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NON-CLASSICAL FREE-RADICAL POLYMERIZATION. PART 1. THE POLYMERIZATION OF MONO-2-PHENOXYETHYL AND MONO-2-PHENYLETHYL ITACONATES

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ABSTRACT

We have compared the free-radical self-initiated bulk polymerization, at total conversion, of mono-2-phenoxyethyl and mono-2-phenylethyl itaconates, using differential thermal analysis (DTA). By fitting theoretical equations to experimental data, we have obtained the kinetic orders for the monomers in the temperature interval 181–225°C. The kinetic orders found are not very different and, in order to explain this behaviour, we have proposed a kinetic scheme. Finally, we have calculated the global activation energy E_A and the collision frequency factor A using the Arrhenius equation.

INTRODUCTION

Thermal methods, such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are becoming increasingly popular for the determination of kinetic constants.

The usual starting point for the analysis of the experimental data is the classical equation

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

where H is the heat of reaction, ΔH_{sp} is the specific enthalpy of reaction and n is the number of moles of monomer. This equation can be expressed as

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

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Assuming that the degree of conversion of total monomer to polymer is obtained as the ratio of the partial to total thermogram area, the kinetic order is calculated by integration of the equation

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

This paper is concerned with the developments in the field of non-classical free-radical polymerization carried out in the temperature range 181–225 °C: The kinetic parameters and reaction order of polymerization of mono-2-phenoxyethyl and mono-2-phenylethyl itaconates were also calculated.

EXPERIMENTAL

To obtain the mono-2-phenoxyethyl and mono-2-phenylethyl itaconates (Figs. 1a and 1b) the following procedure was adopted. Recently distilled acetyl chloride (3 ml), used as catalyst, was added to a warmed mixture of appropriate alcohol (3 mol) and itaconic acid (1 mol). The mixture was refluxed until complete consumption of the itaconic acid (monitored by thin-layer chromatography (TLC)) was achieved (20 min). Then, the reaction mixture was cooled to room temperature and evaporated under vacuum up to three times from a benzene/petroleum ether mixture (1:1) to obtain pure monoitaconate as a crystalline solid. In Table 1 the physical data for both monomers are given.

Each monomer was characterized by IR and ^{1}H NMR. The resulting IR and NMR spectra were wholly consistent with the expected structures, and the proton NMR assignments are listed in Table 2.

Weighed amounts of the monomers (approximately 8 mg) were placed into standard aluminium crucibles. The cells were sealed and weighed using a Mettler balance with a precision of ±0.000005 g, before being placed in the DTA furnace at room temperature.

For each monomer, we carried out a dynamic polymerization in order to establish the polymerization temperature range. Then, polymerization was performed at several constant temperatures in order to calculate the kinetic

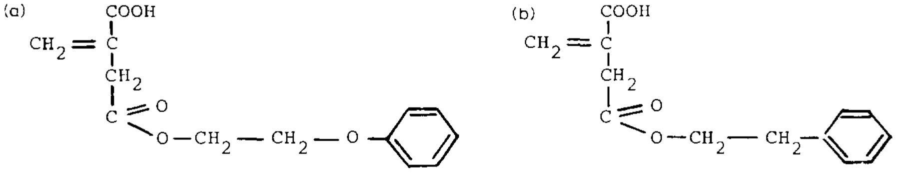

Fig. 1. Chemical structure of: (a) mono-2-phenoxyethyl and (b) mono-2-phenylethyl itaconates.

TABLE 1

Physical data for the monomers

Monomer	T_f(°C)	Yield [a] (%)	R_f [b]
1a	126.52	45	0.23
1b	82.23	40	0.30

[a] Yield of pure crystallized product. [b] R_f, coursed distance by the pattern/coursed distance by the eluent. For thin-layer chromatography, Merck Kieselgel GF254 plates (0.2 mm thick) were used. Eluent: CH_2Cl_2/CH_3OH (9.5:0.5).

order, kinetic constants and the activation energy of the polymerization process.

