Thermochimica Acta, 220 (1993) 91–101
Elsevier Science Publishers B.V., Amsterdam

The kinetics of bulk polymerization of itaconate derivatives.
Part 2. Diphenyl, dibenzyl and di-2-phenylethyl itaconates

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(Received 12 October 1992; accepted 20 October 1992)

Abstract

The synthesis, characterization and radical bulk polymerization of diphenyl, dibenzyl and di-2-phenylethyl itaconates have been studied by differential scanning calorimetry (DSC). The bulk polymerization of diphenyl itaconate was carried out with α,α'-azobis-isobutyronitrile (AIBN) as initiator. The polymerization was self-initiated in the other two cases. The activation energy, reaction order and frequency factor are determined. We found that the polymerization mechanism is controlled by diffusion processes. For dibenzyl itaconate two different activation energies were found.

INTRODUCTION

Itaconic acid derivatives are a very interesting family of monomers derived from non-oil origins. Itaconic acid can be obtained from large-scale fermentation processes [1]. Itaconic acid esterification was first described in 1873 [2] and ester polymerization was reviewed in 1967 by Tate [3]. The chemical structures of these monomers are very similar to acrylic and methacrylic esters.

Differential scanning calorimetry (DSC) measures the enthalpy changes which occur in a sample by comparison with some inert reference material, when they are both heated, and this can be used to measure the rate of the reaction. This can, in principle, be used to obtain information on the kinetic parameters and mechanisms of the polymerization process [4].

This paper reports a study on the bulk polymerization kinetics to

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complete conversion of diphenyl itaconate using α,α'-azobisisobutyronitrile (AIBN) as initiator and of dibenzyl and di-2-phenylethyl itaconates without initiator, with the aim of quantifying the influence of the side groups on the reactivity of the monomers in polymerization.

EXPERIMENTAL

Synthesis of the diitaconate esters

The diphenyl, dibenzyl and di-2-phenylethyl itaconates (Fig. 1) were prepared as follows: sulphuric acid was added dropwise to catalyse the diesterification of itaconic acid (1.0 mol) and the appropriate alcohol (3.0 mol). The reaction mixture was refluxed until complete consumption of the itaconic acid. The process was monitored by thin layer chromatography (TLC) carried out on 0.2 mm silica gel 60 F_{254} Merck plates, using UV light as the developing agent. Immediately after the reaction mixture was cooled to room temperature, methylene dichloride (CH_2Cl_2) was added and the crude product was washed with aqueous $NaHCO_3$. The organic phase was separated, dried and the solvent was removed under vacuum. The mixture containing the diester was separated on a chromatographic column of silica gel 60 Merck (granulometry 0.063–0.200 nm, 70–230 Mesh ASTM) by eluting with dichloromethane to confirm the presence of pure diitaconate [5]. The purity of the diphenyl itaconate was checked by DSC; the purity was greater than 99.9%.

The physical data for the diitaconates are given in Table 1.

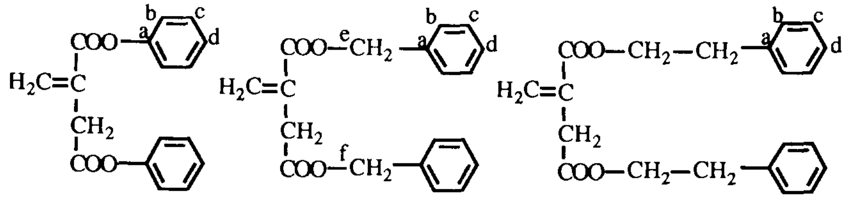

Fig. 1. Chemical structure of diphenyl, dibenzyl and di-2-phenylethyl itaconates.

TABLE 1

Physical data for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	M [a]	R_f [b]	T/K	n_D	Yield % [c]
Diphenyl itaconate	282	0.96	334.2	–	42
Dibenzyl itaconate	310	0.91	–	1.538	69
Di-2-phenylethyl itaconate	338	0.69	–	1.531	62

[a] Monomer molar mass/(g mol^{-1}). [b] CH_2Cl_2/MeOH 9.8/0.2. [c] Pure crystalline compound.

