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KINETICS OF METHACRYLIC DERIVATES BULK POLYMERIZATION BY DTA. STUDY OF THE INFLUENCE OF THE MONOMER SIDE GROUP

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ABSTRACT

The kinetics of a set of methacrylates (t-butylphenyl methacrylate, 2,6-diisopropylphenyl methacrylate and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate) bulk self-initiated polymerization were determined by DTA in the temperature range 413–493 K, and in the presence of 1,2-azobisisobutyronitrile in the temperature range 373–453 K. The polymerization reaction orders, and the activation energies E_a were found to be dependent on the nature of the methacrylate side group as well as on the enthalpies involved in these processes. The influence of the monomer side group on the polymerization process is discussed.

INTRODUCTION

Although thermal analysis had its origins with Le Chatelier [1] in 1887, its application to polymers was restricted until about 15 years ago. Since then, there have been innumerable applications of differential thermal analysis (DTA) to polymers both for research and for routine analysis.

The DTA technique is based on the principle that almost all materials undergo changes in physical state or chemical composition when they are heated.

Differential thermal analysis (DTA), the oldest and most popular of the thermoanalytical techniques, and its close cousin differential scanning calorimetry (DSC) both measure heat flow into or out of a sample.

The great versatility of DTA and DSC stems from the fact that most physical or chemical changes in a sample will result in an energy change,

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with consequent heat flow. Consequently, the kinetics of polymerization which is an exothermic reaction can be easily followed by DTA or DSC, isothermally as well as dynamically.

Early studies of this type were carried out in liquid monomers, in bulk polymerizations for several vinyl monomers [2–8]. In previous papers we have studied the bulk polymerization kinetics of methacrylic dimethylaminoethyl ester acid [7] and 1-vinyl imidazole [9,10] by DTA in the temperature ranges 428–438 and 363–393 K, respectively. They are also applicable in the study of copolymerization kinetics [11,12].

This paper reports a study of the bulk polymerization kinetics, at total conversion, of several methacrylates: t-butylphenyl methacrylate, 2,6-diisopropylphenyl methacrylate and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate, using 1,2-azobisisobutyronitrile (AIBN) as initiator and without it, with the aim of quantifying the influence of monomer side groups in the process.

EXPERIMENTAL

The monomer, 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate (Fig. 1a) was prepared by the reaction of methacryloyl chloride with 4-(1,1,3,3-tetramethyl)phenol in benzene solution and *N*,*N*-dimethylaniline at reflux temperature for 96 h. Purification was achieved by repeated crystallization from methanol/water, to a constant melting point of 326 K; yield 82%. The purity of the monomer was checked by IR (KBr): 3030, 2850, 1750, 1640, 1600, 1460, 1380 and 830 cm^{-1}; and also by ^{1}H NMR ($CDCl_3$): $\tau = 7.2(4H)$, 6.35(3H), 5.75(1H), 2.1(3H), 1.8(2H), 1.4(6H) and 0.78(9H).

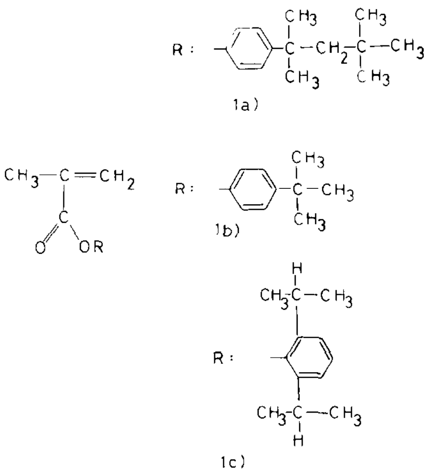

Fig. 1. Chemical structures of the monomers.

Para-t-butylphenyl methacrylate (Fig. 1b) was prepared by the reaction of methacryloyl chloride and the sodium salt of t-butylphenol according to the technique described by Patai et al. [13].

2.6-Diisopropylphenyl methacrylate (Fig. 1c) was prepared by reaction of methacryloyl chloride and 2,6-diisopropylphenol in benzene solution in the presence of diethylamine according to the technique described by Otsu et al. [14].

A weighed amount of 1,2-azobisisobutyronitrile (AIBN) (0.03–0.05 mg) was mixed with purified monomer (3–8 mg) and the mixture was placed in an aluminium standard crucible. For determinations without initiator, samples were prepared by placing 4–6 mg of monomer in aluminium standard crucibles. The cells were sealed and weighed using a Mettler balance with a precision of 5×10^{-6} g before being placed in the DTA furnace.

