Kinetic Study by Differential Scanning Calorimetry of the Bulk Copolymerization of 2-Hydroxyethylmethacrylate with Ethyleneglycoldimethacrylate

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ABSTRACT: This article presents a kinetic study of the copolymerization of 2-hydroxyethylmethacrylate (HEMA) with ethyleneglycoldimethacrylate (EGDMA). First, the rate constant of decomposition, k_d, of azobisisobutyronitrile (AIBN) used to initiate the copolymerization was investigated. Then, the reactivity ratios, r_1 and r_2, of the monomers (HEMA and EGDMA), and the termination rate constant, k_t, were determined. Rate constants were obtained by differential scanning calorimetry (DSC) experiments. The decomposition rate constant of AIBN follows an Arrhenius law in the temperature range 320–400 K. Copolymerizations were carried out in the pans of the DSC apparatus at 353 K. The reactivity ratios, determined after analysis of the mixture composition by gas chromatography, exploitation of the data using the Meyer and Lowry equation, and a numerical method, were found equal to $r_1 = 0.811$ and $r_2 = 6.548$. Also from the reaction rate obtained by DSC, the dependence of the termination rate constant with conversion and temperature has been established. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1220–1228, 2001

Key words: DSC; kinetics; copolymerization; hydroxyethylmethacrylate; reactivity ratios

INTRODUCTION

Over the last decade, great interest has been taken in the copolymers of 2-hydroxyethylmethacrylate (HEMA) and ethyleneglycoldimethacrylate (EGDMA) for use in biomedical applications. A general review, including applications, can be found in the paper of Montheard and Chatzopoulos.[1] For example, several uses concern endovascular occlusion in the case of tumour,[2] preparation of contact and intraocular lenses used after cataract extraction, or sorbents in various types of chromatography. Poly(2-hydroxyethylmethacrylate) (PHEMA) (alone or as a copolymer) has been widely used in the biomedical field because of its nontoxicity, antigenicity, and excellent compatibility with living organism tissue. Indeed, hydrophilic polymers based on HEMA have been used as substitutes for metals, and to suppress corrosion and inflexibility. Also, a sufficient purity and a high swelling ability can be attained by this type of polymer.[2] For biomedical applications, large spherical beads based on PHEMA with very narrow size distribution are required; suspension polymerization is the most suitable process to produce these beads. This has already been achieved by several authors who have dispersed HEMA in an organic solvent. However, the

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polymer obtained in this condition is contaminated by the presence of residual solvent and is not appropriate for biomedical applications. Therefore, another method has been reported, where HEMA and water form two separate phases, which were obtained by adding salt to decrease the solubility of the monomer in water. HEMA and EGDMA form droplets, dispersed in water, that are stabilized by addition of magnesium oxide, MgO,[3,4] or magnesium dihydroxyde, $Mg(OH)_2$.[5,6] Although extensive work has been carried out in the biomedical field, it appears that several kinetic parameters for the copolymerization of HEMA with EGDMA have not been determined. Mikos and Peppas[7] proposed a kinetic analysis based on three parameters: the number of methacrylate groups of HEMA, the number of pendent groups of EGDMA, and the number of crosslinks per chain. In their kinetic model they have taken into account the gel effect via one parameter, the mean number of crosslinks per chain, which depends on two moments. However, in the absence of data, the kinetic constants used in their work refer to MMA homopolymerization. In this work, the kinetic parameters of the copolymerization of HEMA with EGDMA are determined and used in the model proposed by Mikos and Peppas.

It appears that one of the major goals of reaction engineering is to develop mathematical models to predict molecular and morphological properties. In this way, physical and chemical aspects are coupled in a systemic approach. Therefore, valid kinetic constants are needed for polymerization modeling. With this objective, we present here a convenient and reliable method for the determination of several kinetic parameters for the bulk copolymerization of HEMA with EGDMA using azobisisobutyronitrile (AIBN) as an initiator. Thus, the dissociation rate constant of AIBN, the reactivity ratios, and the termination rate constant are reported. Results were obtained from differential scanning calorimetry (DSC) measurements. The procedure for the determination of the reactivity ratios was first applied to the bulk copolymerization of HEMA with MMA to test the reliability of the method of combining DSC and gas chromatography (GC), and to compare our data with that reported in the literature for 353 K. Then, the same procedure was used to determine the reactivity ratios of the system HEMA and EGDMA copolymerized in bulk. The termination rate constant of the copolymerization was also determined by DSC in the 343–363 K temperature range. As dispersed drops can be considered as microreactors in suspension polymerization, the kinetic parameters, so determined, can be used in a second step to model the kinetics of the suspension copolymerization of HEMA with EGDMA in a continuous reactor. More details can be found in Ajzenberg's work.[8]

