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KINETICS OF MONO ALKYL ITACONATES BULK POLYMERIZATION BY DTA

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ABSTRACT

The kinetics of mono alkyl itaconates (methyl, ethyl and propyl) bulk self-initiated polymerization were determined by DTA in the temperature range 428–458 K and in the presence of 1,2-azobisisobutyronitrile in the temperature range 363–403 K. The polymerization reaction orders, and the activation energies E_a were found to depend on the itaconate nature as well as the enthalpies involved in these processes.

INTRODUCTION

At present many of the monomers which are used in industry come from oil, but alternative sources are being investigated. Itaconic acid is structurally similar to the acrylic and methacrylic acids, and shows obvious potential for obtaining materials with properties comparable with theirs.

Itaconic acid was first isolated in 1837 from the citric acid pyrolysis process. However, it has not been possible to synthesize it in considerable amounts using this process. Nowadays, it is obtained industrially by molasses fermentation processes using *Aspergillus itaconicus* and *Aspergillus terreus* fungi.

In recent years, differential thermal analysis (DTA) and differential scanning calorimetry (DSC), both equivalent techniques, have become increasingly important in the study of macromolecular chemistry. These techniques have very important advantages which make them especially useful for the study of the kinetics of polymerization, because its exothermic character can be easily followed by DTA or DSC, isothermally as well as dynamically.

Early studies of this kind were carried out in liquid and solid monomers, in bulk polymerizations for several vinyl monomers [1–7].

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In the present work we report a study of several mono alkyl itaconates, specifically the methyl, ethyl and propyl itaconic acid mono esters polymerization kinetics above their melting points using 1,2-azobisisobutyronitrile (AIBN) as initiator and without it, by DTA and DSC in the whole polymerization temperature range.

EXPERIMENTAL

Mono esters of itaconic acid were synthesized, according to Cowie and Hag [8], from itaconic acid and the respective alcohols using the molar ratio 1 : 3 (itaconic acid/alcohol) with acetyl chloride as catalyst.

Monomers (Fig. 1) were purified by successive crystallizations using a benzene/petroleum ether mixture (50 : 50 v/v). Their purity was checked by paper chromatography and verified by IR and NMR spectroscopy. The melting points of the purified monomers were 342, 329 and 309 K for the mono methyl (Fig. 1a), mono ethyl (Fig. 1b) and mono propyl (Fig. 1c) itaconates, respectively.

The calorimetric measurements (dynamic as well as isothermal) were carried out using a Mettler TA 2000 differential thermal analyser instrument, equipped with a scanning auto-zero device for obtaining a straight baseline. The data were calibrated in absolute units by comparison with the specific heat of a sample of indium (28.0 J g^{-1}). Temperature calibration was performed with the International Confederation for Thermal Analysis certified reference material indium ($T_M = 429.7$ K).

The absolute sample temperature was calculated using the following expression

$$T_{s1} = T_{p1} - \tau(\mathrm{d}T_p/\mathrm{d}T) + \Delta U_1/S$$

where T_{s1} is the sample temperature at point T_1, T_{p1} is the program temperature at point T_1(°C), τ is an intrinsic DTA constant (0.411), $\mathrm{d}T_p/\mathrm{d}T$ is the heating rate, ΔU_1 is the signal at point T_1 (μV) and S is the sensitivity of the thermocouple.

Before carrying out the isothermal polymerizations a dynamic calorimetric determination of the sample was made in order to determine the

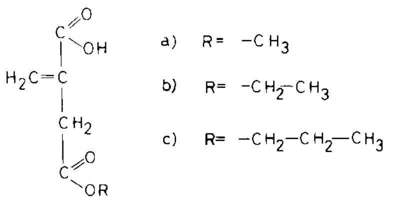


Fig. 1. Chemical structures of mono alkyl itaconates.

temperature range in which the mono esters of itaconic acid monomers undergo polymerization.

The isothermal polymerizations were carried out by placing into an aluminium standard crucible a weighed amount of AIBN (0.03–0.05 mg) mixed with purified monomer (3–8 mg). For determinations without initiator, samples were prepared by placing 4–6 mg of the monomer into the cells, which were sealed and weighed using a Mettler balance model H51AR with a precision of 5×10^{-5} g before being placed in the DTA furnace.

