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Reactivity of Benzoyl Peroxide/Amine System as an Initiator for the Free Radical Polymerization of Dental and Orthopaedic Dimethacrylate Monomers: Effect of the Amine and Monomer Chemical Structure

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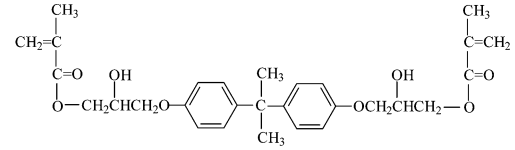
ABSTRACT: The free radical homopolymerization of Bis-phenol-A-bis(glycidyl methacrylate) (Bis-GMA), a urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA) induced by a benzoyl peroxide (BPO)/amine redox couple was studied by differential scanning calorimetry. As amine, para-substituted *N*,*N*-dimethylaniline derivatives were used. Amines with electron-donating para-substituents, such as $-CH_3$, $-CH_2CH_2OH$, or $-CH_2COOH$, are efficient co-initiators for polymerization at 37 °C. On the contrary the amine with the electron-withdrawing para-substituent $-COOCH_2CH_3$, could not initiate polymerization at 37 °C, but only at higher temperatures. The kinetic parameters of polymerization are strongly affected also by the chemical structure of the monomer. UDMA showed the highest values for the maximum polymerization rate followed by Bis-GMA and TEGDMA. TEGDMA showed the highest degree of final conversion (ca. 70%) followed by UDMA (ca. 40%) and Bis-GMA (ca. 27%).

Introduction

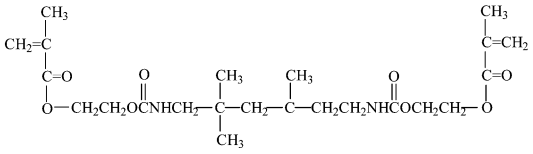
Polymers based on methacrylates have been extensively used in dental and orthopaedic applications for nearly 50 years. Initially, methyl methacrylate (MMA)-based polymers were developed for use in dentistry, for denture construction and prevention of tooth decay, and then were transitioned into orthopaedics by Charnley (1960, 1961) for the stabilization of metallic femoral hip endoprostheses.[1,2] Poly(methyl methacrylate) (PMMA)-based materials (homopolymers of MMA or copolymers with higher methacrylates) are thermoplastic elastic materials with limited strength; therefore, the dental industry focused on stronger more inelastic systems for use as dentures, crowns, bridge prostheses, and tooth restorative materials (with or without inorganic filler particles). This research led to the development of systems based on dimethacrylate monomers, which produce cross-linked polymers, that are stronger and more durable than the PMMA-based polymers.[1−4] The most important dimethacrylate is Bis-phenol-A-bis(glycidyl methacrylate) (Bis-GMA), which is typically copolymerized with triethylene glycol dimethacrylate (TEGDMA) used as a viscosity diluent. Other commonly used dimethacrylate monomers are the ethoxylated Bis-phenol-A-dimethacrylate (Bis-EMA) and a urethane dimethacrylate (UDMA). (Figure 1). Following the path of PMMA, the Bis-GMA-based systems have recently been introduced into orthopaedics for use in vertebral augmentation, repair of cranial defects, stabilization of prosthetics, and as a fixative for various screw and plate constructs in osteoporotic bone.[5−8]

Dental and orthopaedic MMA-based or Bis-GMA-based materials are polymerized at ambient temperature by using a photoinitiation system or a redox initiation system. In the first case (light-cured materials) the most common photoinitiation system is based on a combination of camphoroquinone (CQ) with an amine, which produces free radicals on exposure to 450−500 nm radiation. The photopolymerization kinetics of dimethacrylates initiated by a CQ/amine couple has been extensively studied.[9−13] Redox initiation system, generally used in the so-called "two-part" (powder/liquid or paste/paste) dental and orthopaedic materials, is a combination of benzoyl peroxide (BPO) and *N*,*N*-dimethyl-*p*-toluidine (DMT). However, DMT is highly toxic, and much research has been directed toward the use of alternative tertiary amines with improved biocompatibility. Vazquez et al.[14] reviewed the amines proposed.



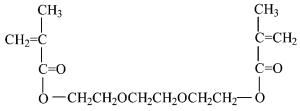
Bis-GMA

2,2-bis[p-(2'-hydroxy-3'methacryloxypropoxy)phenylene]propane



UDMA

Urethane dimethacrylate



TEGDMA

Triethylene glycol dimethacrylate

Figure 1. Chemical structure of the dimethacrylate monomers studied.

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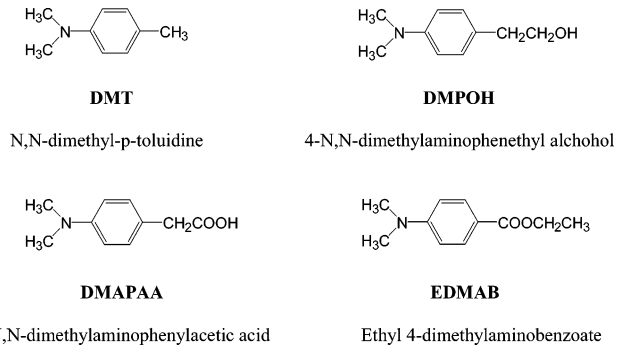


Figure 2. Chemical structure of the para-substituted derivatives of dimethylaniline, used as co-initiators with benzoyl peroxide.

Among them, 4-(*N*,*N*-dimethylamino)phenethyl alchohol (DMPOH),[15−19] 4-(*N*,*N*-dimethylamino)phenylacetic acid (DMAPAA),[15,19−21] and ethyl 4-(dimethylamino)benzoate (EDMAB)[22] are included (Figure 2). Generally, in the "two part" materials one of the parts incorporates the amine and the other the BPO and a stabilizer to control the start of polymerization, usually butyl hydroxytoluene (BHT). When the two parts are mixed in air at room temperature, the monomers of the mixture start to polymerize after a short time and the material starts to harden. The desired mixing time and hardening time, which is defined by the clinical application, can be adjusted by varying the content of the BPO, stabilizer, and the amine. Thus, the control of the polymerization kinetics is very important for a successful application.

The objective of this paper is the study of homopolymerization of Bis-GMA, UDMA, and TEGDMA, initiated by a BPO/amine couple using as amine the DMT, DMPOH, DMAPAA, or EDMAB. To the best of our knowledge there are not data in the literature about the kinetics of these polymerizations. Some experimental results of homopolymerization of TEGDMA and Bis-EMA initiated by the BPO/DMPOH couple have been reported in our previous paper.[23] This work is an attempt to study the relationship between the reactivity of the BPO/amine couple and the chemical structure of the amine co-initiator and dimethacrylate monomer used.

