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Kinetics of bulk polymerization of itaconic acid derivatives Part 1. Monophenyl, monobenzyl and mono-2-phenylethyl itaconates

Issa Katime, Ana Madoz and J.L. Velada

Grupo de Nuevos Materiales, Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco, Campus de Lejona, Apartado 644, Bilbao (Spain)

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Abstract

The bulk polymerization of monophenyl, monobenzyl and mono-2-phenylethyl itaconates using α,α'-azobis(isobutyronitrile) (AIBN) as initiator at several temperatures has been studied by DTA. The order with respect to the monomer and the apparent activation energy of the polymerization process were determined. We found that the obtained values of the order with respect to the monomer are influenced by the diffusion process.

INTRODUCTION

Whenever a monomer reacts chemically, heat is liberated. Modern differential thermal calorimeters are designed to determine the difference between the enthalpy changes which occur in a sample and that in some inert reference material, when they are both heated. Differential thermal analysis (DTA) provides the opportunity for measuring not only the enthalpy change but also the rate of the reaction. This can lead, in principle, to information about the kinetic parameters and mechanisms of the polymerization process. To obtain a measure of reaction rate, the calorimeter may be used in either the isothermal or the temperature-scanning mode. In this paper we used the isothermal mode [1].

Itaconic acid and its derivatives are a very interesting family of monomers derived from non-oil origins. In recent times, this family of monomers has become increasingly important because its chemical structure is very similar to acrylic and methacrylic acids.

Itaconic acid esterification was described for the first time in 1873 [2]. However, ester polymerization was not reported until 1967 [3].

The monoitaconates synthesized and studied in this paper are crystalline solids at room temperature and because polymerization occurs in the melt state, it is of great importance to know the variables of the melting process of the monomers.

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EXPERIMENTAL

Synthesis of monoitaconate esters

To obtain the monophenyl, monobenzyl and mono-2-phenylethyl itaconate (Fig. 1) the following procedure was adopted. Freshly distilled acetyl chloride (5 ml), used as catalyst, was added dropwise to a warmed mixture of appropriate alcohol (3 mol) and itaconic acid (1 mol). The reaction mixture was refluxed until complete consumption of the itaconic acid was achieved. The process was monitored by thin-layer chromatography (TLC) carried out on 0.2 mm silica gel 60 GF-254 Merck plates using UV light as the developing agent. Then the reaction mixture was cooled at room temperature and evaporated under vacuum to remove the excess of the used alcohol. After this, dichloromethane was added and the mixture washed with aqueous NaOH (0.5 M). The aqueous phase was separated, treated with HCl (0.5 M) and extracted with dichloromethane.

The solvent was evaporated from the washed and dried extracts to obtain the corresponding monoitaconate, which was column chromatographed on silica gel 60 Merck (granulometry 0.063–0.200 nm, 70–230 Mesh ASTM) by eluting with dichloromethane (gradually polarized with methanol to obtain the elution mixture dichloromethane/methanol, 9.8/0.2) to afford the monoester in sufficient purity for crystallization. The different monoitaconates were crystallized from a toluene/*n*-hexane mixture. Physical data are given in Table 1.

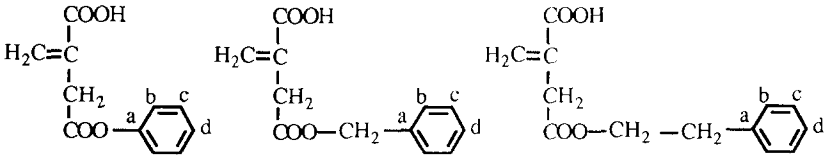

Fig. 1. Chemical structure of monophenyl, monobenzyl and mono-2-phenylethyl itaconate.

TABLE 1

Physical data for monophenyl, monobenzyl and mono-2-phenylethyl itaconates

Monomer	T_m (K)	R_f [a]	Yield (%)
Monophenyl itaconate	367.4	0.38	58
Monobenzyl itaconate	352.5	0.54	71
Mono-2-phenylethyl itaconate	355.3	0.41	63

[a] CH_2Cl_2/MeOH, 9.8/0.2.