The kinetics of polymerization were studied in the temperature range 363–453 K using a Mettler TA 2000 differential thermal analyser system, equipped with a scanning auto-zero device for obtaining a straight baseline. The apparatus was calibrated using the heat of fusion of indium as reference (28.0 J g^{-1}).

The isothermal polymerizations were carried out by placing the aluminium crucibles containing the samples in the pre-heated furnace. For all measurements an empty reference crucible was used, with DTA measurements run at least in triplicate. Before performing the different isothermal polymerizations, the temperature range in which the monomers undergo polymerization and their temperatures of fusion were determined by making a dynamic calorimetric study of the samples. The temperatures of fusion obtained are 307.1, 311.6 and 323.8 K for t-butylphenyl methacrylate, 2,6-diisopropylphenyl methacrylate and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate monomers, respectively. The fusion enthalpies of every monomer were also calculated. The values obtained were 15.1, 22.4 and 27 kJ mol^{-1} for the t-butylphenyl methacrylate, 2,6-diisopropylphenyl methacrylate and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate, respectively. These values are logical considering the monomers' molecular weights and chemical structure.

The monomer reaction rate is calculated by supposing that the reaction heat is proportional to the conversion degree from monomer to polymer at any time

$$\mathrm{d}H = \mathrm{d}n \cdot \Delta H_{\mathrm{sp}} \qquad (1)$$

where ΔH_{sp} is the specific reaction enthalpy and n is the number of monomer moles converted to polymer at any moment. Equation (1) can be expressed as

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

therefore, the reaction rate is then 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 using 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

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

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.

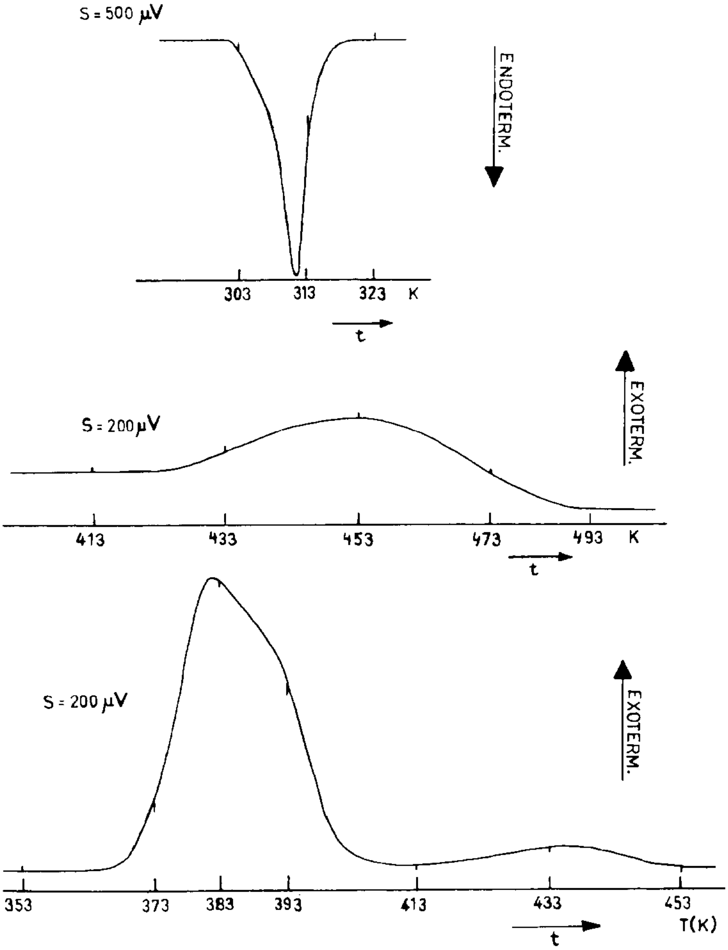

Fig. 2. Thermal behaviour of t-butylphenylmethacrylate, in the temperature range 413–493 K without AIBN, and in the range 353–453 K using AIBN as initiator.