The kinetics of polymerization were studied in the temperature ranges 363–403 and 428–458 K, in the presence of AIBN and without it, respectively.

Isothermal polymerizations were carried out by placing the aluminium crucibles containing the samples into the preheated furnace. For all measurements an empty reference crucible was used. DTA measurements were run at least in triplicate. Before doing the different isothermal polymerizations, the temperature range in which the mono alkyl itaconates (methyl, ethyl and propyl) undergo polymerization and their temperatures of fusion were determined by making a dynamic calorimetric determination of the samples. The temperatures of fusion obtained are 344.8, 330 and 310.5 K for mono methyl, ethyl and propyl itaconates, respectively.

We have also used a Perkin–Elmer Series 7 DSC to verify several polymerization data obtained using the Mettler TA 2000 system. These instruments gave comparable results.

In order to obtain the monomer reaction rate, we supposed that the reaction heat H is proportional to the number of monomer moles n converted to polymer at any moment, i.e.

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

where ΔH_{sp} is the specific reaction enthalpy. 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. Therefore, the reaction rate is directly proportional to the enthalpy change with time, i.e., to the signal obtained on the thermogram.

The determination of the conversion degree and the kinetics order has been carried out using a BASIC program written for a Commodore Amiga-2000 personal computer. The program calculates the partial and total areas of the different thermograms by means of the trapezoidal method. The program is available from the authors.

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

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

where x is the kinetic reaction order and M is the monomer concentration.

The BASIC program allows us to plot the integrated equation corresponding to the different kinetic orders of reaction in order to choose the best one.

The program also calculates the intercept and the slope of the straight line, and the correlation coefficient obtained from the experimental data fitting. The rate constant is calculated from the slope.

RESULTS AND DISCUSSION

Figure 2 shows the thermal behaviour of the three mono alkyl itaconates (A, methyl; B, ethyl; and C, propyl) in the temperature range 343–423 K using AIBN and Fig. 3 shows the same behaviour in the temperature range 403–493 K without initiator. As can be seen the exothermal peaks begin at different temperatures, corresponding to the temperature range where the monomers undergo polymerization. It can be observed that thermal, self-ini-

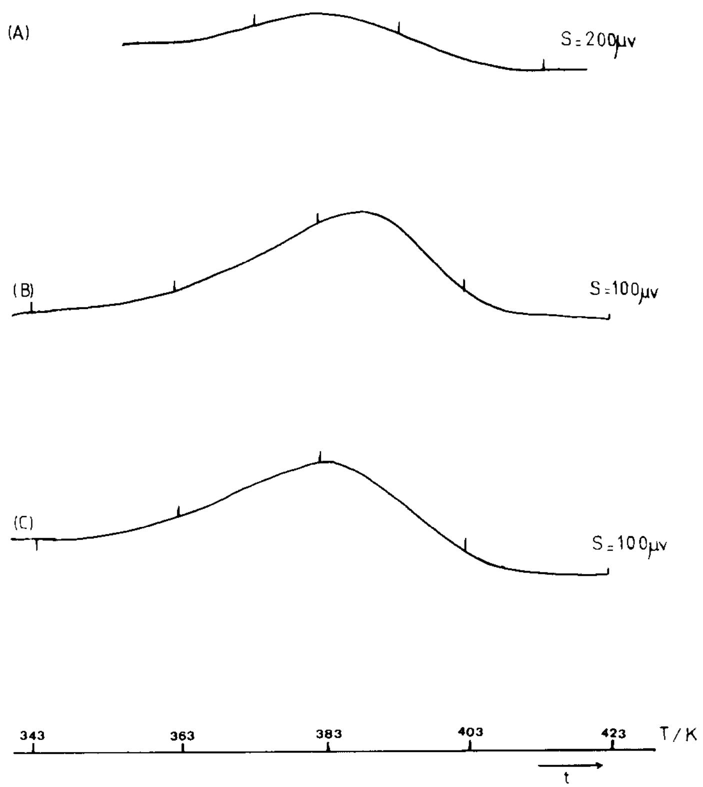


Fig. 2. Thermal behaviour of the different mono alkyl itaconates (A, methyl; B, ethyl; and C, propyl) in the temperature range 343–423 K, using AIBN as initiator.