TABLE 2

^{1}H NMR data ($CDCl_3$/TMS) for monophenyl, monobenzyl and mono-2-phenylethyl itaconate [a]

Monomer	∂ (ppm)
Monophenyl itaconate	9.3 (s, 1H, OH) [b], 7.36 (m, 2H, Ar–H_c), 7.21 (m, 1H, Ar–H_d), 7.08 (m, 2H, Ar–H_b), 6.55 (s, 1H, CH_2=C) [c], 5.95 (s, 1H, CH_2=C) [c], 3.59 (s, 2H, –CH_2–COO)
Monobenzyl itaconate	10.2 (s, 1H, OH) [b], 7.32 (s, 5H, Ar–H) 6.45 (s, 1H, CH_2=C) [c], 5.82 (s, 1H, CH_2=C) [c], 5.14 (s, 2H, –COO–CH_2), 3.38 (s, 2H, –CH_2–COO)
Mono-2-phenylethyl itaconate	11.9 (s, 1H, OH) [b], 7.25 (m, 5H, Ar–H), 6.45 (s, 1H, CH_2=C) [c], 5.70 (s, 1H, CH_2=C) [c], 4.30 (t, 2H, J = 7, COO–CH_2) [d], 3.30 (s, 2H, –CH_2–COO), 2.90 (t, 2H, J = 7, –CH_2–Ar) [d]

[a] The FTIR spectra of these monoitaconates showed bands at 3300 (OH), 1740 (C = O, ester) and 1700 cm^{-1} (C = O, acid).

[b] Exchangeable with D_2O.

[c] Indistinguishable.

[d] J value in hertz.

Spectrometry

Each monomer was characterized by FTIR, ^{1}H NMR and ^{13}C NMR. FTIR spectra were recorded in a Nicolet 520 spectrophotometer and only selected absorptions (cm^{-1}) are reported. NMR spectra were recorded using a Brucker 250 instrument. The resulting FTIR and NMR spectra are in good agreement with the expected structures. Spectral data are recorded in Tables 2 and 3.

TABLE 3

^{13}C NMR data ($CDCl_3$/TMS) for monophenyl, monobenzyl and mono-2-phenylethyl itaconate [a]

Monomer	∂ (ppm)
Monophenyl itaconate	171.52 (COOH), 169.05 (COOR), 150.57 (C [a]), 132.85 (C=CH_2), 131.40 (C [c]), 129.30 (C [d]), 125.80 (C=CH_2), 121.30 (C [b]), 37.38 (–CH_2–)
Monobenzyl itaconate	171.35 (COOH), 170.40 (COOR), 135.56 (C [a]), 133.14 (C=CH_2), 130.76 (C [c]), 128.45 (C [d]), 128.16 (C [b]), 128.05 (C=CH_2), 66.69 (O–CH_2–), 37.21 (–CH_2–)
Mono-2-phenylethyl itaconate	171.51 (COOH), 170.44 (COOR), 137.57 (C [a]), 133.15 (C=CH_2), 130.81 (C [c]), 128.84 (C [b]), 128.42 (C [d]), 126.50 (C=CH_2), 64.45 (O–CH_2–), 37.38 (–CH_2–), 34.89 (–CH_2–Ar)

[a] The FTIR spectra of these monoitaconates showed bands at 3300 (OH), 1740 (C=O, ester) and 1700 cm^{-1} (C=O, acid).

Differential thermal analysis (DTA)

Samples of between 6 and 9 mg were weighed in standard aluminium crucibles on a Mettler microbalance with a precision of ±0.000005 g, before being placed in the DTA furnace at room temperature. The DTA system used was a Mettler TA 2000. The instrument was calibrated using indium as standard (ΔH(fusion) = 28.5 J g^{-1} and melting point 156.4°C). The absolute temperature was calculated using the equation [4]

$$T_s = T_p - \tau \frac{dT_p}{dt} + \frac{\Delta U}{S} \tag{1a}$$

where T_s is the sample temperature at point T_1, T_p is the program temperature at point T_1 (°C), τ is an intrinsic constant of DTA whose value is 0.53, dT_p/dt is the heating rate, ΔU is the signal at point T_1, and S is the sensitivity of the thermocouple.