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

Figures 2–4 show the thermal behaviour of the three methacrylates studied (t-butylphenyl methacrylate = TBFM, 2,6-diisopropylphenyl methacrylate = IPFM and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate = TOFM) in the temperature range 303–503 K, respectively. In these figures, the fusion of the monomers (endothermal peak) are observed as well as some exothermal peaks corresponding to the fused monomer polymerization processes. Note also the very different behaviour of these methacrylates according to the type of initiation utilized in the system. For instance, when initiation is purely thermal or self-initiated, only one exothermal peak is observed for every monomer, which corresponds to the temperature range of polymerization. The temperature ranges obtained are shown in Table 1. As can be seen in this table, as the monomer side group molar volume increases,

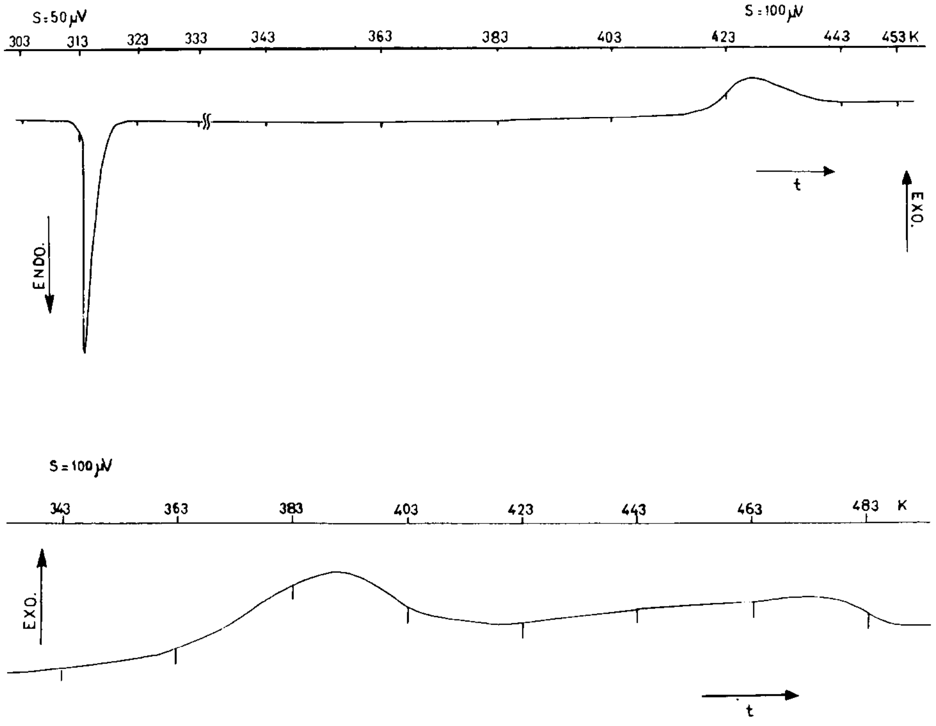

Fig. 3. Thermal behaviour of 2,6-diisopropylphenyl methacrylate, in the temperature range 303–453 K without initiator, and in the range 343–483 K using AIBN as initiator.

