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STUDY OF THE EFFECT OF TWO BPO/AMINE INITIATION SYSTEMS ON THE FREE-RADICAL POLYMERIZATION OF MMA USED IN DENTAL RESINS AND BONE CEMENTS

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ABSTRACT

The kinetics of the free radical bulk polymerization of methyl methacrylate (MMA) was studied by DSC, using the benzoyl peroxide (BPO)/amine initiation system. N,N dimethyl-4-aminophenethyl alcohol (DMPOH), which is a newly synthesized and used amine in the preparation of acrylic dental resins and bone cements was examined, and the results compared to the most commonly used in these applications amine, the N,N dimethyl-p-toluidine (DMT). For both amines, the effect of the molar ratio of BPO/amine and of the reaction temperature, on the polymerization kinetics was investigated. The prepared polymers were characterized by determination of the average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weights distribution ($\bar{M}_w/\bar{M}_n$) using Gel Permeation Chromatography. DMPOH was found to lead in slightly higher polymerization rates, lower gel times and lower molecular weights than DMT. The values of these parameters for both amines were influenced by the molar ratio of BPO to amine, when the product of the concentrations of these was kept constant. The highest polymerization rate occurred in the lowest gel time, resulting in polymers with the lowest molecular weight,

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and was observed when a molar ratio of about 1.5 BPO/amine was used. However, the final monomer conversion was found to be independent of the molar ratio and amine used. The activation energy of polymerization was found to be 51.8 kJ/mol K for BPO/DMPOH and 47.1 kJ/mol K for BPO/DMT.

Key Words: BPO/amine initiation system; Dental materials; Free radical polymerization of MMA; Orthopaedic materials

INTRODUCTION

Tertiary aromatic amines have been used for a number of years together with benzoyl peroxide (BPO) as an effective initiation system in the free radical polymerization of acrylic resins and especially, methyl methacrylate (MMA).[1,2] The resulting polymers have been widely used as biomaterials in dentistry (denture construction, repair and relining, temporary crown and bridge materials), and in orthopaedic surgery as bone cements for the stabilization of metallic femoral hip endoprostheses.[3–6] The role of the amine is to carry out the reaction in a short period of time at room (body) temperature. Although it comprises only a minor component of the material, it significantly influences such important properties as molecular weight, mechanical strength, shade and color stability, and biocompatibility. Much concern has arisen from contamination of the biological system from leaching of the remaining amine. Many amines have been suggested as accelerators, but esthetic and biocompatibility requirements have greatly limited the number of compounds, which can be used for dental or medical applications.

The most commonly used amine is N,N dimethyl-p-toluidine (DMT) which is a suspected, but yet not proven, carcinogen.[3] DMT belongs to the N-dialkylaminoaromatics, a chemical class structurally alert to DNA reactivity, and also a chromosome-damaging agent inducing numerical chromosome alterations. DMT was found to inhibit protein synthesis and interfere with the mineralization processes. Furthermore, it can cause prosthesis failure in hypersensitive patients that develop a florid tissue reaction at the interface between cement and the bone, and can induce contact dermatitis.[7,8] For this purpose, several other amines have been proposed with better biocompatibility than DMT, well reviewed by Vazquez et al.[9]

Brauer et al., in 1981[10] reported the synthesis of a new amine, the 4-N,N dimethylaminophenethyl alcohol (DMPOH), and its use as a highly reactive accelerator for the polymerization of dental composites. With low amine concentration, nearly colorless restorations, having good color stability, were obtained. In 1996, DMPOH, was incorporated into a commercial low-viscosity bone cement, Sulfix 60.[9,11] Fritsch reported that bone cements prepared with DMPOH, showed increased static mechanical properties and fatigue strength, compared with those prepared with DMT.[11] Very recently (1999), Oldfield and Yasuda, studied the polymerization of MMA using the BPO/DMT or BPO/DMPOH redox system, by Electron Spin Resonance Spectroscopy (ESR) recording the conventional nine-line ESR spectrum for the growing polymer radicals at the gel stage of polymerization.[12] They found that DMPOH shows potential for being a more effective accelerator than DMT for bone cement curing and that optimum free macroradical concentration can be obtained by using equimolar BPO/amine concentration. They suggest that concentrations outside the equimolecular range should be avoided in bone cement preparations. This finding is in agreement with that of Vazquez et al., who studied the effect of BPO and DMT concentrations on curing characteristics and properties of experimental bone cements based on PMMA.[13] However a much older study of the effect of molar ratio BPO/amine on the polymerization rate of a trimethacrylate monomer, measured as the minimum gel time, showed that the maximum rate is observed, when the molar ratio BPO/amine is about 1.5.[14] Also, recent studies on experimental dental acrylic composites showed that a much larger molar excess of BPO is required (about 6.5) in order to obtain the fastest cure.[10,15] It is noteworthy that generally it is undesirable to have an excess of amine or BPO remaining in the polymer, due to possible adverse effects on its properties and biocompatibility.