For each monomer, we carried out a dynamic polymerization in order to establish the melting and polymerization temperature range. The monomers did not show the exothermic peak corresponding to the polymerization reaction. Then, radical polymerization was tried using α,α'-azobis(isobutyronitrile) (AIBN) as initiator. In these cases, the polymerization was carried out without problems at temperatures higher than the melting point of monomers. Polymerization reactions were then performed at several temperatures in order to calculate several kinetic parameters.

Calculation of the kinetic parameters is often based on the assumption that the reaction can be described by the differential equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

where α is the degree of conversion of monomer to polymer, which is defined in terms of the change of heat evolved ($\alpha = (\Delta H_{tot} - \Delta H_t)/\Delta H_{tot}$), $k(T)$ is the temperature-dependent rate constant and $f(\alpha)$ is a function which represents the hypothetical model for the reaction mechanism. In the polymerization reaction, in order to obtain the reaction order, we have supposed that the heat of reaction, ΔH, is proportional to the number of monomer moles converted to polymer at every moment. Therefore the rate of reaction can be obtained from

$$\frac{d\alpha}{dt} = \frac{dH}{dt} \frac{1}{\Delta H_{sp}}$$

where ΔH_{sp} is the specific reaction enthalpy and $d\alpha/dt$ can be obtained from the DTA curve. The partial and total areas of the different thermograms were calculated using a Commodore CBM 128/64 computer which integrates the experimental peak areas with an accuracy of better than ±1%.

RESULTS AND DISCUSSION

Figure 2 shows the thermal behaviour of monophenyl, monobenzyl and mono-2-phenylethyl itaconate in the temperature range 50–250 °C in the absence of initiator.

The first endothermic peak corresponds to the melting of the monomers. The obtained melting points were 94.4 ± 0.02, 79.5 ± 0.02 and 82.3 ± 0.02 °C for monophenyl, monobenzyl and mono-2-phenylethyl itaconate, respectively and were corrected using Eqn. (1a). From the area of each peak it is possible to calculate the melting enthalpy of the three monomers; we have obtained the following values: -27.8 kJ mol^{-1} (monophenyl itaconate), -26.4 kJ mol^{-1} (monobenzyl itaconate) and -19.4 kJ mol^{-1} (mono-2-phenylethyl itaconate). As can be seen in Fig. 3, the melting enthalpy of the studied monoitaconates increases with the molar mass as expected. This behaviour means that the larger the lateral group of the different monoitaconates the worse is the packing of the molecules, probably owing to the fact that the methylene groups have a greater possibility of rotation.