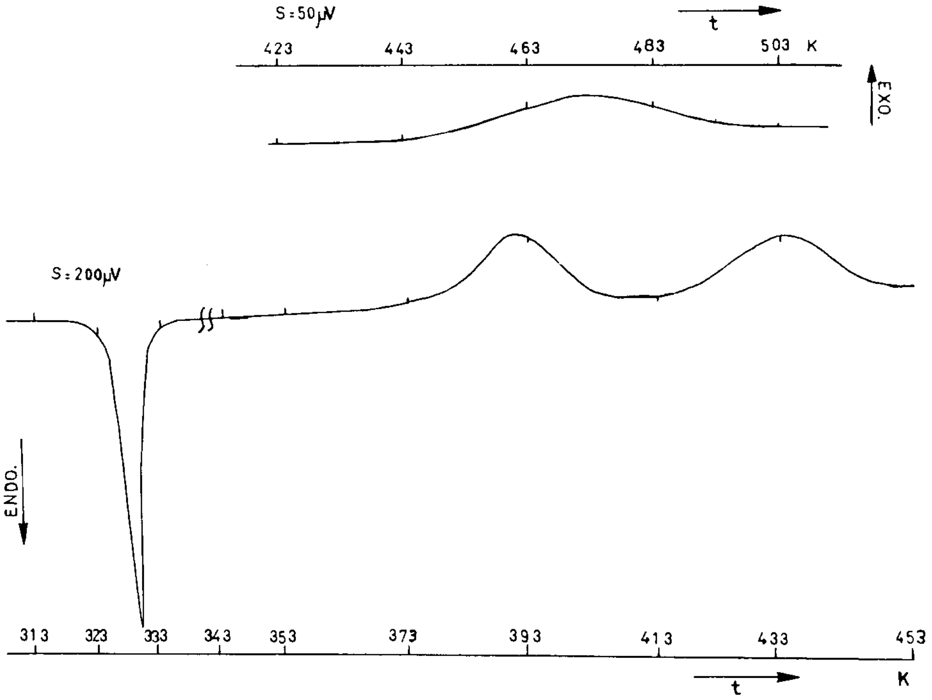

Fig. 4. Thermal behaviour of 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate, in the temperature range 423–503 K without AIBN, and in the range 343–453 K using AIBN.

the monomers become more difficult to polymerize. However, when AIBN is used as initiator, the kinetic situation changes considerably: two exothermal peaks at different temperature ranges are observed, and these start at lower temperatures than those for the self-initiated polymerization.

TABLE 1

Polymerization ranges of t-butylphenyl methacrylate (TBFM), 2,6-diisopropylphenyl methacrylate (IPFM) and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate (TOFM) monomers, with and without initiator

Monomer	Polymerization range (K)	
	Without AIBN	With AIBN
TBFM	415–480	373–413 423–453
IPFM	415–455	373–403 413–453
TOFM	450–495	373–413 423–453

AIBN, 1,2-azobisisobutyronitrile.

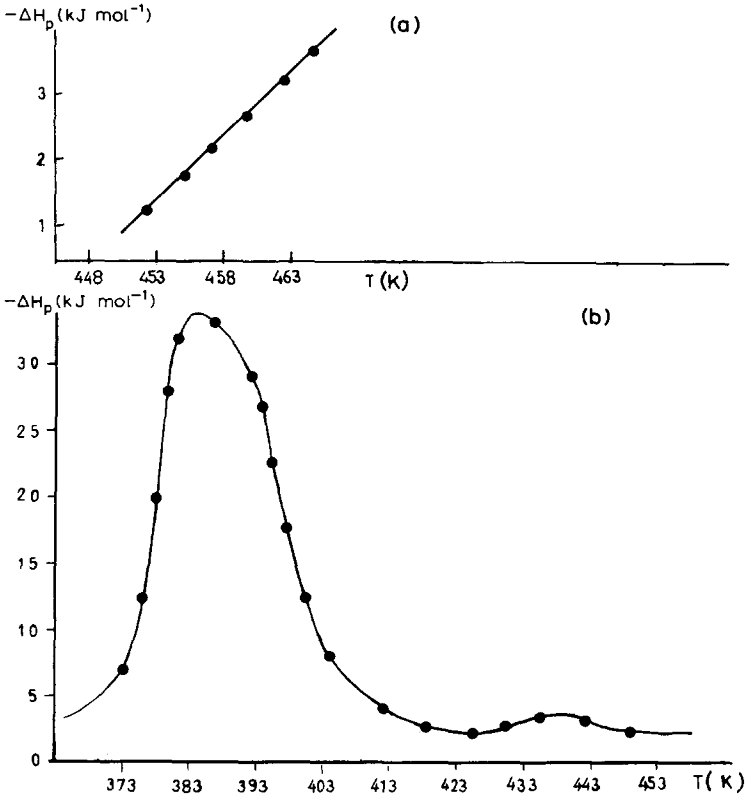

Fig. 5. Polymerization enthalpies of t-butylphenyl methacrylate obtained at constant temperature. (a) Without AIBN in the temperature range 448–463 K; (b) using AIBN in the temperature range 373–453 K.

For the three cases studied, the most important exothermal peak is always the one appearing at the lower temperature range. In order to explain this we have supposed that some radicals can remain trapped inside the polymer until the diffusion rates are increased (as a consequence of temperature increase) re-starting the polymerization process. Besides, if we compare the relative areas of these exothermal peaks (Figs. 2–4) we observe that the importance of this phenomenon increases from TBFM to TOFM. Because of this, we think that the cause of this behaviour may be the side group of the monomer.