The aim of this work was to study by Differential Scanning Calorimetry (DSC) the efficiency of DMPOH in comparison to that of DMT, and the effect of molar ratio BPO/amine on the polymerization kinetics of MMA. DSC is a very sensitive and precise technique for measurement of the polymerization rate as a function of time, by monitoring the rate at which heat is released from the polymerizing sample. The first to study the course and the kinetics of the free-radical polymerization of methyl methacrylate by DSC were Horie et al.[16] The main advantages of the DSC include the use of a small sample mass, which assures that the reaction will be carried out isothermally during the whole conversion range and especially in the autoacceleration region.[17,18] The kinetic parameters and activation energy of MMA polymerization for both initiating systems were determined under the same experimental conditions. Finally, the average molecular weights and molecular weights distribution of the final polymer products were measured using Gel Permeation Chromatography (GPC).

EXPERIMENTAL

Materials and Methods

MMA, stabilized with 100 ppm of hydroquinone (MERCK), was purified by passing it through an inhibitor-remover column (ALDRICH), by a dropwise addition of the monomer to the column. DMT and DMPOH (mp = 59–61°C) (ALDRICH) were used without further purification. BPO (FLUKA) was purified by fractional recrystallization from ethanol (mp = 104°C). All other chemicals used were reagent grade. Three solutions in MMA were prepared, one containing BPO (2% w/w) and the other DMT (1% v/v) or DMPOH (1% v/v).

The bulk free radical polymerization of MMA was investigated using the DSC-Pyris 1 (Perkin-Elmer) equipped with Pyris software for Windows. Indium was used for the enthalpy and temperature calibration of the instrument. In each experiment, 12 μL of MMA containing the BPO/amine initiating system was used, prepared by placing it into a standard Perkin-Elmer sample pan, 5, 6, 7 or 8 μL of the BPO solution and the corresponding volume of 7, 6, 5 or 4 μL of the amine solution (DMT or DMPOH) in MMA. The molar ratio BPO/amine in these solutions was 0.8, 1.12, 1.57 and 2.25, respectively, while the product [BPO][amine] was held constant and equal to 0.001, as reported in Ref. 14. Polymerizations were carried out at 37°C. MMA contained BPO and DMT or DMPOH with a molar ratio 1.12, was also polymerized isothermally at various temperatures for the determination of the activation energy of polymerization. The reaction temperature was recorded and held constant (within ± 0.01°C) during the entire conversion range. The samples were weighed (approximately 10 mg, sealed, and placed into the appropriate position of the instrument. The reaction exotherm (in normalized values, W/g) was recorded as a function of time at a constant temperature. The rate of heat release ($d(\Delta H)/dt$) measured by the DSC was directly converted into the overall reaction rate (dx/dt) using the following formula:

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

where ΔH_T denotes the total reaction enthalpy.

The polymerization enthalpy and conversion were 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). The residual monomer content and total reaction enthalpy were determined by heating the sample from the polymerization temperature to 180°C at a rate of 10 K/min. The sum of enthalpies of the isothermal, plus the dynamic experiment, was the total reaction enthalpy. This showed values between 54 and 57 kJ/mol, in accordance to the literature values.[17] After the end of the polymerization, the pans were weighed again, and a negligible monomer loss (less than 0.2 mg) was observed only in a few experiments. All the experimental results reported below in the Results and Discussion section are taken from an average of at least two experiments.

The molecular weights of the prepared polymers determined by GPC from Polymer Laboratories and included a pump (Marathon III HPLC pump), an Evaporative Mass Detector (PL-EMD 950), and a Plgel 5 μ MIXED-D column. The elution solvent was tetrahydrofuran (Riedel-de-Haen) at a constant flow rate 1 mL/min. Calibration of GPC was carried out with standard polystyrene samples (Polymer Laboratories) by using the universal calibration technique. The Mark-Houwink constants for the PMMA used were $K = 10.4\,10^{-5}$ dL/g and $\alpha = 0.697$. From the chromatogram, the number average molecular weight ($\bar{M}_n$) and the weight average molecular weight ($\bar{M}_w$) together with the polydispersity index ($\bar{M}_w/\bar{M}_n$) were calculated.