EXPERIMENTAL

Materials

The initiator, AIBN, supplied by Janssen, was used as received because several experiences have proved that, when AIBN was recrystallized, the peak obtained by DSC was shifted, but the area remained unchanged. HEMA was supplied by Aldrich and EGDMA by Fluka. HEMA and EGDMA were purified by distillation at reduced pressure (HEMA: T_{eb} = 67°C/3.5 mm and EGDMA: T_{eb} = 98–100°C/5 mm). MMA was supplied by Acros and distilled at atmospheric pressure (T_{eb} = 100°C/760 mm).

Measurements

Rate constants were determined by DSC (Setaram DSC 92). Steel pans were used and indium was the reference. For the determination of the dissociation rate of AIBN, the sample pans were filled with 1 to 2 mg of AIBN. To determine the reactivity ratios, 1 wt % of AIBN was added to a mixture of HEMA and EGDMA. Several experiments were carried out with the following mole fractions of HEMA: 70, 80, 90, 95, and 98% for the copolymerization of HEMA with EGDMA. For the second investigated system, the mole fraction of MMA in the mixture of HEMA/MMA was: 20, 30, 50, 70, and 90%. Monomer composition was determined by GC (890 Gas Chromatography, Hewlett-Packard) with helium as carrier gas. The instrument was equipped with a capillary column (O.V., 30 m × 0.32 mm) and with an integrator (D-2500 Chromato-Integrator, Merck). The operating conditions were: $P = 1.1 \times 10^5$ Pa, T_{injector} = 533 K, T_{oven} = 463 K (temperature corresponding to the highest boiling point of the monomers, i.e., EGDMA), T_{detector} = 553 K. The temperatures of the injector and of the detector were chosen so that they were higher than the boiling point of the products analyzed. V_{injected} = 0.5 μL,

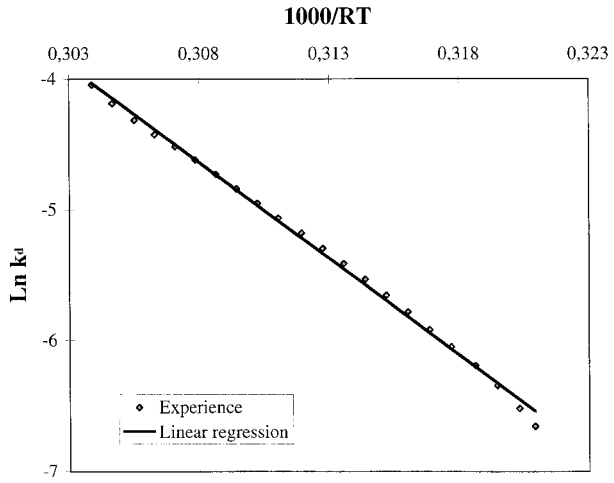

Figure 1 Arrhenius plot for the decomposition of AIBN. Heating rate: 2°C/min. Experimental data and linear regression.

and the following concentrations of HEMA or EGDMA in 1-methyl-2-pyrrolidinone (Fluka) were used for calibration: 8.10^{-3}, 6.10^{-3}, 4.10^{-3}, and 2.10^{-3} mol.l^{-1}. For MMA, the concentrations were: 10^{-2}, 8.10^{-3}, 6.10^{-3}, and 4.10^{-3} mol.l^{-1}.

Decomposition Rate of AIBN

It has already been pointed out that DSC is a reliable tool for determining kinetic constants of chemical reactions.[9,10,11] Only small amounts of sample are required and the kinetic constants are obtained from a simple run. The procedure also gives the heat of decomposition.

AIBN was heated from 20 to 180°C and the heat flow was recorded with time and temperature. The total area, A(J), under the DCS curve corresponds to the total heat of reaction, ΔH. The area a (J) under the heat flow curve versus time corresponds to the heat evolved during the time interval taken between zero and a given time t. Assuming that the heat evolved is proportional to the number of reacted moles of monomer, n, the following relation is derived:

$$\frac{a}{A} = \frac{n}{n_0} \tag{1}$$

where n_0 is the initial mole number of monomer.

Therefore, at any time t, the number of unreacted monomer is given by

$$n = n_0 - \frac{n_0 a}{A} \tag{2}$$

Neglecting the volume variation during the reaction, the kinetic constant can be expressed by the following relation:

$$k_d = \frac{[(AV)/n_0]^{x-1}(dH/dt)}{(A-a)^x} \tag{3}$$

where n_0/V is the initial concentration, x is the order of the reaction, k_d is the rate constant (s^{-1}), and dH/dt, the heat flow at time t (J.s^{-1}).