We have also determined the enthalpies of polymerization ΔH of both systems (with and without initiator) in the whole temperature range studied. This dependence is shown in Figs. 5–7. First of all, it is necessary to point out that the dependence of the polymerization enthalpy on temperature in the self-initiated systems is very different from the dependence observed when AIBN is employed. For instance, for the purely thermal polymerization of these three monomers linear dependence is observed, while for the

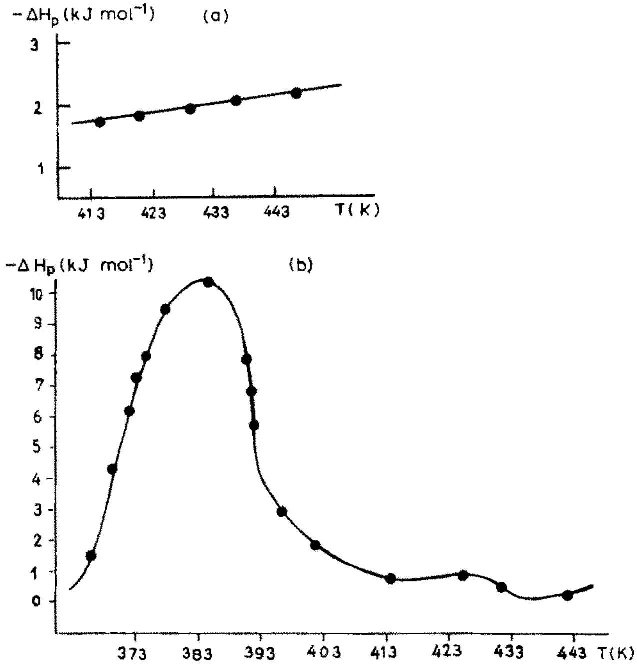

Fig. 6. Polymerization enthalpies of 2,6-diisopropylphenyl methacrylate constant temperature. (a) Without AIBN in the temperature range 413–443 K; (b) using AIBN in the temperature range 373–443 K.

TABLE 2

Overall rate constants and reaction orders for t-butylphenyl methacrylate (TBFM), 2,6-diisopropylphenyl methacrylate (IPFM) and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate (TOFM) in the temperature range 413–493 K, without initiator

Monomer	T (K)	k_{ov} [min^{-1} (mol/l)$^{1/2}$]	Order
TBFM	448	0.1685	1/2
	453	0.2252	1/2
	458	0.2193	1/2
	463	0.2095	1/2
IPFM	413	0.4065	1/2
	423	0.4965	1/2
	433	0.6376	1/2
	443	0.6703	1/2
	453	0.7408	1/2
TOFM	468	0.1861	1/2
	473	0.2312	1/2
	488	0.3603	1/2
	493	0.4459	1/2

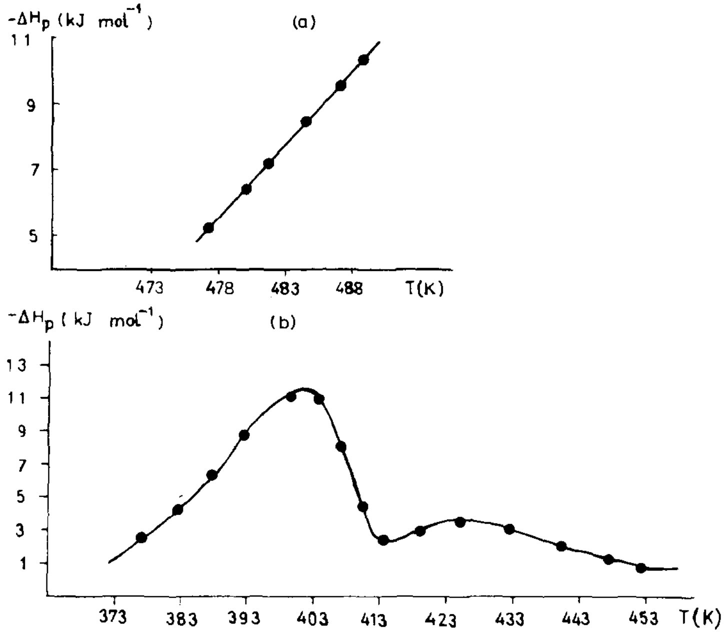

Fig. 7. Polymerization enthalpies of 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate at constant temperature. (a) Without AIBN in the temperature range 473–488 K; (b) using AIBN in the temperature range 373–453 K.

