Polymer Bulletin (2024) 81:4221–4235
https://doi.org/10.1007/s00289-023-04832-3

ORIGINAL PAPER

Photoinitiated polymerization of a dental formulation, part 2: kinetic studies

Afaf Bouzidi[1] · **Samir Bayou**[2] · **Nawal Khier**[3] · **Mohamed Dehamchia**[4]

Received: 8 September 2022 / Revised: 4 March 2023 / Accepted: 5 May 2023 /

Abstract

This work examines the classic dental formulation of dimethacrylate resins Bis-GMA and TEGDMA with camphorquinone (CQ)/*N,N*-dimethylaminoethyl methacrylate, which is recognized as the most efficient photoinitiator system for this type of formulation. The kinetics of photoinitiated polymerization of this formulation was studied using isothermal photocalorimetry. Two kinetic models were applied. First, it is shown that an autocatalytic model can describe the reaction satisfactorily. As long as the reaction system has not reached its freezing point, the reaction follows the autocatalytic pattern perfectly. The analysis of the linear part of the curve then allows us to obtain the values of the coefficients $m = 0.4$ and $n = 1.6$. The reaction temperature does not influence the orders m and n of the reaction, but the phenomenological rate constant k varies with temperature according to the Arrhenius law up to 60 °C. In addition, the ratio of the rate constants k_p and k_t were calculated by means of a mechanistic model. Their evolution with conversion has been studied for different reaction temperatures, and the results effectively illustrate the importance of the reactive diffusion mechanism.

Keywords Dimethacrylate oligomer · Photocross-linking · Phenomenological and mechanistic model

---

✉ Samir Bayou
bayou-samir@univ-eloued.dz

[1] VTRS Laboratory, Department of Chemistry, Faculty of Exact Sciences, University of El Oued, PO Box 789, 39000 El-Oued, Algeria

[2] LEPCMAE, Faculty of Chemistry, USTHB, El-Alia, PO Box 32, 16025 Bab-Ezzouar, Algeria

[3] Laboratory of Bioinformatics, Applied Microbiology and Biomolecules, University of Boumerdès, 35000 Boumerdès, Algeria

[4] Laboratory of Biodiversity and Biotechnology Application in Agriculture Domain (BABDA) Heterocyclic Organic Synthesis and Biotechnology GroupDepartment of Biology, University of El Oued, PO Box 789, 39000 El-Oued, Algeria

Introduction

The use of polymeric materials is increasing in odontology [1–3]. Dental composites for dental restoration in odontology consist of a photopolymerizable resin matrix reinforced by mainly mineral particles. This matrix consists of monomers and oligomers with dimethacrylate functions [4, 5], and the most commonly used monomers are Bis-GMA and TEGDMA. The Bis-GMA monomer with aromatic nuclei ensures the rigidity and strength of the composite and presents a low volume contraction during polymerization [6, 7]. This low volume contraction reduces the internal stresses and increases the service life of the restoration [8, 9]. On the other hand, its high viscosity restricts the mobility of the reaction medium, which limits the conversion of methacrylic functions [10, 11]. This results in an alteration of the physical and biological properties of the material obtained [12–14]. Therefore, TEGDMA is usually added as a reactive diluent, which improves the conversion [15–18] and thus the physical and biological properties of the final material, but it also generates a volume contraction in larger material [6, 19, 20].

The photochemical polymerization of methacrylates multifunctional monomers is one of the most effective methods for creating high-density three-dimensional polymer networks [21, 22]. The kinetic behavior of polymerization is a complex process, and a number of characteristic phenomena are observed. These include auto-acceleration and auto-deceleration, incomplete conversion of functional groups, delayed volume shrinkage relative to equilibrium and unequal reactivity of the double bonds of dimethacrylate monomers [23].

One of the main characteristics of the polymerization reactions of multifunctional monomers is the presence of an auto-acceleration phase and an auto-deceleration phase. This result is a dependent on the reaction rate and the conversion with passage through a maximum, of which the position depends on the nature of the monomer and the reaction conditions. This phenomenon is similar to that of autocatalytic reactions, which makes it possible to consider the polymerization of multifunctional monomers as an autocatalytic process (unlike reactions of order n, which predict the maximum reaction rate at the origin of the conversion). Generally, the autocatalytic effect is due to the formation of intermediate species that greatly accelerate the reaction. In the case of the polymerization of multi-vinyl monomers, this effect is due to the decrease in the rate of termination due to the reduced diffusion of the ends of growing reactive chains. Thus, the resulting increase in radical concentration leads to higher curing rates. The autocatalytic model has already been used in the literature to describe the polymerization of multifunctional methacrylic monomers [23–25]. The kinetic model of the formulations consists of determining an appropriate kinetic equation for the system analyzed to measure the reaction orders, activation energies, and reaction parameters.

