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NON-CLASSICAL FREE-RADICAL POLYMERIZATION. PART 2. THE POLYMERIZATION OF MONO-2-METHOXYETHYL AND MONO-2-ETHOXYETHYL ITACONATE

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ABSTRACT

The free-radical self-initiated bulk polymerization, at total conversion, of mono-2-methoxyethyl and mono-2-ethoxyethyl itaconate has been studied by differential thermal analysis. By fitting the theoretical equations to experimental data, global rate constants and kinetic orders for both monomers in the temperature interval 491–523 K were obtained. A kinetic scheme to explain the kinetic behaviour is proposed. Finally, the global activation energy E_A and the collision frequency factor A have been calculated by means of the Arrhenius equation.

INTRODUCTION

Recent years have seen a growing interest in itaconic acid, owing to the fact that it is the starting point for a family of interesting polymers. Of particular interest is the fact that the acid can be obtained easily from fermentation processes [1].

Another point of interest is that the radical polymerization of mono-itaconate esters is known to be very sensitive to steric effects, probably as a result of the influence of the side group.

The calorimetric techniques of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) facilitate the study of polymerization kinetics [2–12] because only a small quantity of monomer sample is

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required for the experiments (a few milligrams), manipulation is convenient, performance is rapid, and temperature control is versatile and precise.

When a polymerization process occurs, the usual starting point for analysis of the experimental data is the known equation

$$\mathrm{d}H = \mathrm{d}n \, \Delta H_{\mathrm{SP}} \tag{1}$$

where $\mathrm{d}H$ is the differential heat of reaction, ΔH_{SP} the specific enthalpy of reaction, and $\mathrm{d}n$ the differential number of monomer moles expended in a differential time $\mathrm{d}t$. This equation can be written as

$$\mathrm{d}n/\mathrm{d}t = (\mathrm{d}H/\mathrm{d}t)(1/\Delta H_{\mathrm{SP}}) \tag{2}$$

where $\mathrm{d}n/\mathrm{d}t$ can be determined from the DTA curve.

Assuming total conversion of the monomer to polymer, the conversion degree is obtained as the ratio of the partial to total thermogram area. The kinetic order and the kinetic constant are calculated by integrating the equation

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k[\mathrm{M}]^{x} \tag{3}$$

where [M] is the concentration of monomer M.

In previous papers [13–15] we have reported on studies of the kinetics of polymerization of several mono-itaconate esters. In this paper, we compare the bulk free-radical polymerization, carried out in the temperature interval 491–523 K, of mono-2-methoxyethyl and mono-2-ethoxyethyl itaconate.

EXPERIMENTAL

The mono-2-methoxyethyl and mono-2-ethoxyethyl itaconates (Fig. 1a and 1b) were obtained by the following method. Freshly distilled acetyl chloride (3 ml) was used to catalyse the reaction between itaconic acid (0.062 mol) and the appropriate alcohol (0.187 mol). The reaction mixture was refluxed until the itaconic acid was completely consumed. After this, the reaction mixture was cooled and dissolved in dichloromethane. The resulting solution showed the presence (by thin-layer chromatography) of three spots, attributable to the expected monoester, the di-itaconate and the excess of the alcohol used. The mixture was washed with aqueous NaOH (0.5 M), and the resulting aqueous phase was separated by means of a solution of HCl (0.5 M), and extracted with dichloromethane. Evaporation of the solvent produced the corresponding mono-itaconate, which was then purified by column chromatography on silica gel by eluting with dichloromethane/methanol (9.9 : 0.1).

The mono-2-methoxyethyl and mono-2-ethoxyethyl itaconates were fully characterized by ^{1}H NMR and IR spectroscopy. The spectroscopic results were consistent with the expected structures. The proton NMR assignments are listed in Table 1.

