I_a \cdot \phi_i)^{1/2}$$

and, according that,

$$\phi_i = \phi_r \cdot f$$

where ϕ_i is a quantum yield for the initiation process, ϕ_r is the photoreduction quantum yield, and f is the efficient factor (fraction of active free radicals that initiates polymerization), then the R_p^2/ϕ_r ratio value will measure the efficiency factor of the corresponding amino radical when identical experimental conditions are used. Thus, from the R_p and ϕ_r parameters it will be possible to compare the efficiencies of the radical derived from the above tertiary amines. From the R_p^2/ϕ_r values shown in Table III, the important differences in the relative radical efficiencies of the dimethylamino derivatives can be appreciated, which can be attributed to the nature and position of the substitutes of the aromatic ring in agreement with Mateo et al.,[22] in spite of the complexity of the formulations studied here. Conversely, in spite of the higher rate of radical production by TEA and DMAEM, all the R_p^2/ϕ_r values obtained for aromatic amines are appreciably higher than the radical efficiency calculated for both aliphatic tertiary amines (TEA and DMAEM), which is also in agreement with the results obtained for polymerization in solution of monoacrylates[23] and is related to the electron-withdrawing character of the groups attached in the β position with respect to the N atom.[24]

Influence of amine concentration

As mentioned above, the efficiency of the initiator system in the visible-light-cured resin is dependent on the concentration of the reducing agent (coinitiator) and this efficiency affects some clinically important properties such as the depth of cure, the thickness of the oxygen-inhibited layer, and the aesthetic properties of the photocured formulations. For example, the excess of amine can cause instability of the color because of the formation of oxidation products. Furthermore, the residual amine increases the potential toxicity of such products by virtue of its toxic and mutagenic nature.[1,5,8,9] For these reasons, the optimization
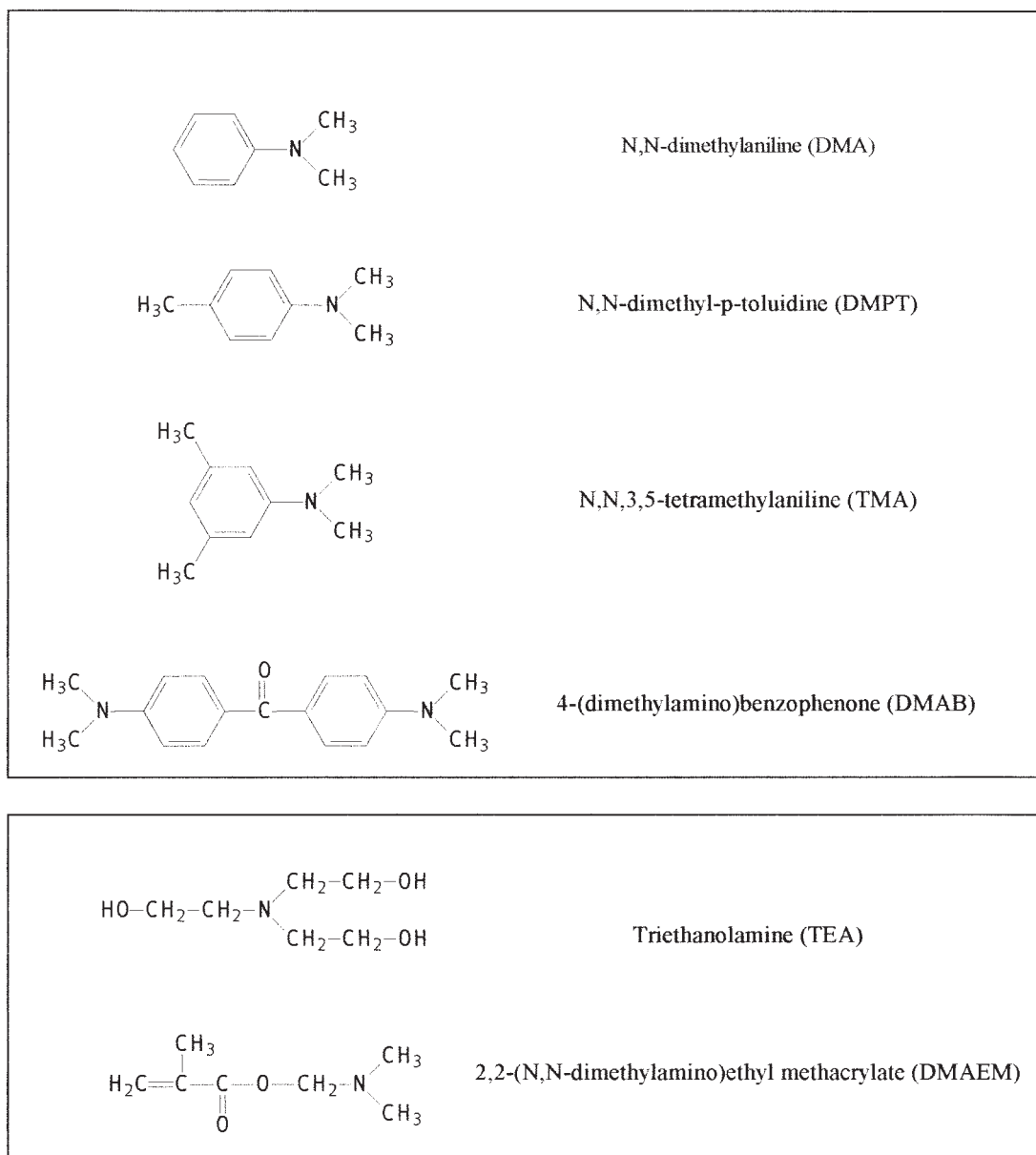
Scheme 1