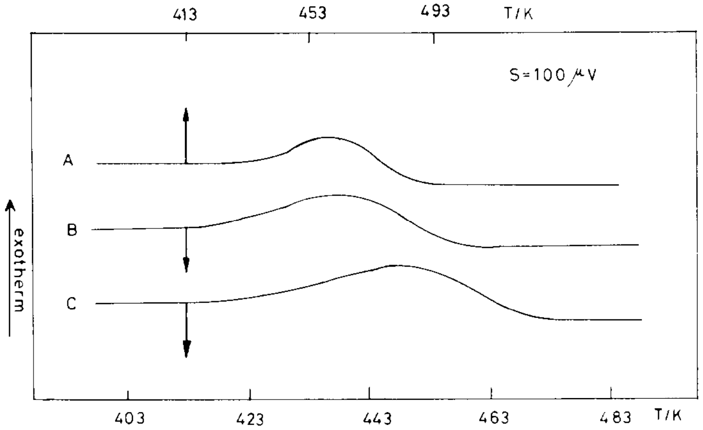


Fig. 3. Thermal behaviour of the different mono alkyl itaconates (A, methyl; B, ethyl; and C, propyl) in the temperature range 403–493 K, without initiator.

tiated polymerization shows higher polymerization temperatures than the ones initiated by AIBN. Figure 4 shows three endothermal peaks which correspond to the fusion processes of these monomers. The values obtained are concordant with the ones given in the literature [8] with a difference smaller than 0.8% between them, which means that differential thermal analysis is a suitable technique which offers great accuracy for determination of this kind of parameter.

We have also determined the enthalpy of polymerization, ΔH_p, of both systems in the whole range of temperature studied at constant temperature. This behaviour is shown in Fig. 5. As can be seen the thermal variation of enthalpy of polymerization is very similar with and without initiator. However, it is necessary to point out that the values obtained are very low if we compare them with other vinyl monomers. In order to verify these results we have also determined the polymerization kinetics of these monomers in the temperature range 433–448 K using a Perkin–Elmer DSC-7 calorimeter. A sample of these results is shown in Fig. 6. The differences between the results obtained for the two systems are less than 1.5%. The use of this kind of monomer whose polymerization enthalpies are so low is very interesting, because in this way the problem of dissipating great quantities of heat from the system during polymerization is avoided, which is one of the greatest and most common problems for the polymeric materials synthesis industries. This fact also contributes to the "Gel Effect", also named the "Trommsdorff Effect" [9] elimination, which produces a self-acceleration in the polymerization process with consequent variation of the molecular weight and molecular weight distribution of the resulting polymer. The control of these parameters would obviously be easier in the poly alkyl itaconates.

In general, methacrylic or acrylic monomers [10–12] show higher values than mono alkyl itaconates. This behaviour has been attributed to two

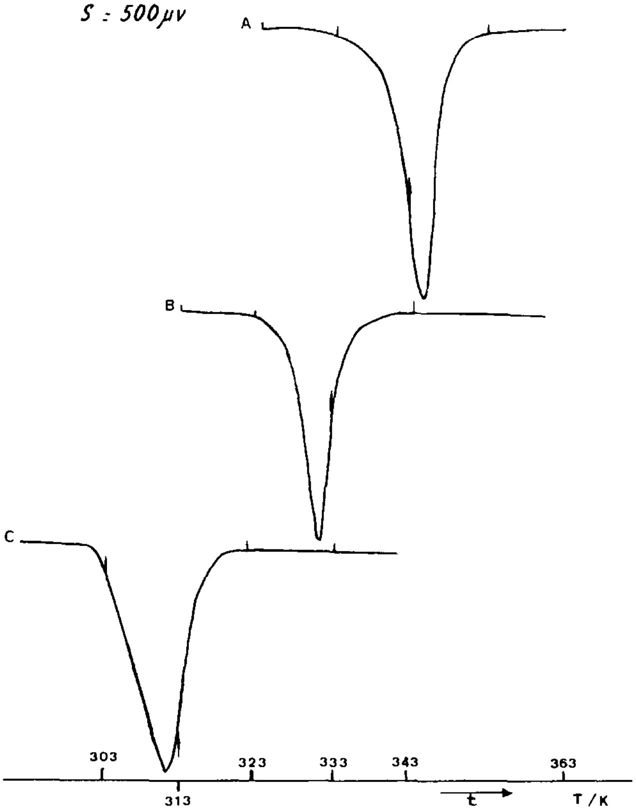


Fig. 4. Thermal behaviour of the different mono alkyl itaconates (A, methyl; B, ethyl; and C, propyl) in the temperature range 303–363 K, using AIBN as initiator.