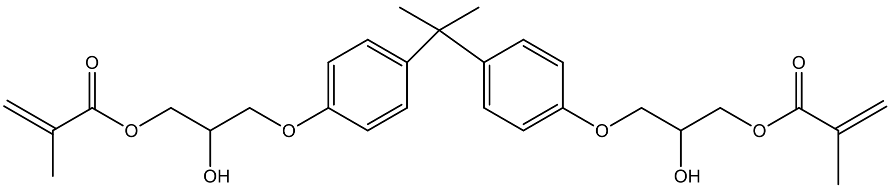
We performed a kinetic study of dental formulation consisting of a mixture of monomers (Bis-GMA/TEGDMA) and a CQ / DAMEMA photoinitiator system, which is the base resin of many dental composites [26]. Previous work was carried out to determine how to control the homogeneity of the materials formed, and we studied the polymerization by subjecting the formulations to several experimental conditions: different concentrations of photoinitiator and diluent, different light intensities, and different temperatures. The influence of various parameters on the evolution of the photopolymerization reaction of Bis-GMA/TEGDMA was studied by photocalorimetry. The results obtained made it possible to determine the optimal polymerization conditions (by weight composition of 75% Bis-GMA/25% TEGDMA and a concentration of the initiator system of 1% by weight (CQ/DMAEMA (1/1))). The optimal final conversion remains below 100% due to the transition to a vitreous state, which causes the blocking of the reactive species and stops the polymerization [27].

Based on the results of previous studies, this article describes kinetic models of the photoinitiated polymerization reaction of this formulation. To this end, we first use a phenomenological model to experimentally determine the various parameters of the kinetic equations, such as the velocity constant k, reaction orders m and n, and activation energy E. Secondly, we will be interested in a mechanistic model that takes into account the diffusional control of the reaction.

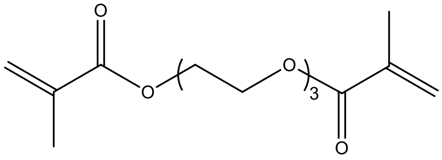
Experimental

Materials

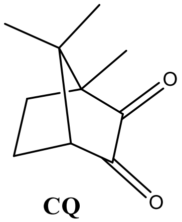
The monomers used in this work are commercial monomers of the di-methacrylate type: Bis-GMA (98%) and TEGDMA (95%, containing 200 ppm. of monomethylether hydroquinone). They were used without prior purification. The system used to prime the photopolymerizable formulations was camphorquinone/2-(dimethylamino)ethylmethacrylate (CQ/DMAEMA). The camphorquinone (CQ > 98%) was chosen as photoinitiator, given its wide use in dental formulations [28]. This molecule absorbs light in the visible range, which requires a hydrogen donor molecule to generate radicals by electron and proton transfer from its triplet-excited state. The 2-(dimethylamino)ethylmethacrylate (DMAEMA > 99% from Aldrich) is a co-initiator or photoaccelerator donor of hydrogen. These reagents were purchased from Aldrich (Lyon, France) and were used without further purification.



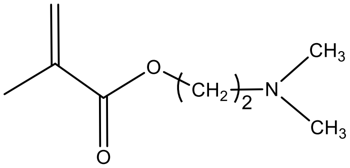
2,2-bis[4-(2-hydroxy-3-methacryloyloxyprop-1-oxy)phenyl]propane (**Bis-GMA**)



Triethylene glycol dimethacrylate (**TEGDMA**)



CQ



DMAEMA

Preparation of the photopolymerizable mixture

The photopolymerizable dental formulations were prepared by mixing the monomers (75% Bis-GMA/25%TEGDMA) by weight. The CQ/DMAEMA priming system (1%/1% by weight) was incorporated into the monomer mixtures. The reagents were mixed under magnetic stirring for 30 min at 50 °C in dark conditions. The formulations obtained were kept old and protected from light before their use to avoid any crosslinking reaction.

Analysis technique

The kinetic analysis of the photopolymerization reaction was followed by photocalorimetry (Photo-DSC), which was done using a differential scanning calorimeter (DSC7 Perkin Elmer, Waltham, MA, USA) with an irradiation unit: a dental halogen office lamp emitting quasi-monochromatic radiation at 465 nm (LA500 Blue Light, Philippines Union Commercial Inc., New Manila, Quezon City, Philippines). The heat flow was recorded as a function of time in isothermal mode under nitrogen atmosphere. The optical part of the calorimeter, sample preparation and thermogram processing have been described elsewhere [29]. The calculation of the conversion rate and the reaction rate was carried out according to previously published work [27].

Results and discussion

Photopolymerization of formulations

The photopolymerization of multifunctional monomers (methacrylates) leads to the formation of a strongly cross-linked polymer network. The polymerization reaction of the Bis-GMA/TEGDMA formulation initiated by the CQ/DAMEMA initiation system is schematised in Fig. 1.

In general, the process of this radical reaction involves three steps: initiation, propagation and termination.

The first step begins with the breakdown of camphorquinone (CQ) [30, 31]. After absorbing a quantum of light energy, CQ finds itself in an excited state and associates with the amine DMAEMA to form an excimer. The latter eventually decomposes after transfer of hydrogen to α of the amine to form an initiator amine radical and a camphorquinone radical. The amine radical formed, denoted ($R^{\bullet}$), can form a covalent bond with the double bond of the monomer. The cetyl radical (camphorquinone) does not initiate the polymerization reaction. It generally recombines with another cetyl radical to form a pinacol or returns to its primary form or even forms the secondary alcohol (Fig. 2).

