The Radical Polymerization of C12–C18 Alkylmethacrylates in Semibatch Conditions

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SYNOPSIS

The radical polymerization of C12–C18 alkylmethacrylates in solution of mineral oil has been studied in semibatch condition by using 2,2'-azobis (2-methylbutyrronitrile) as initiator. Many kinetic runs of polymerization have been performed in different operative conditions. A kinetic model has been developed to interpret and simulate these runs. C12–C18 alkylmethacrylate polymerization in mineral oil concentrated solution occurs through a classical radical chain mechanism. Kinetic parameters for the initiator decomposition and for the radical chain propagation rate resulted the same as reported by the literature. A particular behavior of this system is the intervention of the gel effect observed from the beginning of the reaction as a consequence of the high initial viscosity. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyalkylmethacrylates are commonly used as additives of lubricating oils and are produced by radical chain polymerization of alkylmethacrylates dissolved in mineral oil.

The reological properties of the lubrificating oil strongly depend on both concentration and molecular weights distribution (MWD) of the added polyalkylmethacrylates. The MWD is strictly related to the modalities adopted to perform the radical chain polymerization of the alkylmethacrylates. Therefore, to study the kinetics of the polymerization is useful in order to identify the main factors influencing the MWD, to optimize the operative conditions, and to describe the behavior of the reacting system.

Many articles have been published on both batch and continuous methylmethacrylate polymerization;[1-25] very few, on the contrary, have been published on the kinetics of the alkylmetacrylates,[26,27], despite the relevant importance of these monomers for lubricating oils industry.

In this article, the radical chain polymerization of C12–C18 alkylmetacrylates in solution of mineral

oil has been studied in semibatch condition by using 2,2'-azobis (2-methylbutyrronitrile). Many kinetic runs of polymerization have been performed in different conditions. A kinetic model has been developed to interpret and simulate these runs. Kinetic parameters of model have been determined by mathematical regression analysis on the runs performed. "Gel effect" has great influence on the kinetics of this polymerization and must be considered already at the starting of the reaction as a consequence of the initial viscosity of the reaction mixture. This behavior is different from that observed in the polymerization of methylmethacrylate[1-25] and has been described with the aid of semiempyrical relation containing two parameters.

Finally, kinetic parameters obtained are discussed and compared with the corresponding values found in literature.

EXPERIMENTAL

Methods, Techniques, and Reagents

Kinetic runs of polymerization have been performed in a 50 liter jacketed, well-stirred, stainless steel reactor. The scheme of the reactor used is reported in Figure 1. Polymerization is strongly exothermic;
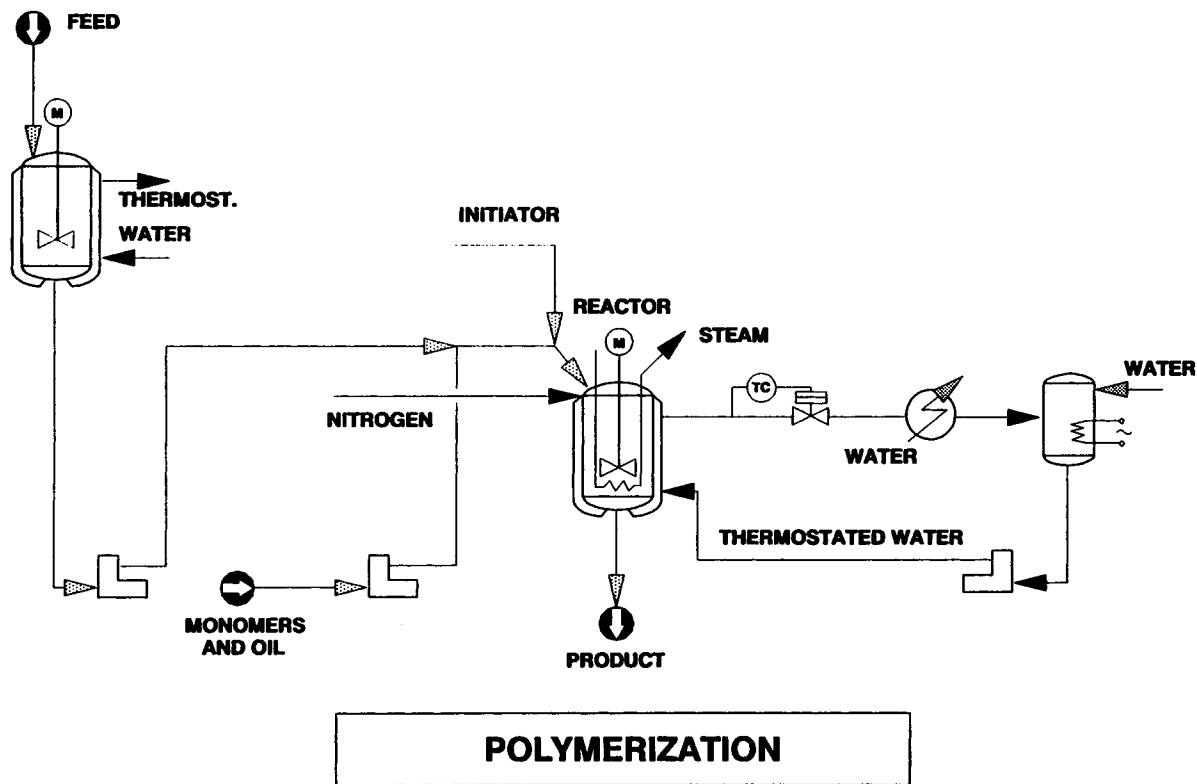

