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The kinetics of bulk polymerization of itaconic acid derivatives.
Part 3. Mono-2-diphenyl and mono-4-diphenyl itaconates

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Abstract

The synthesis and characterization of mono-2-diphenyl and mono-4-diphenyl itaconates have been carried out. The course and kinetics of the isothermal bulk polymerization of mono-2-diphenyl and mono-4-diphenyl itaconates have been studied by differential thermal analysis (DTA). The initiator used was α,α'-azobisisobutyronitrile (AIBN). The polymerization has been investigated at temperatures between 100 and 150°C. The reaction order with respect to the monomer, the activation energy and frequency factor of the polymerization process have been determined. The kinetic order with respect to the monomer shows that the polymerization mechanism is 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 in some inert reference material when they are both heated. Differential thermal analysis (DTA) provides an opportunity for measuring not only the enthalpy change but also the rate of 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 in the temperature-scanning model. In this paper we have used the isothermal mode [1].

Itaconic acid and its derivatives are a very interesting family of monomers not derived from oil. Itaconic acid can be obtained from large scale fermentation process [2]. Itaconic acid esterification was described for the

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first time in 1873 [3] and polymerization of esters was reviewed in 1967 by Tate [4]. Finally, this family of monomers have become increasingly important due to the fact that their chemical structure is very similar to that of acrylic and methacrylic acids.

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

In previous papers we reported the results of DTA studies of the kinetics of polymerization of a series of aryl itaconates [5–7]. In this paper we report the results obtained by the same method for bulk polymerization kinetics at total conversion of mono-2-diphenyl and mono-4-diphenyl itaconates using α,α'-azobisisobutyronitrile (AIBN) as initiator.

EXPERIMENTAL

Synthesis of the monoitaconate esters

The synthesis of mono-2-diphenyl and mono-4-diphenyl itaconate (Fig. 1) was performed as described in previous papers [5–7].

The monoitaconates were 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 monoesters in sufficient purity for crystallization. The different monoitaconates were crystallized several times from a toluene/*n*-hexane (80/20) mixture until the melting temperature of each monomer was constant.

The R_f of mono-2-diphenyl and mono-4-diphenyl itaconates was calculated 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. The

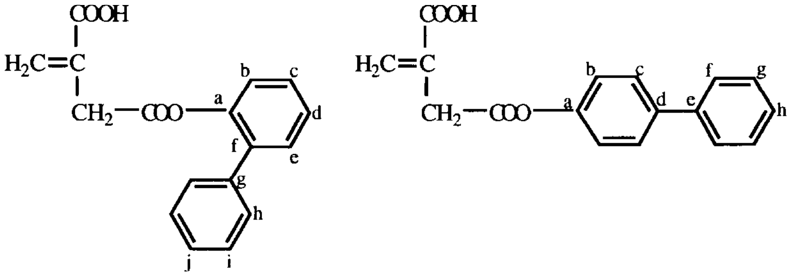

Fig. 1. Chemical structure of mono-2-diphenyl and mono-4-diphenyl itaconates.

TABLE 1

Physical data for mono-2-diphenyl and mono-4-diphenyl itaconates

Monomer	$M^a/(\mathrm{g\,mol^{-1}})$	R_f^b	T_m/K	Yield[c]/%
Mono-2-diphenyl itaconate	282	0.27	372.9	68
Mono-4-diphenyl itaconate	282	0.32	432.6	52

[a] Monomer molar mass. [b] Solvent, CH_2Cl_2/MeOH 9.8/0.2. [c] Compound pure crystallizate.

melting temperature was determined by DTA. These data are shown in Table 1.

Characterization of monoitaconate esters

Each monomer was characterized by FTIR, ^{1}H NMR and ^{13}C NMR. FTIR spectra were recorded with a Nicolet 520 spectrophotometer and only selected absoprtion bands (cm^{-1}) are reported. NMR spectra were recorded using a Brucker AC250. The resulting FTIR and NMR spectra are in good agreement with the expected structures. Spectral data are recorded in Tables 2–4.