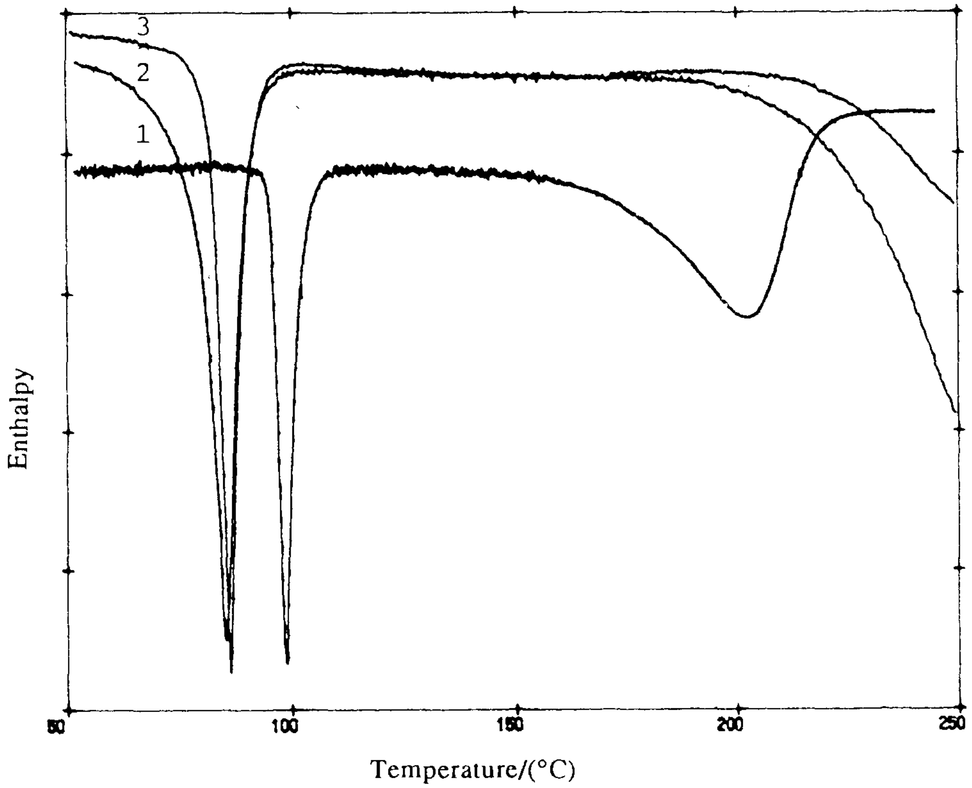

Fig. 2. Thermal behaviour for monophenyl (curve 1), monobenzyl (curve 2) and mono-2-phenylethyl itaconate (curve 3). In this figure no temperature correction has been made.

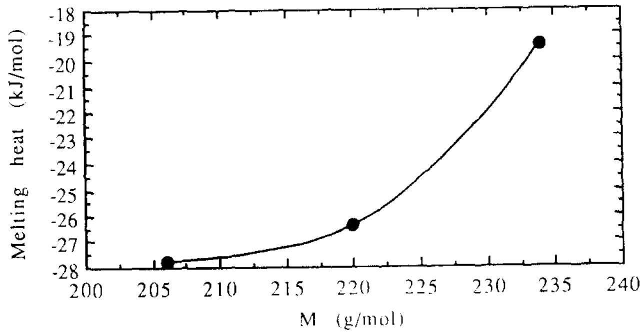

Fig. 3. Heat of melting vs. molar mass for monophenyl, monobenzyl and mono-2-phenylethyl itaconate.

For these monomers it was necessary to employ an initiator to carry out the polymerization reaction. We used α,α′-azobis(isobutyronitrile) (AIBN). Figure 4 shows the results obtained using AIBN. As can be seen in this figure, an exothermic peak appears in all monomers at a temperature a