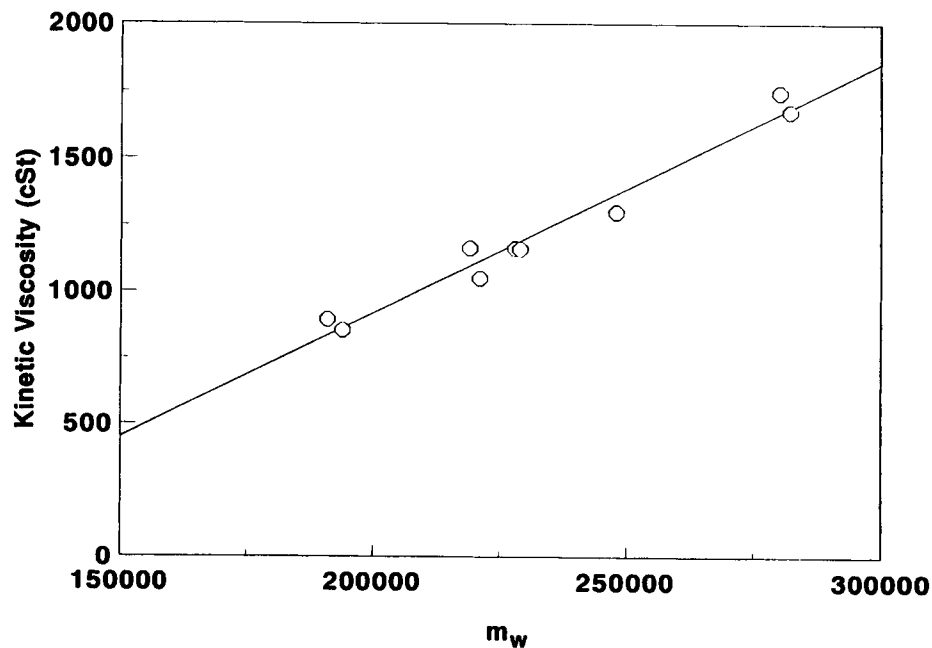**Figure 1**   Scheme of the apparatus employed for the polymerization runs.

Figure 2   Correlation existing between the viscosity mesaured at 100°C of a solution of polymer at 50% in weight in oil and the mean molecular weight M_w.
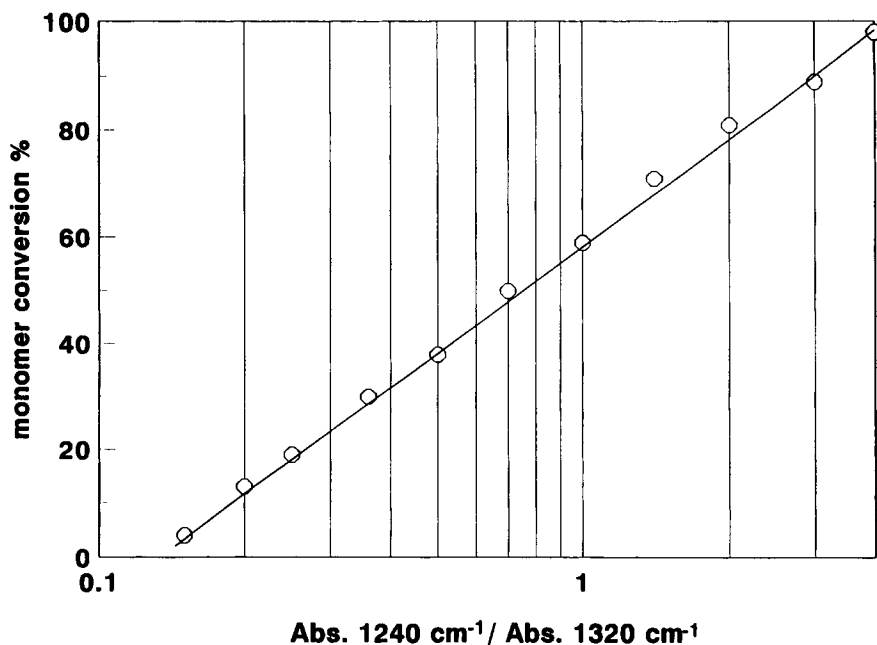
Figure 3 Correlation observed between the monomer conversion and the ratios of the IR spectroscopy adsorbances at 1240 cm^{-1} and 1320 cm^{-1}, respectively, that is, between the concentration of formed polymer in respect to residual monomer.

therefore, the temperature of the reactor is controlled by feeding thermostated water in the reactor jacket and is measured during the reaction with a thermocouple.

