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THERMOGRAVIMETRIC ANALYSIS OF POLYTHIOCARBONATES: THERMAL DECOMPOSITION TEMPERATURES AND KINETIC PARAMETERS

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ABSTRACT

The thermal stability and the kinetic parameters of a series of polythiocarbonates with aliphatic, aromatic, and cycloaliphatic side groups were studied. The thermal decomposition temperatures (TDT) are influenced by the structure of the polythiocarbonate because when the bulk of the side group increases the TDT values also increase. The activation energies were determined using the Arrhenius relationship and obey first-order kinetics, except for one polythiocarbonate which corresponds to zero-order kinetics. The activation energies are also related to the structure of the side groups. The activation energy of the polythiocarbonate from bisphenol A is very similar to that of the respective polycarbonate.

INTRODUCTION

Dynamic thermogravimetric analysis (TGA) has been widely used as a tool of investigation of the thermal stability of polymers, and has become prominent particularly in applications to fibres, plastics and other synthetic polymeric materials.

In TGA, weight changes of a sample are continuously recorded as a function of time or temperature as the sample is heated. Thermograms provide information concerning the sample composition, thermal stability and surface area as well as kinetic data relating to the chemical changes which occur on heating [1].

Polythiocarbonates are a new family of polymers which can offer parallel properties and applications to polycarbonates. In this field, only the thermal degradation of bisphenol A polycarbonate has been studied and the kinetic parameters determined; it has an attractive combination of mechanical properties and good stability, which makes it one of the most versatile engineering plastics [2].

The thermogravimetric behaviour of polythiocarbonates has not been reported in the literature, and the aim of this work is to prepare several polythiocarbonates having different side groups and to carry out thermogravimetric analysis to study the influence of the side groups on the thermal decomposition temperatures (TDT) and to determine their kinetic parameters.

EXPERIMENTAL

Polythiocarbonates were synthesized by phase transfer catalysis from the diphenols and thiophosgene using several quaternary ammonium and phosphonium salts in dichloromethane as solvent. The synthesis and characterization of these polymers have been described in our previous papers [3–4].

Dynamic thermogravimetric analyses were carried out in a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (5–7 mg) were placed in the platinum sample holder and the thermal degradation measurements were carried out between 25 °C and 650 °C at 20 °C min^{-1} under an N_2 atmosphere.

RESULTS AND DISCUSSION

Thermal decomposition temperatures

The structures of the polythiocarbonates studied are shown in Table 1, and are coded by the numbers **I–XVII**. Table 1 shows the values of the TDTs for each polythiocarbonate which were taken as the first strong change in the slope of the thermogravimetric curve.

Figure 1 shows the thermogravimetric curves for polythiocarbonates **I–III**, which degrade in a single-stage process and for which the TDT values are very similar. There is no great influence of the side chain on the degradation.

Thermogravimetric analyses of polythiocarbonates **IV** and **V** show similar behaviour, a single-stage process, but the side chain has some influence, as can be seen in Fig. 2; when the bulk of the side chain increases the TDT values also increase.

In polythiocarbonates **VI–VIII** (Fig. 3), which all have an aromatic side ring, the TDT values increase when the bulk of the aliphatic side chain increases. Polythiocarbonate **VI** shows a greater residue than polythiocarbonates **VII** and **VIII**, which is probably owing to the lack of an aliphatic group as a side chain.

Polythiocarbonates **IX** and **X**, without side chains, especially that which has no group between the aromatic rings, have low values of TDT as can be seen in Fig. 4. The residue in both polythiocarbonates is relatively high (40–50%) at the upper temperature, which is similar to those polythiocarbonates with an aromatic side ring.

TABLE 1

Thermal decomposition temperatures of polythiocarbonates

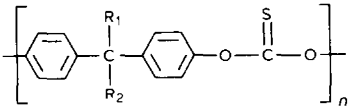
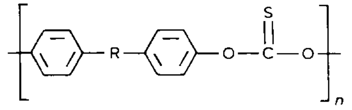
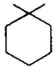
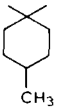
Polymer structure	TDT (°C)
	