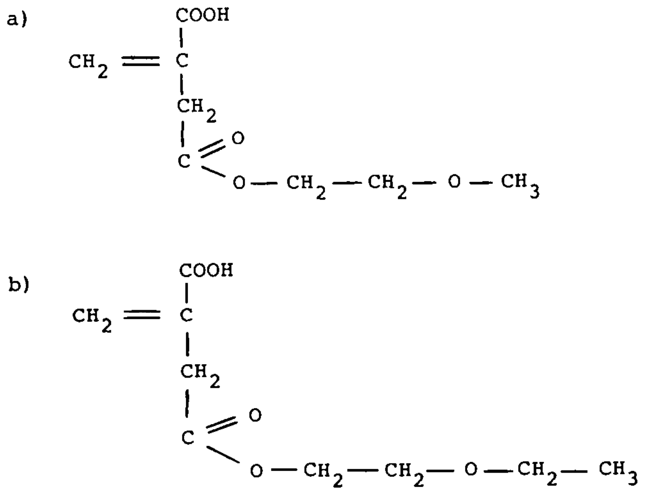

Fig. 1. Chemical structure of (a) mono-2-methoxyethyl and (b) mono-2-ethoxyethyl itaconates.

The calorimetric measurements, dynamic as well as isothermal, were performed using a Mettler TA 2000 differential thermal analyser, equipped with a scanning auto-zero device for obtaining a straight base line, which was calibrated using the heat of fusion of indium (28.0 J g^{-1}).

The measurements were performed in aluminium crucibles filled with monomer quantities of approximately 8 mg for each polymerization experi-

TABLE 1

Physical and ^1H NMR data for mono-2-methoxyethyl (**1**) and mono-2-ethoxyethyl itaconates (**2**)

Monomer	Yield [a] (%)	R_f^b	^1H NMR chemical shifts [c,d,e] (δ ppm)
1	30	0.35	8.22 (s, 1H, -COOH), 6.42 (s, 1H, $CH_2{}^f$=C), 5.81 (s, 1H, $CH_2{}^f$=C), 4.28 (t, 2H, J = 4.5 Hz, -COO-CH_2-), 3.60 (t, 2H, J = 4.5 Hz, -CH_2-O-), 3.39 (s, 3H, -CH_3), 3.38 (s, 2H, =C-CH_2-)
2	51	0.38	8.10 (s, 1H, -COOH), 6.42 (s, 1H, $CH_2{}^f$=C), 5.80 (s, 1H, $CH_2{}^f$=C), 4.29 (t, 2H, J = 4.8 Hz, -COO-CH_2-), 3.66 (t, 2H, J = 4.8 Hz, -CH_2-O-), 3.52 (q, 2H, J = 7 Hz, -O-CH_2-CH_3, 3.38 (s, 2H, =C-CH_2-), 1.21 (t, 3H, J = 7 Hz, -CH_3)

[a] Yield of chromatographically pure compound.

[b] For thin-layer chromatography, Merck Kieselgel GF254 plates (0.2 mm thick) were used. Eluent, CH_2Cl_2/CH_3OH (9.5 : 0.5).

[c] The 250 MHz ^1H NMR spectra were obtained using a Bruker WM-250 spectrometer at ambient temperature, with TMS as internal standard.

[d] In $CDCL_3$.

[e] s, singlet; d, doublet; t, triplet; q, quadruplet.

[f] Indistinguishable protons.

ment. Dynamic and isothermal polymerization were carried out by placing the aluminium crucibles containing the monomer into the furnace. Dynamic polymerization allows us to establish the polymerization interval. Isothermal polymerization permits study of the influence of temperature upon the polymerization rate.

The data were acquired and the numerical calculations performed using a Commodore 64/128 personal computer, running a BASIC program. This program plots dynamic and isothermal thermograms according to the integrated equations corresponding to different kinetic orders of reaction, in order to select the best reaction order for each monomer. Finally, the program calculates the kinetic rate constant from the slope of the straight line. The listing of this program is available upon request.

RESULTS AND DISCUSSION

The thermal behaviour of mono-2-methoxyethyl and mono-2-ethoxyethyl itaconate in the temperature ranges 288–630 and 288–600 K is shown in Figs. 2 and 3 respectively. The first endothermic peak in Fig. 2 corresponds to the melting point of mono-2-methoxyethyl itaconate, and the second to