Experimental Section

Materials. The dimethacrylate monomers, Bis-GMA (from Polysciences Europe, Lot No. 495282, F_p > 240 °F), TEGDMA (from Aldrich Chem. Co. Lot No. 461111, inhibited, bp 162 °C at 1.2 mm), and UDMA (from Ivoclar AG, Lot No. B00338), were used as received without further purification. Generally, the monomers for dental restorative resins are not purified and are used as delivered. They contain inhibitors to prevent premature polymerization during storage and working time. Nevertheless, it was suggested that chromatographic column purification did not affect the polymerization kinetics of TEGDMA.[24,25] The amines DMT (99%, bp = 211 °C), DMPOH (98%, mp = 59−61 °C), and DMAPAA (mp = 105−108 °C) (all from Aldrich Chem. Co.) were used as received. EDMAB (99+%, mp = 64−66 °C) (also from Aldrich Chem. Co.) was recrystallized[26] from an ethanol−water mixture and then dried at 60 °C under vacuum in the presence of phosphorus pentoxide. This recrystallization improved its purity, as revealed by its melting peak. BPO (from Fluka) was also recrystallized from the chloroform−methanol mixture (mp = 104 °C).

Procedure. First, in 5 g of each individual monomer the appropriate amount of BPO or amine (DMPOH or DMAPAA) was dissolved, with the aid of an ultrasonic bath, to prepare a solution of BPO in monomer (0.5 mol %) and a solution of amine in monomer (0.5 mol %). In the case of DMT, which is a liquid, a solution was prepared (1.4% v/v in dichloromethane), and the appropriate amount of this solution (0.5, 0.55, or 0.9 mL) was added correspondingly to 5 g of Bis-GMA, UDMA, or TEGDMA to obtain a solution of DMT in monomer (0.5 mol %). The CH_2Cl_2 was removed by using vacuum pump (∼15 in.Hg) at room temperature. Dichloromethane was also used for the preparation of solutions of BPO or amine in Bis-GMA because this monomer is too viscous.

Instrumentation. The polymerization kinetics of the various formulations was studied using differential scanning calorimetry (DSC). Experiments were performed using the DSC-Pyris 1 (Perkin-Elmer) equipped with the Pyris software for windows. Indium was used for the enthalpy and temperature calibration of the instrument. In each experiment, equal amounts (∼0.5 g) from the two solutions, BPO in monomer and amine in monomer, were mixed in air atmosphere, and from this new solution a standard mass (15−20 mg) was placed in an aluminum Perkin-Elmer sample pan, accurately weighed, sealed in air, and placed into the appropriate position of the instrument. The time that passed from the beginning of mixing of the two solutions up to the introduction of the sealed pan into the nitrogen environment of the DSC was always 2 min. Also, the time passed for the instrument equilibration to the desired temperature was 0.5 min. Thus, the DSC recording was started exactly 2.5 min after the initial mixing of the two solutions. The inhibition time reported in the following section was obtained directly from the DSC recording. Thus, it corresponds to the time passed after this initial "dead time" until the observation of an increase in the heat flow produced during the reaction. Isothermal runs were performed at 37 °C, circulating oxygen-free nitrogen in the DSC cell outside the sealed pans, to avoid atmospheric oxygen supply into the sample. The reaction temperature was continuously recorded and maintained constant (within ±0.01 °C) during the whole conversion range.

The reaction exotherm (in normalized values, W/g) at a constant temperature was recorded as a function of time. All polymerizations showed the presence of an inhibition time, during which no reaction was observed. This is due to the inhibitor contained in the commercial monomers used and the oxygen, dissolved in the monomer during the mixing performed in air atmosphere, as in all dental and orthopedic applications. The presence of an inhibition time is however beneficial for our study because it enabled to stabilize the sample temperature in DSC and obtain a good baseline before the beginning of polymerization. The period midway between the start of DSC recording and the time when the maximum polymerization rate was reached was defined as the hardening time of each studied polymerization.

The rate of heat release (d(ΔH)/d*t*) measured by the DSC was directly converted into the overall reaction rate (d*X*/d*t*) using the following formula:

$$\frac{dX}{dt} = \frac{1}{\Delta H_T}\frac{d(\Delta H)}{dt} \quad (1)$$

in which ΔH_T denotes the total reaction enthalpy calculated from the product of the number of double bonds per monomer molecule ($n = 2$) times the standard heat of polymerization of a methacrylate double bond ($\Delta H_0 = 54.9$ kJ/mol)[23] over the monomer molecular weight, i.e., $\Delta H_T = n\Delta H_0/MW_m$.

The degree of conversion was calculated by integrating the area between the DSC thermograms and the baseline established by extrapolation from the trace produced after complete polymerization (no change in the heat produced during the reaction). All the experimental results reported in the Results and Discussion were taken from an average of at least two experiments.

Results and Discussion

Formation of Initiating Radicals. The BPO/DMT redox system has been used and studied for a long time. In the 1950s Horner and his group proposed[28] a mechanism in which the rate-determining step is the formation of a complex, which subsequently leads to the formation of peroxide and aminium

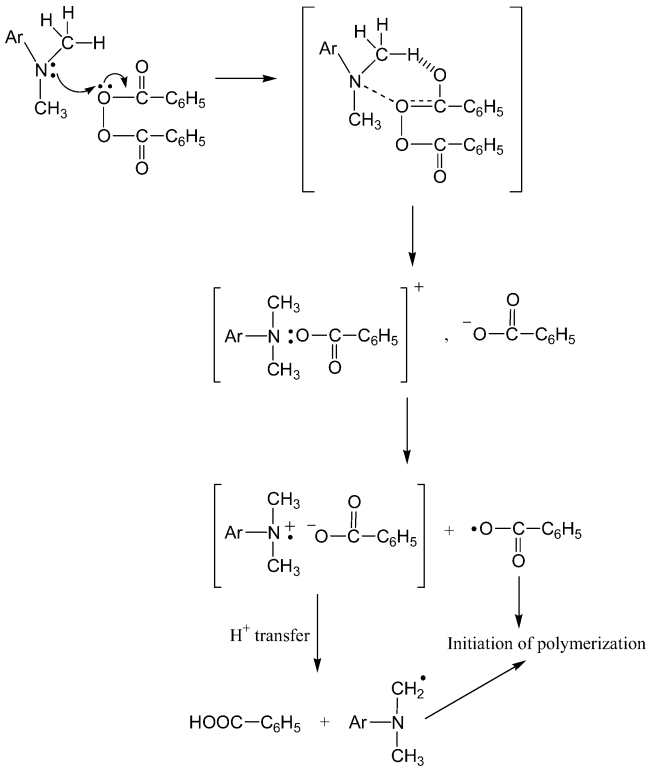


Figure 3. Mechanism of redox initiation by the benzoyl peroxide/amine system.[33b]

radicals by means of an electron transfer from the unshared pair of nitrogen to the peroxide (eq 2). The benzoylate anion is also formed in this reaction, which can remove a proton from the aminium cation and gives rise to benzoic acid. On transfer of an electron from the carbon to the nitrogen, free radicals are formed which could act as polymerization initiators in the presence of vinyl compounds.

$$\mathrm{DMT} + \mathrm{BPO} \xrightarrow{\mathrm{SET}} \mathrm{DMT}^{\bullet+} + \mathrm{BPO}^{\bullet} + \mathrm{BPO}^{-} \qquad (2)$$

In 1958, Walling and Indictor suggested the rapid equilibrium formation of a complex intermediate, although they proposed as the rate-controlling step a nucleophilic S_N2 displacement on the BPO by DMT to yield a quaternary hydroxylamine derivative (eq 3).[27]

$$\mathrm{DMT} + \mathrm{BPO} \xrightarrow{\mathrm{SN2}} \mathrm{Ph{-}N^{+}(Me)_2 - OBP} + \mathrm{BPO}^{-} \qquad (3)$$

This derivative has only transient existence and decomposes into aminium radical, benzoylate anion, and benzoyloxy radical as shown in Figure 3. Pryor and Hendrikson were able to distinguish this mechanism from a process involving single electron transfer, through a study of the kinetic isotope effect.[28] The initiation mechanism of peroxy/amine systems was also studied by De Feng;[29] the results obtained supported the theory that in the nucleophilic displacement a cyclic transition molecular complex and the subsequent benzoate ion pair are formed, as shown in Figure 3.