RESULTS AND DISCUSSION

Tertiary aromatic amines accelerate the free radical decomposition of BPO by a complex mechanism which involves first a $S_N{}^2$ nucleophilic displacement leading to an intermediate adduct and finally, to the formation of a benzoyloxy radical, benzoic acid and a N-methylene radical as is shown in Sch. 1.[2,19,20]

The formation of N-methylene radical was confirmed by electron spin resonance (ESR),[21] and the presence of the mentioned radical was detected by UV analysis in the polymer formed, indicating the efficiency of this radical in the initiation process of polymerization.[20]

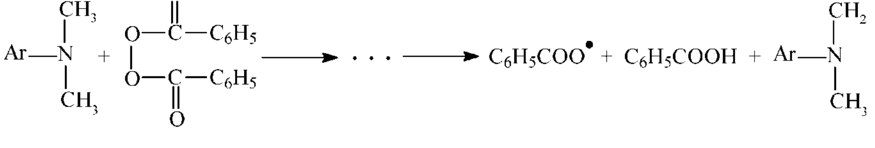
If A is used to denote the amines used in this work ($Ar = C_6H_5\text{-}CH_3$ for DMT and $Ar = C_6H_5\text{-}CH_2\text{-}CH_2\text{-}OH$ for DMPOH) and I the BPO molecules, respectively, then the above reaction can be rewritten as:

$$A + I \xrightarrow{k_d} I^\bullet + A^\bullet + Z \tag{1}$$

The formed radicals can both react then with the monomer molecules to initiate polymerization according to:

$$I^\bullet + M \xrightarrow{k_{i1}} P_1^\bullet \tag{2}$$

$$A^\bullet + M \xrightarrow{k_{i2}} P_1^\bullet \tag{3}$$



Scheme 1.

The polymerization of MMA continues with the following classical consecutive elementary reactions:
propagation step

$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet \tag{4}$$

and *termination step* (assuming that the primary radicals I* and A* do not participate in termination reactions):

$$P_n^\bullet + P_m^\bullet \begin{cases} \xrightarrow{k_{tc}} D_{n+m} & \text{combination} \\ \xrightarrow{k_{td}} D_n + D_m & \text{disproportionation} \end{cases} \tag{5}$$

According to the above kinetic scheme, the rate of initiation of polymerization is finally given by the equation:

$$R_I = (f_1 + f_2)k_d[\mathrm{I}][\mathrm{A}] \tag{6}$$

where f_1 and f_2 denote the efficiency factors and represent the fraction of primary radicals I* and A* formed by Eq. (1) that can eventually escape from their "cages" to react with monomer molecules, thus initiating the chain polymerization reaction.

During the initial stage of polymerization (i.e., conversion less than 5%) where the effect of diffusion-controlled phenomena on the reaction rates is negligible and the steady-state approximation for macroradicals holds, the overall initial rate of polymerization, R_p, is:

$$R_p = \left(\frac{k_p^2(f_1 + f_2)k_d}{k_t}\right)^{1/2} [M]([I][A])^{1/2} \tag{7}$$

or

$$R_p = k[M]([I][A])^{1/2} \tag{8}$$

This equation based on the monomer conversion (x) can be expressed as:

$$R_p = \frac{dx}{dt} = k(1 - x)([I][A])^{1/2} \tag{9}$$

or after integration

$$-\ln(1 - x) = k't \tag{10}$$

where $k' = k([\mathrm{I}][\mathrm{A}])^{1/2}$

This constant (k'), known as the overall initial rate constant, can be easily determined from the DSC thermograms and can be used as a measure of an amine efficiency for MMA polymerization. According to Eq. (10), the value of k' for a certain BPO- amine pair and experimental conditions, should be depend only on the product [BPO][amine] and not on their individual concentrations or their ratio.

In Figs. 1 and 2, the DSC thermograms obtained for MMA polymerization at 37°C initiated by various molar ratios of BPO/amine, but a constant product [BPO][amine], are presented.