different factors. The first is the loss of conjugation energy in going from monomer to polymer, and the second the energy loss associated with the appearance of stresses on formation of the polymeric chain from substituted mono alkyl itaconates owing to interactions between side groups. Then $-\Delta H = 22.5 - Q_{\text{conj}} - Q_{\text{ster}}$, where 22.5 is the difference of energy between a double C=C bond (145.5 kcal mol^{-1}) and the formation energy of two simple C–C bonds (84×2 kcal mol^{-1}). In our case the energy loss due to steric effects is high. Because of this the polymerization becomes thermodynamically difficult, it being necessary to employ high polymerization temperatures (as can be seen in Figs. 2 and 3). On the other hand, the value of Q_{conj} is affected by the presence of initiator in the system. Figures 2 and 3 show this effect in the Q_{conj} term. As can be seen the polymerization temperatures are lower in the system initiated with AIBN than those in the self-initiated one. In the mono alkyl itaconates the π-electrons of the double bond are in conjugation with the π-electrons of the carboxylic groups ($>$C=O). This fact also contributes to decreasing the heat of polymerization, making the polymerization process difficult.

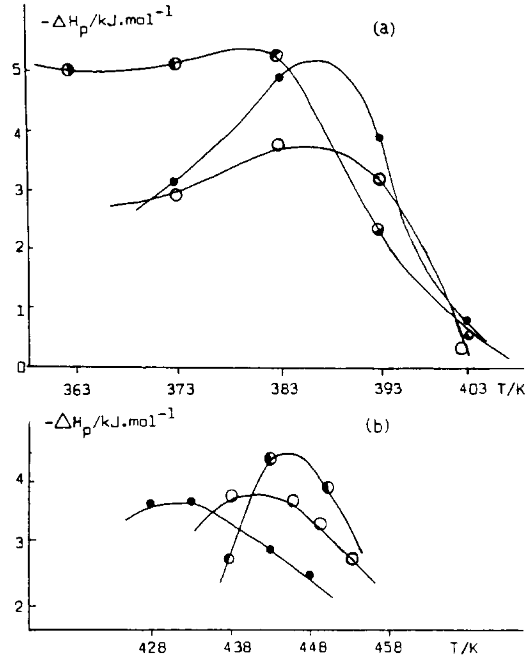


Fig. 5. Polymerization enthalpies of different mono alkyl itaconates (○, methyl; ●, ethyl; and ◐, propyl): (a) using AIBN, and (b) without initiator.