It has been suggested that the amine radical cation is not directly involved in initiating chains and that most polymerization is initiated by the benzoyloxy radicals.[30,31] However, Sato et al.[32] employed spin trapping and ESR spectroscopy to demonstrate that aminomethyl radicals (A$^{\bullet}$) were formed from the radical cation by loss of proton and proposed that these radicals also initiate polymerization. The presence of the above radicals has also been verified through UV analysis of the polymer formed with the characteristic band as the end group.[29] Therefore, it is accepted that both the aminoalkyl radicals and benzoyloxy radicals (RO$^{\bullet}$) are efficient initiators for free radical polymerization.[14,29,33]

$$\mathrm{RO}^{\bullet} + \mathrm{M} \rightarrow \sim\sim\sim\mathrm{M}^{\bullet} \qquad \text{initiation of polymerization} \qquad (4a)$$

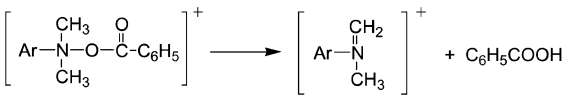
$$\mathrm{A}^{\bullet} + \mathrm{M} \rightarrow \sim\sim\sim \mathrm{M}^{\bullet} \qquad (4b)$$

in which M is a monomer molecule and $\sim\sim\sim$M$^{\bullet}$ is a macroradical.

In the CQ/amine initiating system only the amine-derived radical formed by the CQ*−amine interaction initiates polymerization, whereas the camphoroquinone ketyl radical (CQH$^{\bullet}$) is relatively inactive.[13] In a previous work we studied the kinetics of MMA polymerization initiated by the BPO/DMT or BPO/DMPOH redox system.[34] The maximum polymerization rate (R_p^{max}) depends on their individual concentrations and for a fixed BPO concentration there is an optimum amine concentration and vice versa for certain experimental conditions. Thus, the R_p^{max} obeys expression 5.

$$R_p^{max} \approx [\mathrm{BPO}]_0^{\chi}[\mathrm{AH}]_0^{\psi} \qquad (5)$$

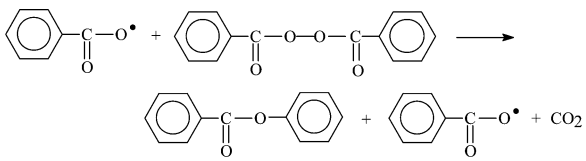
The no half-order dependence of R_p^{max} on the initial BPO and AH concentration shows that these are also wasted by side reactions and/or that their primary radicals, RO$^{\bullet}$ and A$^{\bullet}$, participate in termination reactions. It may also be due to a decrease in initiator efficiency f with increasing initiator concentration.[31] The efficiency f is defined as the fraction of radicals formed that then initiates polymerization (by eqs 4a and 4b). The initiator efficiency is considered exclusive of any BPO and AH wastage reactions. Also, Walling reported that the quaternary hydroxylamine may decompose by another path, resulting in nonradical products, and decrease the initiator efficiency.[27]



(6)

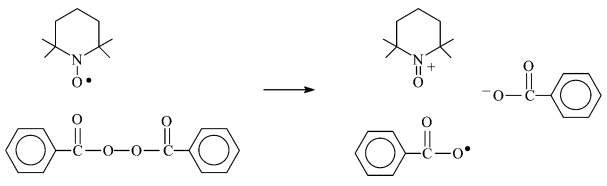
Enamine

Side Reactions of BPO, Amine, and Their Primary Radicals. A possible side reaction of BPO is its reaction with radicals present in the reaction mixture, such as benzoyloxy radicals[33,34] (eq 7a)



(7a)

or nitroxides formed from an excess of amine[33,34] (eq 7b).



(7b)

BPO may also participate in chain-transfer reactions[31] as well as the amines which are very effective chain transfer agents.[35,36]

$$RO{-}OR + {\sim\sim\sim}M^{\bullet} \rightarrow {\sim\sim\sim}\ MOR + RO^{\bullet}$$
chain transfer reactions (8a)

$$AH + {\sim\sim\sim}M^{\bullet} \rightarrow {\sim\sim\sim}\ MH + A^{\bullet} \quad (8b)$$

The benzoyloxy and *N*-methylene radicals may react with macroradicals and terminate the propagation[37] (eqs 9a and 9b).

$$RO^{\bullet} + {\sim\sim\sim}M^{\bullet} \rightarrow {\sim\sim\sim}\ MOR$$
primary radical termination (9a)

$$A^{\bullet} + {\sim\sim\sim}M^{\bullet} \rightarrow {\sim\sim\sim}\ MA \quad (9b)$$

Primary radical termination and the accompanying change in the order of dependence of R_p on initiator are generally important in systems in which primary radicals are produced at too high concentration and/or in the presence of too low monomer concentration to be completed and rapidly scavenged by monomer. It may be also found under conditions where bimolecular termination between propagating radicals becomes difficult because of the increased viscosity.[37]

Reactions with Oxygen. In the presence of dissolved oxygen, as it is our case, additional reactions occur. Oxygen is an inhibitor of free radical polymerization

$$M^{\bullet} + O_2 \rightarrow MOO^{\bullet}$$
inhibition polymerization reactions (10a)

$$\sim\sim\sim M^{\bullet} + O_2 \rightarrow \sim\sim\sim\ MOO^{\bullet} \quad (10b)$$

Also, *N*-methylene radicals react readily with oxygen, yielding an aminoalkylperoxy radical, decreasing the oxygen concentration via a chain reaction, and giving hydroperoxides.

$$A^{\bullet} + O_2 \rightarrow AOO^{\bullet} \quad (10c)$$

$$AOO^{\bullet} + AH \rightarrow AOOH + A^{\bullet} \quad (10d)$$

The rate of oxygen scavenging is directly depended on the structure of the amine as well as its concentration, which thus affects the inhibition time.[38]

The equilibrium concentration of oxygen dissolved in a typical methacrylate monomer is about 10^{-3} mol/L and the steady-state oxygen concentration that allows polymerization is 4.2×10^{-6} mol/L.[39] Therefore, the extent of inhibition time (t_{inh}) strongly depends on how fast oxygen and traces of inhibitor (INH) contained in the monomer are consumed.

$$RO^{\bullet}\ (\text{or } A^{\bullet}) + INH \rightarrow \text{inactive products}$$
inhibition of polymerization (11)

Peroxy radicals ($MOO^{\bullet}$, $\sim\sim\sim MOO^{\bullet}$, and/or $AOO^{\bullet}$) are relatively unreactive toward the C=C double bond of the monomer but may recombine with each other giving peroxides, e.g.

$$2AOO^{\bullet} \rightarrow AOOA + O_2$$
formation of peroxides (12)

or may react with monomer radicals or propagating radicals.[40]

$$MOO^{\bullet} + M^{\bullet} \rightarrow MOOM \quad \text{inhibition} \quad (13)$$

$$MOO^{\bullet} + {\sim\sim\sim}M^{\bullet} \rightarrow {\sim\sim\sim}MOOM \quad \text{termination} \quad (14)$$

Peroxides and hydroperoxides are stable at low temperatures[31,40] as those usually used in polymerizations initiated with BPO/amine systems and may not be involved in the initiation process.