(I) $R_1 \equiv -H$; $R_2 \equiv -CH_3$	415
(II) $R_1 \equiv -H$; $R_2 \equiv -CH_2CH_3$	387
(III) $R_1 \equiv -H$; $R_2 \equiv -CH_2CH_2CH_3$	420
(IV) $R_1 \equiv -H$; $R_2 \equiv -CH(CH_3)_2$	400
(V) $R_1 \equiv -H$; $R_2 \equiv -CH(CH_2CH_3)_2$	430
(VI) $R_1 \equiv -C_6H_5$; $R_2 \equiv -H$	325
(VII) $R_1 \equiv -C_6H_5$; $R_2 \equiv -CH_3$	385
(VIII) $R_1 \equiv -C_6H_5$; $R_2 \equiv -CH_2CH_3$	440
(IX) $R_1 \equiv R_2 \equiv -$	320
(X) $R_1 \equiv R_2 \equiv -H$	350
(XI) $R_1 \equiv R_2 \equiv -CH_3$	355
(XII) $R_1 \equiv -CH_3$; $R_2 \equiv -CH_2CH_3$	365
(XIII) $R_1 \equiv -CH_3$; $R_2 \equiv -CH_2CH(CH_3)_2$	405
(XIV) $R_1 \equiv R_2 \equiv -CH_2CH_3$	395
	
(XV) R = 	320
(XVI) R = 	397
(XVII) R = 	415

Figure 5 shows the thermogravimetric analyses of the polythiocarbonates **XI**–**XIV**, with two aliphatic side groups; there is an increase in the TDT values when the bulk of one of the side groups increases. This increase is more well known when there is a non-linear side group, such as *t*-butyl in polythiocarbonate **XIII**. The TDT value of polythiocarbonate **XIV**, with two ethyl groups, is very similar to that of polythiocarbonate **XIII**.

The thermal degradation of polythiocarbonates with cyclic central groups (**XV**–**XVII**) is shown in Fig. 6, and an important increase in the TDT values can be seen when the size of the cycle increases from cyclopentyl to

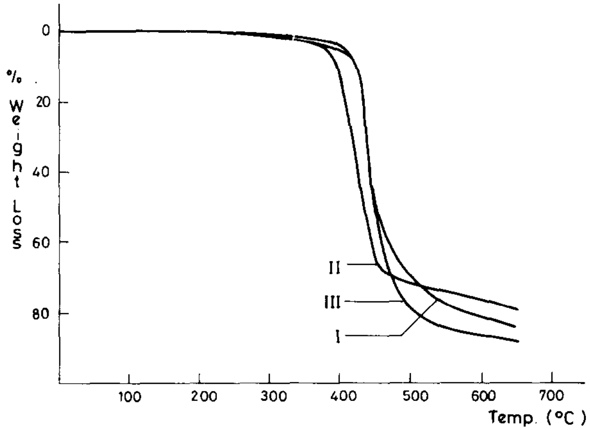


Fig. 1. Thermogravimetric curves of polythiocarbonates **I–III**.

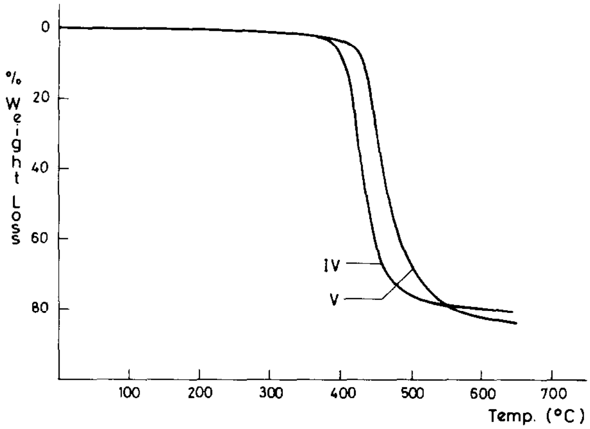


Fig. 2. Thermogravimetric curves of polythiocarbonates **IV** and **V**.

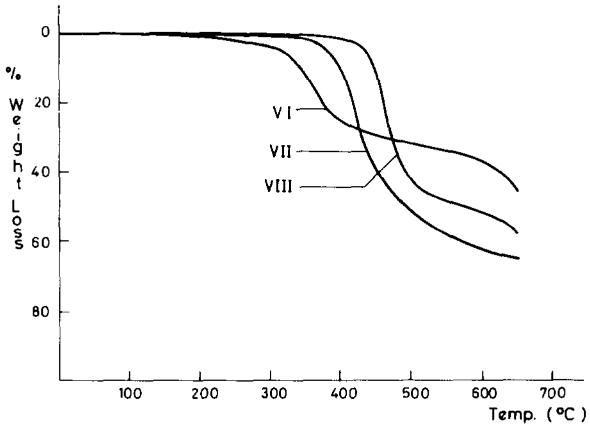


Fig. 3. Thermogravimetric curves of polythiocarbonates **VI–VIII**.