Kinetic runs were performed by introducing 10 kg of mineral oil (SN150) and 7 kg of C12–C18 alkylmethacrylate. The reactor was purged with nitrogen for 1 h and heated at 80°C. Then the initiator 2,2'-azobis (2-methylbutyrronitrile) was added. The initiator was always added at 80°C so that, depending on prefixed polymerization temperature, there is a different interval (from a minimum of 3° to a maximum of 13°C) between the two temperatures. At this point, 3 kg of monomer were added with constant feed rate in 30 min. Samples of the reaction mixture were withdrawn at different reaction times and, after chemical quenching, analyzed by IR spectroscopy and GPC in order to evaluate the conversion of the monomer, the molecular weights distribution (MWD), and the average molecular weights (M_n, M_w, M_z).

Viscosities were measured at 100°C on the final products with a capillary viscosimeter. In Figure 2 the viscosity observed for different mean molecular weights of C12–C18 polyalkylmethacrylates dissolved in mineral oil (SN150) with a concentration of 50% by weight is reported. As it can be seen in the field examined, a linear correlation exists.

The conversion of the monomer can be determined by IR spectroscopy by comparing the absorbance at 1240 cm^{-1} and 1320 cm^{-1}. Signal at 1240 cm^{-1} can be related to the formed polymers, while the signal at 1320 cm^{-1} corresponds to the residual monomer. It is possible to correlate the ratio of two mentioned absorbances to the monomer conversions, as reported in Figure 3. This plot, showing a linear trend, has been made by preparing solutions containing monomer and polymer with known concentrations. The molecular weights distributions have been determined by gel permeation chromatography GPC, by using a FL-Gel mixed column. Standards used for the calibration of instruments are samples of polystyrene of known mean molecular weights (200 mL, 0.1% in THF at 30°C). Molecular weights of the polyalkylmethacrylates have been calculated with the method suggested by Grubisch et al.[28] The parameters employed in the Mark-Houwink-Sakurada relationship:

$$[\eta] = kM_w^a \tag{1}$$

are the followings:

Standards[29] $k = 1.4 \ 10^{-3}$ (mL/g) $a = 0.70$

Samples[29], referred to Poly(octadecyl methacrylate)

$$k = 2.5 \ 10^{-4} \text{ (mL/g)} \quad a = 0.75$$

Table I List of the Kinetic Runs Performed with the Corresponding Operative Conditions

Run	T°C	I%	M_n 10^{-5}	M_w 10^{-5}	M_z 10^{-5}	η^a (cSt)
1	91	0.247	0.90	1.91	3.14	895
2	91	0.183	1.00	2.21	3.71	1050
3	85	0.247	1.03	2.48	4.30	1300
4	85	0.183	1.10	2.80	4.99	1748
5	93	0.215	0.92	1.94	3.20	854
6	83	0.215	1.10	2.82	5.10	1677
7	88	0.215	1.01	2.29	3.87	1161
8	88	0.215	0.96	2.19	3.73	1164
9	88	0.215	0.98	2.28	3.90	1163

[a] Viscosity measured at 100°C.

The monomers have been furnished by Euron Company, the mineral oil SN150 by AGIP Petroli Company, while the initiator was supplied by Dupont de Nemours.

Reaction Pattern and Kinetic Model

The radical polymerization of alkylmethacrylates should occur according to a classical reaction scheme.[8]

Assuming that I is the initiator, M is the monomer, R_j is the radical with j monomeric units, P_j is the dead polymer with j monomeric units, k_d is the kinetic constant for the initiation reaction, k_p is the kinetic constant for the propagation reaction, and k_{td} is the kinetic constant for the termination reaction.

In this scheme, we assume that only the termination by disproportion is operative (this assumption is explained later). From these reactions, the material balance for each component in a semibatch reactor, by assuming the quasi steady-state approximation that is very good for methylmethacrylate polymerization,[5] can be written as follows:

$$R = [(2fk_dI)/k_{td}]^{1/2} \qquad (2)$$

$$dI/dt = -k_dI \qquad (3)$$

$$dM/dt = -k_pMR + F/V \qquad (4)$$

$$dP_n/dt = k_{td}R^2(1 - \alpha)\alpha^{n-1} \qquad (5)$$

where

$$\alpha = (k_pM)/(k_pM + k_{td}R) \qquad (6)$$

R is the overall concentration of the radicals, F is the molar monomer feed.