TABLE 2

^{1}H-NMR spectral data for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	^{1}H-NMR ($CDCl_3$/TMS) δ/(ppm), J/(Hz)
Diphenyl itaconate	7.4 (m, 4 H, Ar–H_c), 7.2 (m, 2 H, Ar–H_d), 7.1 (m, 4 H, Ar–H_b), 6.65 (s, 1 H, $CH_2{=}C$)^a, 6.01 (s, 1 H, $CH_2{=}C$)^a, 3.7 (s, 2 H, –CH_2–COO)
Dibenzyl itaconate	7.3 (m, 10 H, Ar–H), 6.4 (s, 1 H, $CH_2{=}C$)^a, 5.7 (s, 1 H, $CH_2{=}C$)^a, 5.1 (s, 4 H, COO–CH_2–), 3.4 (s, 2 H, –CH_2–COO)
Di-2-phenylethyl itaconate	7.2 (m, 10 H, Ar–H), 6.28 (d, 1 H, J = 1, $CH_2{=}C$)^a, 5.65 (d, 1 H, J = 1, $CH_2{=}C$)^a, 4.3 (t, 4 H, J = 7, COO–CH_2–), 3.3 (s, 2 H, –CH_2–COO), 2.9 (t, 4 H, J = 7, –CH_2–Ar)

[a] Not resolvable.

TABLE 3

^{13}C-NMR spectral data for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	^{13}C-NMR ($CDCl_3$/TMS) δ/(ppm)
Diphenyl itaconate	169.0 (–CH_2–COOR), 164.5 (=C–COOR), 150.55 (C_a), 133.1 ($C{=}CH_2$), 130.4 (C_c), 129.4 (C_d), 125.7 ($C{=}CH_2$), 121.4 (C_b), 37.8 (–CH_2–)
Dibenzyl itaconate	171.0 (–CH_2–COOR), 164.8 (=C–COOR), 138.3 (C_a), 136.0 ($C{=}CH_2$), 128.65 (C_c), 128.35 (C_d), 127.75 (C_b), 127.1 ($C{=}CH_2$), 72.16 (C_e), 66.4 (C_f), 46.3 (–CH_2–COO)
Di-2-phenylethyl itaconate	170.4 (–CH_2–COOR), 165.8 (=C–COOR), 127.6 (C_a), 133.7 ($C{=}CH_2$), 128.8 (C_c), 128.4 (C_b), 127.0 (C_d), 126.4 ($C{=}CH_2$), 65.3 (O–CH_2–), 37.5 (–CH_2–COO), 34.88 (–CH_2–Ar)

Characterization of diitaconate esters

Each monomer was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR. The FTIR spectra were recorded on a Nicolet 520 spectrophotometer and only some selected absorption bands (cm^{-1}) are reported. The NMR spectra were reocrded on a Bruker 250 MHz spectrometer. The resulting FTIR and NMR spectra were in good agreement with the expected structures. Spectral data are recorded in Tables 2, 3 and 4.

Differential scanning calorimetry (DSC)

Between 6 and 9 mg of the monometer were weighted in a standard aluminium crucible on a Mettler microbalance to a precision of $\pm 5\ \mu g$,

TABLE 4

Characteristic FTIR frequencies for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	IR (KBr) $\nu/(\mathrm{cm}^{-1})$
Diphenyl itaconate	3068.3 and 3043.4 (st, ArC–H), 2935 (st, C–H), 1762.9 (st, C=O), 1641.5 (st, C=C), 1196.3 (st as, C–O)
Dibenzyl itaconate	3065.1 and 3032.7 (st, ArC–H), 2929.96 and 2258.7 (st, C–H), 1744.9 (st, C=O), 1643.8 (st, C=C), 1232.7 (st as, C–O)
Di-2-phenylethyl itaconate	3061.8 and 3029.1 (st, ArC–H), 2958.3 and 2904.5 (st, C–H), 1737.2 (st, C=O), 1639.1 (st, C=C), 1245.2 (st as, C–O)

before being placed in the DSC furnace at room temperature. The DSC system used was a Mettler TA 4000.

For each monomer, dynamic calorimetry was carried out in order to establish the melting and polymerization temperature range. The dibenzyl and di-2-phenylethyl itaconates showed an exothermic peak corresponding to their polymerization reaction. However, the diphenyl itaconate showed an endothermic peak due to a melting process but did not show the exothermic peak corresponding to polymerization. We tried to polymerize this monomer by using a radical initiator, α,α'-azobisisobutyronitrile (AIBN). In this case the polymerization reaction was achieved without problem. Then isothermal experiments at several temperatures were carried out over the polymerization temperature range in order to calculate the fundamental kinetic parameters: reaction order n, overall rate constant k_{ov}, overall activation energy E_a and frequency factor A. In each experiment we confirmed the complete conversion of monomer to polymer by carrying out a second thermal scan.

