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THERMOGRAVIMETRIC ANALYSIS OF POLYCARBONATES AND POLYTHIOCARBONATES FROM DIPHENOLS WITH METHYL GROUPS

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ABSTRACT

The thermal behaviour of polycarbonates and polythiocarbonates derived from biphenols with methyl groups in the aromatic rings was studied by dynamic thermogravimetry. The thermal degradation temperatures (TDT) were determined, showing that polythiocarbonates are more stable than the corresponding polycarbonates. The kinetic parameters of the thermal decomposition were determined by using the Arrhenius relationship, and showed two steps for the degradation of the polycarbonates, the first being a zero-order process and the second having first-order kinetics; the steps were associated with two different reaction mechanisms. Polythiocarbonates degraded according to first-order kinetics.

INTRODUCTION

Thermogravimetry, a simple technique in which a sample is heated and weighed continuously, has been widely used to study the thermal stability of polymers. It provides kinetic information on the degradation and the mechanism of the process. Many of the applications of thermogravimetry have been in the characterization of polymeric materials, which include comparisons of relative thermal stability, studies of degradation kinetics, analysis of copolymeric systems, and others.

Bisphenol A polycarbonate, the best known of this kind of polymer, is a versatile engineering plastic, the thermogravimetric behaviour of which has been widely studied [1–4]. Davis and Golden [1–3] and Abbas [4] described the mechanism of the degradation of this polycarbonate. When the polycarbonate was heated in a sealed and evacuated vessel, it underwent random scission, but when the studies were carried out in a continuously evacuated system, the polycarbonate rapidly cross-linked by condensation reactions and formed an insoluble gel. These authors also studied the most significant volatile products, and found that CO_2, phenol and bisphenol A were the major products of the decomposition; it was concluded that the carbonate linkage was the most reactive group in the polymer.

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Several other studies have been carried out for determination of the kinetic parameters and the mechanism of the decomposition of several polymers. In their studies of degradation of polystyrene by dynamic thermogravimetry, Anderson and Freeman [5] suggested that the differences in activation energy and reaction order could be due to two different reaction mechanisms; one would be dominant in a lower temperature range and the other in a higher range. A similar result was reported by Rudin et al. [6].

Recently, two sets of work on the thermal decomposition of polymers containing the –S–C(O)–O– group have been reported. The thermal degradation of these polymers occurs through the decomposition of this group, with the evolution of CO, CO_2 and COS and the formation of thioether groups [7,8].

Polythiocarbonates are a new family of polymers, which we have synthesized, under phase transfer conditions, from several diphenols and thiophosgene [9–12]. The solution and thermal properties of these polymers have been studied over recent years [13–19]. Some polycarbonates were also synthesized using the same technique, and their thermal properties were studied [20,21].

In continuation of our work on the thermal degradation of polymers [21], in this paper we have studied the thermal decomposition and kinetic parameters of polycarbonates and polythiocarbonates derived from biphenols with methyl groups in the aromatic rings and several groups bonded to the central carbon atom.

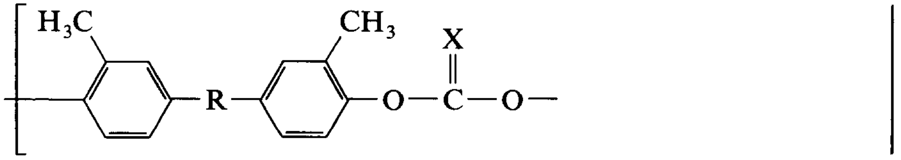
EXPERIMENTAL

The synthesis and characterization of polythiocarbonates (**Ib**–**IVb**) were described in a previous paper [11]. Polycarbonates (**Ia**–**IVa**) were synthesized from the diphenols and phosgene (20% in toluene solution) under phase transfer conditions, using quaternary ammonium salts as catalysts and CH_2Cl_2 as solvent, according to the procedure described in a previous paper [20], and were characterized by IR and ^{1}H NMR spectroscopy and elemental analysis.

Dynamic thermogravimetric analyses were carried out in a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (3–6 mg) were placed in the platinum sample holder, and the thermal degradation measurements were carried out between 25 and 650 °C at 20 °C min^{-1} under an N_2 atmosphere.

RESULTS AND DISCUSSION

The following polycarbonates and polythiocarbonates, synthesized under phase transfer catalysis conditions, were studied:

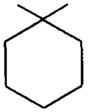


where

R = $CH_3-\overset{|}{\underset{|}{C}}-CH_3$ **Ia** X = O
Ib X = S

$CH_3-\overset{|}{\underset{|}{C}}-CH_2CH_3$ **IIa** X = O
IIb X = S

$CH_3-\overset{|}{\underset{|}{C}}-C_6H_5$ **IIIa** X = O
IIIb X = S



IVa X = O
IVb X = S

Figures 1–4 show the thermogravimetric curves for polymers **I**–**IV** respectively, and Table 1 gives the thermal decomposition temperatures (TDT), which were taken as the first marked change in the slope of the thermogravimetric curve.