The value of volume (V) is calculated after each integration step

$$V = \frac{w_s}{d_s} + \frac{w_M}{d_M} + \frac{w_p}{d_p} \qquad (7)$$

where d_s is the solvent density, d_M the monomer density, d_p is the polymer density. The weight of solvent w_s is constant, while the weight of monomer w_M and the weight of polymer w_p are calculated as follows:

$$dw_M/dt = m_w VdM/dt \qquad (8)$$

$$dw_p/dt = m_w Vk_pMR \qquad (9)$$

where m_W is the molecular weight of monomer.

Solution of Eqs. (2–9) would give the initiator, radicals, monomer, and polymeric chains concentration, but it would be time consuming owing to the high values of n, so we have used the moments of the molecular weight distribution (λ_i) to describe the evolution of the number average molecular weight (M_n), the weight average molecular weight (M_w) and the z average molecular weight (M_z).

The moments are related to the molecular weight averages by:

$$M_n = m_W\lambda_1/\lambda_0 \quad M_w = m_w\lambda_2/\lambda_1 \quad M_z = m_w\lambda_3/\lambda_2 \qquad (10)$$

Table II Parameters Used in the Simulation of the Kinetic Runs

Kinetic Parameters		
f	0.26*	
β	9.91*	
φ_p^*	0.11*	
Pre-exponential Factors		Activation Energies (cal/mol)
k_d	$9.77\ 10^{14}$ (s^{-1})	30800
k_p	$4.92\ 10^5$ (l/mol s)	4350
k_{td}	$3.38\ 10^{7*}$ (l/mol s)	701
Other parameters		
Monomer density		0.87 g/cm^3
Polymer density		0.94 g/cm^3
Solvent density		0.87 g/cm^3
Mean molecular weight of monomer		276.
Mean molecular weight of solvent		442.

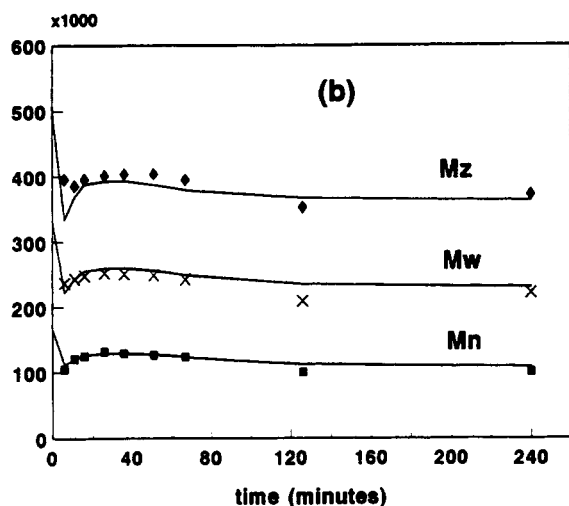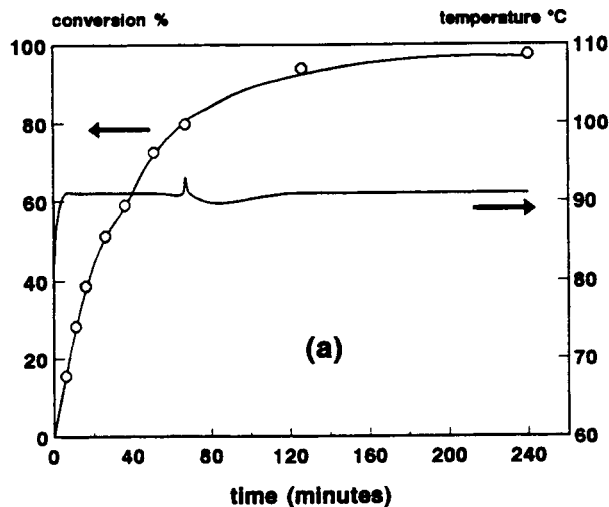Asterisks indicate the parameters obtained by regression on the experimental data.

Figure 4 Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 2 of Table I. Dots are experimental, lines are calculated.

The moments of order 0, 1, 2, and 3 can be calculated as follows:[30]

$$d\lambda_0/dt = k_{td}R^2\alpha \tag{11}$$

$$d\lambda_1/dt = [k_{td}R^2\alpha(2 - \alpha)]/(1 - \alpha) \tag{12}$$

$$d\lambda_2/dt = [2k_{td}R^2\alpha]/(1 - \alpha)^2 + d\lambda_1/dt \tag{13}$$

$$d\lambda_3/dt = [6k_{td}R^2\alpha^2]/(1 - \alpha)^3 + 3d\lambda_2/dt + 2d\lambda_1/dt \tag{14}$$

In the radical polymerization kinetic parameters can be affected by diffusional limitation. According to Soh and Saudeberg,[21,22] radical polymerization can

occur through four different phases. In phase I, that is, initial phase, we have low conversion of the mean molecular weight. In phase II, the viscosity of the reaction system strongly increases and the well-known "gel effect" appears. In this case, the rate of polymerization strongly increases because termination constant decreases as a consequence of the reduced mobility of growing radical chains, that is, the probability of collision between two growing radical chains is strongly reduced.