Kinetic Parameters, Rate, and Conversion Profiles of Homopolymerization of the Bis-GMA, UDMA, or TEGDMA, Initiated by BPO/DMT, DMPOH, or DMAPAA Redox System at 37 °C. The DSC thermograms obtained for these polymerizations allowed the calculation of a number of important kinetic parameters, which are presented in Table 1. The initiator concentration was selected such that the polymerization would be completed in a short time, since the specification for dental "two part" filling resins requires a minimum working time of 1.5 min and a maximum hardening time of 8 min.[41] Also, the amine concentration must not exceed 50 mM due to material yellowing and biocompatibility reasons.[42] Figures 4−6 show the profiles of polymerization rate vs time or conversion for the monomers studied. Data presented in Table 1 and Figures 4−6 clearly show that the chemical structure of both monomer and amine co-initiator affect the polymerization kinetics.

Bis-GMA polymerization showed a sharp maximum rate soon after the beginning (<2 min) and a very low conversion (<5%). It seems that the structure of amine has a slight influence on kinetic parameters, with the DMAPAA giving better results followed by DMPOH (Figure 4). Polymerization of UDMA like that of Bis-GMA showed also a sharp maximum rate at about 9% for all the amines and with DMPOH giving better results followed by DMAPAA (Figure 5). The polymerization rate is a function of the product of initiator efficiency and decomposition constant ($f k_d$). Not all the free radicals produced are capable of initiating polymerization because alternate pathways exist which do not lead to initiation of polymerization. Any such wastage reactions lower the efficiency. It was found that efficiency of the BPO/amine system is enhanced by the presence of electron-withdrawing substituents on the aniline.[43] Also, it was found that electron-donating substituents which increase the nucleophilicity of the amine increase the rate constant of decomposition. The substituents p-CH_2CH_2OH and p-CH_2-COOH of DMPOH and DMAPAA, respectively, have electron-donating character as the p-CH_3 group of DMT. The Hammett constant σ_p for p-CH_3 is −017 and for p-$CH_2COOC_2H_5$ is −0.16, but no data were found in the literature for the σ_p of p-CH_2CH_2OH and p-CH_2COOH. Therefore, it is difficult to explain the observed slightly higher reactivity of BPO/DMPOH and BPO/DMAPAA initiating system compared to that of BPO/DMT for the polymerization of Bis-GMA (Figure 4) and UDMA (Figure 5).

Polymerization of TEGDMA, on the contrary, to that of Bis-GMA and UDMA showed an initial rapid increase in the rate, followed by a break that leads to a maximum rate at about 25% (Figure 6). This shoulder observed clearly in both rate−time and rate−conversion plots is also mentioned by Cook for the photopolymerization of TEGDMA initiated by the system CQ/*N*,*N*,3,5-tetramethylaniline[44] and also by Dickens et al. for the photopolymerization of TEGDMA by CQ/EDMAB.[45] In TEGDMA, which has a particularly flexible aliphatic ether spacer group compared with connecting groups present in Bis-GMA and UDMA, the propagation initially occurs more extensively by intramolecular attack of the radical site on the pendant double bond (primary cyclization) rather than intermolecular attack which leads to network formation (cross-linking). Cyclization causes a delay in the gel effect.[46] The effect of diffusion-controlled phenomena on the termination reaction causes k_t to decrease and the polymerization rate to increase. The termination mechanism initially is controlled by segmental diffusion, while as the polymerization proceeds it turns to translational diffusion-controlled. The change in the termination mechanism occurs near the shoulder. Termination becomes increasingly slower and

Table 1. Kinetic Data of the Polymerization of Bis-GMA,[a] UDMA,[a] or TEGDMA,[a] at 37 °C, Initiated by Benzoyl Peroxide (0.5% mol/mol) and an Amine (0.5% mol/mol): Maximum Rate of Polymerization (R_p^{max}), Time and Conversion at Which R_p^{max} Appears (t_{peak} and X_{peak}), Inhibition Time (t_{inh}), and the Maximum of the Conversion (X_{max})

monomer	amine[b]	$R_p^{max} \times 10^3$ (s^{-1})	t_{peak} (s)	X_{peak} (%)	t_{inh} (s)	X_{max} (%)
Bis-GMA	DMT[a] (9.75 mM)	1.40	59	3.5	9	26.6
Bis-GMA	DMPOH[a] (9.75 mM)	1.77	85	2.5	47	27.4
Bis-GMA	DMAPAA[a] (9.75 mM)	1.96	95	4.5	55	28.5
UDMA	DMT (10.64 mM)	2.35	149	8.7	106	37.0
UDMA	DMPOH (10.64 mM)	3.75	137	8.6	62	40.5
UDMA	DMAPAA (10.64 mM)	3.03	144	8.8	98	39.9
TEGDMA	DMT (17.47 mM)	1.62[d] (0.42)[e]	338[c] (1191)[e]	24.7[d] (62.1)[e]	35	72.2
TEGDMA	DMPOH (17.47 mM)	2.00[d] (0.40)[e]	293[d] (1107)[e]	21.3[d] (60.2)[e]	29	67.7
TEGDMA	DMAPAA[c] (34.94 mM)	1.63[d] (0.84)[e]	326[d] (787)[e]	24.7[d] (61.8)[e]	45	74.9

[a] The chemical structure of monomers is shown in Figure 1 and of amines in Figure 2. [b] The values in parentheses express the concentration of amine in millimolal units mM, which are usually used in many publications. [c] The concentration of DMAPAA and BPO in this polymerization is 1.0% mol/mol (34.94 mM) because for 0.5% mol/mol the polymerization was too slow. [d] These values correspond to the first peak of polymerization shown by TEGDMA. [e] The values in parentheses correspond to the second smaller peak.