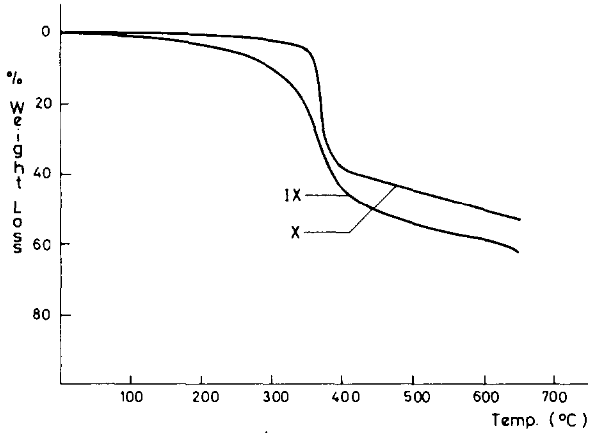


Fig. 4. Thermogravimetric curves of polythiocarbonates **IX** and **X**.

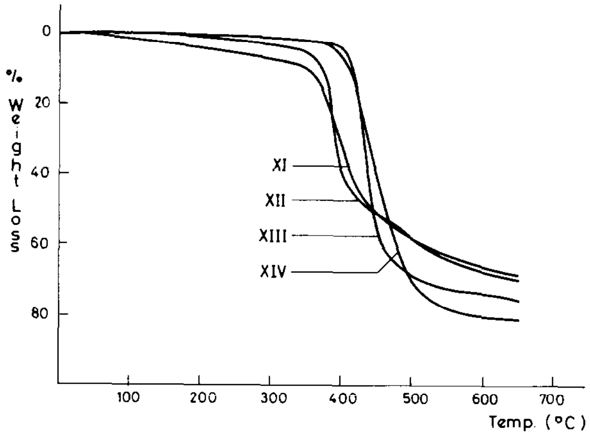


Fig. 5. Thermogravimetric curves of polythiocarbonates **XI–XIV**.

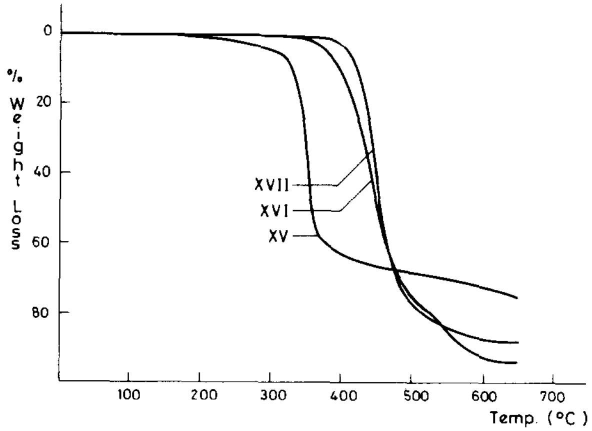


Fig. 6. Thermogravimetric curves of polythiocarbonates **XV–XVII**.

cyclohexyl. The increase in TDT when the size of the cycle increases from cyclohexyl to 4-methylcyclohexyl is smaller. The trend of the degradation curves is also a single-stage process, and the residue at 650 °C is high when the group is smaller.

From the above results we can see that the steric hindrance of the side groups appears to be responsible for the improved thermal stability and resistance of C–C bond scission in each group of the polythiocarbonates studied. Similar results have been reported for styrene-alkyl methacrylate copolymers and terpolymers [5]. However, in other systems such as the poly(alkyl acrylate) [6], poly(alkyl methacrylate) [7] and poly[*N*-(*n*-alkyl)-maleimide] systems [8], the thermal stability decreases when the bulk of the side chain increases. This opposite behaviour is probably because in polythiocarbonates the side chains are linked directly to the main chain, and in the other polymers the side chains are separated from the main chain by the ester group.

The thermograms obtained show that polythiocarbonates degrade in a single-stage process which is characteristic of the thermal decomposition of a great number of macromolecular compounds, and gives evidence that no other preferred or competitive and simultaneous process occurs.