Azo compounds, such as AIBN, obey a first order kinetics,[12] so eq. (3) becomes

$$k_d = \frac{dH/dt}{A-a} \tag{4}$$

and k_d can be easily determined from the thermogramme.

Experiments were carried out at three different heating rates: 2, 5, and 10°C/min. This determined dH/dt, A, and a. Then, k_d values were calculated using eq. (4) for the different heating rates. More explanations on the procedure can be found in Barrett or Ajzenberg's work.[8,12]

The variation of the decomposition rate constant of the initiator with temperature follows an Arrhenius law:

$$k_d = A_f \exp\left(-\frac{E}{RT}\right) \tag{5}$$

where A_f is the frequency factor (s^{-1}), $R = 8.314$ J.mol^{-1} K^{-1}, and E is the activation energy (J.mol^{-1}). A_f and E have been determined for three heating rates by plotting Ln k_d versus $1/T$ (Fig. 1).

It has been noted[13] that the area, A, under the peak of the DSC trace, corresponding to the total decomposition of the initiator depends on the

Table I Reactivity Ratios

System	
HEMA	MMA
$r_1 = 0.110$	$r_2 = 0.814$
HEMA	EGDMA
$r_1 = 0.811$	$r_2 = 6.548$

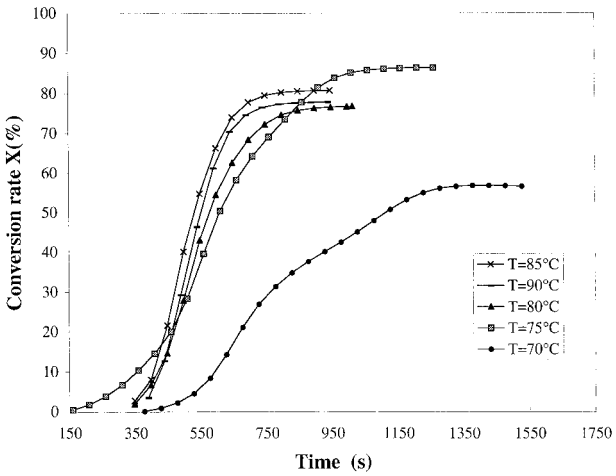

Figure 2 Copolymerization of HEMA with EGDMA initiated by AIBN. Variation of the conversion with time at several temperatures. Data obtained by DSC measurements.

heating rate. Consequently, k_d, determined by this method, depends on dT/dt. Therefore, k_d was extrapolated to a value which corresponds to a heating rate equal to 0°C/min. Then, k_d was plotted versus $1/T$, and the following equation was established:

$$k_d(\mathrm{s}^{-1}) = 1.9510^{19} \times \exp\left(-\frac{158644\ \mathrm{J.mol}^{-1}}{RT}\right) / \qquad 320 < T(\mathrm{K}) < 400 \quad (6)$$

This relation is valid in the temperature range 320–400 K, where the best linearity is observed.

Reactivity Ratios

The determination of the reactivity ratios, when two monomers are reacting, requires a sensitive analytical technique and a statistically valid method. The experimental procedure proposed by Maeder and Renken[14] was used here. The procedure was first validated by the copolymerization of HEMA with MMA,[8] monomers having a chemical structure similar to HEMA and EGDMA. Several experiments have been carried out at T = 353 K. The only modified parameter was the molar fraction. After 2 min of copolymerization, the reaction was stopped by plunging the pans