Based on these data for low degrees of monomer conversion ($x < 5\%$), the $-\ln(1-x)$ was plotted against time (Fig. 3). From the slopes of these lines, the values of k' were calculated, and are presented in Table 1. In this Table, the values of the initiation rate of polymerization (R_I) are also shown, calculated from the equation $k' = (k_p^2 R_I / k_t)^{1/2}$, taking into account the following values of constants k_p and k_t for the bulk free radical polymerization of MMA:[22]

$$k_p = 10^{6.427} \exp\left(\frac{-22.36\,\text{kJ/mol}}{R \times T}\right) \text{L/mol/s} \quad \text{and}$$

$$k_t = 9.810^{7} \exp\left(\frac{-701\,\text{cal/mol}}{R \times T}\right) \text{L/mol/s}$$

The Table 1 data first shows that the system BPO/DMPOH is a slightly more efficient initiator than BPO/DMT for the polymerization of MMA. The k' and R_I values for the first system was always higher than the latter. More interesting, however, is the finding that for both initiation systems the value of k' is not constant, but varies with the molar ratio BPO/amine, showing the highest value for BPO/amine = 1.57. This result is in agreement with that observed by Bowen and Argentar.[14] The effect of BPO/amine molar ratio on polymerization kinetics is more profound as the polymerization proceeds at higher monomer conversions (Figs. 1 and 2). The largest value of the maximum rate of polymerization ($R^{\max}{}_p$), the shortest time at which it appears (gel time)($t_{\max}$), and the shortest inhibition time (t_{inh}) of polymerization presented in Table 2, are observed for both initiation systems at the molar ratio BPO/amine = 1.57. It is noteworthy, however, that, the monomer conversion at the maximum rate of conversion ($x_{R,\max}$) and at the end of polymerization ($x_{\max}$) are roughly the same in all molar ratios and independent of the amine used.

Although the product of their concentrations was held constant, the fact that the value of k' in the studied polymerizations was not constant for the various molar ratios of BPO to amine, reveals that the decomposition reaction of BPO by an amine (Eq. 1) does not follow first order kinetics with respect to their concentrations and some of it is wasted by side reactions.

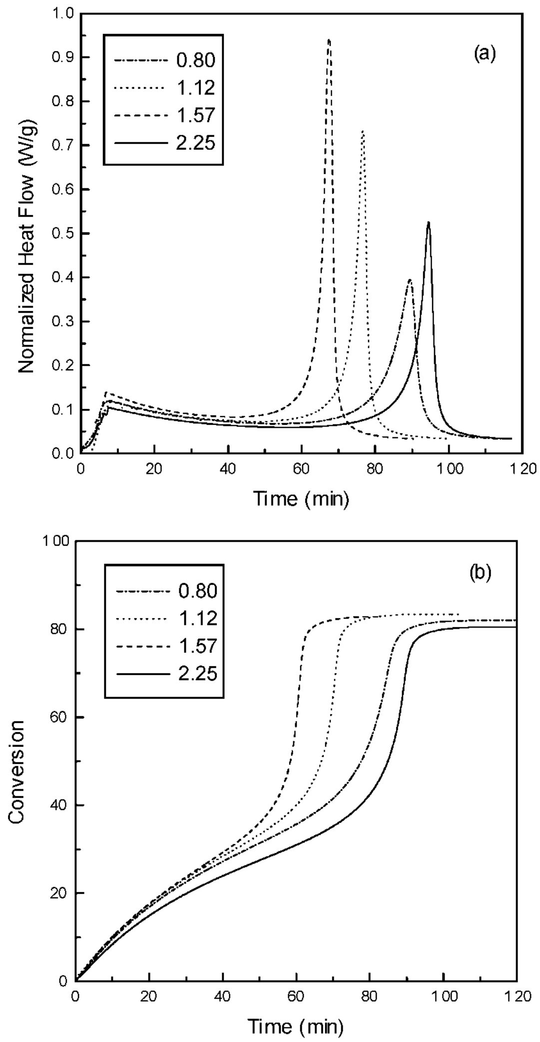


Figure 1. (a) Normalized DSC curves for the bulk free-radical polymerization of MMA at 37°C, initiated by various molar ratios of BPO/DMPOH; (b) the corresponding conversion–time curves.

There is an old report cited in Ref. 3, that BPO can be decomposed by benzoyloxy radicals according to the reaction shown in Sch. 2.