The thermograms show that the residues are high (40–50%) in polythiocarbonates with a phenyl group as a side chain (**VI**) or when there are no side chains (**IX** and **X**). In polythiocarbonates with one or two aliphatic side chains or with a cycle between the main groups the residue is low (10–20%).

Kinetic parameters

The thermal decomposition kinetics of the thermogravimetric weight loss data were attributed to the kinetic equation

$$\frac{-\mathrm{d}\alpha}{\mathrm{d}t} = k_n(1-\alpha)^n \tag{1}$$

where α is a fraction of the sample weight reacted at time t and k_n is the specific rate with a reaction order n. The reaction rates $\mathrm{d}\alpha/\mathrm{d}t$ were calculated using a differential technique and directly incorporating the heating rate (20 °C min^{-1}) into the data of temperature vs. sample weight fraction [5]. The specific rates k_n were obtained from the Arrhenius relation

$$k_n = A\exp(-E/RT) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, T is the absolute temperature and R is the gas constant. The expressions (1) and (2) were combined and used in logarithmic form

$$\beta = \ln\left[\frac{-\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \tag{3}$$

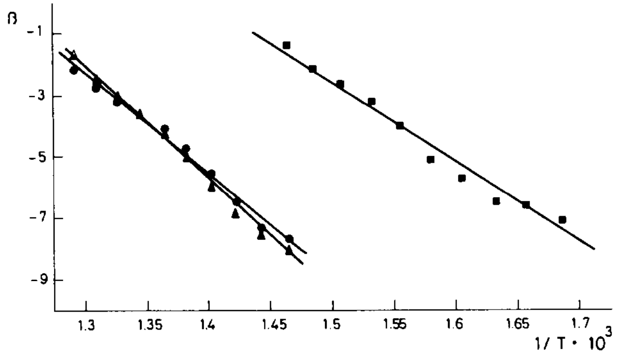


Fig. 7. Arrhenius plot for the degradation of polythiocarbonates **I** (●), **II** (■) and **III** (▲).

A linear multiple regression program was developed to calculate the kinetic parameters E and A from a linear least-squares fit of the data in a semilogarithmic plot of β vs. $1/T$. The first-order model was the best fit for the kinetic data of each polythiocarbonate, except for polythiocarbonate **IX** which fitted with $n = 0$. The kinetic parameters derived from the plots of Figs. 7–12 are summarized in Table 2. The linearity of each plot is good, although some scatter at the beginning and end of the decomposition was detected which can be attributed to the difficulty of obtaining accurate measurements at the beginning and end of an experiment, as is frequently encountered in kinetic measurements.

The activation energies obtained for each polythiocarbonate group with a similar side group show, in general, the same tendency as the values of TDT, in the sense that when the bulk of the side group increases the E values also increase.

The E value for polythiocarbonate **I** is surprisingly high in comparison with **II** and **III** (Fig. 7) but the trend is the same as that for the TDT values.

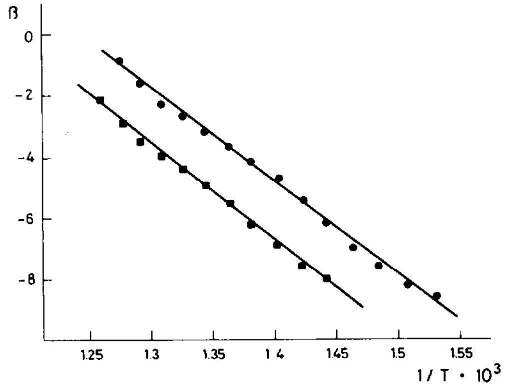


Fig. 8. Arrhenius plot for the degradation of polythiocarbonates **IV** (●) and **V** (■).

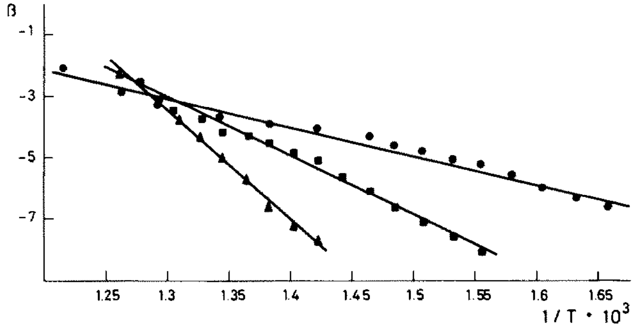


Fig. 9. Arrhenius plot for the degradation of polythiocarbonates **VI** (●), **VII** (■) and **VIII** (▲).