The propagation of the polymerization is due to a series of reactions between the radials formed and the vinyl of the starting monomers. Chain growth can lead to bridging and the formation of new polymerization sites (Fig. 3).

The termination reaction can be done either by the combination of two macroradical chains to give a new carbon–carbon bond or by disproportionation by the transfer of hydrogen from one macroradical chain to another to give a saturated and an unsaturated macromolecule. The crosslinked material obtained may contain reactive species, which are frozen inside the polymer network [32].

Phenomenological model

The kinetics of the photochemical reaction of multifunctional monomers obeys mainly to two types of kinetics: reaction of order n and autocatalytic reactions. For crosslinks, which follow a reaction of order n, the reaction rate is given by:

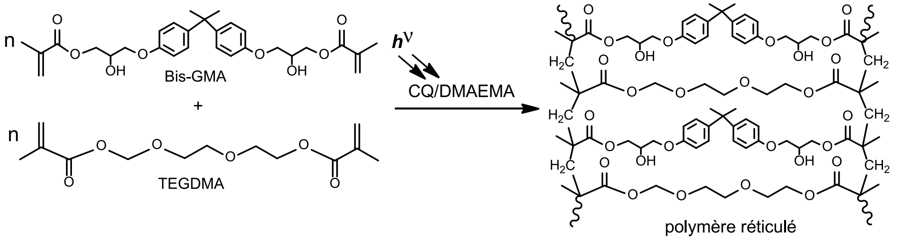


Fig. 1 Formation of a crosslinked polymer by polymerization of Bis-GMA/TEGDMA formulation

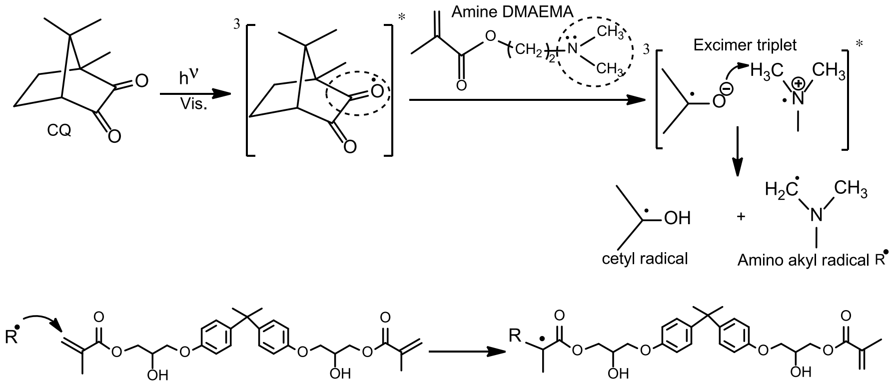


Fig. 2 Mechanism of CQ decomposition and formation of the first radical monomer

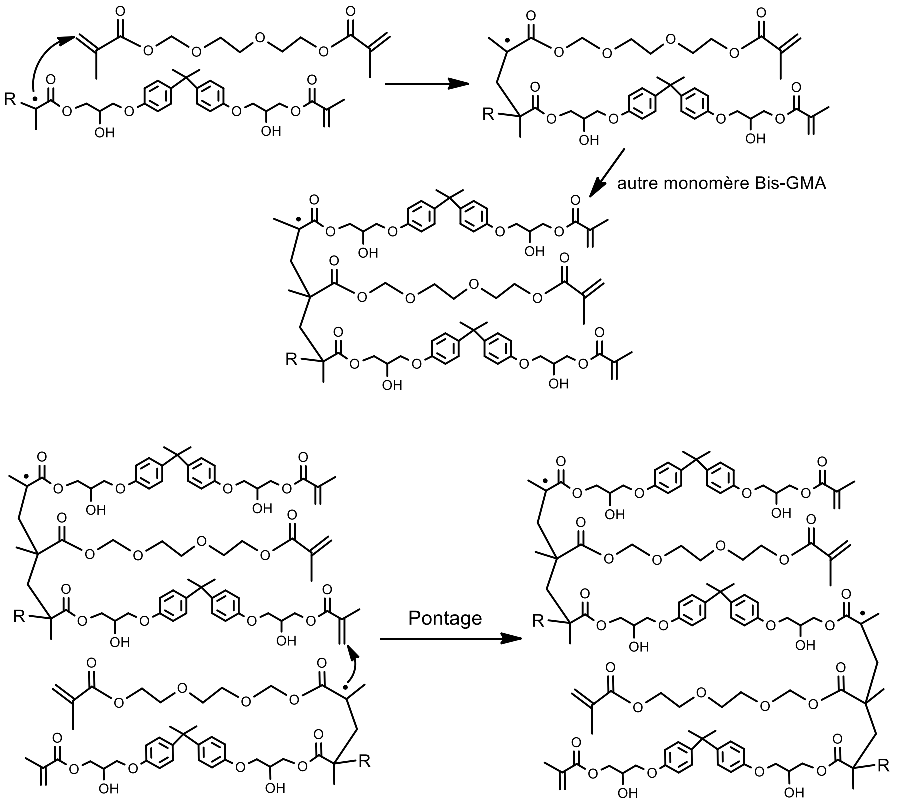


Fig. 3 Reactions involved in the propagation step

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k(1 - C)^n \tag{1}$$

where C is the conversion rate, k is the rate constant and n is the order of the reaction.