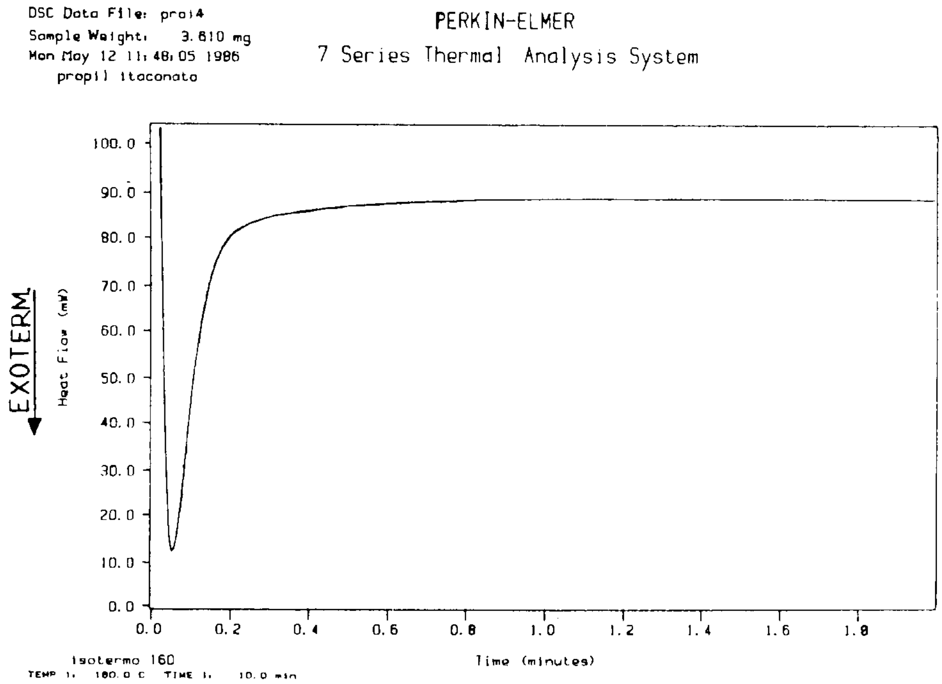


Fig. 6. Thermogram of mono propyl itaconate using a Perkin–Elmer DSC-7 calorimeter.

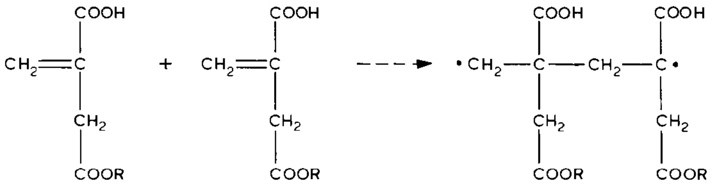
Consider the expression

$$\Delta G = \Delta H_p - T\Delta S$$

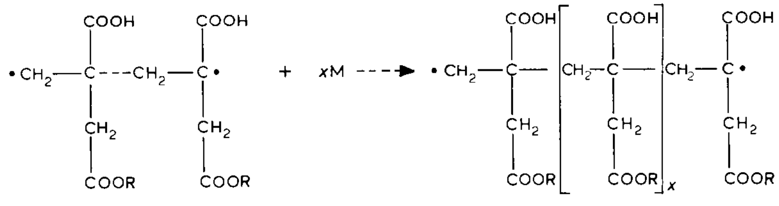
where ΔG is the Gibbs free energy. Whenever $\Delta G < 0$ it is possible to polymerize any monomer. In our case, as the ΔH_p are very low the polymerization process in this type of monomer is governed by the entropic term. This means that it is possible to find a temperature at which $\Delta H_p = T\Delta S$. For these three processes the ceiling temperatures found are 408, 403 and 413 K for the mono methyl, ethyl and propyl itaconates, respectively when initiator is employed. However, when the polymerization is thermally self-initiated the values found are 483, 463 and 473 K for the mono methyl, ethyl and propyl itaconates, respectively.

These divergencies between the ceiling temperatures must have their origin in the propagation steps, because this is the step which controls the ceiling temperature. If the following mechanisms are assumed for these monomers