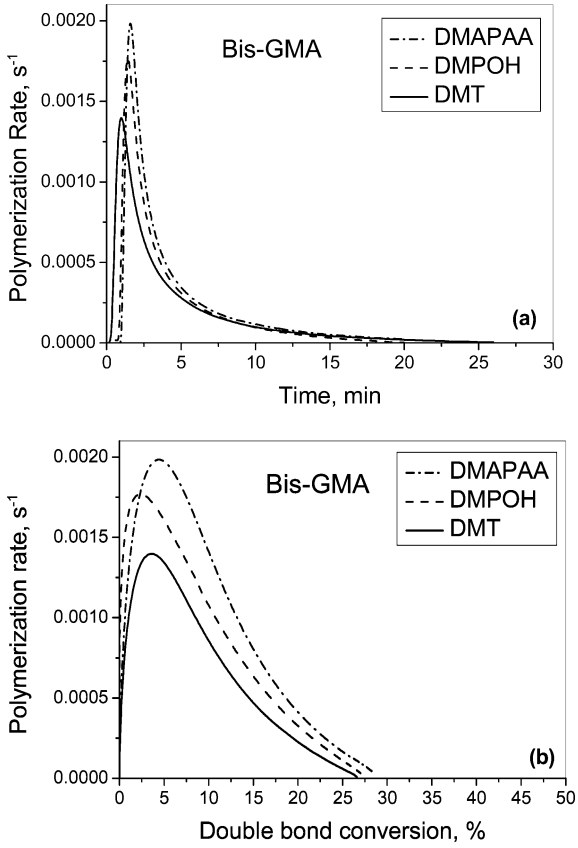


Figure 4. Effect of the amine chemical structure on the profile of the polymerization rate vs time (a) or double-bond conversion (b) for the Bis-phenol-A-bis(glycidyl methacrylate) (Bis-GMA) polymerization at 37 °C, initiated by the benzoyl peroxide (BPO)/amine system. [BPO] = [amine] = 0.5 mol %.

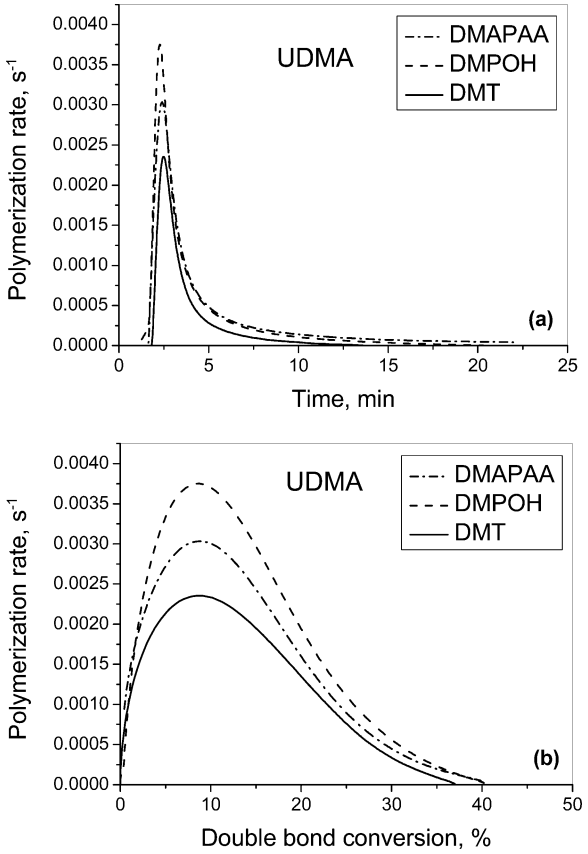


Figure 5. Effect of the amine chemical structure on the profile of the polymerization rate vs time (a) or double-bond conversion (b) for the urethane dimethacrylate (UDMA) polymerization at 37 °C, initiated by the benzoyl peroxide (BPO)/amine system. [BPO] = [amine] = 0.5 mol %.

the rate higher (gel effect). As the viscosity increases, an alternative termination mechanism the so-called reaction diffusion is appeared. When the termination mechanism from translational diffusion controlled changes to reaction diffusion controlled, a maximum rate appears. In the case of the more viscous monomers UDMA and mainly Bis-GMA, the termination mechanism is from the beginning of polymerization reaction diffusion-controlled and shows an immediate autoacceleration region. However, an interesting finding is that the polymerization of TEGDMA showed a second maximum rate at higher conversion (~60%). The ratio of the maximum rate at about 25% to that at 60% conversion for DMT, DMPOH, or DMAPAA was 4, 5, or 2, respectively (Table 1). The formation of two R_p maxima also has an effect on the kinetics of the conversion p, which has in each case two slopes. The presence of two well-defined maxima has been also observed in the photopolymerization of TEGDMA initiated by CQ/DMT in air atmosphere.[25] Formation of the second R_p maximum has been explained by the different mobility of the initiating monomer radicals in the polymer matrix as the polymerization proceeds. Accordingly, in our case in the early stage the $RO^{\bullet}$ and $A^{\bullet}$ radicals initiate polymerization (eqs 4a and 4b), whereas the peroxy radicals $MOO^{\bullet}$ and $AOO^{\bullet}$ formed during the inhibition period (eqs 10a and 10c) are accumulated. As the polymerization proceeds, these radicals that are trapped in the microgel domain slowly start to react with vinyl groups, and the second R_p maximum appears. The assumption that the presence of oxygen is responsible for the second peak observed was also confirmed by additional experiments carried out with open (instead of

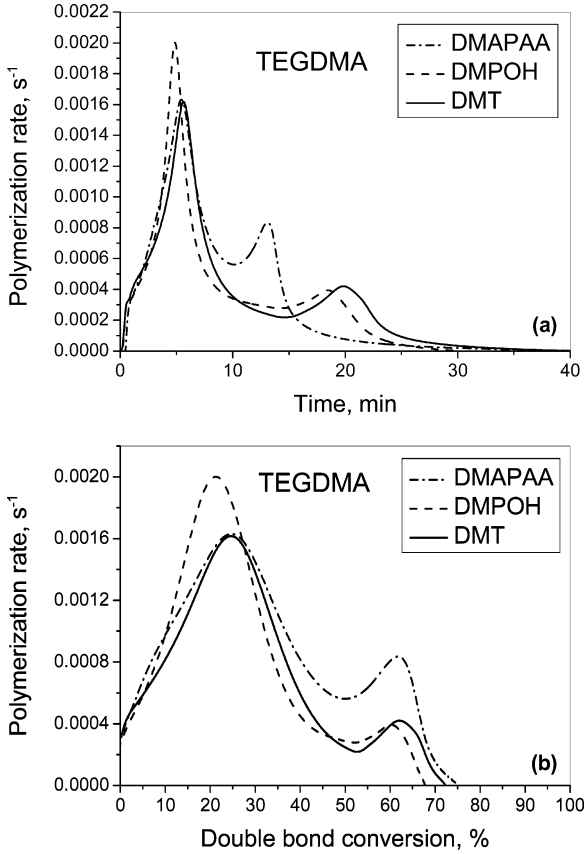


Figure 6. Effect of the amine chemical structure on the profile of the polymerization rate vs time (a) or double bond conversion (b) for the triethylene dimethacrylate polymerization at 37 °C, initiated by the BPO/amine system. [DMPOH] = [DMT] = [BPO] = 0.5 mol %; [DMAPAA] = [BPO] = 1 mol %.