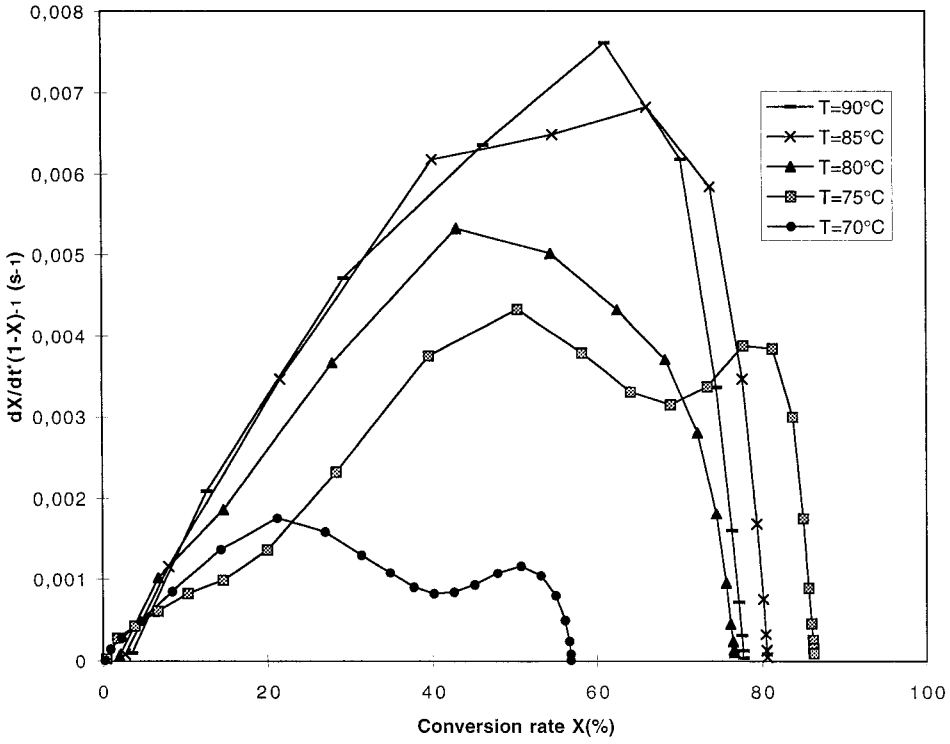

Figure 3 Copolymerization of HEMA with EGDMA initiated by AIBN. Variation of $(dX/dt)/(1-X)$ with conversion at several temperatures.

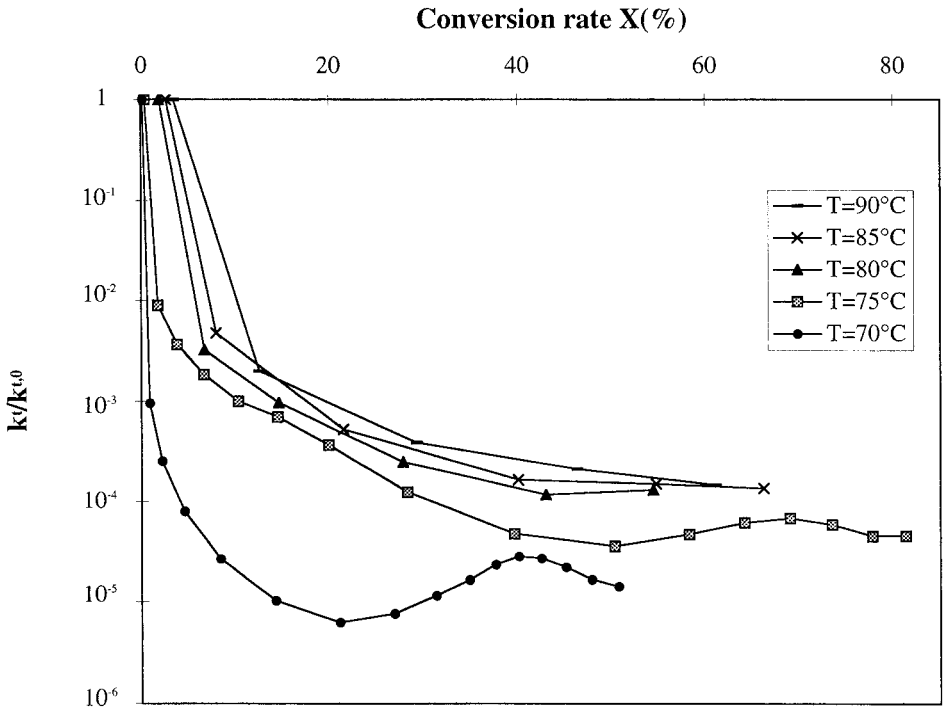

Figure 4 Variation of $k_t/k_{t,0}$ with conversion (%) at several temperatures.

into ice. Pans were pierced and placed in a vial with 1 mL of 1-methyl 2-pyrrolidinone. After 2 days under mechanical stirring, the content was analyzed by GC. From these experiments, the monomer conversions X_1 and X_2 were calculated. According to Meyer and Lowry,[15] the overall conversion X is related to the monomer composition in the mixture and to the reactivity ratio r_1 and r_2 by the following equation:

$$X = 1 - \left(\frac{f_1}{f_{1,0}}\right)^{\alpha}\left(\frac{1-f_1}{1-f_{1,0}}\right)^{\beta}\left(\frac{f_{1,0}-\delta}{f_1-\delta}\right)^{\gamma} \qquad (7)$$

and

$$\alpha = \frac{r_2}{1-r_2}; \quad \beta = \frac{r_1}{1-r1}; \quad \gamma = \frac{1-r_1r_2}{(1-r_1)(1-r_2)}; \quad \delta = \frac{1-r_2}{2-r_1-r_2}$$

where $f_{1,0}$ is the initial mole fraction of monomer 1 (HEMA) in the reacting mixture, and f_1 is the mole fraction of HEMA after the reaction was stopped.