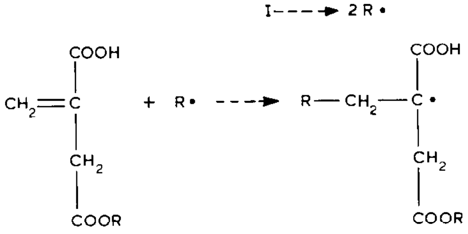
Thermal initiation



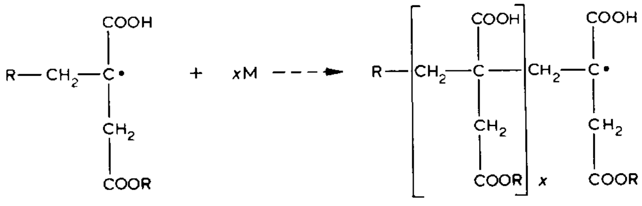
Propagation



Radical initiation



Propagation



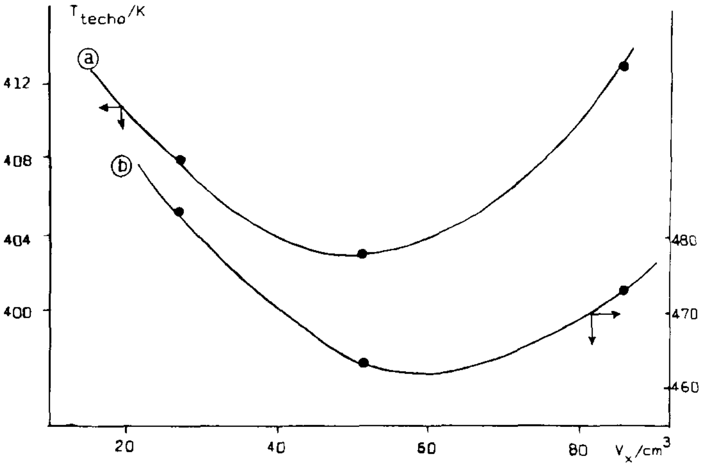


Fig. 7. Dependence of ceiling temperature on monomer side group V_x: (a) without initiator, and (b) using AIBN.

we can observe that according to the type of initiation, two different propagating species are formed; this fact necessarily influences the ceiling temperature. Besides, the nature of the side group also affects the ceiling temperature values as can be seen in Fig. 7, where the representation of the ceiling temperature vs. the side group molar volume is shown.

As can be seen in Fig. 5, there is in the ΔH dependence on temperature a maximum that depends on the monomer molecular structure. As the monomer becomes bulkier the value of ΔS increases as a consequence of a greater difficulty in ordering the molecules of the system. This leads to polymerization of the mono alkyl itaconates at higher temperatures as the monomer side group molar volume decreases. From this figure it is possible to find the ceiling temperature by extrapolating the ΔH values to zero. The ceiling temperature is that at which the propagation and depropagation rates are equal.

In Tables 1 and 2 the variation of the overall rate constants with temperature for the three mono alkyl itaconates studied, polymerized with and without initiator, as well as the respective polymerization kinetics reaction orders are shown.

As can be seen in these tables both for the kinetics carried out with initiator and for the ones made without it, the overall rate constants increase with temperature. This must affect the molecular weight variation with temperature, because when initiation is produced by thermal decomposition of AIBN we have

$$\frac{\mathrm{d}\ln X}{\mathrm{d}T}=\frac{(E_{\mathrm{p}}-E_{\mathrm{t}}/2)-E_{\mathrm{i}}/2}{RT^2}<0$$

TABLE 1

Overall rate constants and reaction order for the mono methyl, ethyl and propyl itaconates in the temperature range 363–403 K using AIBN as initiator

Monomer	T (K)	k_{ov}	Order
Mono methyl itaconate	373	0.2109	3/4
	383	0.3187	3/4
	393	0.694	3/4
	403	1.235	3/4
Mono ethyl itaconate	373	0.2348	3/4
	383	0.3180	3/4
	393	0.6057	3/4
	403	1.397	3/4
Mono propyl itaconate	363	0.1214	3/4
	373	0.2121	3/4
	383	0.3762	3/4
	393	0.6576	3/4
	403	1.4880	3/4

whereas, for purely thermal initiation we have

$$\frac{\mathrm{d}\ln X}{\mathrm{d}T}=\frac{E_p-E_t/2}{RT^2}>0$$

where X is the polymer polymerization degree and E_i, E_p and E_t are the activation energies of initiation, propagation and termination processes, respectively.

In theory, for thermally self-initiated polymerizations the reaction order with respect to monomer should be 2. However, as can be seen in Table 2, the experimental order obtained is smaller (1 and 4/5). These differences may be caused by the difficulty of monomers in diffusing towards the active

TABLE 2

Overall rate constants and reaction order for the mono methyl, ethyl and propyl itaconates in the temperature range 428–453 K without initiator

Monomer	T (K)	k_{ov}	Order
Mono methyl itaconate	446	0.5262	1
	450	0.6360	1
	453	0.7497	1
Mono ethyl itaconate	428	0.3480	4/5
	433	0.3963	4/5
	438	0.5089	4/5
	448	0.6965	4/5
Mono propyl itaconate	441	0.3786	4/5
	443	0.4009	4/5
	451	0.6674	4/5

centres (due to the great viscosity of the environment) and/or the appearance of other termination processes. Since the termination reaction involves two chain radicals, it might be expected that these radicals have to diffuse together before they can react. When this transport-diffusive process is the rate-determining step, it is then customary to refer to the termination reaction as being diffusion-controlled. Furthermore, it is generally assumed that the termination step involves a three-stage process, that is, two chain radicals diffuse together so that certain segments are in contact (translational diffusion). Once the proximate pair has been formed, rearrangement of the radical chains may occur (intermolecular segmental diffusion) so that the reactive radical ends are close enough and are properly oriented for chemical reaction to take place. This concept of diffusion-controlled termination steps is largely due to North and co-workers [13–16].