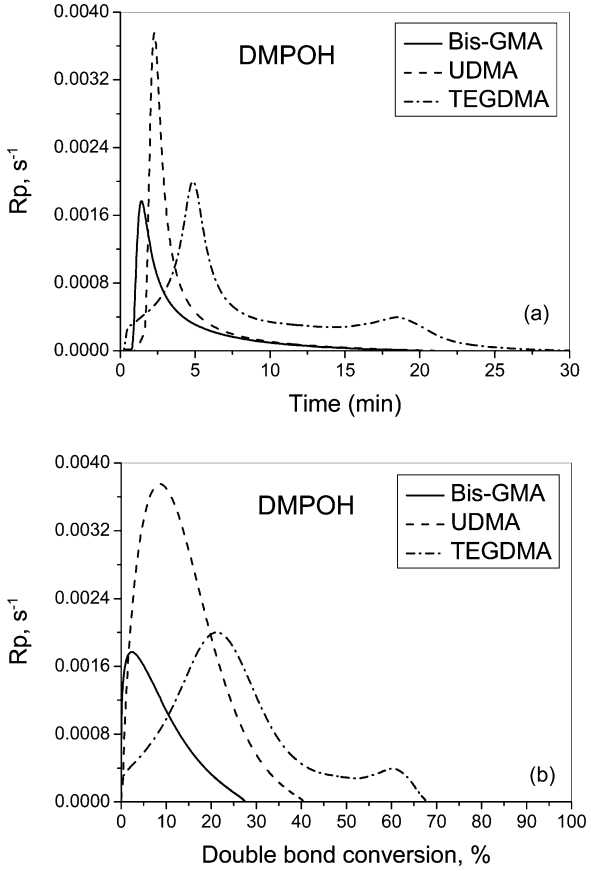


Figure 7. Effect of the monomer chemical structure on the profile of the polymerization rate vs time (a) or double bond conversion (b) for the BPO/DMPOH-initiated polymerization at 37 °C. [DMPOH] = [BPO] = 0.5 mol %.

sealed) pans in the nitrogen atmosphere of the DSC. Under these conditions a second maximum in the heat flow was not observed.

Polymerization of TEGDMA initiated by the BPO/DMAPAA system showed much lower reactivity than DMPOH and DMT, since a twice higher amount of the amine and BPO was used to give comparable results with the other amines (Table 1, Figure 6).

Figures 7 and 8 show the effect of the monomer chemical structure on the rate profiles of polymerizations initiated by the same BPO/amine couple. UDMA compared with Bis-GMA showed a higher value for R_p^{max} for all the amines, especially for DMPOH ($\sim 4 \times 10^{-3}$ s^{-1}); R_p^{max} for Bis-GMA was about 2×10^{-3} s $^{-1}$. The much higher reactivity of UDMA than Bis-GMA monomer was also observed by Dickens[45] in their photopolymerization with CQ/EDMAB; this behavior was attributed to both the greater flexibility of the UDMA molecular structure and the possible hydrogen abstraction and a chain transfer reaction mechanism, which enhances radical initiation or causes an alternate polymerization pathway. The higher reactivity of UDMA than Bis-GMA monomer was also observed in our previous work.[47]

TEGDMA showed the highest values of degree of conversion followed by UDMA and Bis-GMA (Table 1) as was observed and in our previous work.[47] It seems that the degree of conversion is mainly affected by the chemical structure of monomer, which defines the mobility of the polymer network being formed and the system viscosity, and it is not affected significantly by the structure of the amine used.

Kinetic Parameters, Rate, and Conversion Profiles of Homopolymerization of Bis-GMA, UDMA, or TEGDMA, Initiated by the BPO/EDMAB System at Various Temperatures. Although EDMAB is an efficient co-initiator with CQ for the photopolymerization of (meth)acrylates at room temperature, it was not able to initiate, in combination with BPO, the polymerization of the studied monomers at 37 °C. Study of photopolymerization of butyl acrylate initiated by CQ/EDMAB or CQ/DMT showed that the radicals derived from EDMAB have higher initiation efficiency f than those derived from DMT.[11] This difference was attributed to the electron-withdrawing character of the $-COOCH_2CH_3$ substituent of EDMAB, in contrast to the electron donor character of $-CH_3$ of DMT; the initiation efficiency, f, is proportional to the σ_p value defined in the Hammett equation.[11] The σ_p value for the ethyl ester group is $+0.45$ and for the methyl group -0.17. Moreover, in another study it was found that the decomposition constant k_d of BPO induced by several p-substituted diethylanilines depends on the amine nucleophilicity and is linearly correlated with the Hammett constant σ_p.[43] The lower the amine nucleophilicity, the lower the k_d constant. Therefore, according to these literature data, it seems that EDMAB must have much lower k_d than DMT, DMPOH, and DMAPAA which contain electron-donor p-substituents and thus can decompose the BPO at 37 °C.

The polymerization of Bis-GMA, UDMA, and TEGDMA by BPO/EDMAB was carried out isothermally at various higher temperatures. The results obtained are presented in Table 2. The shape of rate curves are strongly influenced by the temperature (Figure 9); as the temperature increases, the curve becomes less broad, the R_p^{max} increases, and it is observed at higher conversion. Also, the rate curves for TEGDMA do not show the second

Table 2. Kinetic Data of the Polymerization of Bis-GMA,[a] UDMA,[a] or TEGDMA[a] at Various Temperatures, Initiated by BPO (1 mol % 34.94 mM) and EDMAB[b] (1 mol %, 34.94 mM): Maximum Rate of Polymerization (R_p^{max}), Time and Conversion at Which R_p^{max} Appears (t_{peak} and X_{peak}), Inhibition Time (t_{inh}), and Maximum Double-Bond Conversion (X_{max})

monomer	temp (°C)	$R_p^{max} \times 10^3$ (s^{-1})	t_{peak} (s)	X_{peak} (%)	t_{inh} (s)	X_{max} (%)
Bis-GMA	60	0.42	591	2.7	480	13.9
Bis-GMA	70	1.69	233	5.2	180	24.0
Bis-GMA	80	4.44	84	6.6	58	32.9
Bis-GMA	90	10.41	44	10.7	24	42.8
UDMA	60	0.45	334	3.1	192	11.0
UDMA	70	1.87	227	7.9	152	25.0
UDMA	80	3.92	81	10.8	38	42.1
UDMA	90	10.76	48	16.2	19	47.7
TEGDMA	70	1.16	1566	48.8	163	77.8
TEGDMA	80	2.69	498	50.7	51	84.6
TEGDMA	90	24.15	108	41.1	10	87.5
TEGDMA	100	26.26	33	24.9	9	91.4

[a] The chemical structure of monomers is shown in Figure 1. [b] The chemical structure of amine EDMAB is shown in Figure 2.