Considering the overall monomer conversion, X

$$X = f_{1,0}X_1 + f_{2,0}X_2 \qquad (8)$$

and

$$f_1 = \frac{\frac{n_{1,0}}{n_{2,0}}(1-X_1)}{\frac{n_{1,0}}{n_{2,0}}(1-X_1) + (1-X_2)} \qquad (9)$$

where $n_{1,0}$ is the initial molar amount of monomer 1 in the reacting mixture $n_{2,0}$ is the initial amount of monomer 2 and $f_{2,0}$ is the initial mole fraction of monomer 2 (MMA or EGDMA).

From X_1 and X_2 values determined by GC and from eq. (8) and eq. (9), X and f_1 were calculated. Then the reactivity ratio, r_1 and r_2, was obtained after resolution of eq. (7) using Excel Solver.

The criterion for the resolution of the equation was minimization between experimental and calculated conversion. To test the validity of the method, the copolymerization of HEMA with MMA was also investigated. Results are reported in Table I. For the system HEMA–MMA, values

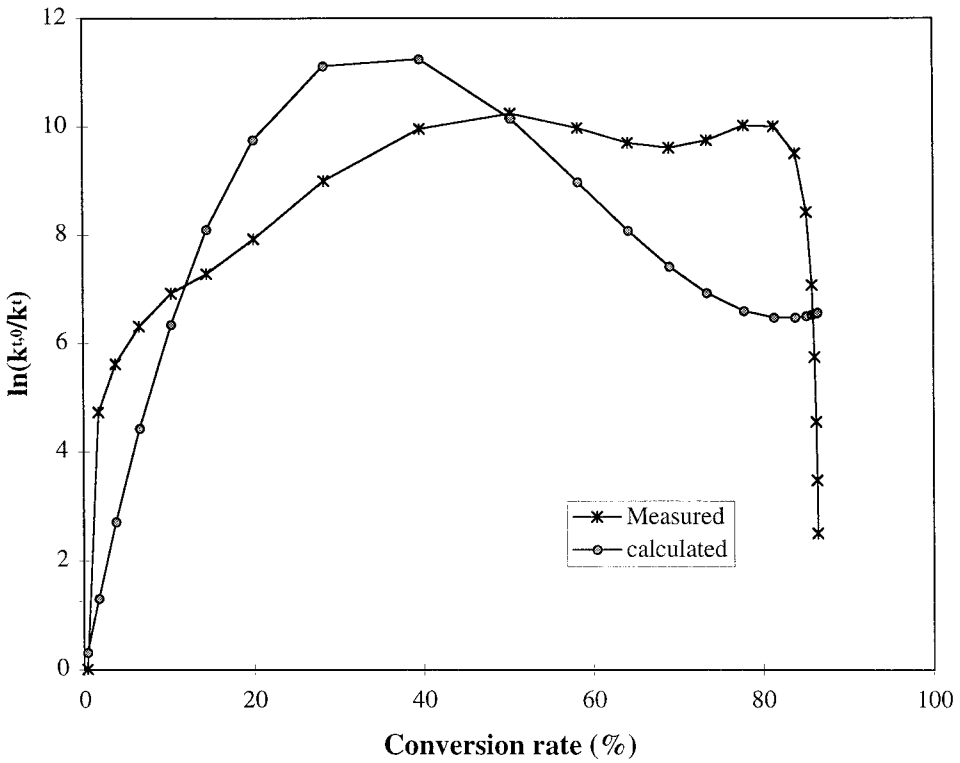

Figure 5 Variation of $\ln(k_{t,0}/k_t)$ with conversion at $T = 348$ K. Experimental and calculated values (method 1).

are in agreement with those reported in the literature. The difference between experimental results and calculated values using the Meyer and Lowry equation is 2.1% for the first system and 4% for the second one.

For the copolymerization of HEMA with EGDMA, $r_2 \gg r_1$ ($r_1 < 1$ and $r_2 \gg 1$), which means that both types of radicals react preferentially with EGDMA. There is a tendency for successive homopolymerization of the two monomers. Therefore, a heterogeneous network is formed.