However, a recent study on the bulk polymerization of MMA by BPO showed that the above reaction is nearly suppressed in the presence of MMA.[23] It is known that BPO undergoes a facile decomposition by nitroxides as is shown in Sch. 3.[2]

In the presence of a nitroxide, the study of the bulk polymerization of styrene initiated by BPO showed that, when the concentration of the nitroxide is above 0.05 M, it induces the decomposition of BPO to benzoic acid

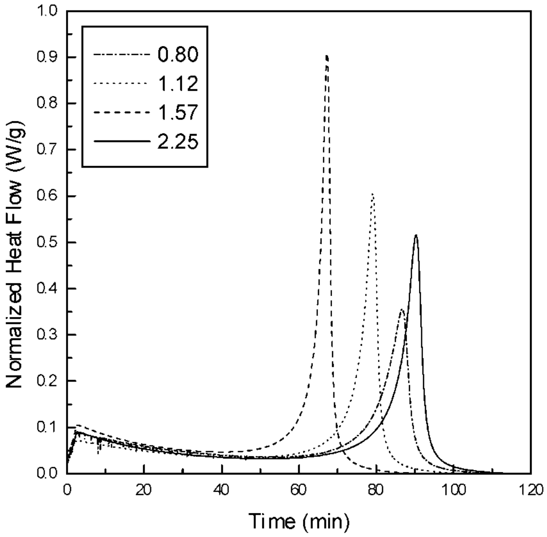


Figure 2. Normalized DSC curves for the bulk free-radical polymerization of MMA at 37°C, initiated by various molar ratios of BPO/DMT.

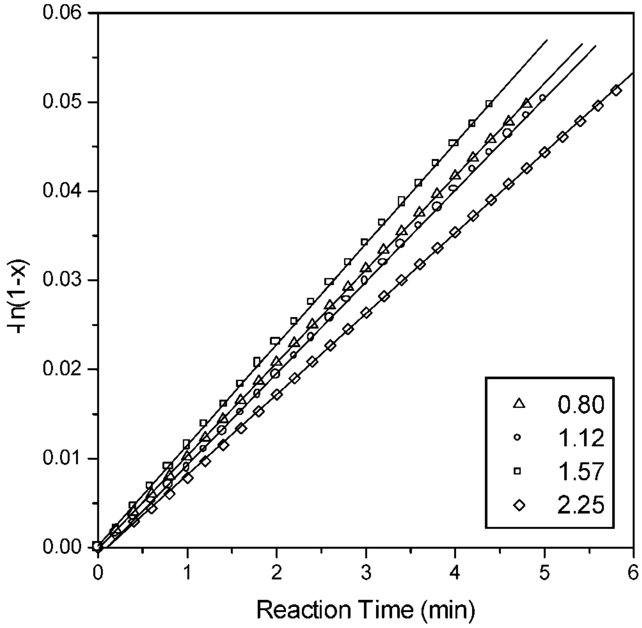


Figure 3. Determination of overall initial rate constant (k') from the initial (conversion <5%) rates of MMA polymerization at 37°C, using various molar ratios of BPO/DMPOH.

Table 1. Values of Initial Overall Rate Constant k', and Initiation Reaction Rate R_I of the Free Radical Polymerization of MMA at 37°C, Induced by Various Initial Molar Ratios of the BPO/Amine System; Values of the Molecular Weight Averages ($\bar{M}_n$ and $\bar{M}_w$) and the Polydispersity Index ($\bar{M}_w/\bar{M}_n$) of the Corresponding Prepared Polymers

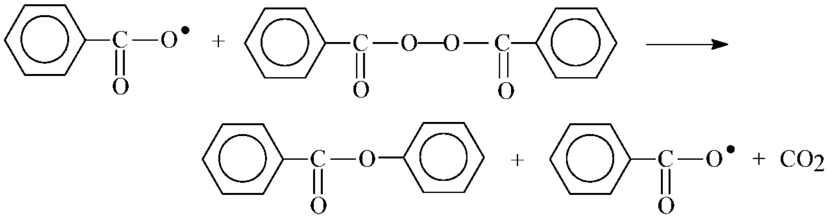
Amine	Molar Ratio [BPO]/Amine	$k' \times 10^4$ (s^{-1})	$R_I \times 10^6$ (mol/L s)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
DMPOH	0.80	1.74	4.55	146,000	424,860	2.91
	1.12	1.72	4.46	139,500	386,400	2.77
	1.57	1.88	5.29	128,000	349,000	2.72
	2.25	1.56	3.66	149,500	405,800	2.71
DMT	0.80	1.71	4.40	179,400	544,400	3.03
	1.12	1.53	3.50	155,000	471,200	3.04
	1.57	1.86	5.10	127,800	405,900	3.17
	2.25	1.60	3.85	153,530	481,270	3.13

and benzoyloxy radicals. The latter, can in turn, be trapped by the nitroxide to form stable alkoxyamines.[2,24,25] Oldfield and Yasuda, in their study of MMA polymerization by BPO/DMT or BPO/DMPOH, detected the presence of nitroxides when an excess amount of amine is used.[12] According to the above literature data, it is most probable that in the studied polymerizations some of the BPO amount is decomposed by nitroxides formed from the amine.