Translational diffusion

Intermolecular segmental diffusion

Relying on this mechanism we have supposed for our case that termination is basically produced by intramolecular segmental diffusion of monomer units which form the macrodiradical, destroying themselves afterwards.

Intramolecular diffusion

The reaction order decrease might be partly explained by supposing the existence of an intramolecular segmental diffusion contribution in our systems. This hypothesis is supported, in part, by the fact that when temperature increases, the reaction order decreases, because the rotational degrees of freedom of the macromolecular coil are favoured, in this way increasing the probability of production of intramolecular segmental diffusion processes.

A similar phenomenon is also possible in polymerization initiated by the initiator, even though in this case the order decrease with respect to the theoretical one is much smaller than in the previous case, which may mean a smaller contribution of these termination processes with respect to the theoretically foreseen ones.

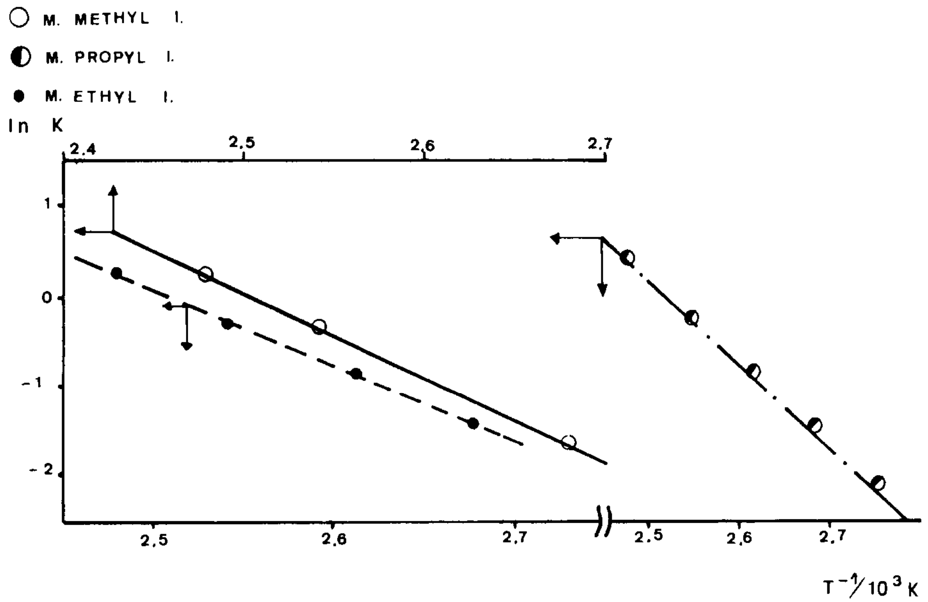


Fig. 8. Arrhenius plot for the three mono alkyl itaconates using AIBN.

On the other hand, as the overall kinetic rate constants depend greatly on temperature, using the Arrhenius equation

$$k_{ov} = A \exp(-E_a/RT)$$

where A is a constant called the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature. By plotting ln k_{ov} against $1/T$ in the customary fashion, E_a and A may be determined from the slope and the intercept of the straight line obtained. In Figs. 8 and 9 we can see the Arrhenius plot for our systems, in the presence and absence of initiator, respectively. The calculated E_a values are very different in the two systems. For the polymerizations initiated with AIBN we obtained approximately the same E_a values (73.0, 73.9 and 74.8 kJ mol^{-1}) for the three mono alkyl itaconates. However, for the polymerizations without initiator the E_a values are very different for the three monomers: 83.8, 88.5 and 97.6 kJ mol^{-1} (see Table 3). In general, the polymerizations carried out with initiator show lower E_a values than those without, and are similar to those obtained in other vinyl monomers, such as 1-vinyl imidazole [7], vinyl acetate [17], etc. The differences found between the systems with and without initiator can be explained by taking into account that the possibility of getting free radicals in the system by decomposition of the initiator is greater than that of collision between monomer molecules.