Termination Rate Constant

Using mixtures having the following initial proportions of the components: 0.03 mole EGDMA/mole HEMA and 0.015 mole AIBN/mole HEMA,[4] a series of DSC experiments was carried out at fixed temperature and for several times of reaction. The fractional conversions of the monomers were calculated from the area of the thermogrammes obtained for the complete conversion by increasing the temperature from 20 to 180°C. The variation of the conversion with time is shown in Figure 2 at several temperatures.

For radical polymerization, the variation of the conversion with time is given by

$$\frac{dX}{dt} = k_p[R^*](1 - X) \tag{10}$$

where X is the monomer conversion (%), k_p is the propagation rate constant ($\text{l.mol}^{-1}.\text{s}^{-1}$), and $[R^*]$ is the total polymer radical concentration (mol.l^{-1}).

From data reported in Figure 2, the quantity $\frac{dX}{dt}\frac{1}{1-X}$ can be calculated, and its variation with monomer conversion is shown in Figure 3 at different temperatures. As $\frac{dX}{dt}\frac{1}{1-X}$ values increase, $X < X_c$, $[R^*]$ increases, but k_p is considered constant. The reaction of termination is controlled by diffusion and decreasing k_t. Because $\frac{dX}{dt}\frac{1}{1-X}$ values decrease when $X > X_c$, both rate constants, k_p and k_t, decrease when the conversion increases. In this case, the reaction of propagation is also controlled by diffusion.

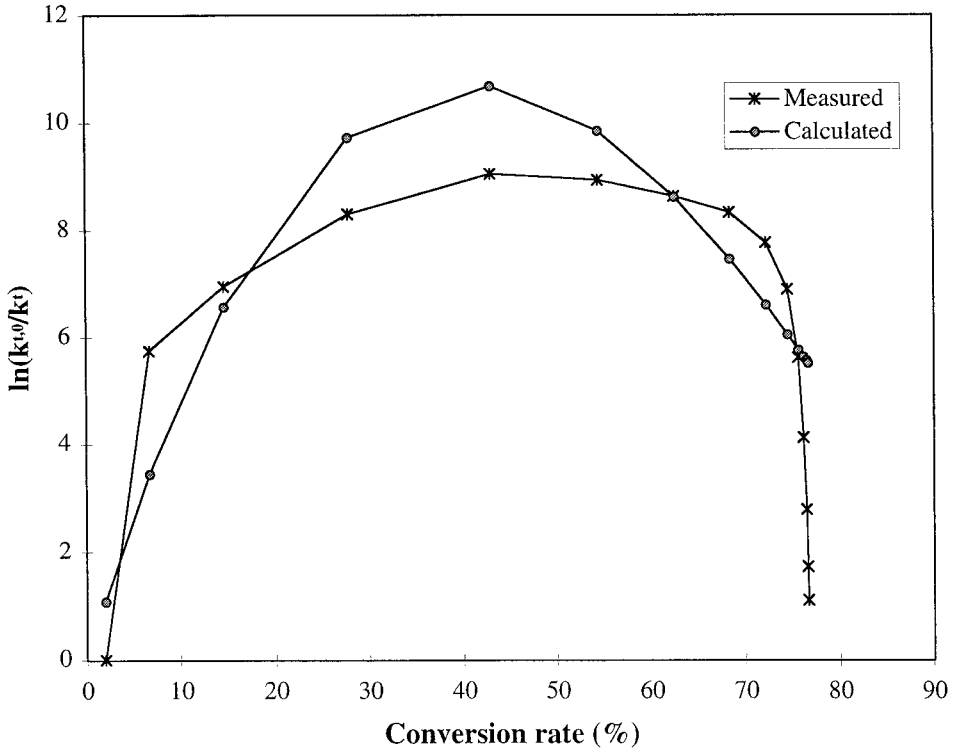

Figure 6 Variation of $\ln(k_{t,0}/k_t)$ with conversion at $T = 353$ K. Experimental and calculated values (method 1).

Assuming that k_p is constant for conversion lower than a critical value, X_c, corresponding to the occurrence of the glass effect, it follows:

$$\frac{[R^*]}{[R_0^*]} = \left(\frac{fk_{t,0}}{f_0 k_t}\right)^{1/2} \tag{11}$$

where f and f_0 are, respectively, the initiator efficiency and its value for low conversion; k_t and $k_{t,0}$ ($\text{l.mol}^{-1}.\text{s}^{-1}$) are, respectively, the termination rate constant and its value for low conversion. Assuming that the initiator efficiency remains constant for conversions lower than X_c, $f = f_0$, the variation of $[(R^*)/(R^*)_0]^2$ with conversion is the same as the rate constant ratio, $k_{t,0}/k_t$. Figure 4 shows the variation of $k_t/k_{t,0}$ with conversion at several temperatures. The ratio decreases when the conversion increases.