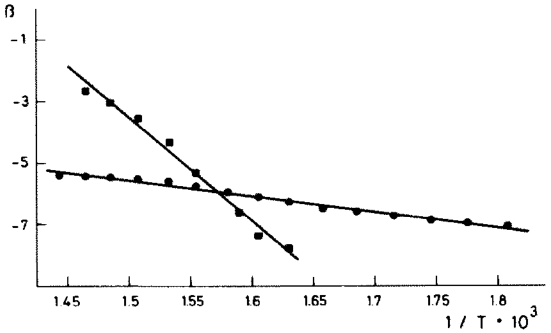


Fig. 10. Arrhenius plot for the degradation of polythiocarbonates **IX** (●) and **X** (■).

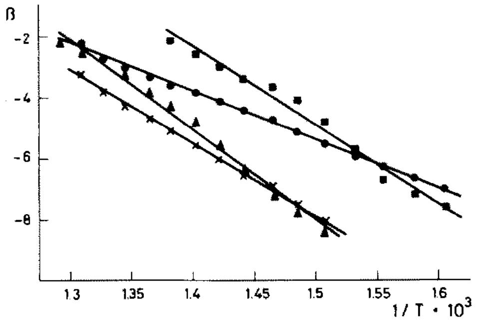


Fig. 11. Arrhenius plot for the degradation of polythiocarbonates **XI** (●), **XII** (■), **XIII** (▲) and **XIV** (×).

For polythiocarbonates **VI**–**VIII** (Fig. 9) the *E* values increase when the size of the side group increases, probably owing to additional hindrance effects of the aliphatic side chains.

Polythiocarbonates **IV** and **V** (Fig. 8) present high and similar *E* values and there is no influence of the side groups on the kinetic parameters. It is

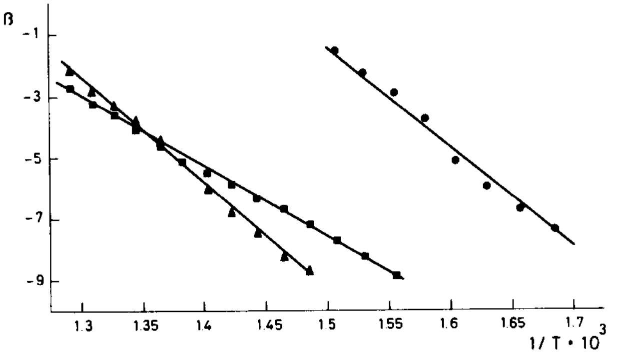


Fig. 12. Arrhenius plot for the degradation of polythiocarbonates **XV** (●), **XVI** (■) and **XVII** (▲).

probable that the non-linear structure of the side chain is responsible for these high values. Polythiocarbonate **XIII**, with a *t*-butyl group, shows a similar *E* value.

Polythiocarbonate **IX** (Fig. 10) shows a zero reaction order, which means that $-\mathrm{d}\alpha/\mathrm{d}t$ is constant, implying that if the sample mass is increased the rate of decrease in mass remains unchanged [9], probably because due to the lack of a carbon atom between the rings the rigidity of the chain is

TABLE 2

Kinetic parameters for polythiocarbonates

Polythiocarbonate	$A(\mathrm{s}^{-1})$	$E(\mathrm{kcal\ mol}^{-1})$
I	1.87×10^{17}	64.3
II	2.23×10^{14}	47.4
III	5.72×10^{19}	72.6
IV	2.80×10^{16}	60.6
V	9.87×10^{14}	58.3
VI	1.02×10^{4}	18.7
VII	6.80×10^{9}	39.1
VIII	6.44×10^{17}	68.0
IX	8.09	10.2
X	3.84×10^{18}	61.7
XI	1.78×10^{8}	32.3
XII	4.45×10^{14}	51.2
XIII	2.77×10^{16}	60.9
XIV	4.79×10^{12}	49.2
XV	7.57×10^{22}	71.3
XVI	1.23×10^{12}	47.0
XVII	1.34×10^{19}	70.8

enhanced. In polythiocarbonate **X** with a $-CH_2-$ group between the main rings, the flexibility of the chain and the E value increase with a first-order rate reaction.