TABLE 2

^{1}H NMR spectral data for mono-2-diphenyl and mono-4-diphenylitaconates

Monomer	^{1}H NMR ($CDCl_3$/TMS) δ/ppm
Mono-2-diphenyl itaconate	7.25 (m, 9 H, Ar–H), 6.36 (s, 1 H, CH=C)[a], 5.64 (s, 1 H, CH_2=C)[a], 3.30 (s, 2 H, $-CH_2-$)
Mono-4-diphenyl itaconate	7.42 (m, 9 H, Ar–H), 6.42 (s, 1 H, CH_2=C)[a], 5.73 (s, 1 H, CH_2=C)[a], 3.18, (s, 2 H, $-CH_2-$)

[a] Indistinguishable.

TABLE 3

^{13}C NMR spectral data for mono-2-diphenyl and mono-4-diphenylitaconates

Monomer	^{13}C NMR ($CDCl_3$/TMS) δ/ppm
Mono-2-diphenyl itaconate	171.38 (COOH), 168.89 (COOR), 147.60 (C^a), 137.31 (C^g), 134.81 (C=CH_2), 132.50 (C^f), 130 (ArC), 127.44 (C=CH_2), 126.41 (C^d), 122.70 (C^b), 36.97 ($-CH_2-$)
Mono-4-diphenyl itaconate	171.23 (COOH), 169.56 (COOR), 148.15 (C^a), 141.58 (C^c), 133.21 (C=CH_2), 130 (ArC), 126.85 (C=CH_2), 121.37 (C^b), 35.48 ($-CH_2-$)

TABLE 4

FTIR spectral data for mono-2-diphenyl and mono-4-diphenylitaconates

Monomer	IR (KBr) ν/cm^{-1}
Mono-2-diphenyl itaconate	3500–2500 (st, COO–H), 3063.4 and 3030.1 (st, ArC–H), 2967.5 and 2933.7 (st, C–H), 1748.0 (st, C=O, ester), 1699.2 (st, C=O, acid), 1637.0 (st, C=C), 1321.8 (st as, C–O), 1151.6 (st s, C–O)
Mono-4-diphenyl itaconate	3500–2500 (st, COO–H), 3064.5 and 3037.2 (st, ArC–H), 2967.3 (st, C–H), 1748.0 (st, C=O, ester), 1702.6 (st, C=O, acid), 1635.8 (st, C=C), 1313.6 (st as, C–O), 1194.4 (st s, C–O)

Key: as, asymmetric; s, symmetric; st, stretch.

Differential thermal analysis (DTA)

In each experiment 6–9 mg monomer plus initiator, were weighed into a standard Mettler aluminium crucible which was then placed in the sample holder assembly of the calorimeter whose temperature had previously been set to the desired value. The DTA system used was a Mettler TA 2000. Calibration of the calorimeter was performed by determining the heat of fusion of indium ($\Delta H_f = 28.5$ J g^{-1}, m.p. = 156.4°C).

For each monomer, we carried out a dynamic polymerization in order to establish the melting and polymerization temperature range. Monomers alone did not show an exothermic peak corresponding to a polymerization reaction. Then, radical polymerization was tried using α,α'-azobisisobutyronitrile (AIBN) as initiator. The initiator was recrystallized from absolute alcohol and stored in the dark at −20°C. Its melting point was checked calorimetrically. Each aluminium crucible was checked for tightness and almost no leakage was observed. In this case polymerization was carried out without problems. Isothermal experiments, at several temperatures in the polymerization temperature range, were carried out to measure the kinetic parameters: reaction order (n), overall rate constant (k_{ov}), overall activation energy (E_a) and frequency factor (A). Each experiment was repeated at least four times. The mean standard deviation was estimated to be ±3%. The residual monomer content was determined calorimetrically. After each isothermal polymerization the sample was heated to 250°C at a heating rate of 10°C min^{-1}. In the thermogram which was subsequently recorded the baseline was obtained by the extrapolation of the straight line of the final stage of polymerization [8]. The areas between the curve and the baseline in the DTA thermograms were measured using a computer.

The treatment of DTA experimental data was performed as described previously [5–7].