To describe mathematically the dependence of k_t on conversion, Li et al.[16,17] proposed the following equation:

$$\frac{k_t}{k_{t,0}} = \exp(A_1X + A_2X^2A_3X^3) \tag{12}$$

where A_i ($i = 1$ to 3) coefficients depend linearly on temperature and X is the monomer conversion. To determine the A_i ($i = 1$ to 3) coefficients, two approaches were followed. In the first approach, eq. (12) was solved by considering simultaneously conversion and temperature parameters. $Ln(k_{t,0}/k_t)$, obtained experimentally by DSC and calculated values (by a mean square method with Excel Solver) is represented as a function of the conversion rate, respectively at 348 and 353 K, in Figures 5 and 6. In Figure 5, differences between experimental and calculated values can be observed; in particular, the simulation does not show a second maximum at high conversion.

A better agreement between experimental and calculated values was obtained for $T > 348$ K. For this temperature, the second peak is probably due to the limit of the gel effect or to impurities that can be present in the mixture. Both assumptions suggest an inhibition effect, which is not visible at higher temperature. Also, this behaviour points out that temperature has a strong influence on the $k_t/k_{t,0}$ estimation at $T = 343$ K. Therefore, a second method for the simulation of

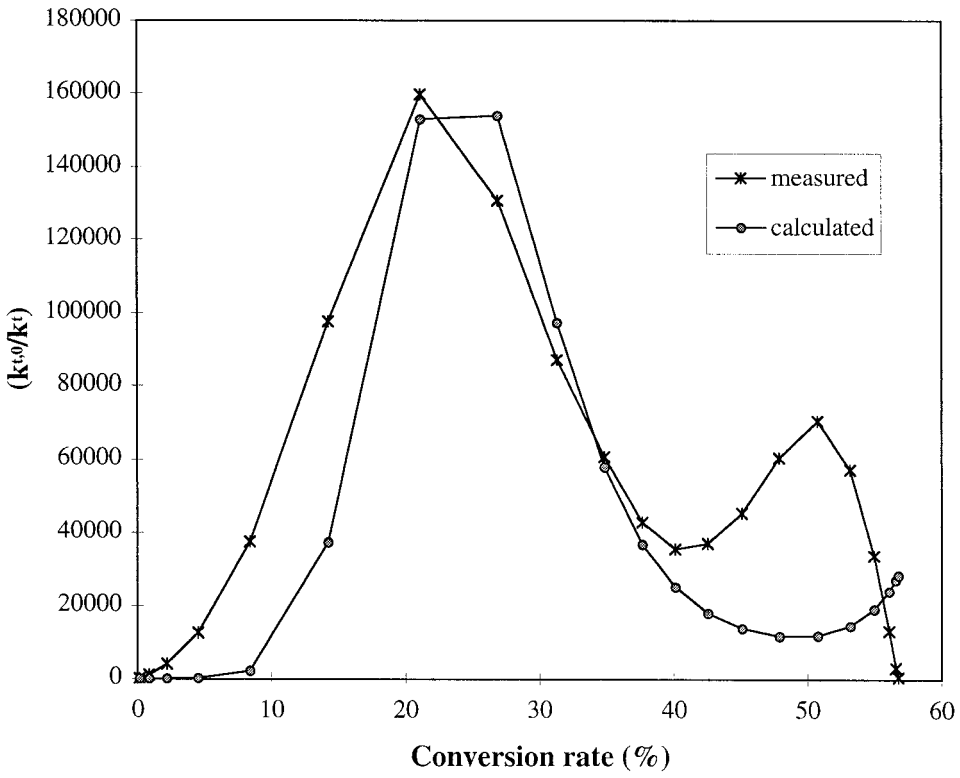

Figure 7 Variation of $(k_{t,0}/k_t)$ with conversion at $T = 343$ K. Experimental and calculated values (method 2).

the variation of the termination rate constant with conversion has been considered. In this step, the estimation of the A_i ($i = 1$ to 3) parameters has been made, considering different conversion rates at a fixed temperature. So for one temperature, the A_1, A_2, and A_3 parameters, and an expression relating $k_t/k_{t,0}$ with conversion have been determined. Figures 7 and 8 show the variation of $k_{t,0}/k_t$ with conversion at 343 and 363 K, respectively. The method was also applied to the determination of the coefficients at several temperatures.