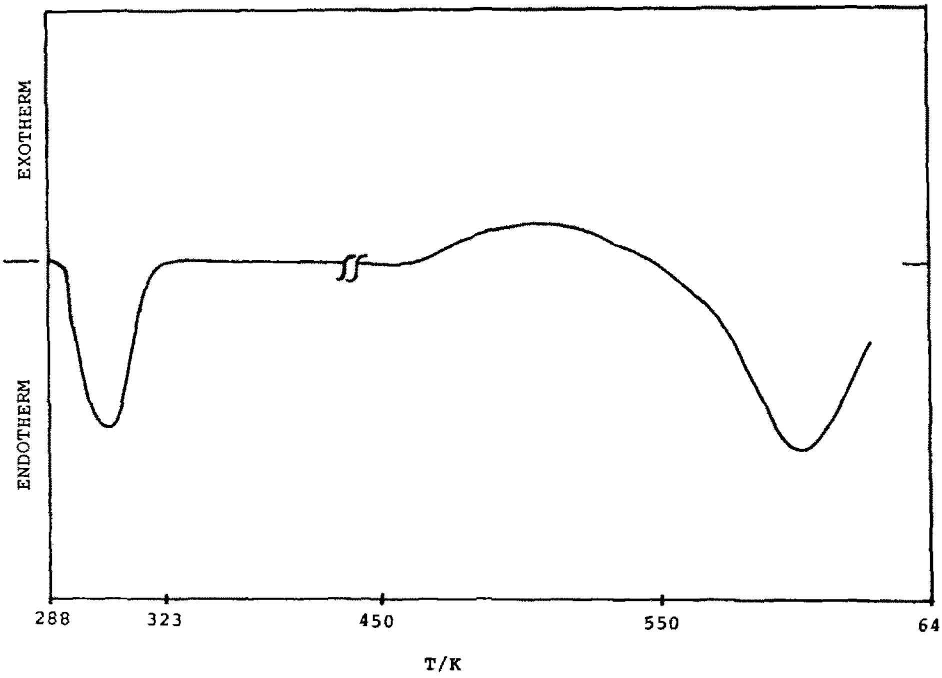

Fig. 2. Thermal behaviour of mono-2-methoxyethyl itaconate in the temperature range 288–630 K.

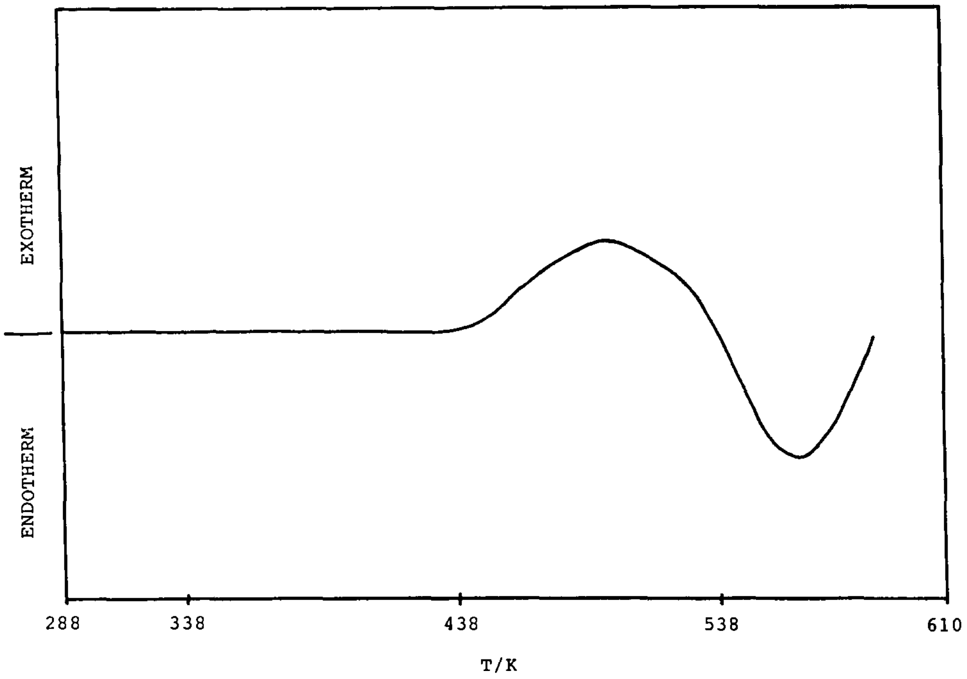

Fig. 3. Thermal behaviour of mono-2-ethoxyethyl itaconate in the temperature range 288–600 K.