The treatment of DSC experimental data to determine the kinetic rate constants and the reaction order, was performed as described in ref. 6.

RESULTS AND DISCUSSION

Figures 2a, b and c show the thermal response of diphenyl, dibenzyl and di-2-phenylethyl itaconates, respectively, in the range 123–523 K in the absence of initiator. As can be seen, only the diphenyl itaconate shows an endothermic peak typical of melting. The melting point was 334.2 ± 0.2 K. From the peak area, the melting enthalpy was found to be 20.0 ± 0.05 kJ mol^{-1}. The other two monomers have no melting process. This can be explained as follows: the methylene or ethylene groups attached to the aromatic rings allow free movement of the side chains, and therefore the molecular packing becomes unfavorable so that these substances do not readily crystallize.

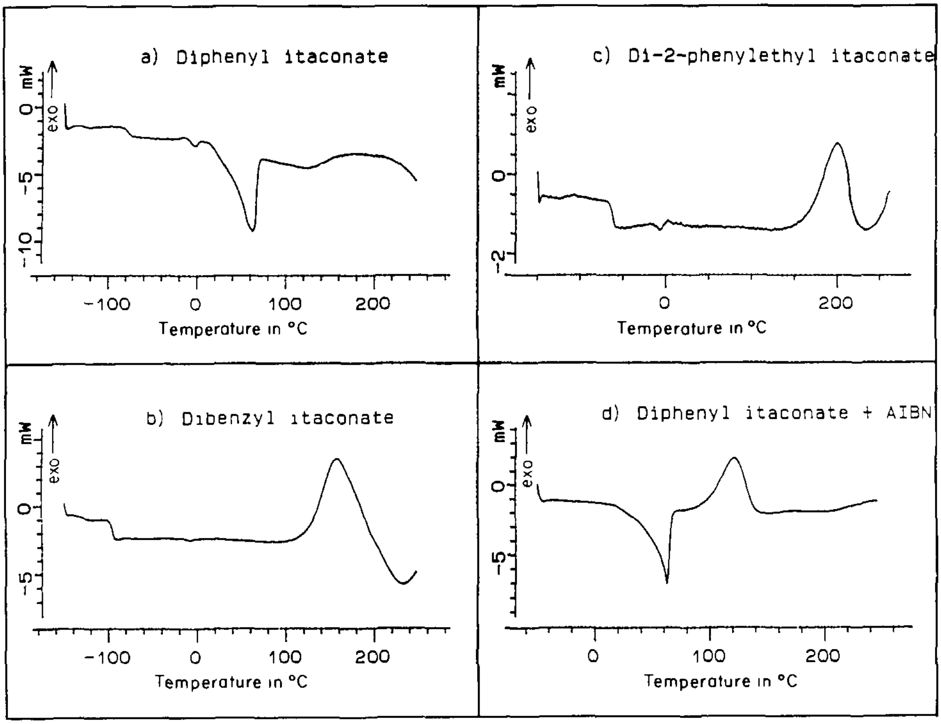

Fig. 2. Thermal behaviour of diphenyl (a), dibenzyl (b) and di-2-phenylethyl (c) itaconates without AIBN, and diphenyl itaconate with AIBN (d) in the temperature range 123–523 K.

The exothermic peaks in Fig. 2b and c correspond to the polymerization of dibenzyl and di-2-phenylethyl itaconates. As can be seen in Fig. 2d, diphenyl itaconate also shows an exothermic peak corresponding to polymerization in the presence of α,α'-azobisisobutyronitrile (AIBN). Table 5 lists the temperatures and heats of polymerization for the three monomers.