The data acquisition and handling was carried out using a Commodore 64/128 personal computer employing a BASIC program. The program allowed us to plot the integrated equations corresponding to the different kinetic orders of reaction so that the best fit could be selected. The program also calculated the constant kinetic rate from the slope of the straight line. The listing of the program is available upon request.

Details of experimental calorimetric procedures are given in previous papers [1–5].

The chromatographic experimental system used was standard and consisted of a Gilson pump model 303, a Rheodyne injector, two μ-Shodex columns (A80M) and a Knauer differential refractometer. The GPC measurements were made in THF, at 298 K, and the columns were calibrated with polystyrene standards.

The weight-molecular weights of poly(mono-2-phenoxyethyl) itaconate and poly(mono-2-phenylethyl) itaconate are given in polystyrene equivalent since it is not necessary, for the aims of this investigation, to know the real

TABLE 2

^1H NMR data of monomers 1a and 1b [a]

Monomer	^1H NMR chemical shifts [b,c] (δ ppm)
1a	11.25 (s,1H,-COOH), 6.88–7.36 (m, 5H, ArO–), 6.46 (s, 1H, CH_2 [d]=C), 5.84 (s, 1H, CH_2 [d]=C), 4.46 (t, 2H, $J = 6$ Hz,-CO_2CH_2–), 4.16 (t, 2H, $J = 6$ Hz, -CH_2OAr), 3.37 (s, 2H, =CCH_2
1b	11.90 (s, 1H, -COOH), 7.25 (m, 5H, ArH), 6.45 (s, 1H, CH_2 [d]=C), 5.70 (s, 1H, CH_2 [d]=C), 4.30 (t, 2H, $J = 7$ Hz,-CO_2CH_2–), 3.30 (s, 2H=CCH_2–),2.90(t, 2H, $J = 7$ Hz,–CH_2Ar)

[a] Spectra were run on Bruker WM-250 (250 MHz) instrument at room temperature, using TMS as internal standard. [b] In $CDCl_3$. [c] s, Singlet; d, doublet; m, multiplet; t, triplet. [d] Indistinguishable protons.

molecular weights of the polymers obtained at the different temperatures studied.

RESULTS AND DISCUSSION

Figures 2 and 3 show the thermal behaviour of mono-2-phenoxyethyl and mono-2-phenylethyl itaconates in the ranges 50–250 and 50–300 °C, respectively. The first endothermic peak corresponds to the melting point of the monomer and the second to the polymerization process. From the first peak we obtained the values of the fusion heat of both monomers. These values are 46.68 ± 0.05 kJ mol^{-1} and 27.30 ± 0.05 kJ mol^{-1}. The melting temperatures of 126.52 and 82.23 °C, respectively, correspond to these two peaks. The presence of the oxygen atom in the mono-2-phenoxyethyl molecule allows a better packing of the phenyl side group of the molecule than in mono-2-phenylethyl itaconate. The consequence of this is a higher stability and, therefore, an increase in the melting point with respect to the mono-2-phenylethyl itaconate. From the exothermic peak the total polymerization heats of both polymers were calculated. The values obtained were -2.34 and -11.66 kJ mol^{-1} for mono-2-phenoxyethyl and mono-2-phenylethyl itaconates, respectively.