the polymerization process. From the first peak we established that the heat of fusion and the melting point are 4.19 kJ mol^{-1} and 293 K respectively. From the exothermic peak the total polymerization heat for the mono-2-methoxyethyl and mono-2-ethoxyethyl itaconates was calculated to be -10.18 kJ mol^{-1} and -17.9 kJ mol^{-1} respectively. Surprisingly, while the methoxy derivative is obtained as a transparent solid compound (m.p. 293 K), the corresponding ethoxy derivative appears as an oily liquid. This is probably due to conformations in mono-2-ethoxyethyl itaconate, because of the possibility of rotation of the ethyl group around the valence cone of the oxygen. In other words, this behaviour is probably determined by steric

TABLE 2

Enthalpy of polymerization ΔH_p and global kinetic constant k at different temperatures, corresponding to the monomer order of 0.9, found for the mono-2-methoxyethyl itaconate

T (K)	$-\Delta H_p$ (kJ mol^{-1})	$k \times 10^{-3}$
499	3.3059	2.31
505	4.2887	2.51
511	4.50079	2.81
517	3.7596	3.31
523	2.9736	3.64

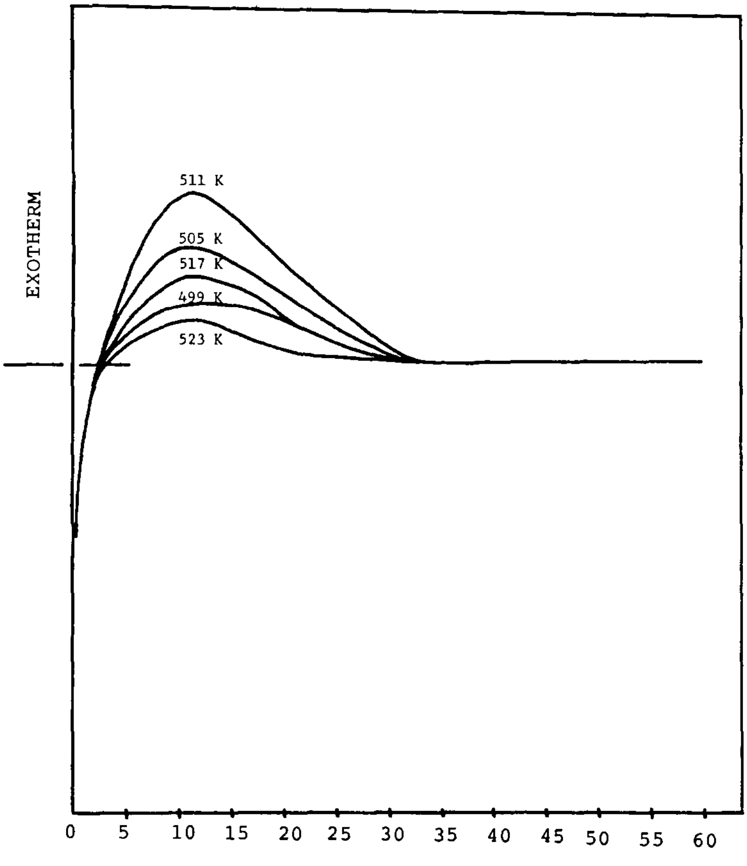

Fig. 4. Thermograms for the isothermal polymerization of mono-2-methoxyethyl itaconate at several temperatures.

interactions. As the potential barrier decreases with increasing chain length, it is possible to obtain more conformers in mono-2-ethoxyethyl itaconate than in mono-2-methoxyethyl itaconate. Transition from one conformation to another can therefore occur more readily. Mono-2-ethoxyethyl itaconate becomes kinetically more flexible. The flexibility of a molecule determines many of its properties (melt viscosity, tendency to crystallize, etc.) so it is for this reason that mono-2-ethoxyethyl itaconate has a lower melting temperature.

Figures 4 and 5 show isothermal thermograms for the bulk polymerization of the two monomers in the temperature range 491–523 K. As was expected, the reaction rate increases with temperature. However, the heat of reaction has a different behaviour: for mono-2-methoxyethyl and mono-2-ethoxyethyl itaconate, the heat of reaction increases (in absolute value) only to temperatures of 511 K and 497 K, respectively, decreasing thereafter (see