We have also studied the influence of the monomer side group: as can be seen in Fig. 10, when the molar volume of the monomer side group increases

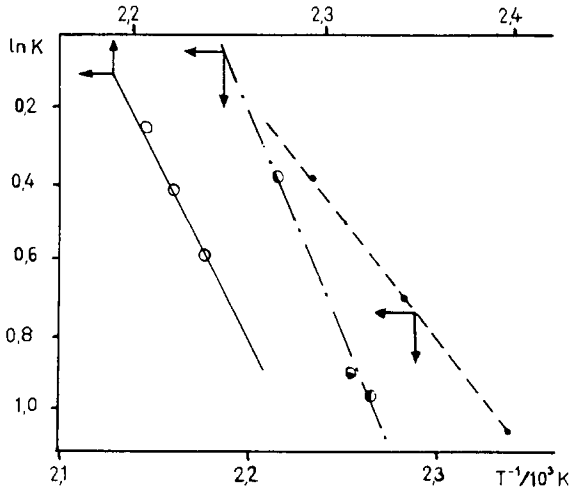


Fig. 9. Arrhenius plot for the three mono alkyl itaconates without initiator.

TABLE 3

Activation energies E_a of the different mono alkyl itaconates obtained with and without initiator and differences between the activation energies of the two processes ΔE_a

Monomer	E_a (kJ mol^{-1})		ΔE_a (kJ mol^{-1})
	With AIBN	Without AIBN	
Mono methyl itaconate	73.0	83.8	10.8
Mono ethyl itaconate	73.9	88.5	14.6
Mono propyl itaconate	74.8	97.6	22.8

AIBN, 1,2-azobisisobutyronitrile.

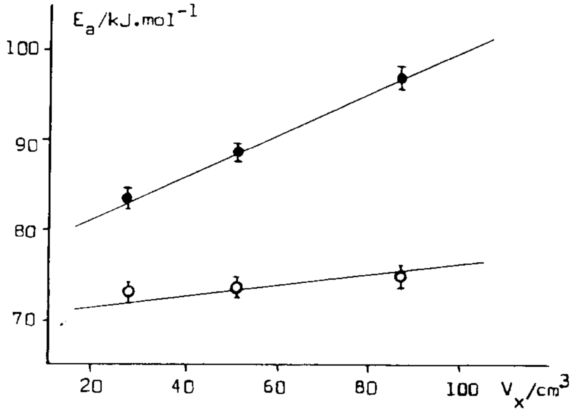


Fig. 10. Plot of activation energy, E_a, against monomer side group molar volume using AIBN (○) and without initiator (●).

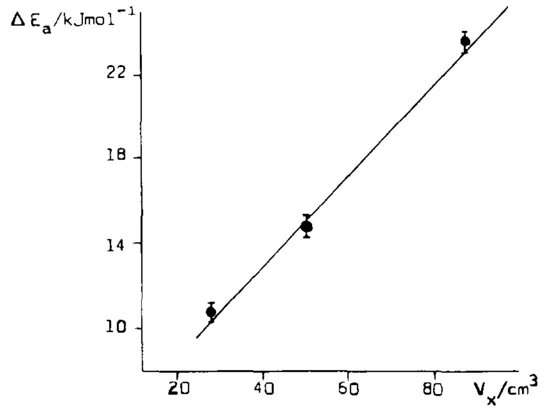


Fig. 11. Plot of $\Delta E_a = E - E_{AIBN}$ against monomer side group molar volume.

the activation energy of the process rises too. We can also see in Fig. 10 that this dependence is greater when initiator is not used. From the slopes of the two straight lines obtained, it is possible to calculate $\partial E_a/\partial V_x$ whose values are: 0.225 and 0.056 kJ cm^{-3}. This means that the dependence of E_a on the molar volume of the side group is four times greater when not using initiator. For both cases, we can see that $\partial E_a/\partial V_x$ is positive, which means that the monomer side group has a great influence in polymerization kinetics.

In Fig. 11 we show the differences between the activation energies of both processes (with and without initiator) as a function of the side group molar volume for our systems. The relation between these two quantities is also linear.

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