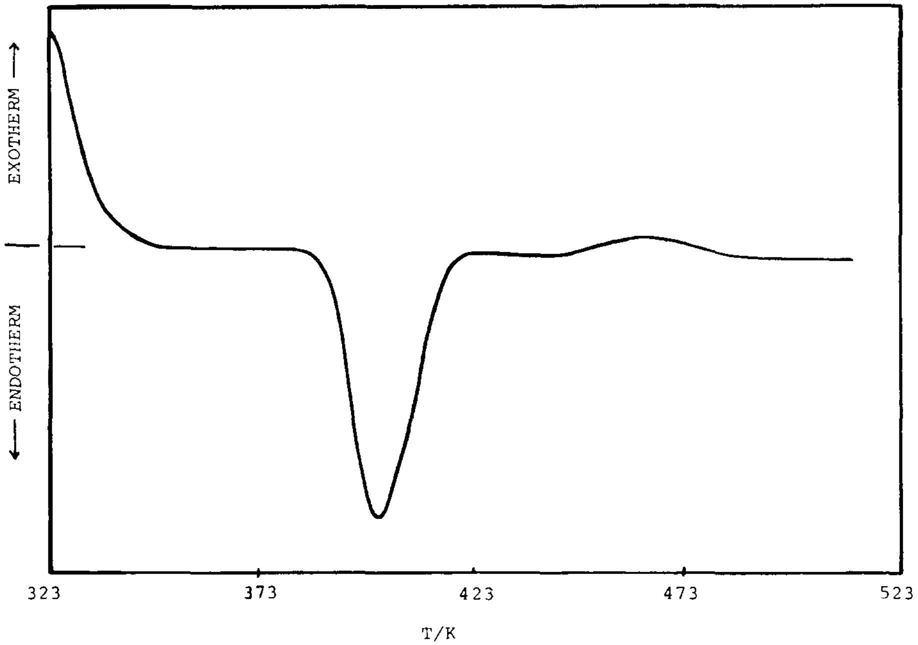

Fig. 2. Thermal behaviour of mono-2-phenoxyethyl itaconate in the temperature range 323–523 K.

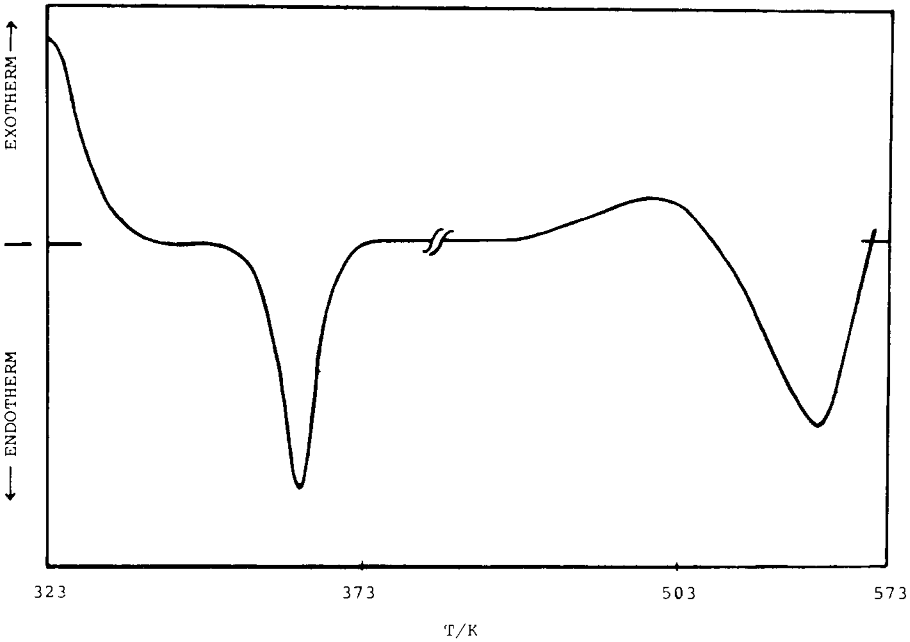

Fig. 3. Thermal behaviour of mono-2-phenylethyl itaconate in the temperature range 323–573 K.

In Figs. 4 and 5 the isothermal thermograms corresponding to the different temperatures of polymerization are shown. The areas of these curves (required for the determination of the kinetics of polymerization) were calculated using a BASIC program which can integrate the experimental peak areas with a precision higher than 1%.