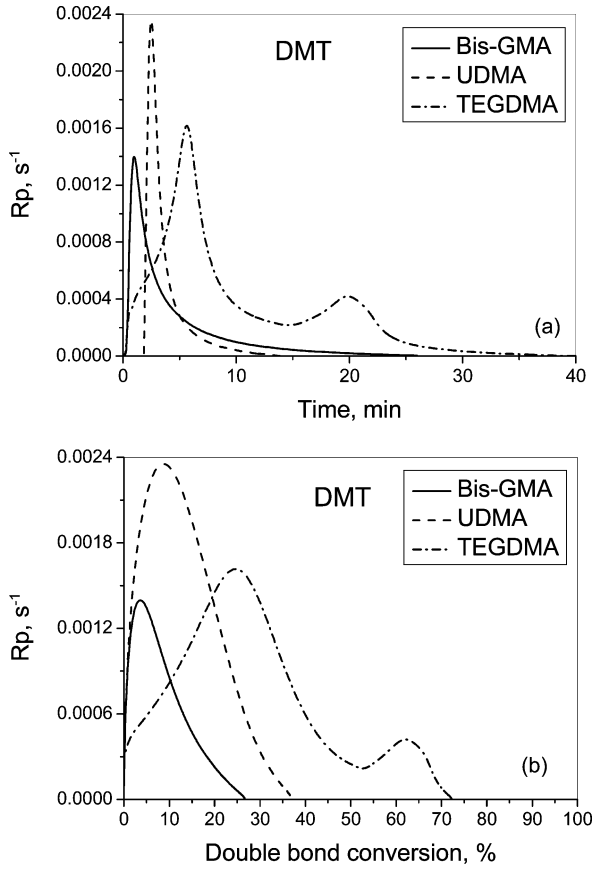


Figure 8. Effect of the monomer chemical structure on the profile of the polymerization rate vs time (a) or double-bond conversion (b) for the BPO/DMT initiated polymerization at 37 °C. [BPO] = DMT = 0.5 mol %.

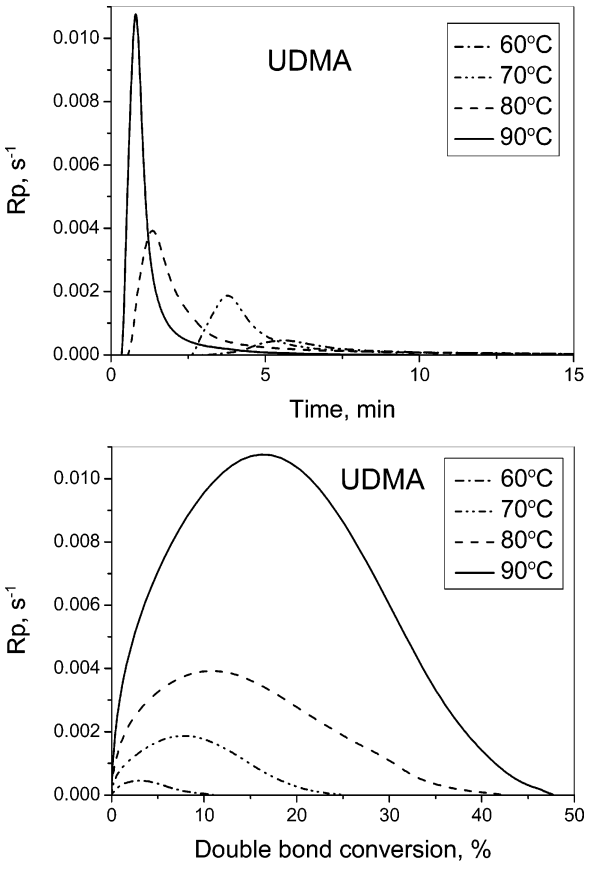


Figure 9. Effect of polymerization temperature on the profile of the polymerization rate vs time (a) or double-bond conversion (b) for the urethane dimethacrylate polymerization initiated by the benzoyl peroxide/ethyl 4-(dimethylamino)benzoate system.

maximum rate at higher conversions; it is known that temperature increases, reducing the solubility of oxygen in the polymerization medium and its effect on the kinetics.[46]

For all monomers a significant increase of the maximum degree of double-bond conversion was observed with increasing temperature, which seems to follow a linear dependence (Figure 10).

During the initial stage of polymerization where the effect of diffusion-controlled phenomena on the reaction rates is negligible and the steady-state approximation for macroradicals holds, the overall rate of polymerization, R_p, is given by

$$R_p = -\frac{d[M]}{dt} = \left(\frac{k_p^2(f_1 + f_2)k_d}{k_t}\right)^{1/2} [M]([ROOR][A])^{1/2} \quad (15)$$

in which k_p and k_t represent the propagation and termination rate constant, respectively, and k_d is the initiator decomposition rate constant, while f_1 and f_2 denote the efficiency factors.

Based on the monomer conversion X, eq 15 becomes

$$\frac{dX}{dt} = k(1 - X)([ROOR][A])^{1/2} \quad (16)$$

in which

$$k = \left(\frac{k_p^2(f_1 + f_2)k_d}{k_t}\right)^{1/2}$$

Assuming that the initiator concentrations do not change significantly during the initial polymerization time, eq 16 can

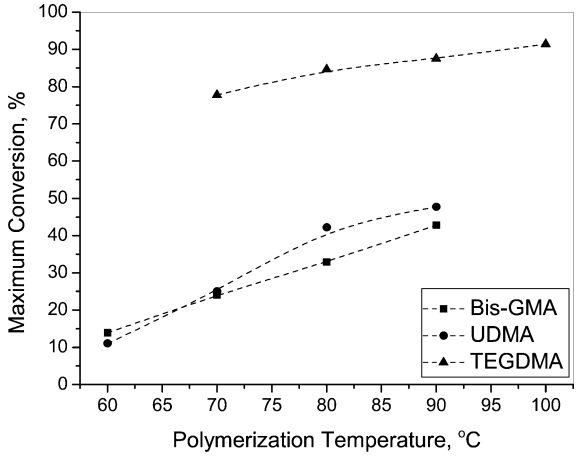


Figure 10. Maximum double-bond conversion vs polymerization temperature for the benzoyl peroxide/ethyl 4-(dimethylamino)benzoate-initiated polymerization of Bis-phenol-A-bis(glycidyl methacrylate), urethane dimethacrylate, and triethylene glycol dimethacrylate.

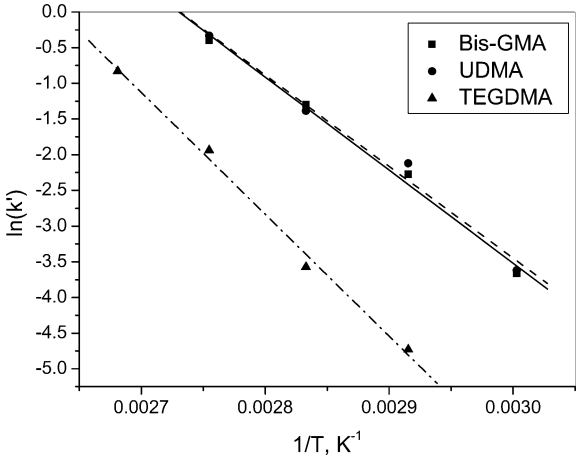


Figure 12. Arrhenious-type plots of the overall kinetic rate constant k' for the benzoyl peroxide/ethyl 4-(dimethylamino)benzoate-initiated polymerization of Bis-phenol-A-bis(glycidyl methacrylate), urethane dimethacrylate, and triethylene glycol dimethacrylate.