RESULTS AND DISCUSSION

Figure 2 shows the thermal behaviour of mono-2-diphenyl and mono-4-diphenyl itaconates in the temperature range 50–250°C without initiator. The endothermic peak corresponds to the melting of each monomer. From the area of this peak it is possible to calculate the melting enthalpy of the monomers. Table 5 shows the melting data obtained for the two monomers.

As can be seen in Table 5, the melting temperature and enthalpy of mono-4-diphenyl itaconate are higher than the mono-2-diphenyl itaconate isomer. This can be explained in that the mono-4-diphenyl itaconate is more planar in structure which gives a better arrangement of the molecules of this compound, and so a greater enthalpy of fusion. Similar behaviour

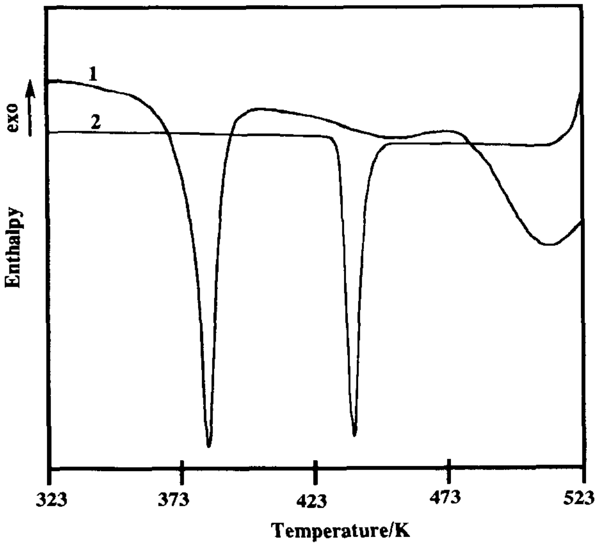

Fig. 2. Thermal behaviour of mono-2-diphenyl (curve 1) and mono-4-diphenyl itaconates (curve 2).

TABLE 5

Melting data for mono-2-diphenyl and mono-4-diphenyl itaconates

Monomer	Melting point/K	$\Delta H_f/(\text{kJ mol}^{-1})$
Mono-2-diphenyl itaconate	373.0	21.34
Mono-4-diphenyl itaconate	432.6	36.88

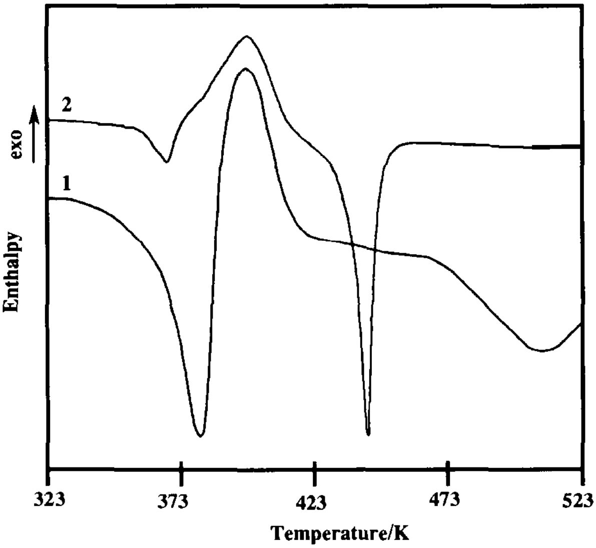

Fig. 3. Thermal behaviour for mono-2-diphenyl (curve 1) and mono-4-diphenyl (curve 2) itaconates using α,α'-azobisisobutyronitrile (AIBN) as initiator.

has been found with other corresponding alcohols. For these monomers it was necessary to employ an initiator to carry out the polymerization reaction. The initiator used was α,α'-azobisisobutyronitrile (AIBN). In Fig. 3 we can see the thermal behaviour for the two monomers using an initiator. The exothermic peaks correspond to the polymerization reaction of mono-2-diphenyl (curve 1) and mono-4-diphenyl (curve 2) itaconates with initiator. From the area of these peaks we can calculate the polymerization enthalpy. Table 6 shows the polymerization data obtained for these monomers.