In order to explain the experimental results the following kinetic scheme is suggested

$$M + M \xrightarrow{k_i} {}^{\bullet}M{-}M^{\bullet} \qquad \text{(i)} \qquad \text{Initiation}$$

$$\left.\begin{array}{ll} {}^{\bullet}M{-}M^{\bullet} + M \xrightarrow{k_p} {}^{\bullet}M{-}M{-}M^{\bullet} & \text{(ii.1)} \\ \vdots \qquad\qquad \vdots & \\ {}^{\bullet}M{-}M_n{-}M^{\bullet} \xrightarrow{k_p} {}^{\bullet}M{-}M_{n+1}{-}M^{\bullet} & (\text{ii}.n+1) \end{array}\right\} \quad \text{Propagation}$$

$$\left.\begin{array}{ll} 2\,{}^{\bullet}M{-}M_n{-}M^{\bullet} \xrightarrow{k_t} \text{polymer} & \text{(iii.1)} \\ {}^{\bullet}M{-}M_n{-}M^{\bullet} + 2M \xrightarrow{k_{tr}} \text{polymer} & \text{(iii.2)} \end{array}\right\} \quad \text{Termination}$$

where M is the monomer, ${}^{\bullet}M{-}M^{\bullet}$ the initial diradical and ${}^{\bullet}M{-}M_n{-}M^{\bullet}$ the propagation diradical. From this kinetic scheme we can obtain the rate of polymerization.

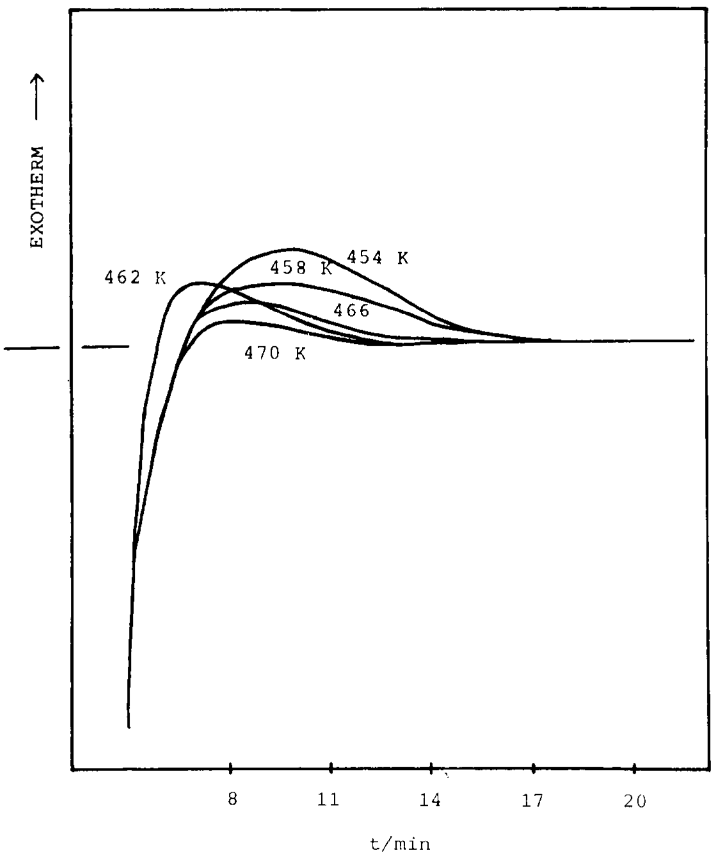

Fig. 4. Thermograms for the isothermal polymerization of mono-2-phenoxyethyl itaconate at several temperatures.

We have considered that the initiation step is probably a dimocular process, because it needs a lower activation energy than a unimolecular process. Thus, the rate of initiation of the radical chain is given by

$$v_i = 2k_i |M|^2 \tag{4}$$

where k_i is the initiation rate constant for the reaction of initiation. Thus, the rate of initiation is of second order with respect to the monomer.

The rate of the propagation step is

$$v_p = k_p |M^\cdot||M| \tag{5}$$

We have proposed two possible termination reactions. If we consider the step (iii.2), then the rate of polymerization is of first order with respect to the monomer concentration. However, if we take the step (iii.1) then we obtain a second monomer reaction order. Comparing the experimental and theoretical equations, the termination step given in ref. 6 seems probable.