Tertiary aromatic amines may also participate in side reactions, most probably in chain-transfer reactions.[2] The side reactions of BPO and amine influence the optimum BPO to amine ratio, which seems to depend on their individual concentrations; that is, for a fixed BPO concentration there will be an

Table 2. Values of Maximum Rate of Polymerization ($R_p^{\max}$), Time at Which $R_p^{\max}$ Appears ($t_{\max}$), Monomer Conversion at Which $R_p^{\max}$ Appears ($x_{R,\max}$), Inhibition Time (t_{inh}), and Maximum Conversion ($x_{\max}$) of the Free Radical Polymerization of MMA at 37°C, Using Different Initial Molar Ratios of the BPO/Amine Initiation System

Amine	Molar Ratio [BPO]/Amine	$R_p^{\max} \times 10^3$ (s^{-1})	$t_{\max}$ (min)	$x_{R,\max}$ (%)	t_{inh} (min)	$x_{\max}$ (%)
DMPOH	0.80	0.80	83	69.3	3.7	82.0
	1.12	1.50	69	68.7	4.0	83.4
	1.57	1.98	61	67.3	2.8	82.9
	2.25	1.11	87	67.4	3.3	80.4
DMT	0.80	0.78	84	70.1	2.9	82.0
	1.12	1.36	77.5	67.4	3.0	80.6
	1.57	1.96	65	68.4	2.5	83.6
	2.25	1.13	87.5	68.4	3.2	82.0



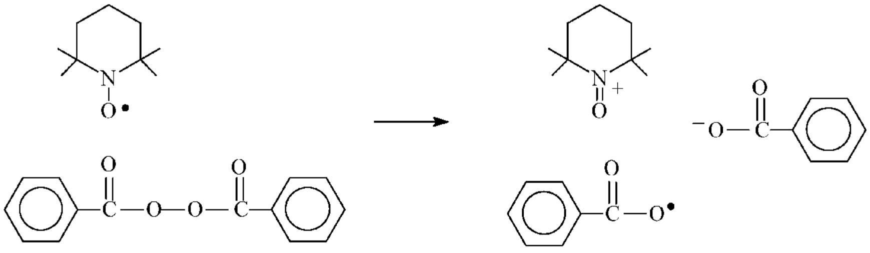
Scheme 2.

optimum amine concentration and vice-versa for certain experimental conditions, justifying the different values reported in the literature for the optimum BPO/amine molar ratio for the polymerization of various acrylic resins.

Table 1 presents the number-average molecular weight $\bar{M}_n$, weight-average molecular weight $\bar{M}_w$, and polydispersity index ($\bar{M}_w/\bar{M}_n$) of the prepared PMMA. These properties were slightly lower for polymers prepared using DMPOH than DMT for all molar ratios BPO/amine studied. A clear dependence of $\bar{M}_n$ on the molar ratio BPO/amine used is observed, which is shown more clearly in Fig. 4 for DMT and Fig. 5 for DMPOH. In the same figure, the time required for the maximum rate to appear is plotted. As can be seen, the two curves exhibit the same shape, reinforcing the assumption that at the molar ratio BPO to amine 1.57, the maximum primary and macroradical concentration occurs, leading in shorter reaction times and lowered $\bar{M}_n$values.

All the prepared polymers showed for the ratio $\bar{M}_w/\bar{M}_n$ a value higher than 2. Taking into account that the value of this ratio depends on the mode of termination and falls between 1.5–2, when the growing macroradicals terminate by recombination and/or disproportionation,[26] it is obvious that, in the studied polymerizations the macroradicals terminate also by other modes, reacting most probably with amine (chain transfer reactions) or with nitroxide formed from amine.[12]

The effect of the reaction temperature on the polymerization of MMA initiated by BPO/DMPOH or BPO/DMT (molar ratio 1.12) is shown, respectively in Figs. 6 and 7. From these figures, the overall reaction rate constant k' and the initiation reaction rate R_I were calculated at monomer



Scheme 3.