Autocatalytic reactions are characterized by the expression:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = kC^m(1 - C)^n \tag{2}$$

where m is also an order of reaction.

For the autocatalytic model, Eq. (2) seems best suited to describe the isothermal crosslinking of multifunctional methacrylic monomers. The shape of the photoinitiated polymerization rate curves is the same as that of the autocatalytic reaction (Fig. 4). Although photoinitiated polymerization is autoaccelerated and not autocatalyzed, this model can be applied to describe these reactions in a purely mathematical manner.

This work focuses on the Kamal and Sourour approach [33] to take into account the kinetics of cross-linking and access to the energy parameters of Arrhénius.

The heat given off during the cross-linking is proportional to the number of double bonds have reacted. Equation (3) defines the conversion rate.

$$C_t = \frac{\Delta H_t}{\Delta H_{\mathrm{theorique}}} \times 100 \tag{3}$$

where ΔH_t is the enthalpy at time t, and $\Delta H_{\mathrm{Theoretical}}$ is the theoretical enthalpy that all methacrylate functions should release.

The integral form of relation (3) leads to the expression (4) [33]:

$$C = \frac{At^B}{1 + At^B} \tag{4}$$

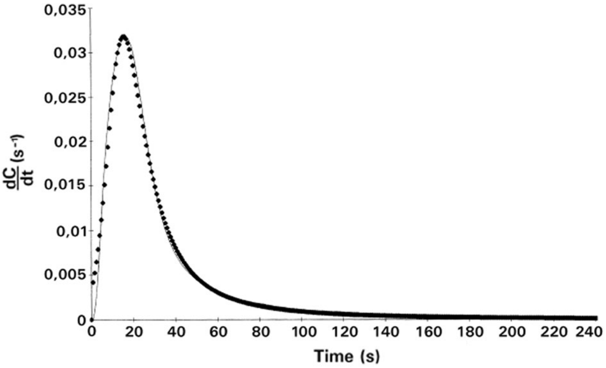


Fig. 4 Typical photoinitiated polymerization rate versus time curve at 50 °C. Experimental curve (——) and modeling (◆)

where t is the time elapsed since the start of the isothermal reaction, and A and B are coefficients related to the parameters m, n, and k of Eq. (2). Equation (4) can be arranged in an equivalent form:

$$\frac{C}{1-C} = At^{B} \tag{5}$$

The derivative of Eq. (4) in relation to time gives:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{At^{B-1}}{(1+At^{B})^{2}} \tag{6}$$

Moreover, the combination of Eqs. (2) and (4) makes it possible to obtain at a different form of the reaction rate:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = kC^{m}(1-C)^{n} = k\left[\frac{At^{B}}{(1+At^{B})}\right]^{m} \cdot \left[\frac{1}{1+At^{B}}\right]^{n} \tag{7}$$

or:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k\frac{A^{m}t^{Bm}}{(1+At^{B})^{m+n}} \tag{8}$$

Equations (6) and (8) can be directly compared and allow us to deduce the relationships between the parameters (m, n, and k) and the coefficients (A and B).

By analogy, we have $m+n=2$ and $B\text{-}1=B.m$, from which we can deduce:

$$m = 1 - \frac{1}{B} \tag{9}$$

$$n = 1 + \frac{1}{B} \tag{9'}$$

$$AB = kA^{m} \tag{10}$$

The photocalorimetric measurements made continuously throughout the reaction make it possible to obtain the heat ΔH_t released at time t and to calculate the C_t conversion from Eq. (3). Once the conversion rate is determined as a function of time, we can obtain Eq. (5) in its logarithmic form:

$$\ln\frac{C}{1-C} = \ln A + B\ln t \tag{11}$$

Figure 5 shows a graphical representation of Eq. (11); i.e., the evolution of *ln (C/(1-C))* as a function of ln (t) for the photopolymerization of the formulation Bis-GMA/TEGDMA ($T=30$ °C, I = 40 mW/cm^2, and 1% by mass CQ/DMAEMA (1/1)).