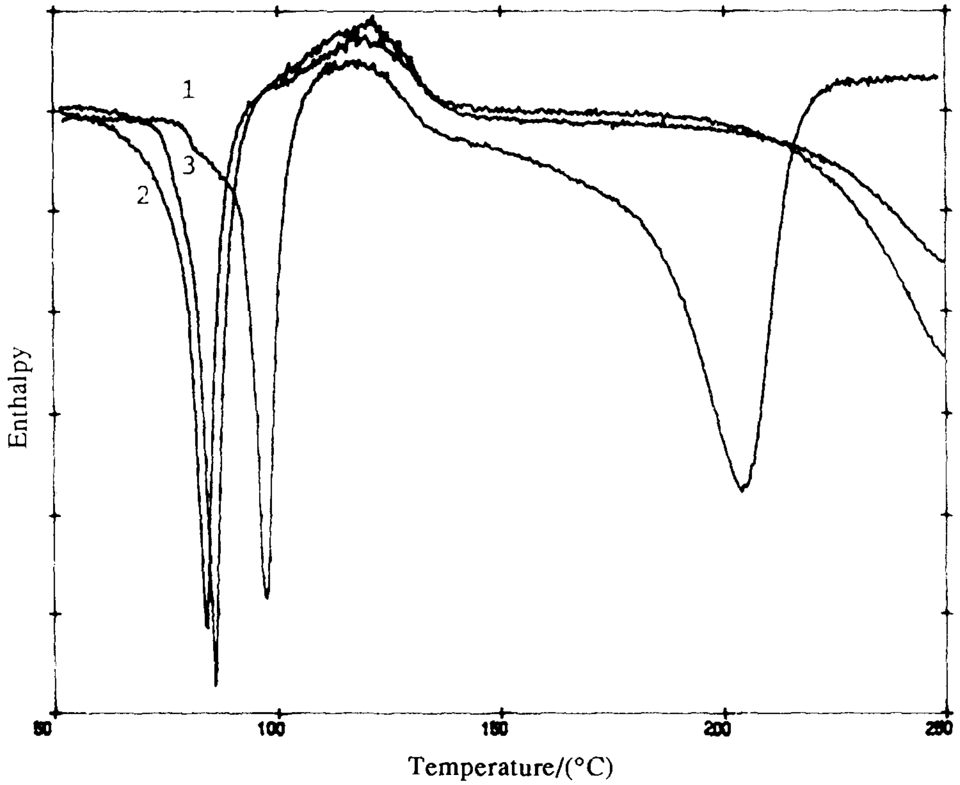

Fig. 4. Thermal behaviour of monophenyl (curve 1), monobenzyl (curve 2) and mono-2-phenylethyl itaconate (curve 3) with AIBN. In this figure no temperature correction has been made.

little above the melting point; these peaks correspond to the polymerization process.

For monophenyl, monobenzyl and mono-2-phenylethyl itaconate the exothermic peaks are located in the temperature intervals 108–140 °C, 95–145 °C and 97–140 °C, respectively and the values were corrected using Eqn. (1a). The maxima of these peaks are 115.4 °C for monophenyl itaconate, 115.8 °C for monobenzyl itaconate and 114.8 °C for mono-2-phenylethyl itaconate; the total polymerization heats, calculated from the areas of the peaks, are 13.2, 12.4 and 6.4 kJ mol^{-1}, respectively.

In the simplest case, the kinetic scheme of free radical polymerization consists of three stages which correspond to initiation, propagation and chain termination. For a radical polymerization initiated with initiator, the polymerization rate is

$$v_p = \frac{k_p}{\sqrt{k_t}} (fk_d)^{1/2} [\mathrm{I}]^{1/2} [\mathrm{M}] = k_{ov} \, [\mathrm{M}]$$

where k_p, k_t and k_d are the propagation, termination and decomposition kinetic rate constants, respectively. For monophenyl itaconate we found an experimental kinetic order of 0.75 with respect to monomer; for monobenzyl itaconate this value was 0.8 and finally for mono-2-phenylethyl itaconate we found a variation of the order with temperature. Between 100 and 115 °C, the kinetic order with respect to monomer was 0.75 and for the temperature range 120–130 °C a value of 0.90 was obtained, very close to the theoretical ones. These differences between the experimental and theoretical kinetic order can be due to the existence of diffusion processes in the monomer, as pointed out by North and co-workers [5–7]. The termination reactions in free radical polymerizations for the three monoitaconates studied are controlled by different diffusion processes. Direct measurements of the second-order termination rate [8–11] have shown that the apparent termination rate constant is inversely proportional to the viscosity of the medium over a thousandfold range of viscosity. The inverse dependence of a rate constant on viscosity can be explained only in terms of a diffusion-controlled process. However, diffusion is not a simple phenomenon, and there are at least two kinds of diffusion which can play a role in bimolecular termination: the translational diffusion of the chain centres and the segmental diffusion of the active centres.

The behaviour observed for mono-2-phenylethyl itaconate with temperature is as expected because the diffusion rate of molecules increases as temperature increases.

The global activation energy E_a for the three monomers has been calculated using the Arrhenius equation

$$k = A \exp(-E_a/RT)$$

where k is the global kinetic constant, A is a constant often called the

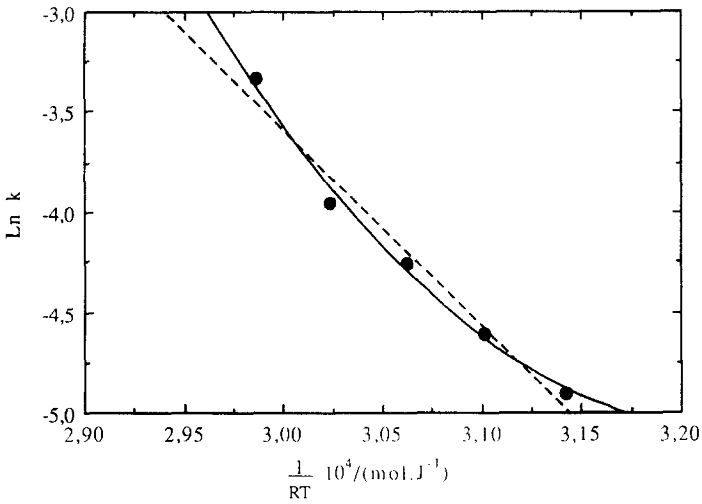

Fig. 5. Arrhenius plot for monophenyl itaconate. The dotted line is calculated using the Arrhenius equation without modification.