In phase III, characterized by high conversion, the viscosity of the reaction mixture increases more and more, but the termination parameter, decreased in the previous phase, reaches a constant value. As
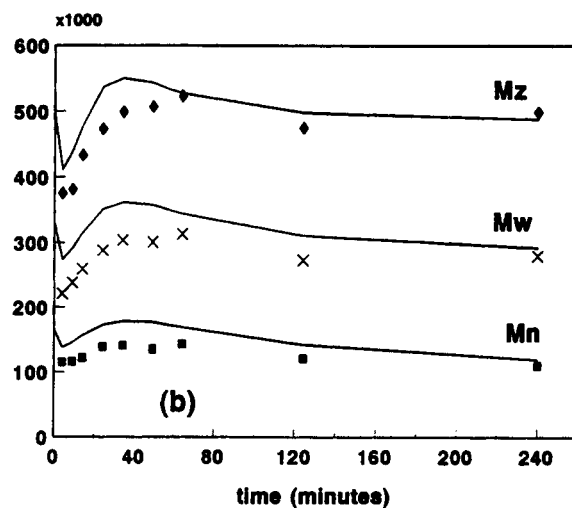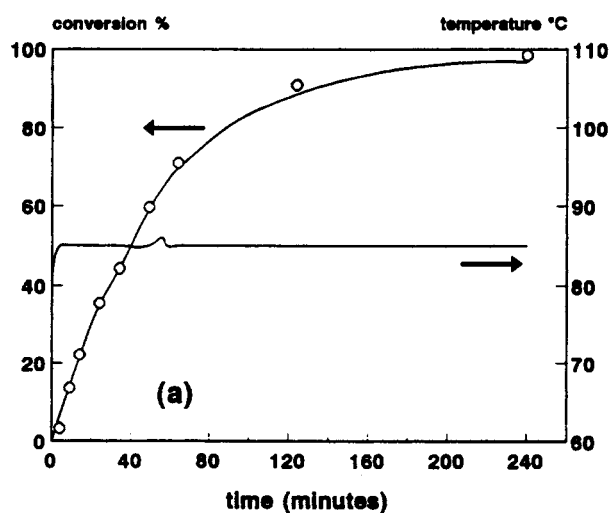

Figure 5 Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 4 of Table I. Dots are experimental, lines are calculated.
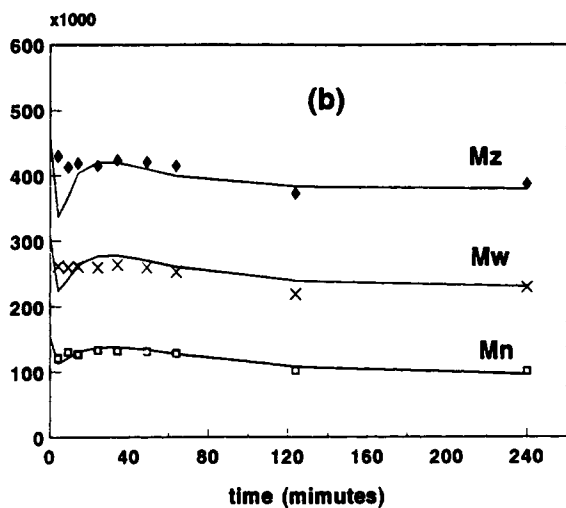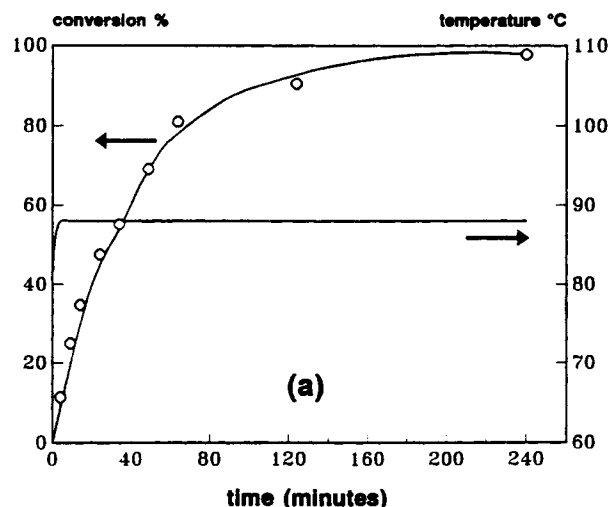
that are lower than the glass transition temperature of polymer.