According to the curve in Fig. 5, as long as the reaction system has not reached its gel point, the reaction follows the autocatalytic model perfectly [34]. Analysis

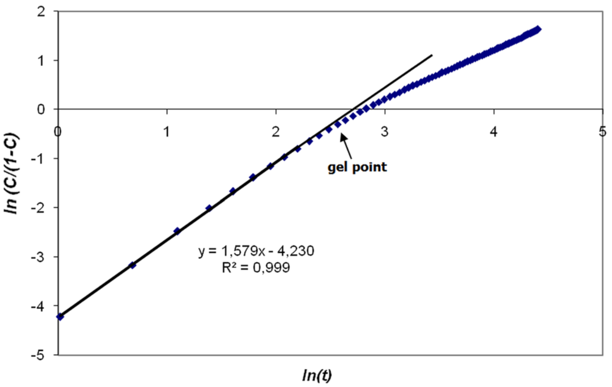


Fig. 5 Curve of ln*(C/(1 – C))* as a function of ln*(t)* for the 75% Bis-GMA/25% TEGDMA formulation

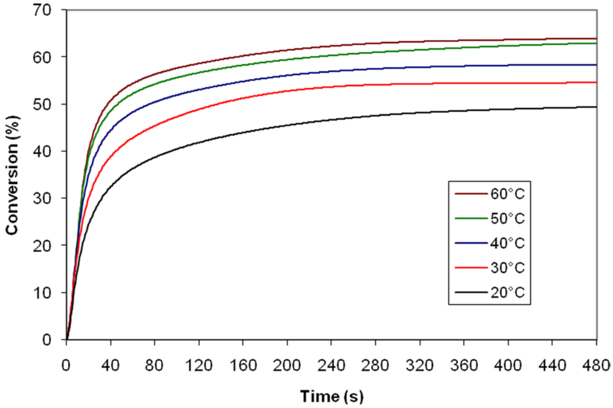


Fig. 6 Evolution of the conversion as a function of the temperature

of the linear part of the curve allows us to obtain the values of the coefficients $m = 0.37$ and $n = 1.63$, which are deduced from the value of the slope, which corresponds to the parameter B. The value of the rate constant k as a function of the conversion before the gel point can then be determined by substituting the calculated m and n values into Eq. (2) or (10).

Some studies have been carried out on the dependence of the orders m and n on these factors [23, 24]. The orders m and n can change considerably with the temperature, surrounding atmosphere, and type of functionality. In this work, we studied the effect of temperature on the m, n, and k values. The photopolymerization kinetics of the 75% Bis-GMA/25% TEGDMA formulation were followed over a temperature range of 20 and to 60 °C (Fig. 6).

From the conversion curves and the graphical representation of Eq. (11), Table 1 shows the values of the kinetic parameters for the Bis-GMA/TEGDMA system obtained with 1% CQ/DMAEMA by weigh at different reaction

Table 1 Values of the kinetic reaction parameters

Temperature (°C)	$k.10^3$ (s^{-1})	m	n
20	100.7	0.38	1.62
30	108.4	0.37	1.63
40	110.4	0.38	1.62
50	118.0	0.42	1.58
60	123.7	0.46	1.54

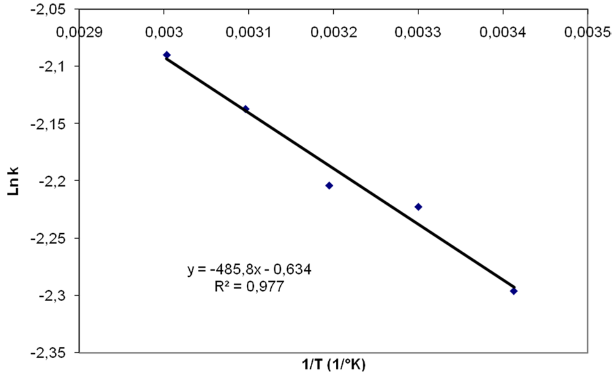


Fig. 7 Evolution of the rate constant k as a function of the reaction temperature

temperatures. The values of n and m were found to be constant and equal to 1.6 and 0.4, respectively, regardless of the reaction temperature. Only the rate constant k varies with temperature (Fig. 7).

The application of the Arrhenius law $k = Ae^{-\left(E_a/RT\right)}$ to the values of k makes it possible to determine the activation energy value as 4.04 kJ/mol and the pre-exponential factor A as 0.53 s^{-1}, which are in agreement with literature. In a study of commercial dental composites based on methacrylate, Morancho et al. [25] showed that the activation energy varies between 4 and 10 kJ/mol.

Mechanistic model

In radical photochemistry, a kinetic model was first proposed by Tryson and Shultz [35], and then extensively developed by Decker et al. [36], and Andrzejewska [37]. This model allows us to access the propagation and termination rate constants with simple knowledge of the evolution of the reaction rate over time. This model involves the classical steps of the polymerization reaction.