A_i ($i = 1$ to 3) parameters determined at $T = 343$ K were found to be different from the values calculated in the temperature range $348 \leq T\,(\mathrm{K}) \leq 363$, because the evolution of the conversion with time is different. This behavior, characterized by a retardation effect, is probably due to the shift of the gel effect or the presence of inhibitor trace in the mixture. These phenomena disappear with increasing temperature. Nevertheless, the method gives a better estimation of A_i ($i = 1$ to 3), which was found equal to

$$T = 343 \text{ K}$$
$$A_1 = -1.2006$$
$$A_2 = 3.7267 \times 10^{-2}$$
$$A_3 = -3.3994 \times 10^{-4}$$
$$348 \leq T(K) \leq 363$$
$$A_1 = 0.0180T - 6.7630$$
$$A_2 = -5.357 \times 10^{-4}T + 0.1941$$
$$A_3 = 4.226 \times 10^{-6}T - 0.0015$$

CONCLUSIONS

The results presented here are based on DSC experiments. The technique has proved to be a reliable tool for the determination of kinetic parameters. Therefore, the method has been applied to the bulk copolymerization of HEMA with EGDMA in the presence of AIBN as initiator. First, and because the results found in the literature are scattered and depend on the solvent and on the method, the dissociation rate constant of AIBN was re-examined. Also, the reactivity ratios of HEMA and EGDMA were determined by combining DSC and GC for the estimation of the

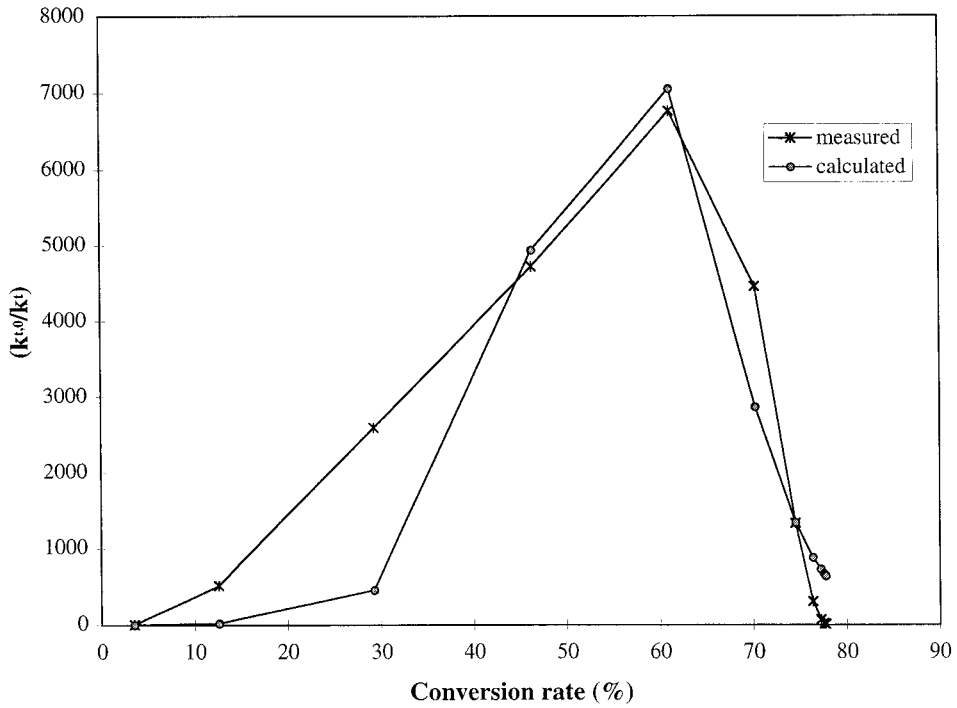

Figure 8 Variation of $(k_{t,0}/k_t)$ with conversion at $T = 363$ K. Experimental and calculated values (method 2).

concentrations of the unreacted monomers in the mixture at 353 K. The methodology is more reliable and gives results with a better precision than when obtained by classic methods. Furthermore, the numerical resolution is more valid than a graphical one and the technique can be used in a large conversion range. Bulk copolymerization of HEMA with EGDMA carried out in the pan of the DSC instrument has permitted us to determine the variation of the termination rate constant with conversion in the temperature range $343 \leq T\,(\mathrm{K}) \leq 363$. A different estimation was found at $T = 343$ K because the evolution of the conversion with time is different at that temperature. The production of HEMA/EGDMA copolymers by a continuous process is attractive. For this reason, the kinetic data obtained here would be helpful for the modeling of such a process.

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