It is necessary to point out that the values obtained for polymerization enthalpy are very low if we compare them with other vinyl monomers. The use of this type of monomer having such a low polymerization enthalpy is very interesting, because in this way the problem of dissipating great quantities of heat from the system during polymerization is avoided (this is one of the greatest and most common problems for industrial synthesis of

TABLE 6

Polymerization data for mono-2-diphenyl and mono-4-diphenyl itaconates

Monomer	Temperature range/K	Temperature peak/K	ΔH_p/ (kJ mol^{-1})
Mono-2-diphenyl itaconate	383–428	391	−19.25
Mono-4-diphenyl itaconate	373–318	385.4	−29.6

polymeric materials). This fact also contributes to the "gel effect" (also named the "Trommsdorff effect" [9]) elimination, which produces 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 with the polyitaconates.

As can be seen in Fig. 3, mono-4-diphenyl itaconate shows the polymerization peak before the melting peak. According to this, mono-4-diphenyl itaconate polymerizes in the solid state. Nevertheless, in Fig. 3 we can see that the endothermic peak, corresponding to the melting process, does not disappear. This can be explained as follows: polymerization in the solid state is very slow, so part of the monomer cannot react during the time corresponding to the polymerization temperature range. This residual monomer is responsible for the melting peak. For this reason, the polymerization enthalpy obtained is not valid because we cannot know the monomer mass that reacts during the polymerization process.

Several isothermal experiments were carried out in the polymerization temperature range for each monomer. This allowed us to calculate the kinetic parameters. The DTA isothermal experiments performed with the two monomers offer the results shown in Table 7 for the kinetic rate constant at several temperatures.

The rate of the process can be described by the two functions

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \qquad (1)$$

where α is the degree of conversion, $\mathrm{d}\alpha/\mathrm{d}t$ the rate of reaction, the function $k(T)$ is the temperature dependent rate constant, while $f(\alpha)$ is a function which represents the hypothetical model of the reaction mechanism. It is the task of empirical kinetics to find the analytical form of both functions;

TABLE 7

Kinetic rate constants for mono-2-diphenyl and mono-4-diphenyl itaconates

Mono-2-diphenyl itaconate		Mono-4-diphenyl itaconate	
T/K	$k_{ov} \times 10^4$ $(\mathrm{mol\,l^{-1}})^{1/4}\,\mathrm{s^{-1}}$	T/K	$k_{ov} \times 10^4$ $(\mathrm{mol\,l^{-1}})^{1/4}\,\mathrm{s^{-1}}$
		378	42.2
383	51.8	383	61.2
388	97.7	388	104.0
393	128.0	393	203.0
398	200.0	398	405.0
403	286.0		
408	351.0		

that is, to determine the so-called kinetic parameters. Provided that all other possible variables are held constant, the thermodynamic process is determined as a function of time by the two quantities α and T. The most common experimental method is based on the investigation of the isothermal course of the process for a set of temperatures. Upon itegration, Eqn. (1) yields

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \times k(T)t \tag{2}$$

The linear dependence of $g(\alpha)$ on t makes it possible to find by way of trial and error the function which best corresponds to the experimental data. In differential thermal analysis the degree of reaction is defined as

$$\alpha = \Delta H_{ov} - \frac{\Delta H_t}{\Delta H_{ov}} \tag{3}$$

where ΔH_{ov} is the peak total area and ΔH_t is the area at a time t.

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

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

where k is the overall kinetic constant, A is a constant often called the frequency factor which is independent of temperature, proportional to the number of successful collisions of the reacting molecules, R is the gas constant (8.31 J mol^{-1} K^{-1}), and T is temperature in kelvin. The Arrhenius parameters (E_a and A) can be determined by plotting ln k against $1/RT$ in the customary fashion, from the slope and intercept, respectively, of the straight line obtained. In Figs. 4 and 5 we can see the obtained Arrhenius plot for the two monomers studied.