In the radical polymerization of C12–C18 alkyl methacrylates, dissolved in oil SN150, we observed only phase II and III. Phase I does not occur because reaction mixture has a high initial viscosity, while phase IV is absent because the reaction temperature is greater than glass transition temperature of the polymer.

By observing the behavior of our kinetic runs performed at lowest temperatures, that is, runs 3, 4, and 6 of Table I, we note that when isothermal conditions are reached a considerable increase in the molecular weight occurred until 30–40% of con-
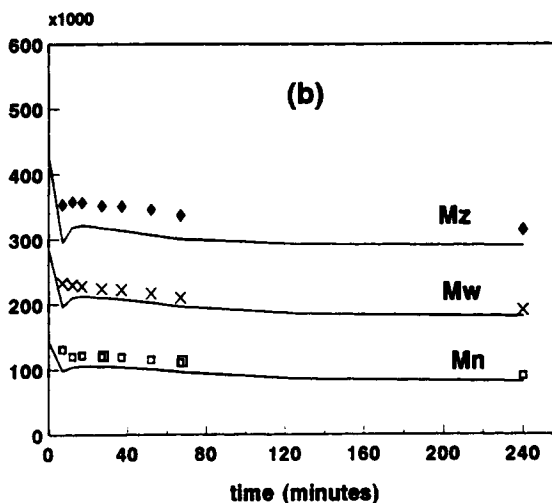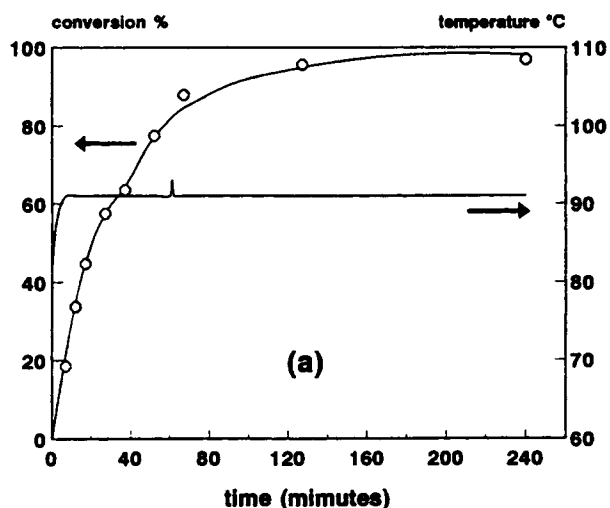

Figure 6 Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 7 of Table I. Dots are experimental, lines are calculated.

a consequence, polymerization rates remain fast and mean molecular weights do not increase or slowly decrease. In this phase, the termination occurs with a different mechanism not requiring the translation of growing radical chains. In fact, during polymerization, the terminal part of the growing chains move in a casual way and a finite probability exists that two radicals collide giving termination. In phase IV, a limit conversion is reached at which the rate of polymerization decreases. In this case, the viscosity of the reaction mixture has become so high that also monomer mobility is prevented; propagation rate is consequently reduced, and polymerization rates slow down. This occurs for polymerization temperatures

Figure 7 Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 1 of Table I. Dots are experimental, lines are calculated.

Figure 8 Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 3 of Table I. Dots are experimental, lines are calculated.
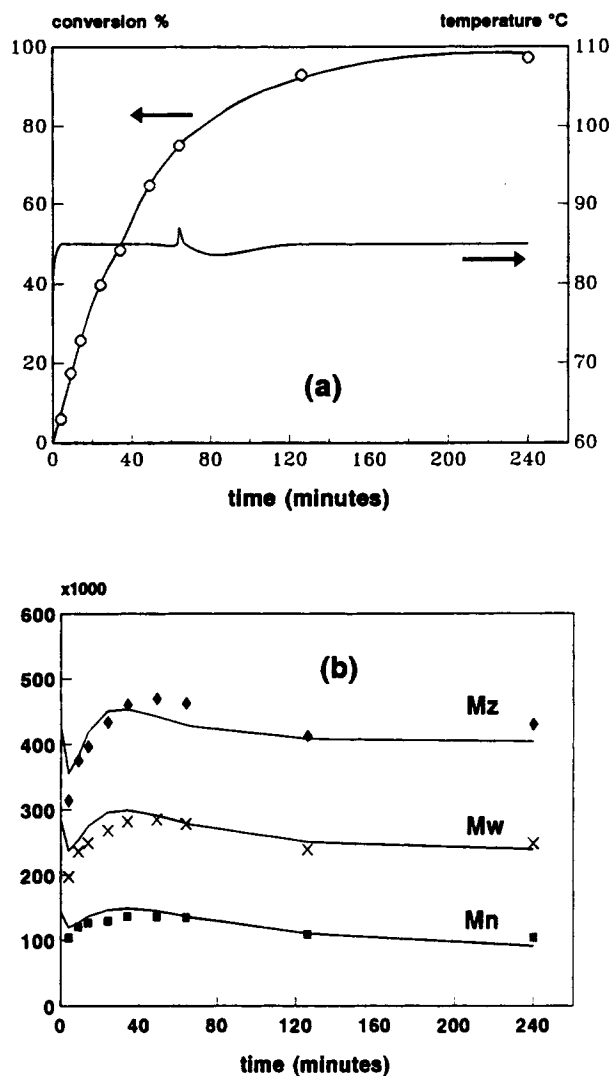
version, corresponding to a volumetric fraction of the polymer of about 0.1. Then, molecular weight slightly decrease. This behavior can be attributed, according to Soh and Sunderberg,[22,23] to decrease of termination constant.