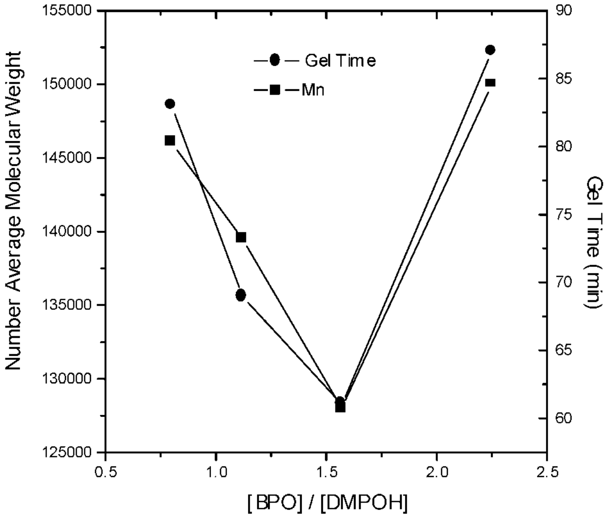


Figure 4. Number average molecular weight of PMMA and gel time of polymerization, as a function of the used initial molar ratio of the BPO/DMPOH at 37°C.

conversion values less than 5% and the results are presented in Table 3. An increase in the value of k' and R_I with increasing temperature was observed for both systems, resulting in a decrease of the molecular weight of the corresponding prepared PMMA (Table 3).

The temperature dependence of the overall rate constants were plotted by an Arrhenious type equation and gave a straight line with a slope equal to

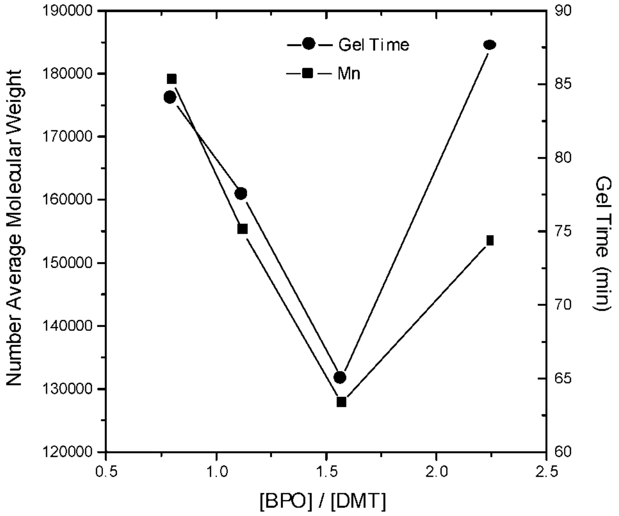


Figure 5. Number average molecular weight of PMMA and gel time of polymerization, as a function of the used initial molar ratio of the BPO/DMT at 37°C.

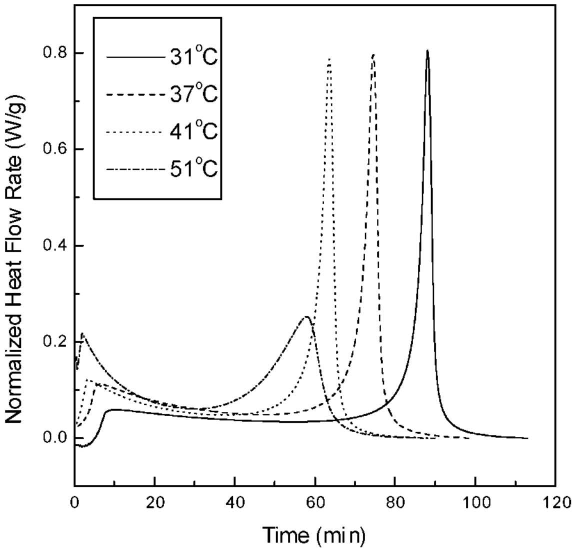


Figure 6. Effect of the reaction temperature on the reaction rate profile for the BPO/DMPOH initiation system at a molar ratio 1.12.

the overall activation energy E_a Fig. 8. This was 51.8 kJ/mol K for the BPO/DMPOH and 47.1 kJ/mol K for the BPO/DMT system. The latter is slightly higher than that of 35.9 kJ/mol reported by De Feng[20] and of 39.23 kJ/mol reported by Elvira et al.,[27] most probably due to the wider temperature range examined in this study than in earlier studies.