The polymerization of the unsaturated compounds involves the opening of one double bond (608.77 kJ mol^{-1}) and formation of two single C–C bonds (702.91 kJ mol^{-1}). The difference between these energies determines

TABLE 5

Polymerization data for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	Temperature range/K	Temperature peak/K	ΔH_p/(kJ mol^{-1})
Diphenyl itaconate	349–413	394.2	−14.9
Dibenzyl itaconate	373–453	415.4	−58.6
Di-2-phenylethyl itaconate	413–473	447.3	−5.9

the heat of the reaction ($94.14\,\mathrm{kJ\,mol^{-1}}$). In our case, the heats of polymerization are smaller than this value (see Table 5). The different heats of polymerization of monomers but the deviation from the theoretical value may be due to two factors. The first arises from the loss of conjugation in going from monomer to polymer, and the second from the energy loss associated with the appearance of stresses on formation of the polymeric chain from substituted olefins, owing to interactions between side groups (steric effect). Then, $-\Delta H = 94.14 - Q_{\mathrm{conj}} - Q_{\mathrm{ster}}$.

In the case of the three itaconates studied here, the π electrons of the double bond are in conjugation with the π electrons of the carbonyl group. The loss of conjugation energy on polymerization of the three diitaconates is approximately equal for compounds of similar chemical structures. The energy loss due to the steric effect is very important. It seems that it is higher for di-2-phenylethyl itaconate and lower for diphenyl itaconate. We are currently calculating its value for each monomer by quantum mechanical calculations. In the case of di-2-phenylethyl and diphenyl itaconates, the energy loss due to steric effects is so high that polymerization becomes very difficult.

The DSC isothermal rate constants measured for the three monomers at several temperatures are shown in Table 6.

The overall activation energy ΔE_a for the three monomers has been calculated using the Arrhenius equation $k = A\exp(\Delta E_a/RT)$ where k is the overall polymerization rate constant, A is the frequency factor which is independent of temperature, R is the gas constant ($8.31\,\mathrm{J\,mol^{-1}\,K^{-1}}$), and T is the temperature (K). The Arrhenius parameters (ΔE_a and A) can be determined by plotting $\ln k$ against $1/RT$ in the customary fashion, from the

TABLE 6

Polymerization rate constants for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Diphenyl itaconate		Dibenzyl itaconate		Di-2-phenylethyl itaconate	
T/K	$k \times 10^4$/ $((\mathrm{mol/l})^{1/5}/\mathrm{s})$	T/K	$k \times 10^4$/ $((\mathrm{mol/l})^{1/4}/\mathrm{s})$	T/K	$k \times 10^4$/ $((\mathrm{mol/l})^{1/2}/\mathrm{s})$
368	17.8	383	40.9	433	27.6
373	21.1	388	44.6	438	37.3
378	38.8	393	49.3	443	52.7
383	56.5	398	55.0	448	67.4
388	75.4	403	59.6	453	104.0
393	108.0	408	67.2	458	118.0
398	181.0	413	76.4	463	170.0
		418	108.0	468	216.0
		423	148.0		
		428	205.0		

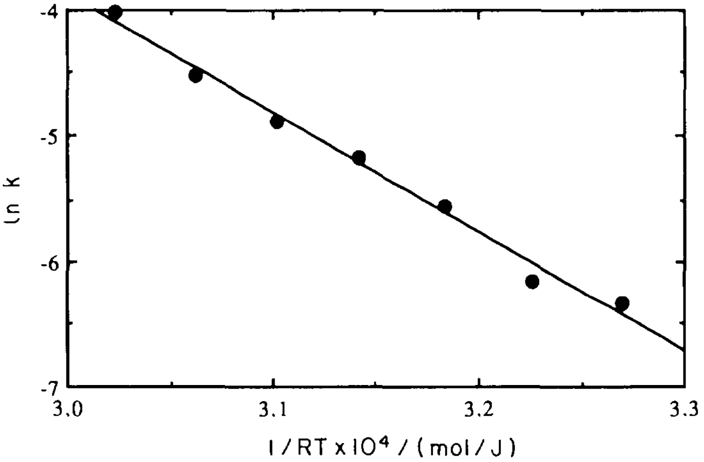

Fig. 3. Arrhenius plot for the polymerization of diphenyl itaconate.

slope and intercept, respectively, of the straight line obtained. Figures 3–5 show the Arrhenius plot for the three monomers studied. The results obtained from the Arrhenius parameters are summarized in Table 7.

For dibenzyl itaconate, two different values for the activation energy were found. For higher temperatures, the activation energy is four times larger than the activation energy in the lower range. This is a greater energy difference than can be attributed to experimental errors. This behaviour can be explained as follows: at higher temperatures the molecule can adopt some high energy conformations. In this state, the polymerization reaction is more easy. This explains the higher activation energy and why the kinetic rate constant increases more rapidly at higher temperatures.