of the photoinitiation system by setting limits in the amine concentration constitutes a crucial step when formulating a dental material with the most favorable characteristics in all aspects.

In order to establish the optimal concentration of reducing agent, DMAEM was selected as coinitiator. This amine possesses an additional advantage because of its possibility of copolymerizing with the monomeric matrix through the methacrylic group of its structure, thus forming harmless polymers.

Polymerization studies were carried out with variable concentrations of DMAEM (0–5 wt %) and a constant concentration of CQ (0.5 wt %). The results are presented in Figure 6, which shows that at low amine concentrations the polymerization rate grows toward a maximum (at 0.5–1% of amine) and then at higher amine contents it decreases. Similar behavior was reported by Cook,[15] who observed that an excess of amine acted as a retardant when TMA was used as a coinitiator for different mixtures of diacrylic monomers. Cook explained the dual action of the amine in accelerating the polymerization at low levels and in retarding this reaction at higher concentrations in terms of a chain transfer process in which the rate of the addition of amine radical to the monomer is much slower than the rate of the propagation reaction. In contrast, it was noticed that in the absence of amine some weak photopolymerization process also took place (R_p = 3.6 × 10^{-4} mol/L s). This appears to be caused by the presence of an impurity in the Bis-GMA
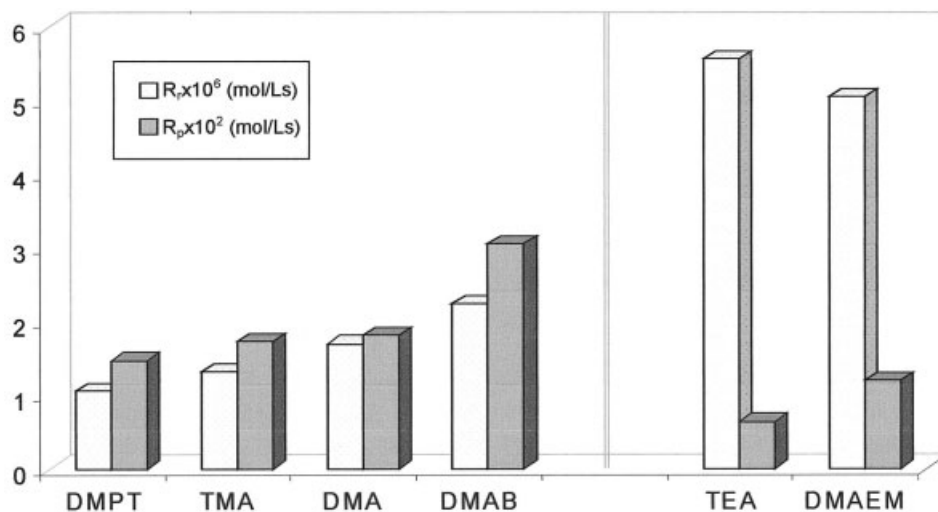
Figure 5 A comparison between the rate of polymerization (R_p) and the rate of CQ photoreduction (Rr) in the presence of amines (40/60 wt % Bis-GMA/TEGDM).