To describe the effect of viscosity on the termination constant, that is, the dependence of k_t from the composition of the reaction mixture, many empirical or semiempirical relation containing two or more parameters have been proposed by literature.[10,12,13,17,24,25]

To simulate our runs we have assumed the following relationship:

$$k_{td} = k_{tdo}\exp(-B\phi_p) \qquad (15)$$

where k_{tdo} is the initial termination constant, B is an empirical parameter, and ϕ_p is the volumetric fraction of the polymer. According to relation (15), the termination constant exponentially decreases by increasing the concentration of polymer, which is strictly correlated with the viscosity of the reaction mixture. Relation (15) is valid until phase III is reached, where a constant value of k_{td} must be assumed. The value of polymer volumetric fraction at which phase III starts (ϕ_p^*) is another empirical parameter of the model.

RESULTS AND DISCUSSION

A list of the kinetic runs performed is reported in Table I, together with the corresponding presetted temperatures and the amounts of initiator used. In the same table, kinetic viscosity and mean molecular weights obtained for each run are also summarized. Runs 7, 8, and 9 have been made by adopting exactly the same conditions in order to verify the reproducibility of the runs that resulted satisfactory. By observing the data reported in Table I it can be concluded that MWD are strongly affected by polymerization conditions adopted. In order to simulate kinetic runs listed in Table I, the kinetic parameters of the described model must be known. Some of these are reported by literature.

The decomposition constant of initiator 2,2′-azobis (2-methylbutyrronitrile), according to Engel,[31] is

$$k_d = 9.77 \ 10^{14}\exp(-30800/RT) \qquad (s-1)$$

The efficiency factor f must be evaluated by mathematical regression on the experimental data; in fact, the only value reported by literature for a C12 alkylmethacrylate polymerization is related to 2,2′-dimethyl-2,2′-azodiproprionitrile and is 0.28.[26]

The propagation constant would be independent of the kind of monomer used;[26,27] therefore, we can write, as reported by literature:[16]

$$k_p = 4.92 \ 10^5\exp(-4350/RT) \qquad (1/mol \ s)$$

The termination constant is given by the sum of two contributions, k_{tc} and k_{td}, that is, constant of termination by radical combination and by disproportion, respectively. It is known that the ratio k_{tc}/k_{td} decreases with the increase of both the length of the alkyl chain[26] and of the temperature;[1] therefore,
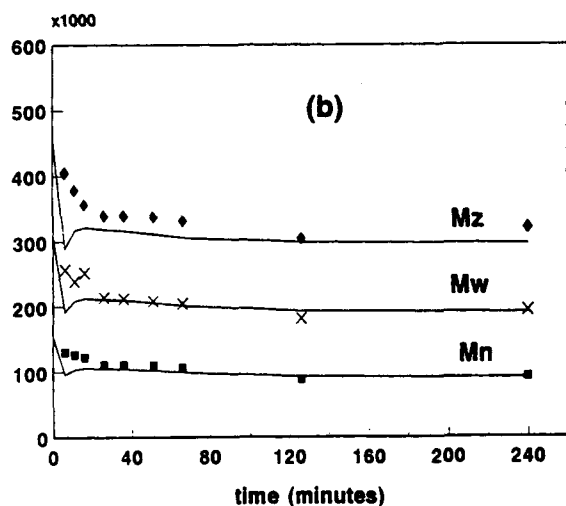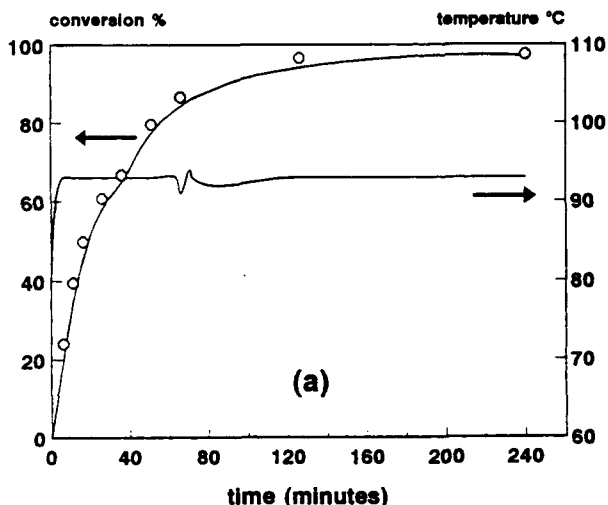
Figure 9   Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 5 of Table I. Dots are experimental, lines are calculated.

in our conditions, only the disproportion mechanism gives a significant contribution to the polymerization. Termination constant; otherwise, propagation is affected by the alkyl chain length of the esterified alcohol,[27] but it is reasonable to assume that only pre-exponential factor and not activation energy can be influenced. Therefore, we assumed 701 cal/mol for the activation energy, as reported by literature, while the pre-exponential factor A_o was determined by regression analysis on the experimental data.