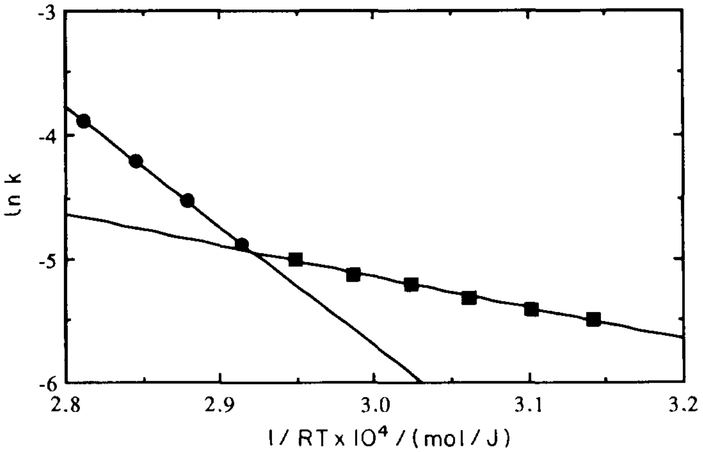

Fig. 4. Arrhenius plot for the polymerization of dibenzyl itaconate.

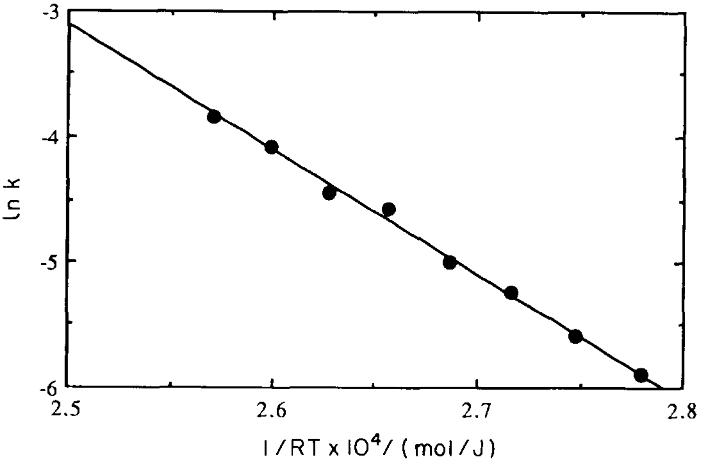

Fig. 5. Arrhenius plot for the polymerization of di-2-phenylethyl itaconate.

For a radical polymerization with an initiator, the polymerization rate is

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

where k_p, k_t and k_d are the propagation, termination and decomposition kinetic rate constants, respectively.

If the polymerization is self-initiated, the polymerization rate expression is

$$v_p = \frac{k_p}{\sqrt{k_t}} fk_i[M]^2 = k_{ov}[M]^2$$

where k_i is the initiation kinetic rate constant.

According to these theoretical kinetic equations, the monomer reaction order must be 1 for diphenyl itaconate, and 2 for the other two monomers. The experimental order for diphenyl itaconate is very close to the theoretical one; however, the values obtained for dibenzyl and di-2-phenylethyl itaconates differ markedly from the theoretical ones. These

TABLE 7

The parameters for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	n [a]	E_a/(kJ mol^{-1})	ln A
Diphenyl itaconate	4/5	94.6	24.51
Dibenzyl itaconate	2/3	25.6, 96.2 [b]	12.81, 23.17 [b]
Di-2-phenylethyl itaconate	1/2	99.6	21.81

[a] n is the overall order in monomer concentration.

[b] The first value corresponds to the range 383–408 K, and the second to 408–428 K.

differences between the experimental and theoretical kinetic orders can be the result of diffusion processes in the monomer, as pointed out by North and co-workers [7–9]. However, the process of diffusion is not a simple phenomenon, and there are at least two kinds of diffusion mechanisms that can play a role in bimolecular termination: the translational diffusion of the chain centres and the segmental diffusion of the active centres [10–13]. Recent work [14] has indicated that segmental diffusion is the slow step in the termination process and, therefore, that it is rate determining.