and TEGDM products, which were used as received, although some authors suggest that CQ itself can initiate the polymerization of multimethacrylates by direct hydrogen abstraction from the monomer molecule by excited CQ.[25]

Influence of presence of pigment

Titanium dioxide, one of the most widely used pigments in the formulation of dental pit and fissures sealants, was used to assess the influence of its pres-

ence on the polymerization rate of the studied system. For this purpose, the 40/60 wt % Bis-GMA/TEGMA mixture was selected and the concentration of TiO_2 was varied from 0 to 2 wt %. It was observed that the R_p underwent a slow decrease from 1.22 to 1.07 mol/L s with the rise of the pigment's content from 0 to 2 wt %. This result may be explained by assuming the presence of TiO_2 in the monomeric composition reduces the intensity of light absorbed by the photoinitiator due to a screening effect. This supposition was confirmed by studying the variation in the absorbance
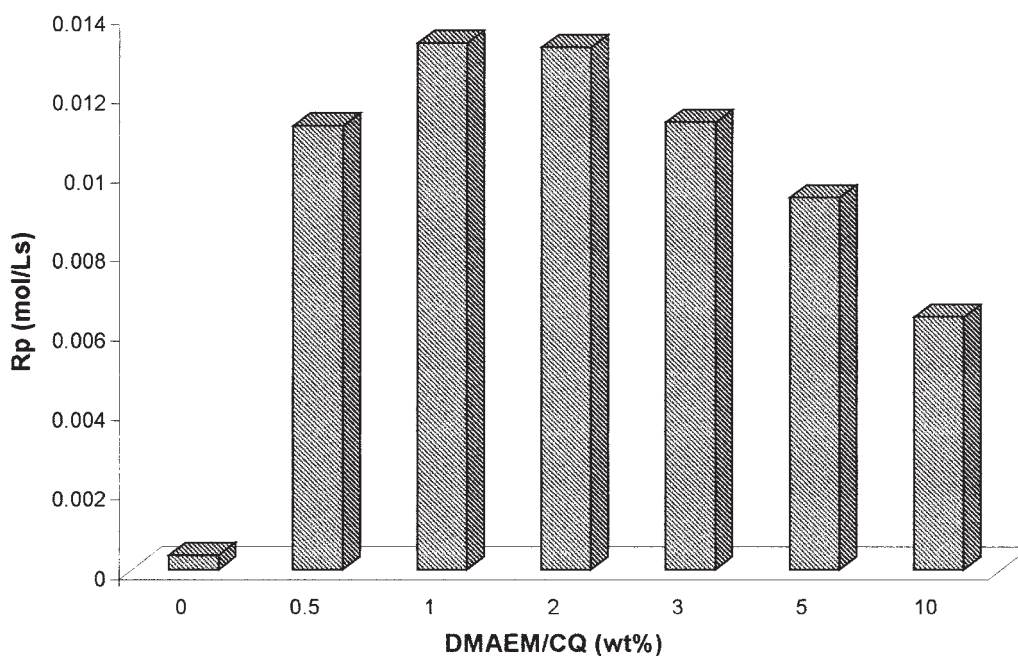

Figure 6 The dependence of the polymerization rate (R_p) on the DMAEM/CQ ratio (40°C, I_0 = 0.50 mcal/s, 0.5 wt % CQ, 40/60 wt % Bis-GMA/TEGDM).

toward visible light by the monomeric mixtures in the presence of the variable amounts of TiO_2, proving some increase in absorbed light intensity with the content of this pigment.

CONCLUSIONS

All the compositions that were studied showed similar kinetic profiles under visible light irradiation, their polymerization rates being directly proportional to the square root of the incident light intensity. This is in agreement with the well-known mechanism for the ideal radical photopolymerization of monofunctional vinyl monomers in solutions.