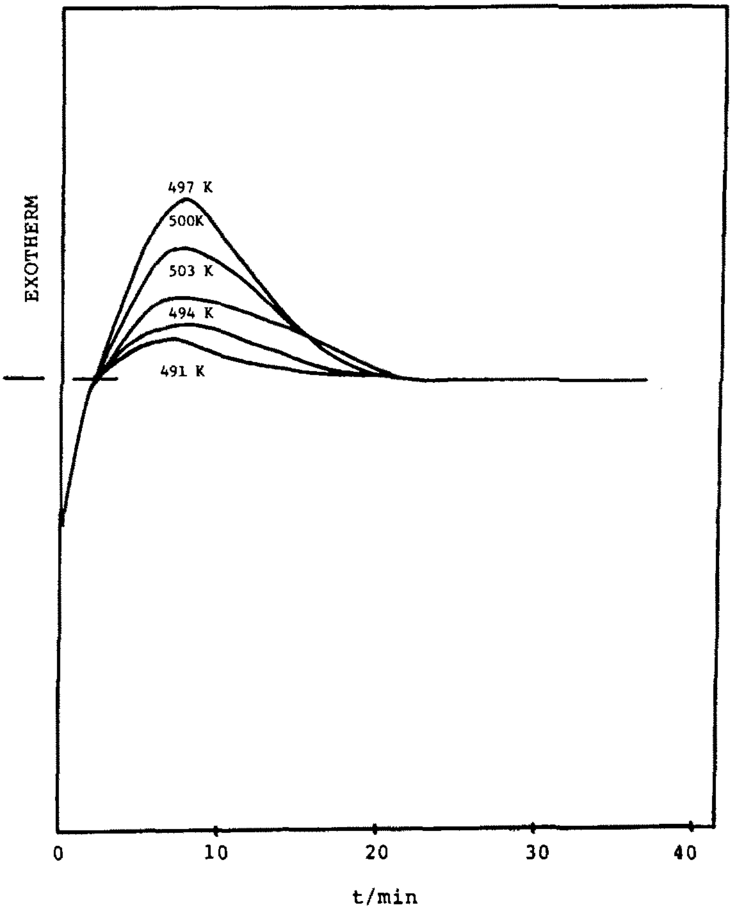

Fig. 5. Thermograms for the isothermal polymerization of mono-2-ethoxyethyl itaconate at several temperatures.

Tables 2 and 3, and Figs. 6 and 7). The areas under the curves shown in Figs. 4 and 5, necessary for determination of the kinetics of the polymerization, have been calculated using a BASIC program which integrates the experimental peak areas with an accuracy of better than 1%.

As the polymerization reaction was achieved by means of thermal initiation we have proposed the following kinetic scheme

$$\begin{array}{lll} \mathrm{M} + \mathrm{M} \xrightarrow{k_i} \cdot\mathrm{M{-}M}\cdot & \text{(i)} & \text{Initiation} \\ \cdot\mathrm{M{-}M}\cdot + \mathrm{M} \xrightarrow{k_p} \cdot\mathrm{M{-}M{-}M}\cdot & \text{(ii.1)} & \left.\right\} \\ \quad\vdots \qquad\qquad \vdots & & \text{Propagation} \\ \cdot\mathrm{M{-}M}_n\mathrm{{-}M}\cdot + \mathrm{M} \xrightarrow{k_p} \cdot\mathrm{M{-}M}_{n+1}\mathrm{{-}M}\cdot & (\text{ii.}n+1) & \left.\right\} \\ 2\ \cdot\mathrm{M{-}M}_n\mathrm{{-}M}\cdot \xrightarrow{k_t} \text{polymer} & \text{(iii.1)} & \text{Termination} \end{array}$$

TABLE 3

Enthalpy of polymerization ΔH_p and global kinetic constant k at different temperatures, corresponding to the monomer order of 1 found for the mono-2-ethoxyethyl itaconate

T (K)	$-\Delta H_p$ (kJ mol^{-1})	$k \times 10^{-3}$
491	2.047	5.17
494	2.408	5.67
497	3.9822	5.95
500	3.5586	6.38
503	3.1435	6.52

where M is the monomer, $\cdot$M–M$\cdot$ the initial diradical, and $\cdot$M–M$_n$–M$\cdot$ the propagation diradical.

We have assumed that the initiation step is a bimolecular process characterized by a second order rate with respect to the monomer

$$v_i = 2k_i[\mathrm{M}]^2 \tag{4}$$

where k_i is the initiation rate constant. The rate of the propagation step is

$$v_p = k_p[\mathrm{M}\cdot][\mathrm{M}] \tag{5}$$

We consider that the termination reaction occurs via step (iii.1) because the global rate of polymerization is first order

$$V = (2k_p k_i/k_t)[\mathrm{M}] \tag{6}$$

which is in good agreement with the experimental results .