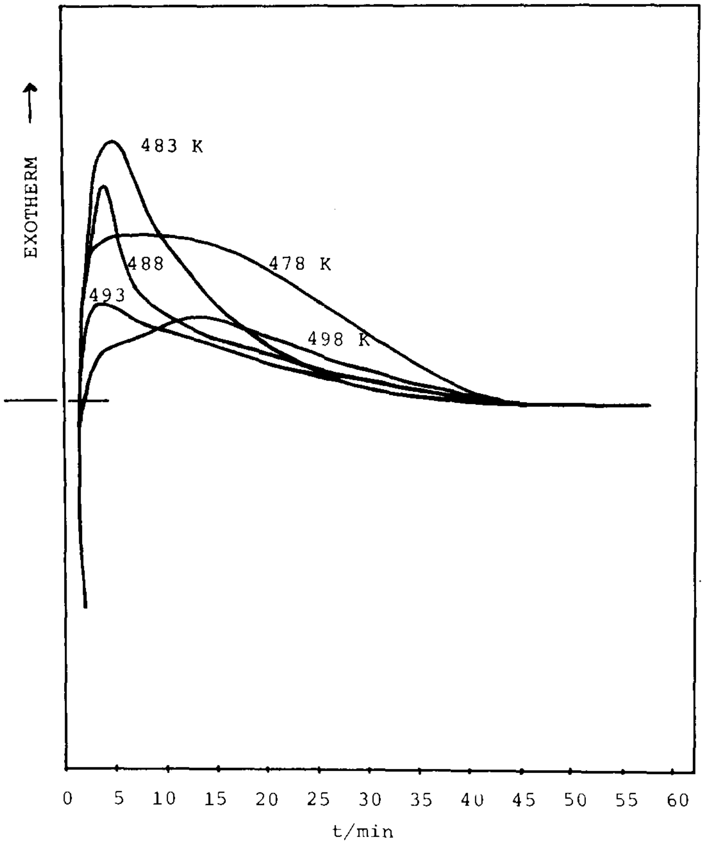

Fig. 5. Thermograms for the isothermal polymerization of mono-2-phenylethyl itaconate at several temperatures.

Consequently the polymerization rate is

$$v = (2k_p k_i / k_{tr}) |M| \tag{6}$$

The proposed mechanism leads to a first-order rate for thermal conversion of monomer.

For mono-2-phenoxyethyl and mono-2-phenylethyl itaconates we found experimental kinetic orders of 0.7 and 0.9 with respect to monomer, respectively. The observed difference between experimental orders may be a result of the diffusion processes of the monomer molecules moving towards the growing radicals. In Tables 3 and 4 the enthalpies of polymerization, and global kinetic constants as a function of temperature are given for the monomers. In Figs. 6 and 7 examples of the kinetic reaction plots are shown. As can be seen the enthalpies of polymerization of the monomers decrease as temperature increases. For mono-2-phenoxyethyl itaconate, the temperature at which the enthalpy of polymerization disappears is 477 K. For mono-2-phenylethyl itaconate this temperature is located at 519.5 K. From these two temperatures it can be seen that is not possible to polymerize the

TABLE 3

Enthalpy of polymerization ΔH_p and global kinetic constant k at various temperatures corresponding to the monomer order of 0.7 found for the mono-2-phenoxyethyl itaconate

T (K)	$-\Delta H_p$ (kJ mol^{-1})	$k \times 10^{-3}$
454	1.63	6.49
458	1.58	8.02
462	0.807	9.72
466	0.50	13.50
470	0.20	18.75

TABLE 4

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

T (K)	$-\Delta H_p$ (kJ mol^{-1})	$k \times 10^{-3}$
478	40.62	0.907
483	32.52	1.068
488	29.25	1.194
493	16.87	1.262
498	10.76	1.372