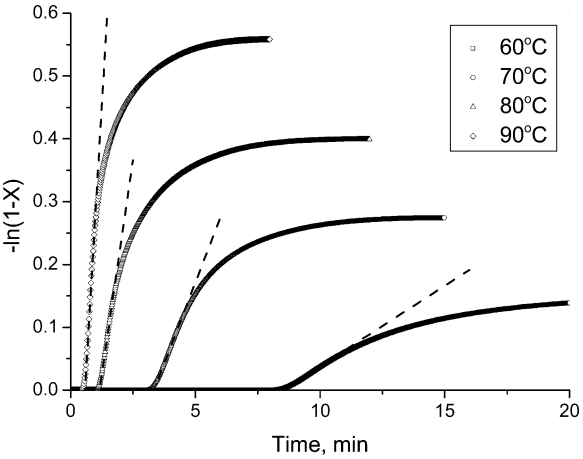


Figure 11. Plots of $-\ln(1 - X)$ vs time for the benzoyl peroxide/ethyl 4-(dimethylamino)benzoate-initiated polymerization of Bis-phenol-A-bis(glycidyl methacrylate) at different reaction temperatures.

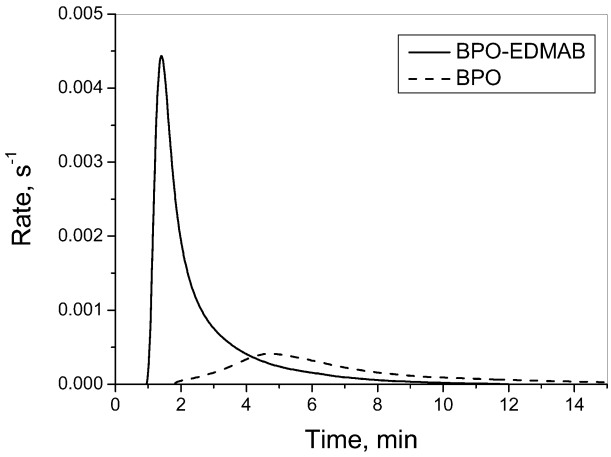


Figure 13. Polymerization rate vs time of Bis-phenol-A-bis(glycidyl methacrylate) at 80 °C using as initiator either the redox system benzoyl peroxide/ethyl 4-(dimethylamino)benzoate or benzoyl peroxide alone.

be integrated to give

$$-\ln(1 - X) = k't \tag{17}$$

in which $k' = k([\mathrm{ROOR}]_0[\mathrm{A}]_0)^{1/2}$.

If eq 17 holds true, then a plot of $-\ln(1 - X)$ vs t should give a straight line with a slope equal to the overall reaction rate k'. Such plots for the BPO/EDMAB-initiated polymerization of Bis-GMA appear in Figure 11. A clear straight line appears at the initial stages of polymerization. The conversion at which this linearity is followed ranges between 1 and 5% at 60 °C to 1 and 10% at 90 °C. The values of the overall kinetic rate constant, k', thus calculated depend on temperature according to an Arrhenius-type form:

$$k' = k'_0 \exp(-E_{\mathrm{eff}}/RT) \tag{18}$$

in which k'_0 is a preexponential factor and E_{eff} is the overall effective activation energy.

Plots of $\ln(k')$ vs $1/T$ for the three monomers studied are presented in Figure 12. Although the number of different temperatures examined is rather low, a very good straight line was drawn for all three monomers studied (correlation coefficient, $R = 0.996$). The slope of the straight lines corresponds to effective activation energies of 108.5, 106.7, and 142.0 kJ/mol for Bis-GMA, UDMA, and TEGDMA homopolymerization, respectively. The viscous Bis-GMA and UDMA monomer exhibit almost the same effective activation energy, while that calculated for the much less viscous TEGDMA was much larger.

It should be pointed here that in such high temperatures (60−90 °C) there is a probability for polymerization, induced by thermal decomposition of the BPO alone. This probability was examined in two ways. First, certain additional experiments were carried out using as initiator only BPO, and indicative results for Bis-GMA polymerization at 80 °C are presented in Figure 13. It can be observed that BPO alone can initiate polymerization but to a much lesser extent and in larger time intervals compared to the binary system BPO/EDMAB. Furthermore, some nonisothermal experiments were carried out using again as initiator only BPO, and the results for Bis-GMA and UDMA polymerization appear in Figure 14. It was noticed that in both monomers an observable amount of heat released appeared at temperatures greater than 100 °C. Therefore, it was concluded that the contribution of the thermal decomposition of BPO in the initiation reaction was negligible.

Conclusions

Para-substituted anilines, *N*,*N*-dimethyl-*p*-toluidine (DMT), 4-(*N*,*N*-dimethylamino)phenethyl alchohol (DMPOH), and 4-(*N*,*N*-dimethylamino)phenylacetic acid (DMAPAA), are effective coinitiators with benzoyl peroxide (BPO) for the polymerization

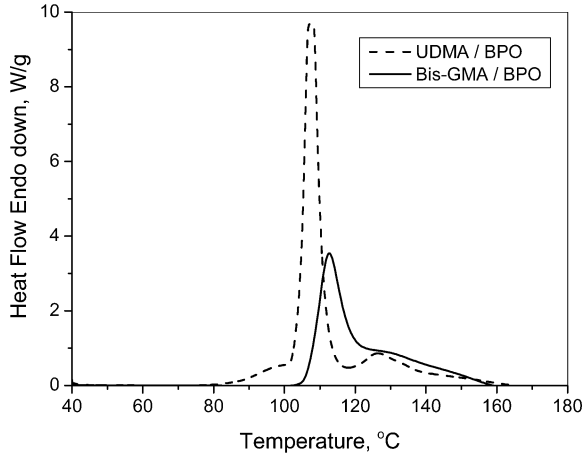


Figure 14. Heat flow released vs temperature for Bis-phenol-A-bis-(glycidyl methacrylate) and urethane dimethacrylate using as initiator the benzoyl peroxide alone.

of Bis-phenol-A-bis(glycidyl methacrylate) (Bis-GMA), a urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA) at 37 °C. DMPOH and DMAPAA showed a slightly higher reactivity than DMT toward the polymerization of Bis-GMA and UDMA. Also, DMPOH and DMT showed comparable results for the polymerization of TEGDMA while DMAPAA was much less reactive. The polymerization kinetics is mainly defined by the monomer chemical structure. UDMA is more reactive monomer than Bis-GMA and TEGDMA. Polymerization of TEGDMA showed an initial shoulder and two well-defined maxima at ∼25% and ∼60% conversion. This showed the highest final degree of conversion (∼70%) followed by UDMA (∼40%) and Bis-GMA (∼27%). Ethyl 4-dimethylaminobenzoate (EDMAB), while is an effective co-initiator with CQ for the photopolymerization of (meth)acrylates, was found to be a noneffective co-initiator with BPO at 37 °C and acts only at higher temperatures.

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