By concluding same experimental (runs 2, 4, and 7) kinetic data of conversion and average molecular weight where subjected to statistical regression

analysis by looking the minimum of the following objective function $\Phi(\beta)^{32}$

$$\Phi(\beta) = \sum_{i=0,n} [(x_{s_i} - x_{c_i})^2/x_{s_i} + (M_{ms_i} - M_{mc_i})^2/M_{ms_i}$$

$$+ (M_{ws_i} - M_{wc_i})^2/M_{ws_i} + (M_{zs_i} - M_{zc_i})^2/M_{zs_i}]$$

where β is the vector of the parameters to be optimized that are, respectively: the efficiency of the initiator f, the pre-exponential factor of termination constant A_o, and the parameters describing the gel effect B and ϕ_p, x is the conversion, the subscript s is related to experimental values, the subscript c is related to calculated values.
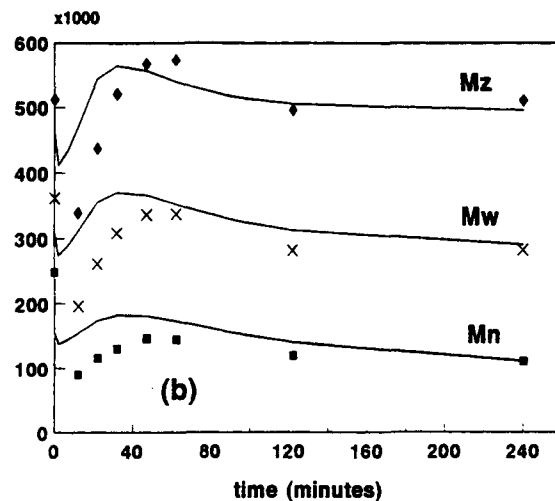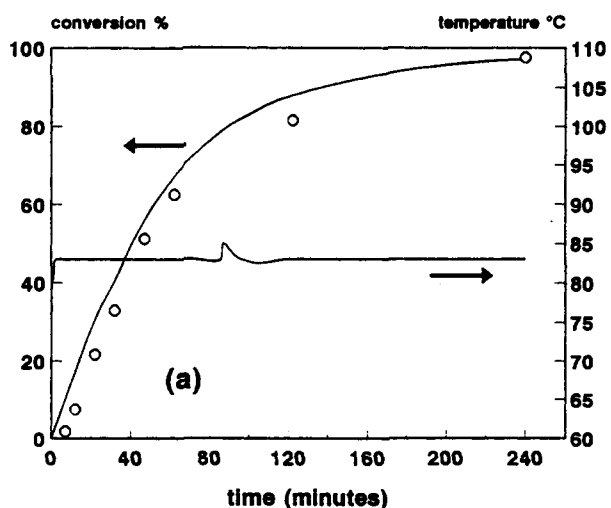

Figure 10   Evolution with time of the monomer conversion and of temperature (a) and of the mean molecular weights (b) for run 6 of Table I. Dots are experimental, lines are calculated.

Statistical regression analysis has been made on the data related to three different runs performed at different temperatures and in the presence of different amounts of initiator. These runs are listed in Table I as runs 2, 4, and 7. The values of the kinetic parameters not subjected to regression analysis are reported in Table II, togheter with the parameter obtained by calculation.

In Figures 4, 5, and 6 the agreement between experimental and calculated data in the simulation of the three runs used for regression analysis can be appreciated. Dots are experimental, lines are calculated. The same model with the same parameters have then been used to simulate the other kinetic runs reported in Table I, that are made in different conditions with respect to the three runs considered in the regression analysis. Examples of the agreements obtained in the simulation can be appreciate in Figures 7-10. As it can be seen, this agreement is quite satisfactory considering the large number of kinetic parameter of the model with respect of the small number of parameters determined by regression analysis.

In conclusion, C12-C18 alkylmethacrylate polymerization in mineral oil concentrated solution occurs through a classical radical chain mechanism. Kinetic parameters for the initiator decomposition and for radical chain propagation are the same reported in the literature. We have found a particular behavior of this system only for the intervention of the gel effect from the beginning of the reaction as a consequence of the high initial viscosity.

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