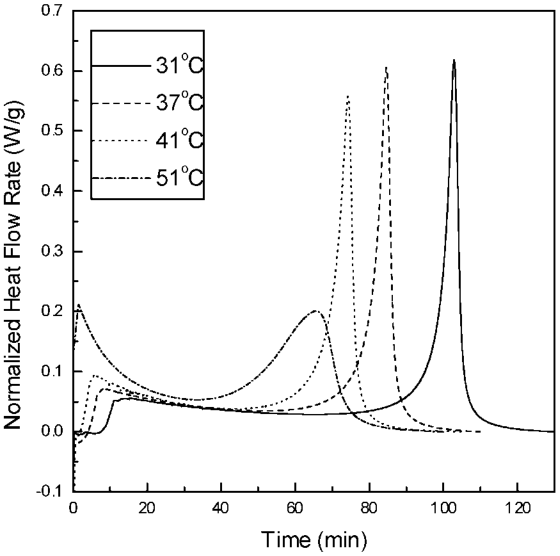


Figure 7. Effect of the reaction temperature on the reaction rate profile for the BPO/DMT initiation system at a molar ratio 1.12.

Table 3. Values at Different Temperatures of the Overall Rate Constant, k' and Initiation Reaction Rate R_I, of the Polymerization of MMA Initiated by a BPO/Amine Initiation System (Molar Ratio BPO/Amine 1.12); Values of Molecular Weights ($\bar{M}_n$ and $\bar{M}_w$) of the Equally Prepared Polymers

Amine	T (°C)	$k' \times 10^4$ (s^{-1})	$R_I \times 10^6$ (mol/L/s)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
DMPOH	31	1.11	2.56	149,100	442,600	2.97
	37	1.76	4.67	139,500	386,400	2.77
	41	2.20	5.95	137,600	418,300	3.04
	51	3.98	11.91	128,000	394,500	3.08
DMT	31	1.11	2.57	158,000	481,900	3.05
	37	1.53	3.52	155,000	471,200	3.04
	41	1.83	4.13	149,800	450,900	3.01
	51	3.50	9.19	143,100	450,480	3.15

CONCLUSION

BPO/DMPOH system was found to be a slightly more efficient initiator with respect to BPO/DMT for the free-radical polymerization of MMA at 37°C, resulting in higher polymerization rates and lower gel times. The prepared polymers, using DMPOH, showed slightly lower molecular weights and polydispersity index than those from DMT. In all cases, this index was

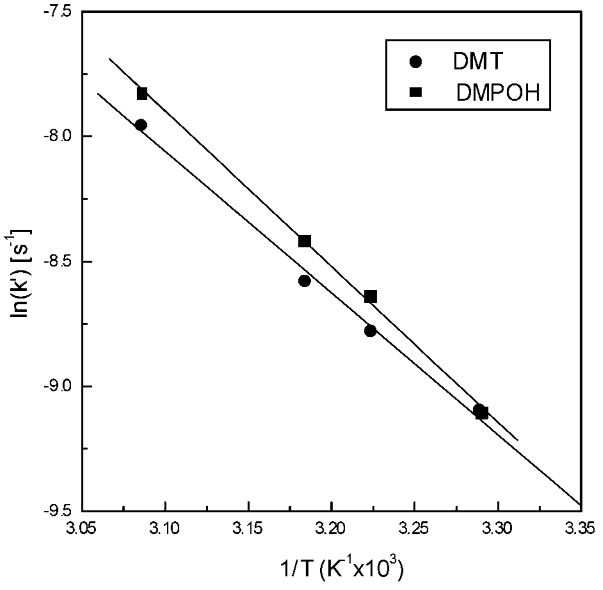


Figure 8. Arrhenious plot of the initial overall kinetic rate constant k' for both initiation systems.

higher than 2, revealing that the macroradicals terminate not only by recombination and/or disproportionation, but also by other modes of reactions. The polymerization rate and molecular weights of the corresponding polymers were found to depend on the molar ratio of BPO to amine when the product of these concentrations was kept constant. The maximum rate and the lowest molecular rate occurred for both amines when 1.57 moles of BPO per mole of amine were used. The activation energy of MMA polymerization was found to be 51.8 kJ/mol K for BPO/DMPOH and 47.1 kJ/mol K for BPO/DMT.

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