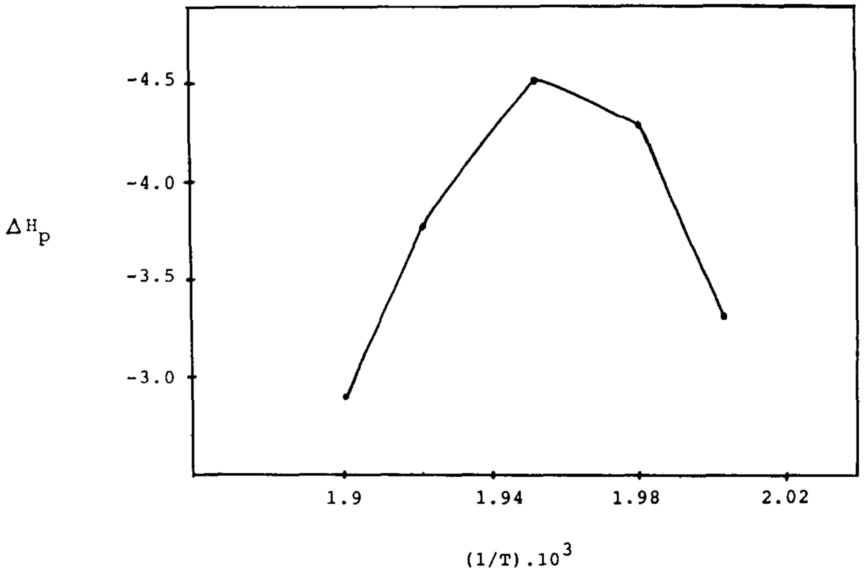

Fig. 6. Heat of polymerization vs. reciprocal temperature for mono-2-methoxyethyl itaconate.

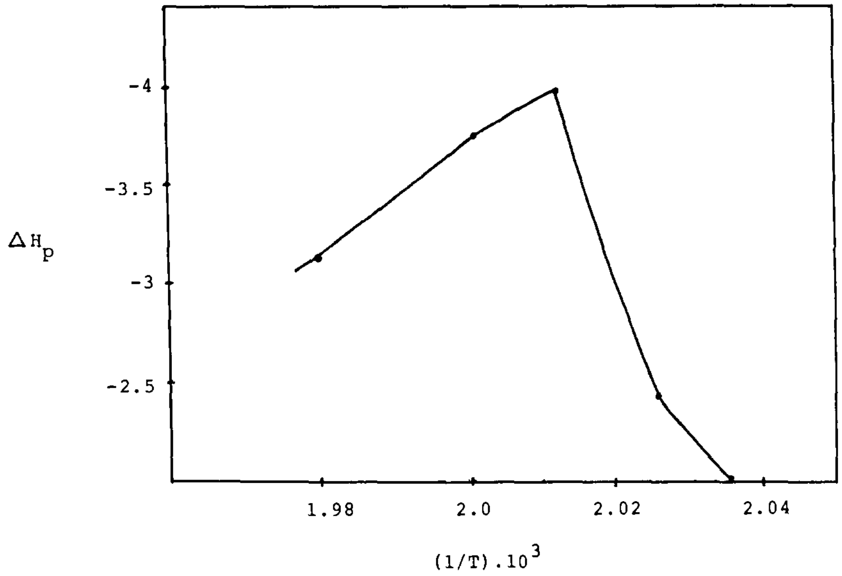

Fig. 7. Heat of polymerization vs. reciprocal temperature for mono-2-ethoxyethyl itaconate.