Initiation:

$$A_2 \xrightarrow{hv} 2A^{\cdot} \quad R_i = 2,3\phi\varepsilon I_0\left[A_2\right]$$

$$A^{\cdot} + M \rightarrow AM^{\cdot} \quad [A_2] = [A_2]_0 e^{-2,3\Phi_0 \varepsilon I_0 t}$$

Propagation:

$$\sim M^{\cdot} + M \xrightarrow{k_p} \sim MM^{\cdot} \quad R_p = -\frac{d[M]}{dt} = k_p[M^{\cdot}][M]$$

Bimolecular termination:

$$\sim M^{\cdot} + {}^{\cdot}M \overset{k_t}{\rightsquigarrow} \sim MM \sim \quad R_t = -\frac{d[M^{\cdot}]}{dt} = 2k_t[M^{\cdot}]^2$$

The principle of this model is to determine the ratio $k_p/k_t^{0.5}$ ratio and the energy of the photopolymerizable formulation by studying the polymerization kinetics under quasi-stationary conditions. The approximation of the quasi-stationary state and the combination of the equations expressing the initiation (R_i), propagation (R_p), and termination (R_t) rates lead to the expression of the following photopolymerization rate:

$$R_p = \frac{k_p}{\sqrt{k_t}} \sqrt{2,3\varphi\varepsilon I_0 [A_2]}[M] \tag{14}$$

$$\frac{k_p}{\sqrt{k_t}} = \frac{R_p}{[M]} \sqrt{\frac{2}{2,3\varphi\varepsilon I_0 [A_2]}} \tag{15}$$

where k_p and k_t are the propagation and termination rate constants, $[A_2]$ and [M] are the photoinitiator and monomer concentrations, respectively, ϕ is the initial quantum yield, ε is the molar extinction coefficient of the photoinitiator, and I_0 is the intensity of the incident radiation.

In order to determine the evolution of $k_p / k_t^{0,5}$, the rate of polymerization must first be followed as a function of the time under continuous irradiation. In our case, from the photo-DSC experiments, Rp is defined as follows:

$$R_p = \frac{[M]_0}{\Delta H_{\text{theor}}} \frac{\mathrm{d}(\Delta H_t)}{\mathrm{d}t}$$

The plot of $\frac{R_p}{[M]}\sqrt{\frac{2}{2,3\varphi\varepsilon I_0[A_2]}}$ plot as a function of the conversion makes it possible to determine the evolution of $k_p/k_t^{0.5}$ during the reaction. The values of $[M]$ and R_p and the conversion to times are obtained directly from the DSC thermograms. This study examined the 75%Bis-GMA/25%TEGDMA formulation while assuming an initial quantum yield of $\phi = 1$.

Figure 8 shows the evolution of $k_p/k_t^{0.5}$ as a function of conversion for different reaction temperatures carried out with a radiation intensity of Io = 40 mW/cm^2. The evolution of these curves indicates that the photopolymerization of Bis-GMA/TEGDMA can be explained as follows. During the first seconds of the reaction, the

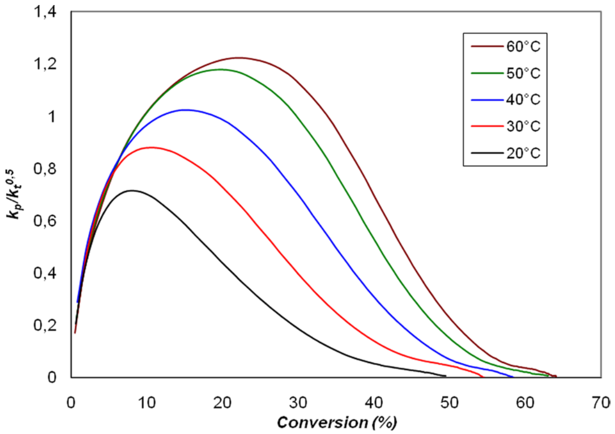


Fig. 8 Variation of $k_p/k_t^{0.5}$ as a function of the conversion of the 75% Bis-GMA/25% TEGDMA system

viscosity of the medium increases rapidly, the segmental or translational diffusion of reactive species is greatly reduced, and it is increasingly difficult for two radicals to meet and reach the termination stage. Therefore, the rate constant k_t is relatively low during this step, which explains the strong increase in the ratio $k_p/k_t^{0,5}$.

The termination mechanism is then no longer controlled by segmental diffusion but by reactive diffusion and assumes a propagation mechanism. From the top of the curve, the viscosity continues to increase, and the mobility of the reactive groups is increasingly reduced. This influences the propagation reaction, which then becomes controlled by diffusion. This step is characterized by the rapid decrease in the ratio $k_p/k_t^{0.5}$. At the end of the reaction, k_p and k_t become very weak and the ratio tends towards 0.

The activation energy of the mechanistic model is calculated from the substitution of the rate constants k_p and k_t by their Arrhenius expressions in the rate Eq. (15). We then obtain the following equation:

$$\ln\left[-\frac{\mathrm{d}[M]}{\mathrm{d}t}\right] = \ln\left(\frac{A_p}{\sqrt{A_t}}\right) + \ln\left([M]\sqrt{2,3\Phi\varepsilon I_0[A_2]}\right) - \frac{E_R}{\mathrm{RT}} \qquad (16)$$
$$\text{with} \quad E_R = E_p - E_t/2$$

According to Fig. 6, when the temperature increases, there is first a slight increase in the initial polymerization rate R_{Pi}, which is assimilated to the maximum slope of the tangents to the conversion curves at the beginning of the reaction $R_P^{\max}$.