The results obtained from Arrhenius performance are shown in Table 8. As can be seen in this table, the activation energy and the frequency factor

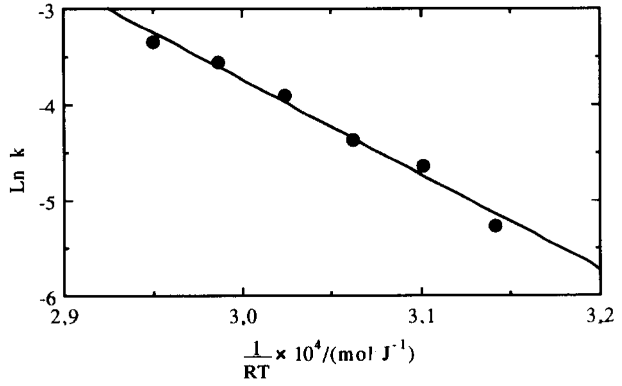

Fig. 4. Arrhenius plot for mono-2-diphenyl itaconate.

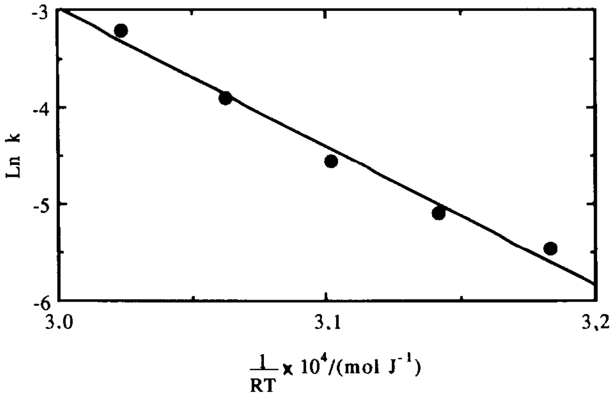

Fig. 5. Arrhenius plot for mono-4-diphenyl itaconate.

for mono-2-diphenyl itaconate are very close to the values obtained for other monoitaconates [5–7]. The solid state polymerization needs more energy that the melting state one; for this reason the Arrhenius equation parameters for mono-4-diphenyl itaconate are bigger than those for mono-2-diphenyl itaconate.

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

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

where k_p, k_t and k_d are the propagation, termination and decomposition kinetic constant rates, respectively. According to the above equations, the monomer order must be unity. For mono-2-diphenyl and mono-4-diphenyl itaconates we found an experimental kinetic order of 0.75 with respect to monomer. These differences between the experimental and theoretical kinetic orders may be due to the existence of diffusion processes in the monomer, as pointed out by North and Reed [10, 11]. However, there are at least two kinds of diffusion mechanism which can play a role in bimolecular termination: the translation diffusion of the chain centres and

TABLE 8

Kinetic parameters for mono-2-diphenyl and mono-4-diphenyl itaconates

Monomer	n	$E_a/(\text{kJ mol}^{-1})$	$\ln A$
Mono-2-diphenyl itaconate	3/4	98.42	25.78
Mono-4-diphenyl itaconate	3/4	142.8	39.86

the segmental diffusion of the active centres [12]. Further, recent work [13] indicates, that segmental diffusion is the slow step in the termination process and is hence rate determining.

The Eyring theory [14] provides a means for calculating the concentration of activated complexes and the rate at which they are converted into products. In this theory it is assumed that activated complexes are in equilibrium with reactants. this allows us to define an equilibrium constant in the activated state, $k^{\#}$. The overall kinetic rate constant k_{ov}, is related to $k^{\#}$ by

$$k_{\text{ov}} = \frac{kT}{h} k^{\#}$$

where k is the Boltzmann constant ($k = 1.38 \times 10^{-23}$ J K^{-1}) and h is Planck's constant ($h = 6.626 \times 10^{-34}$ J s). Taking into account that $k^{\#} = \exp(-\Delta G^{\#\circ}/RT)$ we have

$$k_{\text{ov}} = \frac{kT}{h} \exp(\Delta G^{\#\circ}/RT)$$

since $\Delta G^{\#\circ} = \Delta H^{\#\circ} - T\,\Delta S^{\#\circ}$

$$k_{\text{ov}} = \frac{kT}{h} \exp(-\Delta H^{\#\circ}/RT)\exp(\Delta S^{\#\circ}/R)$$

or

$$\ln\left(\frac{k_{\text{ov}}}{T}\right) = \ln\left(\frac{k}{h}\right) - \frac{\Delta H^{\#\circ}}{RT} + \frac{\Gamma S^{\#\circ}}{R}$$

Plotting $\ln(k_{\text{ov}}/T)$ against $1/T$ the slope and the intercept give $\Delta H^{\#\circ}$ and $\Delta S^{\#\circ}$ respectively. In Figs. 6 and 7 and Table 9 we can see the results obtained for the two monomers studied.