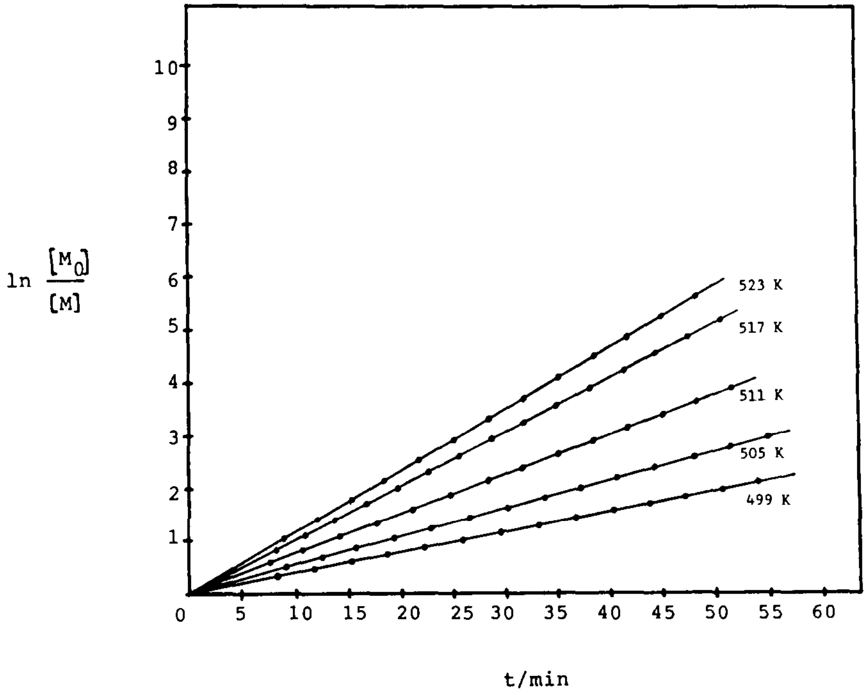

Fig. 8. Conversion vs. time curves for the bulk polymerization of mono-2-methoxyethyl itaconate at several temperatures.

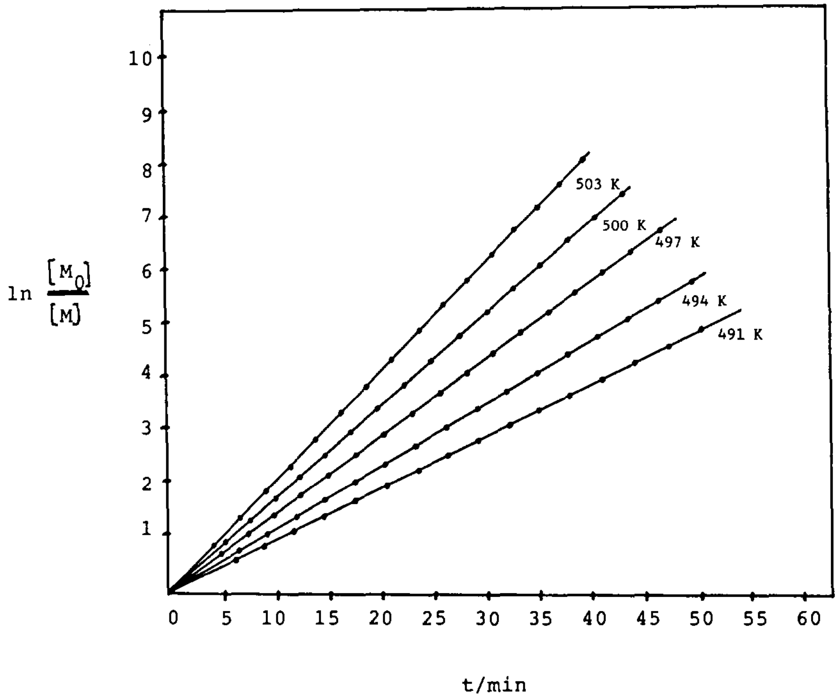

Fig. 9. Conversion vs. time curves for the bulk polymerization of mono-2-ethoxyethyl itaconate at several temperatures.

From the isothermal polymerizations we have found kinetic orders for mono-2-methoxyethyl and mono-2-ethoxyethyl itaconate of 0.9 and 1 respectively (Figs. 8 and 9). The difference observed between the theoretical and experimental orders for mono-2-methoxyethyl itaconate seems to be a result of weak diffusion of the growing radicals of the monomer molecules.