An increase in the monomer diluent content (TEGDM) from 40 to 60% in the monomeric mixture leads to a reduction in the R_p (from 2.86 to 2.73 mol/L s at $I_0 = 1.64–1.8$ mcal/s) but to higher monomer conversion (from 68.2 to 82.7% with 15-min irradiation and the same I_0) and therefore to a decrease of the percentage of residual double bonds. This is explained by a decrease in viscosity of the mixtures, which permits increased mobility of the monomers and macroradicals during the process of propagation, leading to higher monomer conversion. Taking these results into account, it can be tentatively concluded that the behavior shown by the 40/60 mixture of Bis-GMA/TEGMA is the most favorable for producing unfilled dental resins with improved end characteristics because this composition guarantees less quantities of residual monomer, which is the main source of the potential toxicity of these materials as well as the degradation in their physicomechanical properties.

With respect to the initiating system, the best results were obtained with the aromatic tertiary amines DMPT, TMA, DMA, and DMAB. It was established that the efficiency of the coinitiator depends both on its ability to reduce the CQ under irradiation (quantum yield of CQ photoreduction) and on the reactivity of amine-derived radicals toward the initiation of acrylic monomer polymerization. Concerning the amine concentration, the most favorable ratio of CQ to coinitiator was found to be in the interval of 1/1–1/2 (wt %).

References

1. Linden, L. A. In Radiation Curing in Polymer Science and Technology. Practical Aspect and Applications; Fonassier, J. P.; Rabek, J. F., Eds.; Elsevier Applied Science: New York; 1993; Vol. 4, p 394.
2. Abadie, M. J. M.; Appelt, B. K. Dent Mater 1989, 6.
3. Yoshida, K.; Greener, E. H. J Dent 1994, 22, 296.
4. Cook, W. D. Polymer 1992, 33, 2152.
5. Davidenko, N.; Díaz, J. M.; Sastre, R. Rev Plast Mod 1999, 519, 287.
6. Davidenko, N.; Cohen, M. E.; Díaz, J. M.; Sastre, R. J Biomater Sci 1998, 9, 891.
7. Koda, J.; Tsuchiyai, H. J Dent Mater 1990, 6, 13.
8. Ferracane, J.; Berge, H. J Dent Res 1995, 74, 1418.
9. Allen, J. G.; Dart, E. C.; Jones, E. J. Photochemistry 1987, 3, 86.
10. Niinimaki, A.; Rosberg, J.; Saari, S. Contact Dermatitis 1983, 9, 148.
11. Peutzfeldt, A.; Asmussen, E. Acta Odontol Scand 1989, 47, 229.
12. Andrzejewska, E.; Lindén, L. A.; Rabek, J. F. Macromol Chem Phys 1998, 199, 441.
13. Sionkowska, A.; Kamiñska, A.; Lindén, L. A.; Rabek, J. F. Polym Bull 1999, 43, 349.
14. Jun, N. Ph.D. Dissertation, University of Stockholm, 1998.
15. Cook, W. D. Polymer 1992, 33, 600.
16. Cook, W. D. J Appl Polym Sci 1991, 42, 2209.
17. Scranton, A. B.; Bowman, C. N.; Klier, J.; Peppas, N. A. Polymer 1992, 33, 1683.
18. Anseth, K. S.; Kliene, L. M.; Walker, T. A.; Anderson, K. J.; Bowman, C. N. Macromolecules 1995, 28, 2491.
19. Sastre, R.; Conde, M.; Mateo, J. L. J Photochem Photobiol 1988, A44, 111.
20. Sastre, R.; Conde, M.; Catalina, F.; Mateo, J. L. Rev Plast Mod 1989, 393, 375.
21. Kurdikar, D. L.; Peppas, N. A. Polymer 1994, 35, 1004.
22. Mateo, J. L.; Bosch, P.; Lozano, A. E. Macromolecules 1994, 27, 7794.
23. Mateo, J. L.; Bosch, P.; Catalina, F.; Sastre, R. J Polym Sci Part A: Polym Chem 1991, 29, 1955.
24. Mateo, J. L.; Bosch, P.; Lozano, A. E. J Polym Sci Part A: Polym Chem 1997, 35, 2889.
25. Andrzejewskaya, L. A.; Linden, J. P. Macromol Chem Phys 1998, 199, 441.