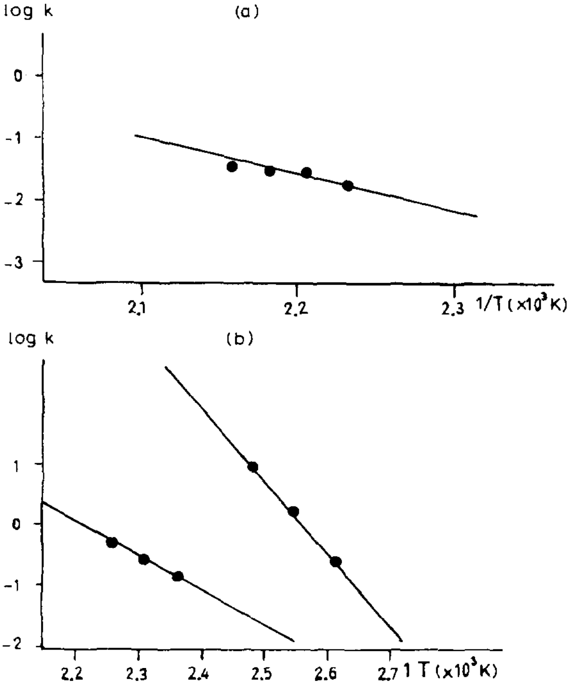

Fig. 8. Arrhenius plot for t-butylphenyl methacrylate. (a) Without initiator; (b) using AIBN as initiator.

TABLE 3

Overall rate constants and reaction orders for t-butylphenyl methacrylate (TBFM), 2,6-diisopropylphenyl methacrylate (IPFM) and 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate (TOFM) in the temperature range 373–453 K, using AIBN as initiator

Monomer	T (K)	k_{ov} (min^{-1})	Order
TBFM	383	0.5705	1
	393	1.293	1
	403	2.721	1
	413	4.932	1
	423	0.439	1
	433	0.606	1
	443	0.778	1
IPFM	373	0.258	1
	383	0.450	1
	393	1.221	1
	403	1.930	1
	413	0.766	1
	423	1.077	1
	443	1.161	1
TOFM	373	0.679	1
	383	1.139	1
	393	1.819	1
	403	2.916	1
	413	4.384	1
	423	0.411	1
	433	0.562	1
	443	0.712	1
	453	1.005	1

polymerization initiated with AIBN a maximum value of the polymerization enthalpy is always observed. The temperature values which correspond to these maxima are 383, 388 and 403 K for TBFM, IPFM and TOFM, respectively. As can be seen, the temperature corresponding to the maximum increases as the side group molar volume V_x increases. This confirms previous results [15], and gives evidence of the importance of the side group in this kind of polymerization.

We have also calculated the overall rate constants of polymerization for the three methacrylates with and without initiator, and the reaction orders of the different kinetics of polymerization using a BASIC program. The values obtained are summarized in Tables 2 and 3.

As can be seen in Table 3, there is an increase of the overall rate constant with temperature in the case of polymerization initiated by AIBN. From the dependence of the rate constants on temperature we have obtained the

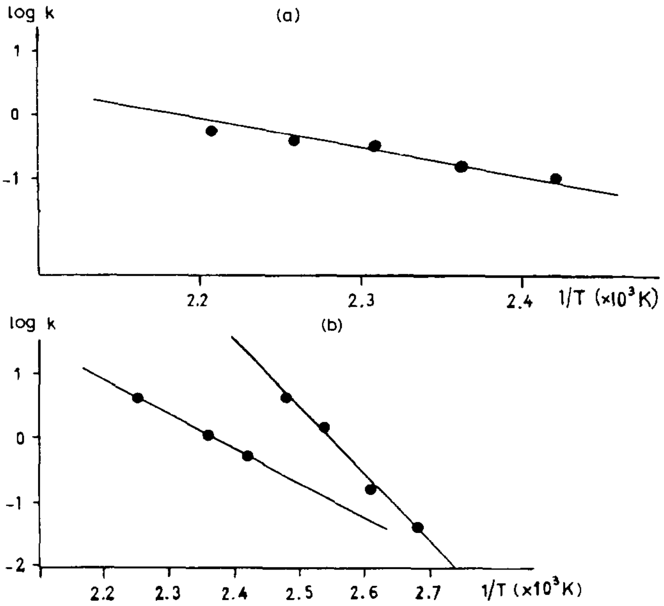

Fig. 9. Arrhenius plot for 2,6-diisopropylphenyl methacrylate. (a) Without initiator; (b) using AIBN as initiator.