We have also calculated global activation energy by applying the Arrhenius equation

$$k = A \exp(-E_A/RT) \tag{7}$$

where A is the collision frequency factor and E_A the global activation energy of the polymerization. Figures 10 and 11 show a plot of ln k against T^{-1} for each itaconate. From these curves we can determine E_A and ln A;

TABLE 4

Logarithm of the collision frequency factor A and activation energy E_A for the mono-2-methoxyethyl (**1**) and mono-2-ethoxyethyl (**2**) itaconates

Monomer	ln A	E_A (kJ mol^{-1})
1	4.2391	42.956
2	4.5225	39.97

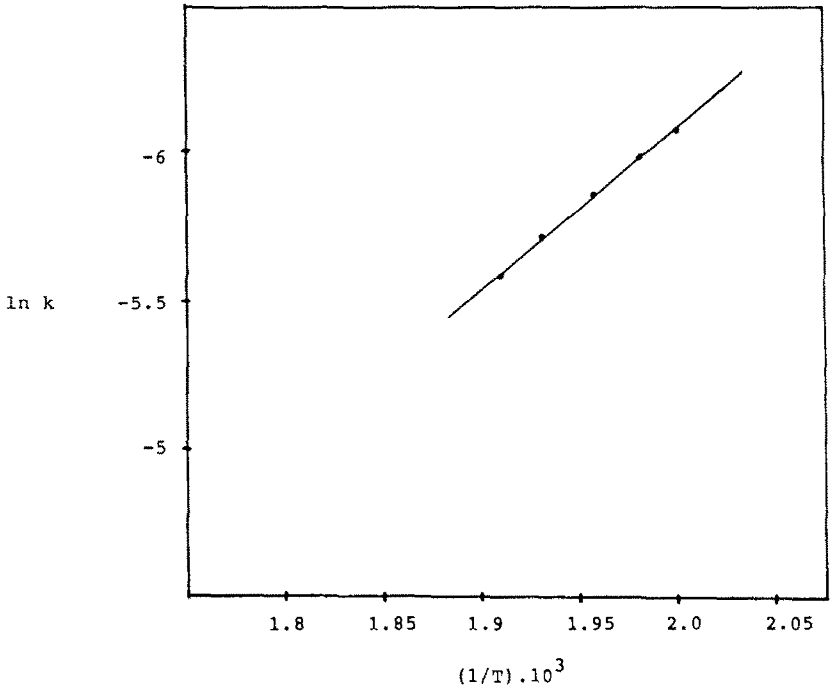

Fig. 10. Arrhenius plot in the temperature interval 499–511 K for mono-2-methoxyethyl itaconate.

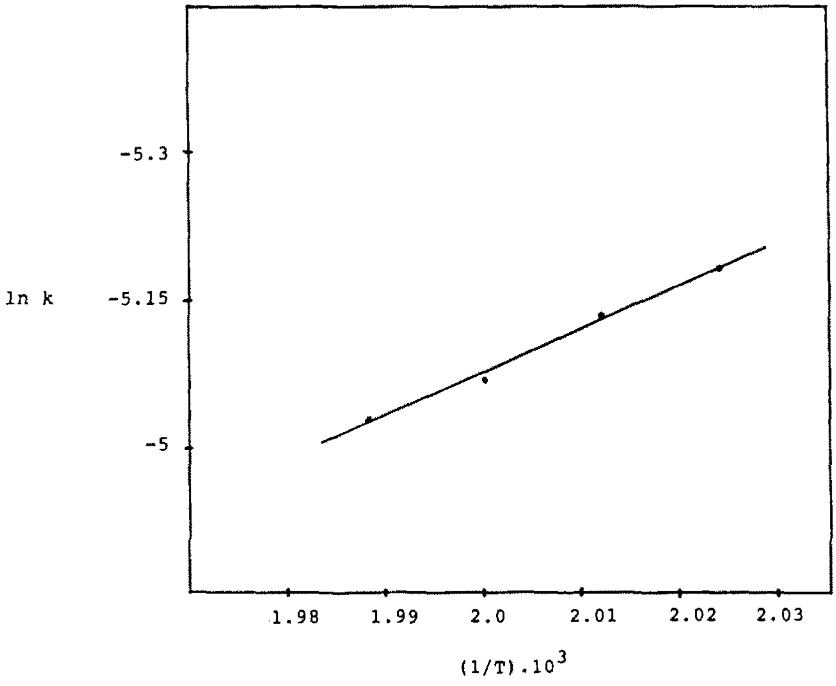

Fig. 11. Arrhenius plot in the temperature interval 491–503 K for mono-2-ethoxyethyl itaconate.

the results obtained are given in Table 4. It is interesting to observe that in order to undergo a reactive process, molecules of mono-2-methoxyethyl itaconate require more energy than do molecules of mono-2-ethoxyethyl itaconate.

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