From Eq. (16), we can plot the evolution of *ln* ($R_P^{\max}$) as a function of 1/T (Fig. 9). The slope of the line gives us a total reaction activation energy of 8.15 kJ/mol. In the case of the phenomenological model, however, the activation energy is 4.04 kJ/mol. This difference can be explained by the fact that the mechanistic model takes into account the reactions that take place during the

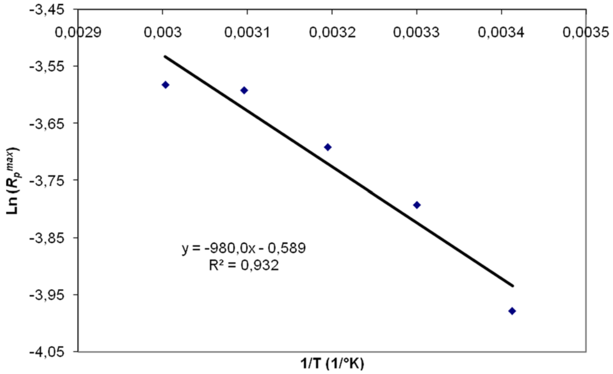


Fig. 9 Evaluation of reaction rate as a function of 1/T of the formulation 75% Bis-GMA/25% TEGDMA

polymerization up to the maximum rate, while the phenomenological model is based on the reaction process up to the gel point.

Conclusion

The progress of the photoinitiated polymerization reaction of the Bis-GMA/TEGDMA system was followed by photocalorimetry (Photo-DSC). The study of the kinetics at different temperatures made it possible to determine the kinetic parameters of the photochemical reaction using two models. The application of the first autocatalytic model based on the relationship

$$\frac{\mathrm{d}C_{\mathrm{t}}}{\mathrm{dt}} = kC_t^m\left(1-C_{\mathrm{t}}\right)^n$$

led to the determination of reaction orders independent of the reaction temperature as 0.4 and 1.6 for *m* and *n*, respectively. The temperature dependence was observed in the evolution of the global rate constant *k*, which followed the Arrhenius law up to 60 °C.

In order to truly take into account the chemical phenomena occurring during the reaction, a second mechanistic model was based on the kinetic equations of the different steps involved in the photopolymerization reaction. This model determined the evolution of the ratio of the propagation rate and termination rate constants during the reaction. The increase in the viscosity of the polymerizing medium had a more marked effect on the termination reactions than on the propagation reactions, which resulted in the passing of $k_p/k_t^{0.5}$ by a maximum.

References

1. Bayne SC (2013) Beginnings of the dental composite revolution. J Am Dental Assoc 144:42S-46S https://doi.org/10.14219/jada.archive.2013.0248
2. Manouchehi F, Sadeghi B, Najafi F, Mosslemin MH, Niakan M (2019) Synthesis and characterization of novel polymerizable bis-quaternary ammonium dimethacrylate monomers with antibacterial activity as an efficient adhesive system for dental restoration. Polym Bull 76:1295–1315. https://doi.org/10.1007/s00289-018-2414-y
3. Beun S, Glorieux T, Devaux J, Vreven J, Leloup G (2007) Characterization of nanofilled compared to universal and microfilled composites. Dent Mater 23:51–59
4. Schroeder WF, Cook WD, Vallo C (2008) Photopolymerization of *N,* N-dimethylaminobenzyl alcohol as amine co-initiator for light-cured dental resins. Dental Mater 24:686–693
5. Gauthier MA, Zhang Z, Zhu XX (2009) New dental composites containing multimethacrylate derivatives of bile acide : Acomparative study with commercial monomers. Appl Mater Interfaces 1:824–832
6. Atai M, Watts DC, Atai Z (2005) Shrinkage strain-rates of dental resin-monomer and composites systems. Biomaterials 26:5015–5020
7. Sarhaadei E, Najafi F, Akbari B (2022) Assessing two dominant methods of dental composites linear polymerization shrinkage management: macromonomers and prepolymerized fillers. Polym Bull 79:8193–8215. https://doi.org/10.1007/s00289-021-03893-6
8. Park JH, Choi NS (2021) Polymerization shrinkage and stress analysis during dental restoration observed by digital image correlation method. J Mech Sci Technol 35:5435–5444. https://doi.org/10.1007/s12206-021-1114-y
9. Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, Leloup G (2006) A physico-chemical explanation of the post-polymerization shrinkage in dental resins. Dent Mater 22(5):405–412
10. Lovell LG, Stansbury JW, Syrpes DC, Bowman CN (1999) Effects of composition and reactivity on the reaction kinetics of dimethacrylate/ dimethacrylate copolymerisation. Macromolecules 32:3913–3921
11. Mendes LC, Tedesco AD, Miranda MS (2005) Determination of degree of conversion as function of depth of a photo-initiated dental restoration composite. Polym Testing 24:418–422
12. Sideridou I, Tserki V, Papanastasiou G (2002) Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. Biomaterials 23:1819–1829
13. Buchwald Z, Sandomierski M, Smulek W, Ratajczak M, Patalas A, Kaczorek E, Voelkel A (2022) Physical-chemical and biological properties of novel resin-based composites for dental applications. Polym Bull, pp 1–24. https://doi.org/10.1007/s00289-022-04606-3
14. Atai M, Nekoomanesh M, Hashemi SA, Amani S (2004) Physical and mechanical properties of an experimental dental composite based on a new monomer. Dent Mat 20:663–668
15. Dewaele M, Truffier-Boutry D, Devaux J, Leloup G (2006) Volume contraction in photocured dental resins: the shrinkage- conversion relationship revised. Dent Mat 22:359–365
16. Lovell LG, Newman SM, Bowman CN (1999) The effects of light intensity, temperature and comonomer composition on the polymerization behavior of dimethacrylate dental resins. J Dent Res 78:1469–1476
17. Dauvillers BS, Aarnst MP, Feilzer AJ (2003) Modelling of visco-elastic behavior of dental light-activated resin composites during curing. Dent Mat 19:277–285
18. Goncalves F, Pfeifer CS, Ferracane JL, Braga RR (2008) Contraction stress determinants in dimethacrylate composites. J Dent Res 87:367–371
19. Carmem SP, Zachary RS, Roberto RB, Dario W, Jose CM, Jeffrey WS (2011) Characterization of dimethacrylate polymeric networks: a study of the crosslinked structure formed by monomers used in dental composites. Eur Poly J 47:162–170
20. Atai M, Watts DC (2006) A new kinetic model for the photopolymerization shrinkage-strain of dental composites and resins. Dent Mat 22:785–791
21. Achilias DS, Karabela MM, Sideridou ID (2008) Thermal degradation of light-cured dimethacrylate resins Part I. Isoconversional kinetic analysis. Thermochim Acta 472:74–83
22. Bayou S, Mouzali M, Lecamp L, Lebaudy P (2013) Simulation of conversion profiles inside a thick dental material photopolymerized in the presence of nanofillers. Polym J 45:863–870