In polythiocarbonates with two aliphatic chains (**XI–XIV**, Fig. 11) the activation energy values increase as the bulk of one chain increases, except for polythiocarbonate **XIV** with two ethyl groups which has a lower value, and the trend is the same as that of the TDT values. In this group of polythiocarbonates only **XI** from bisphenol A has an analogous polycarbonate which has been studied in depth. Several values of activation energy, between 21 and 39.5 kcal mol^{-1}, have been reported by different methods of detection for the polycarbonate of bisphenol A [10–15]. Values of 25 kcal mol^{-1} in sealed vacuum [10] and 33 kcal mol^{-1} in air [13] have been reported using thermogravimetry. The latter value is very similar to that obtained by us in N_2 for the polythiocarbonate of bisphenol A (32.3 kcal mol^{-1}) and it is probable that the structure of the diphenol would have more influence than the carbonyl or thiocarbonyl groups.

Polythiocarbonate **XV** (Fig. 12) with a cyclopentyl group between the aromatic rings shows a higher E value than polythiocarbonates **XVI** and **XVII**, probably owing to the greater rigidity of this ring. Polythiocarbonate **XVII** shows a larger E value than polythiocarbonate **XVI** which has no methyl group in the ring, showing the same trend as the TDT values.

In general, the E values of these polythiocarbonates show a trend similar to that of the TDT values in the sense that when the bulk of the side chain increases the E values also increase in each group of polythiocarbonates, which means that when the size of the side chain is greater, the energy necessary to begin the decomposition is also greater.

CONCLUSIONS

We can conclude that the thermal decomposition temperatures of the polythiocarbonates are greatly influenced by the nature (rigidity and volume) of the groups linked to the carbon atom between the rings of the main chain, in the sense that when the bulk of these groups increases, the TDT values also increase, considering the polythiocarbonates divided in groups with similar side chains. Similar behaviour was found by us when we studied the glass transition temperatures, T_g, of these polythiocarbonates [16].

The kinetic parameters also show the same trend, and obey first-order kinetics, except polythiocarbonate **IX** which shows zero-order kinetics owing probably to an enhanced rigidity of the chain when there is no group between the principal rings.

Finally, the E value obtained for the polythiocarbonate from bisphenol A is very similar to that obtained for the respective polycarbonate, which could mean that the influence of the main and side chains is greater than the carbonyl or thiocarbonyl groups.

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REFERENCES

1 T. Nguyen, E. Zavarin and E.M. Barrall, J. Macromol. Sci., Rev. Macromol. Chem., C20 (1981) 1.
2 K.B. Abbas, Polymer, 21 (1980) 936.
3 L.H. Tagle, F.R. Diaz, J.C. Vega and P.F. Alquinta, Makromol. Chem., 186 (1985) 915.
4 L.H. Tagle, F.R. Diaz and P.E. Riveros, Polym. J., 18 (1986) 501.
5 W.Y. Wen and J.W. Lin, J. Appl. Polym. Sci., 22 (1978) 2285.
6 N. Grassie and J.G. Speakman, J. Polym. Sci., Part A, 9 (1971) 919.
7 S.L. Malhotra, L. Minh and L.P. Blanchard, J. Macromol. Sci., Chem., A-19 (1983) 967.
8 J.M. Mazón-Arechederra and J.M. Barrales-Rienda, Polym. Degrad Stab., 15 (1986) 357.
9 G.G. Cameron and A. Rudin, J. Polym. Sci., Polym. Phys. Ed., 19 (1981) 1799.
10 M. Tomikawa, Chem. High Polym. (Jpn.) 20 (1963) 102.
11 Y. Sekine, K. Ikeda and H. Taketani, Kogyo Kagaku Zasshi, 72 (1969) 791.
12 A. Davis and J.H. Golden, Makromol. Chem., 78 (1964) 16.
13 L.H. Lee, J. Polym. Sci., Part A-1, 2 (1964) 2859.
14 B.M. Kovarskaya, M.S. Akutin, A.I. Sidneo, M.P. Yasvikova and M.B. Neiman, Polymer Sci. USSR, 5 (1963) 1346.
15 A. Davis and J.H. Golden, J. Chem. Soc., B, (1968) 45.
16 M. Yazdani-Pedram, E. Soto, L.H. Tagle, F.R. Díaz, L. Gargallo and D. Radic, Thermochim. Acta, 105 (1986) 149.