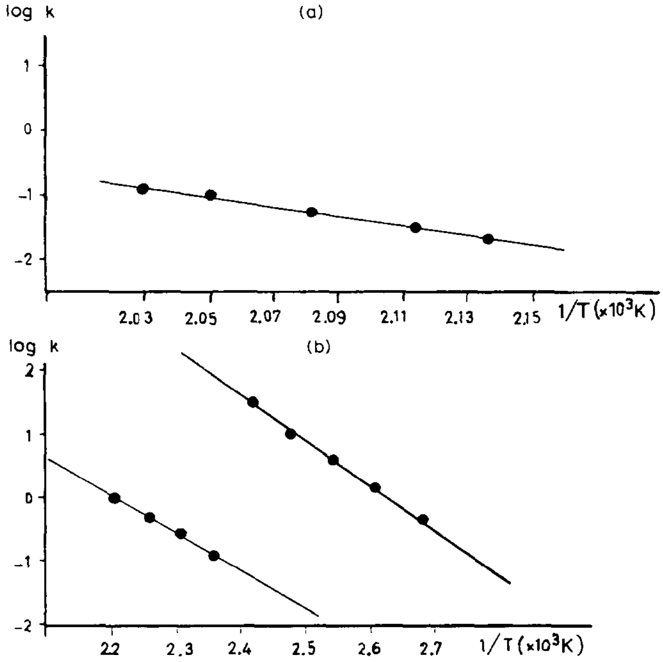

Fig. 10. Arrhenius plot for 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate. (a) Without initiator; (b) using AIBN as initiator.

Arrhenius plot for these systems, and the final results are shown in Figs. 8–10. Note that, for the polymerizations initiated by thermal homolytic dissociation of AIBN, two straight lines are obtained which correspond to the two temperature ranges previously described, and from their slopes the following values of activation energy, E_a, have been obtained

Monomer	E_a (kJ mol^{-1})	
TBFM	84.3 (373–413 K)	47.1 (423–443 K)
IPFM	86.7 (373–403 K)	44.7 (413–453 K)
TOFM	61.8 (373–413 K)	49.9 (423–453 K)

As shown in this table, the activation energy values of the second temperature range reinforce the above-mentioned hypothesis, suggesting that active species inside the polymer may be the cause of the second polymerization. In addition, these new values are nearly constant and lower than those of the first temperature range for all three monomers.

On the other hand, self-initiated polymerizations seem not to have this peculiarity and, as indicated in the next table, a unique temperature range and only one activation energy were obtained

Monomer	E_a (kJ mol^{-1})
TBFM	49.9 (448–463 K)
IPFM	45.7 (413–453 K)
TOFM	59.6 (468–493 K)

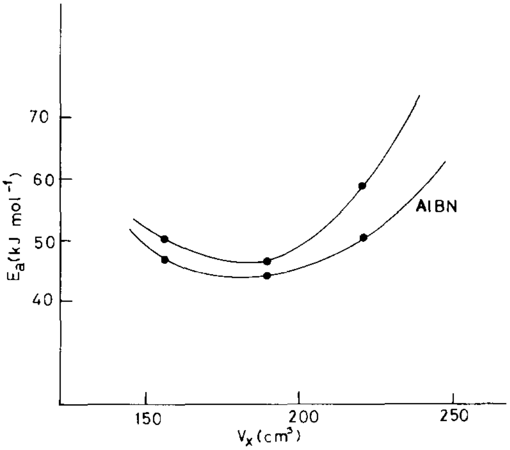

Fig. 11. Dependence of the activation energy, E_a on the molar volume of the monomer side group, V_x.

This behaviour seems to indicate that the AIBN initiator may be responsible for the phenomenon. When the activation energies obtained with and without initiator are compared in the same temperature range, we can see that the latter activation energies are higher, which is in agreement with theoretical predictions.

Likewise, we have determined the correlation between activation energy and monomer side group molar volume. Results are shown in Fig. 11. According to this new expression the result is very similar for the first two monomers: however, differences found for the TOFM monomer are more evident.

Finally we can conclude that the polymerization kinetics of vinyl monomers are influenced by the monomer side group.

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