23. Lecamp L, Youssef B, Bunel C, Lebaudy P (1999) Photoinitiated polymerization of a dimethacrylate oligomer: 2. Kinetic stud Polym 40:1403–1409
24. Bayou S, Mouzali M, Abadie MJM (2005) Etude de la photoréticulation par DPC de deux Systèmes TEGDMA / photoamorceur et Bis-GAA / photoamorceur. C R Chimie 8:905–910
25. Morancho JM, Cadenato A, Fernandez-Francos X, Salla JM, Ramis X (2008) Isothermal kinetics of photopolymerization and thermal polymerization of Bis-GMA/TEGDMA resins. J Therm Anal Cal 92:513–522
26. Raskin A, Salomon JP, Sabbagh J (2005) Les résines composites : classification-évolution. Réal Clin 16:297–312
27. Bayou S, Mouzali M, Lecamp L, Lebaudy P (2017) Photoinitiated polymerization of a dental formulation: 1. Influence of photoinitiating system, temperature and luminous intensity. J Fundam Appl Sci 9(2):685–695
28. Asmusen S, Arenas G, Cook WD, Vallo C (2009) Photobleaching of camphorquinone during polymerization of dimethacrylate-based resins. Dent Mater 25:1603–1611
29. Lecampa L, Youssef B, Bunel C, Lebaudyb P (1997) Photoinitiated polymerization of a dimethacrylate oligomer: 1 Influence of photoinitiator concentration, temperature and light intensity. Polymer 38:6089–6096
30. Kamoun EA, Winkel A, Eisenburger M, Menzel H (2016) Carboxylated camphorquinone as visible-light photoinitiator for biomedical application: Synthesis, characterization, and application. Arab J Chem 9:745–754. https://doi.org/10.1016/j.arabjc.2014.03.008
31. Brandt WC, Schneider LFJ, Frollini E, Correr-Sobrinho L, Sinhoreti MAC (2010) Effect of different photo-initiators and light curing units on degree of conversion of composites. Braz Oral Res Jul-Sep 24(3):263–270. https://doi.org/10.1590/S1806-83242010000300002
32. Amorin BC, Vicentin BLS, Di Mauro E (2020) Post-polymerization reactivity of free radicals trapped in resin-based dental restorative materials by ESR spectroscopy. Polym Bull 77:3249–3262. https://doi.org/10.1007/s00289-019-02914-9
33. Kamal MR, Sourour S (1973) kinetic and thermal characterization of thermoset cure. Polym Eng Sci 13:59–64
34. Abadie MJM, Rouby M (1996) II-Description d'un protocole d'étude pour résines photopolymérisables. J Biomatériaux Dentaires 11:141–148
35. Tryson GR, Shultz AR (1979) A calorimetric study of acrylate photopolymerization. J Polym Sci Polym Phys Ed 17:2059–2075
36. Decker C, Elzaouk K, Decker D (1996) Kinetic study of ultrafast photo-polymerization reactions. J M S Pure Appl Chem A33(2):173–190
37. Andrzejewska E (2001) Photopolymerization kinetics of multifunctional monomers. Prog Polym Sci 26:605–665