frequency factor which is independent of temperature, R is the gas constant (8.31 J mol^{-1} K^{-1}), and T is the absolute temperature. Carrying out a series of experiments over a range of different but constant temperatures and plotting ln k against $1/RT$ in the customary fashion, gives the Arrhenius parameters, the global activation energy E_a and the pre-exponential or frequency factor A from the slope and intercept, respectively, of the straight line obtained. In Figs. 5–7 we can see the Arrhenius plots obtained for the three monomers studied.

The values obtained for the frequency factor A and global activation energy E_a are shown in Table 4. It is usually found that a plot of log k vs.

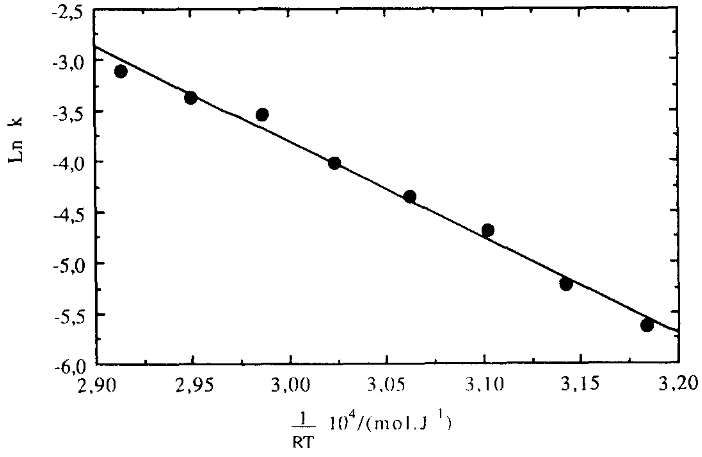

Fig. 6. Arrhenius plot for monobenzyl itaconate.

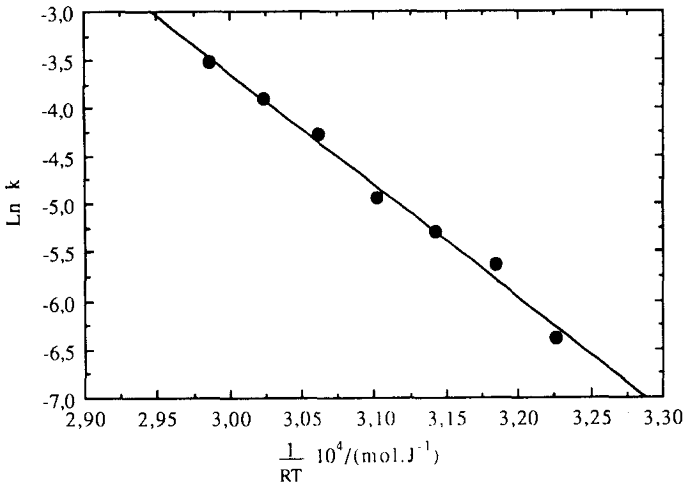

Fig. 7. Arrhenius plot for mono-2-phenylethyl itaconate.

$1/T$ is nearly linear with negative slope. This result is equivalent to the Arrhenius results in

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T}=\frac{E_a}{RT^2} \tag{1b}$$

If E_a is a constant with respect to temperature, integration results in

$$\ln k=-\frac{E_a}{RT}+\text{constant} \tag{2}$$

or

$$k=A\exp(-E_a/RT) \tag{3}$$

A somewhat better fit can often be obtained with an equation of the form [10]

$$k=AT^m\exp(-E/RT) \tag{4}$$

or

$$\ln k=-\frac{E}{RT}+m\ln T+\ln A \tag{5}$$

where m is a small number (positive or negative).