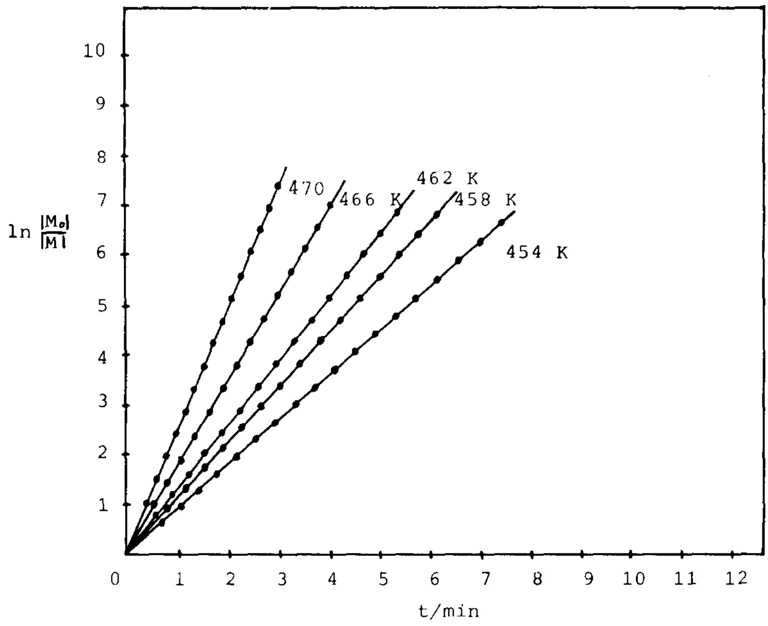

Fig. 6. Kinetic order for mono-2-phenoxyethyl itaconate.

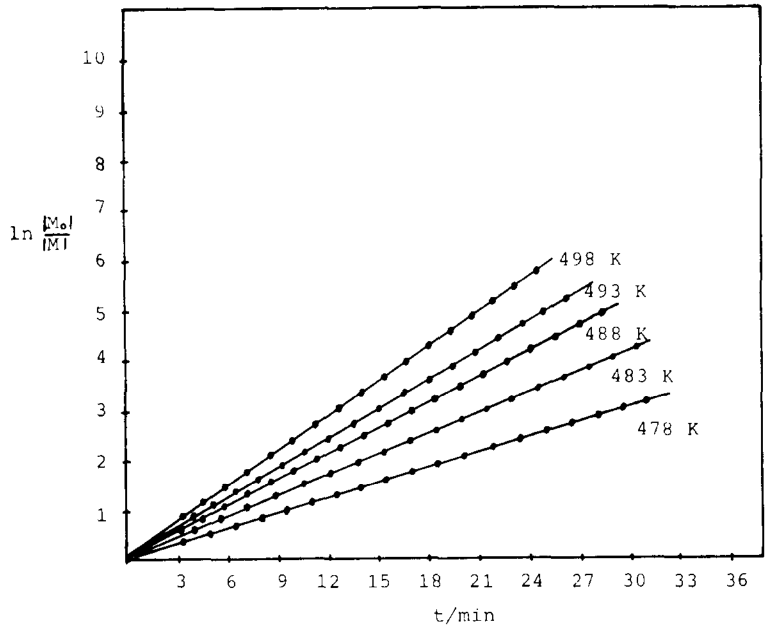

Fig. 7. Kinetic order for mono-2-phenylethyl itaconate.

two monomers.

If we compare the theoretical and experimental monomer orders we can see that there is a slight difference between them. This behaviour can only be explained by taking into account the existence of diffusion processes [7–11] and/or other termination processes in the system. In both cases it seems that the ifluence of these phenomena is not very important. Unfortunately, it is not possible to determine experimentally the existence and extent of these phenomena.

In our case the kinetic chain length is given by

$$\tau = \frac{k_p}{k_{tr}|M|} \tag{7}$$

i.e. the kinetic chain length is inversely proportional to the monomer concentration.