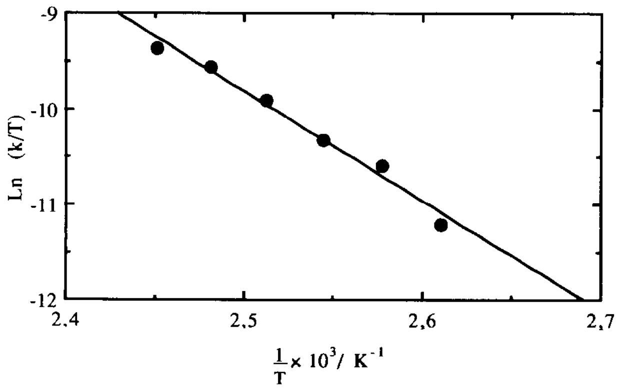

Fig. 6. Plot of $\ln(k_{\text{ov}}/T)$ against $(1/T)$ for mono-2-diphenyl itaconate.

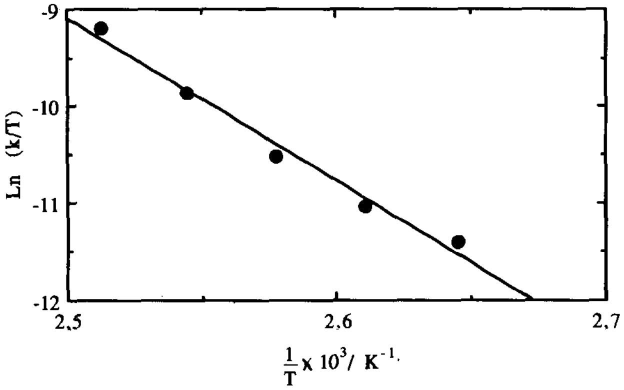

Fig. 7. Plot of $\ln(k_{ov}/T)$ against $(1/T)$ for mono-4-diphenyl itaconate.

TABLE 9

$\Delta H^{\#\circ}$ and $\Delta S^{\#\circ}$ for mono-2-diphenyl and mono-4-diphenyl itaconates

Monomer	$\Delta H^{\#\circ}$/(KJ mol^{-1})	$\Delta S^{\#\circ}$/(J mol^{-1} K^{-1})
Mono-2-diphenyl itaconate	95.1	−41.2
Mono-4-diphenyl itaconate	139.6	75.9

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REFERENCES

1 J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
2 Product Information Sheet Nos. 402–404, Pfizer Europe Chemicals, Sandwich, Kent.
3 S. Swarts, Bull. Acad. R. Belg., 36 (1873) 64.
4 B.E. Tate, Adv. Polym. Sci., 5 (1967) 214.
5 I. Katime, F. Palomares, L. C. Cesteros, C. Laborra and E. Domínguez, Thermochim. Acta, 132 (1988) 193.
6 I. Katime, A. Madoz and J.L. Velada, Thermochim. Acta, 189 (1991) 25.
7 I. Katime, A. Madoz and J.L. Velada, Thermochim. Acta, 220 (1993) 91.
8 K. Horie, I. Mita and H. Kambe, J. Polym. Sci., Part A1, 6 (1968) 2663.
9 E. Trommsdorff, H. Kohle and P. Lagally, Makromol. Chem., 1 (1948) 169.
10 A.M. North, Makromol. Chem., 49 (1961) 241.
11 A.M. North and G.A. Reed, Trans. Faraday Soc., 57 (1961) 859.
12 A.M. North and G.A. Reed, J. Polym. Sci., 41 (1963) 1311.
13 A.M. North and S.W. Benson, J. Am. Chem. Soc., 84 (1962) 935.
14 H. Eyring, J. Chem. Phys., 3 (1935) 107.