TABLE 4

Global activation energy E_a and frequency factor A for several itaconate derivatives

Monomer	ln A	A	E_a (kJ mol^{-1})
Monophenyl itaconate	25.5	1.187×10^{11}	97.1
Monobenzyl itaconate	24.6	4.827×10^{10}	94.8
Mono-2-phenylethyl itaconate	31.4	4.334×10^{13}	116.9

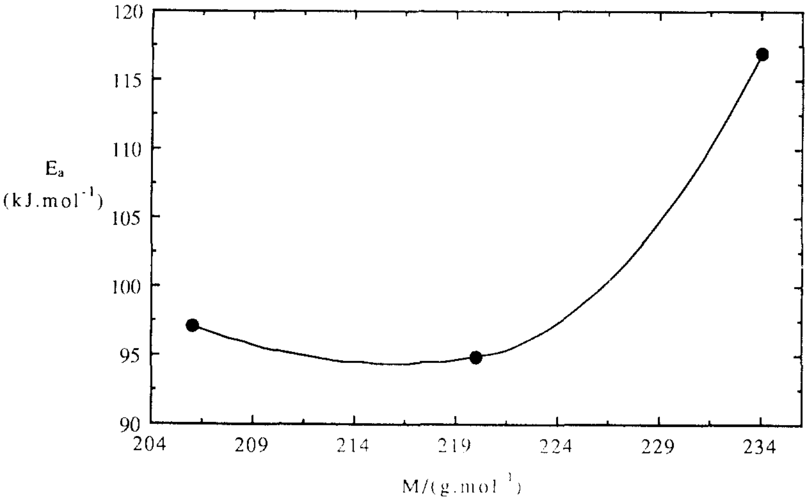

Fig. 8. Activation energy vs. the molar mass of the monomer side group.

In treating experimental data by means of eqns. (2) and (5) the activation energies E_a and E will differ. It is of importance to know the relation between E_a and E. Differentiating eqn. (5) with respect to temperature, assuming E is constant, and setting this equal to eqn. (1) gives

$$\frac{E}{RT^2}+\frac{m}{T}=\frac{E_a}{RT^2} \tag{6}$$

and

$$E=E_a-mRT \tag{7}$$

The difference between the two activation energies will typically be hundreds or a few thousands of joules per mole.

If eqn. (5) is correct with m not zero, a plot of log k vs. $1/T$ will show a slight curvature. The curve may sometimes be resolved into two parts, each of which approaches linearity. This can result if there are two competing reactions with different activation energies and is often observed where the same reaction may occur both homogeneously and heterogeneously. The homogeneous reaction usually has a higher activation energy and so it is favoured at high temperatures, whereas the heterogeneous reaction predominates at lower temperatures. Such is the case of monophenyl itaconate.

Figure 8 shows activation energy E_a as a function of the molar mass of the side group of the investigated monomers. As can be seen, the activation energy increases sharply from monophenyl and monobenzyl itaconate to mono-2-phenylethyl itaconate, probably because of the influence of the monomer side group [12].

Finally, we have calculated the polymerization heat as a function of the molar mass of the monomer side group. As can be see in Fig. 9, the

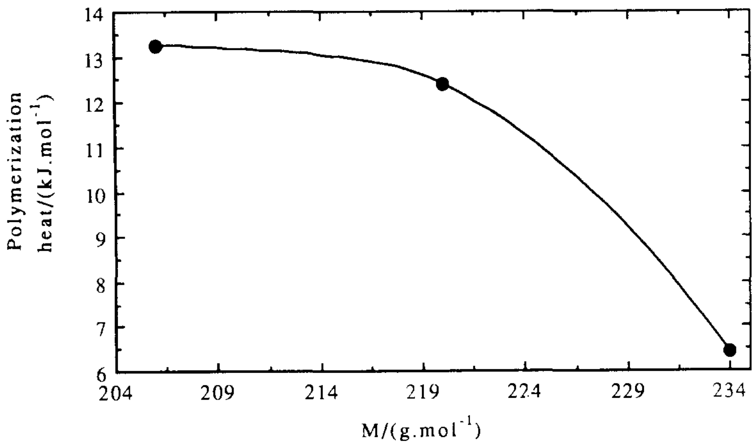

Fig. 9. Polymerization heat vs. the molar mass of the monomer side group.

polymerization heat decreases as the molar mass of the monomer side group increases.

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