From eqn. (7) we can obtain

$$\frac{d \ln \bar{x}_n}{dT} = \frac{E_p - E_{tr}}{RT^2} \tag{8}$$

As d ln $\bar{x}_n/dT$ is positive we can expect to obtain higher molecular weight as the temperature of polymerization increases. GPC measurements confirm this assumption as can be seen in Table 5. However, the GPC measurements reveal that the propagation kinetics of the polymerization of mono-2-pheno-

TABLE 5

Weight-molecular weight and polydispersities of poly(mono-2-phenoxyethyl) itaconate (PMPHEI) and poly(mono-2-phenylethyl) itaconate (PMPEI) obtained from GPC at different temperatures

PMPHEI			PMPEI		
T (K)	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	T (K)	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
189	966	1.11	185	1323	1.23
193	1014	1.14	195	1471	1.22
197	1048	1.14	215	1568	1.21
201	1218	1.20	225	1580	1.22

xyethyl and mono-2-phenylethyl itaconates at very high monomer conversions is greatly affected by the diffusion process of the monomers to the active centres, that are probably completely immobilized in the polymer matrix of the reaction system. Weight-molecular weights and polydispersities of both polymers obtained at various temperatures are shown in Table 5. In this table we can see that, in general, the polymerization process leads to oligomeric species with narrow polydispersities.

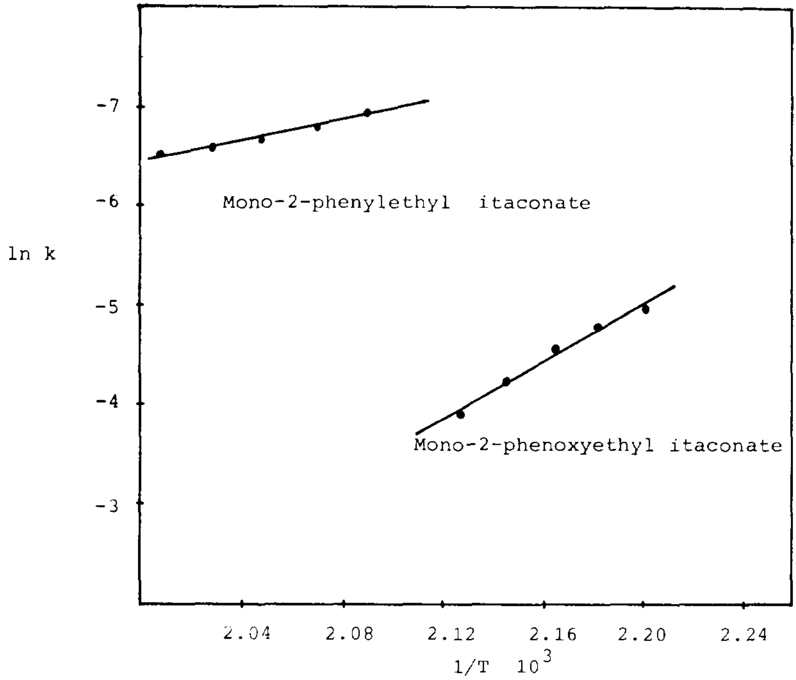

Fig. 8. Arrhenius plot in the temperature intervals 454–470 K and 478–498 K for mono-2-phenoxyethyl and mono-2-phenylethyl itaconates, respectively.

TABLE 6

Logarithm of the collision frequency factor A and activation energy E_A for the mono-2-phenoxyethyl and mono-2-phenylethyl itaconates

Monomer	ln A	E_A (kJ mol^{-1})
1a	25.95	118.00
1b	2.95	39.66

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

$$k = A \exp(-E_A/RT) \tag{9}$$

where A is the collision frequency factor and E_A the global activation energy of polymerization. A plot of ln k against $1/T$ (Fig. 8) allows the determination of both E_A and A from the slope and intercept, respectively. Values of E_A and ln A for both monomers are shown in Table 6. It is interesting to note that the variations in the values of E_A and ln A are much greater in mono-2-phenoxyethyl itaconate than in mono-2-phenylethyl itaconate.

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