Eyring [15] has given a quantitative treatment of the activated complex theory that is very useful for interpreting and predicting reaction rates. This theory provides a mean for calculating the concentrations of activated complexes and the rate at which they are converted to products. In the Eyring theory, it is assumed that activated complexes are in equilibrium with reactants. This allows an equilibrium constant in the active state $k^{\#}$ to be defined. The overall kinetic rate constant is related to $k^{\#}$ by

$$k_{\mathrm{ov}} = \frac{KT}{h} k^{\#}$$

Because $k^{\#} = \exp(-\Delta G^{\#\ominus}/RT)$, we have

$$k_{\mathrm{ov}} = \frac{KT}{h} \exp(\Delta G^{\#\ominus}/RT)$$

and because $\Delta G^{\#\ominus} = \Delta H^{\#\ominus} - T\Delta S^{\#\ominus}$

$$k_{\mathrm{ov}} = \frac{KT}{h} \exp(-\Delta H^{\#\ominus}/RT) \exp(\Delta S^{\#\ominus}/R)$$

or

$$\ln\left(\frac{k_{\mathrm{ov}}}{T}\right) = \ln\left(\frac{K}{h}\right) - \frac{\Delta H^{\#\ominus}}{RT} + \frac{\Delta S^{\#\ominus}}{R}$$

where $\Delta S^{\#\ominus}$ is the activation entropy, $\Delta H^{\#\ominus}$ is the activation enthalpy, K is the Boltzman constant ($K = 1.38 \times 10^{-23}$ J K^{-1}) and h is the Planck constant ($h = 6.626 \times 10^{-34}$ J s). Plotting $\ln(k_{\mathrm{ov}}/T)$ versus $1/T$, the slope and the intercept give $\Delta H^{\#\ominus}$ and $\Delta S^{\#\ominus}$ respectively. Figure 6 shows the results obtained for the three studied monomers, and Table 8 summarizes the $\Delta H^{\#\ominus}$ and $\Delta S^{\#\ominus}$ values calculated with the above equations.

In all cases the polymerization reaction involves a decrease in the entropy of the system. However, the value obtained for dibenzyl itaconate at low temperatures is very high if we compare it with that obtained at high temperatures and with the others. This behaviour is related to the activation energy obtained for this monomer and is discussed above.

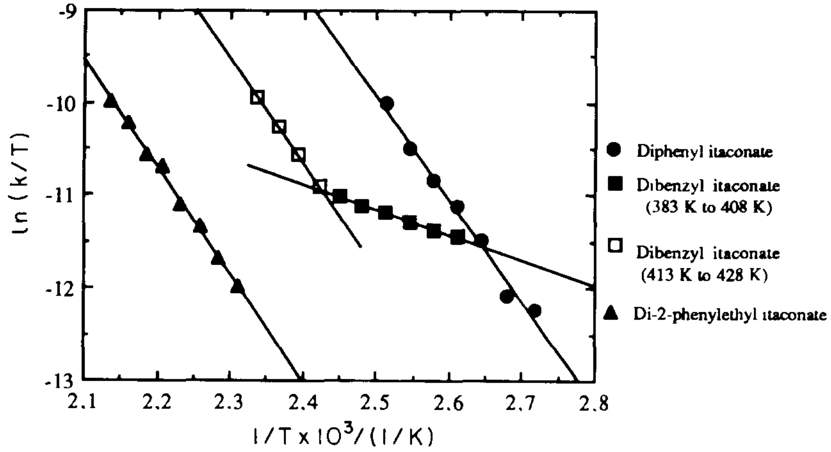

Fig. 6. Plots of $\ln(k_{ov}/T)$ against $(1/T)$ for the polymerization of diphenyl, dibenzyl and di-2-phenylethyl itaconates.

TABLE 8

$\Delta H^{\#\ominus}$ and $\Delta S^{\#\ominus}$ values for diphenyl, dibenzyl and di-2-phenylethyl itaconates

Monomer	$\Delta H^{\#\ominus}$/(kJ mol^{-1})	$\Delta S^{\#\ominus}$/(J mol^{-1} K^{-1})
Diphenyl itaconate	91.43	−51.51
Dibenzyl itaconate (383–408 K)	23.39	−234.20
Dibenzyl itaconate (413–428 K)	92.75	−63.38
Di-2-phenylethyl itaconate	95.91	−75.32

ACKNOWLEDGEMENTS

The authors are grateful to the Ministerio de Educación y Ciencia and Vicerrectorado de Investigación de la Universidad del País Vasco for financial support of this work.

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