By comparing the stability of polycarbonates and polythiocarbonates, it can be seen that the TDT values are practically constant even though the

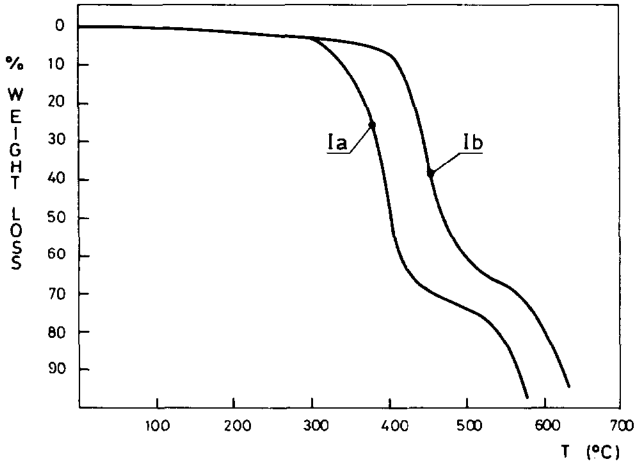


Fig. 1. Thermogravimetric curves for polymers **Ia** and **Ib**.

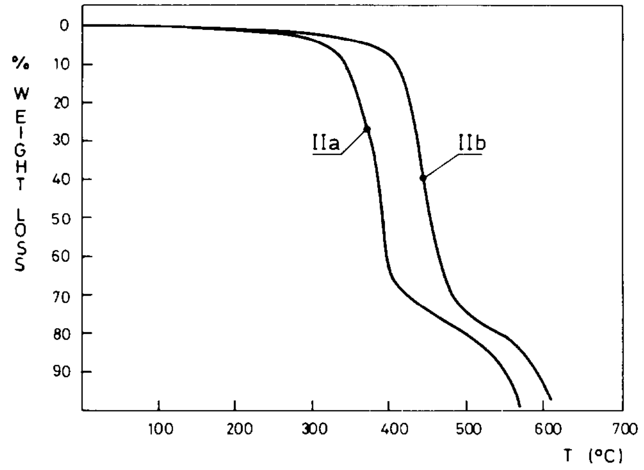


Fig. 2. Thermogravimetric curves for polymers **IIa** and **IIb**.

bulk of the side group, R, is increased, and that polythiocarbonates are more stable than polycarbonates. The variations that can be observed are small and cannot be attributed to structural factors.

In a previous paper we described the thermogravimetric analysis of polythiocarbonates with similar structure, but without methyl groups in the aromatic rings of the main chain. Those polythiocarbonates showed TDT values that depended on the structure of the side group; when the bulk of the side group was increased, the TDT values also increased. This behaviour was attributed to steric hindrance of the side groups, which appears to be responsible for the improved thermal resistance to C–C bond scission [15].

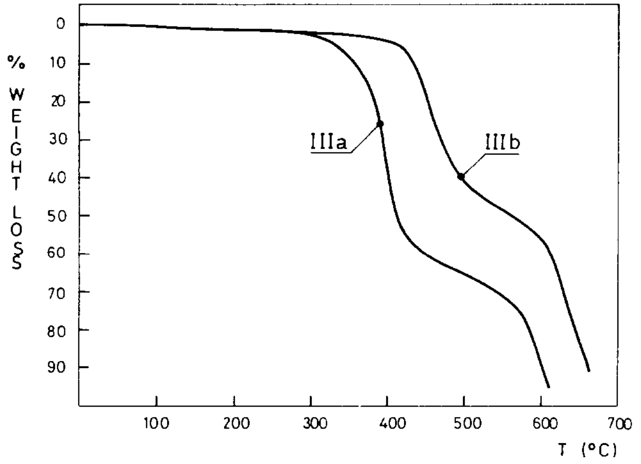


Fig. 3. Thermogravimetric curves for polymers **IIIa** and **IIIb**.

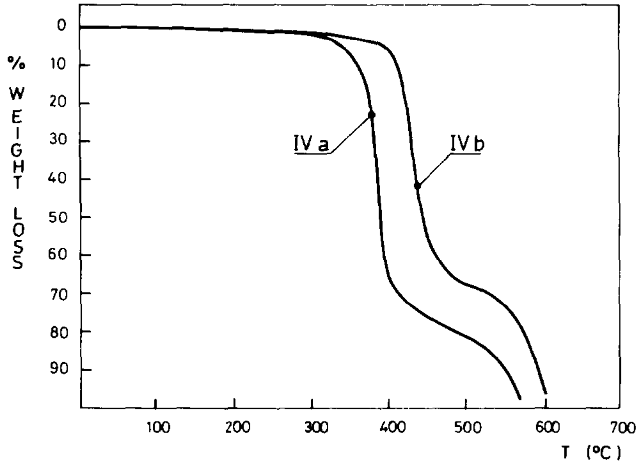


Fig. 4. Thermogravimetric curves for polymers **IVa** and **IVb**.

In the polythiocarbonates studied in this work, the methyl groups bonded to the aromatic rings in the main chain exert important steric hindrance, which was described in the synthetic step with respect to the nature of the phase transfer catalyst [11]. Probably these methyl groups also modify the thermal stability, and if this influence is greater than that of the side groups the TDT values of the polythiocarbonates will be similar.

The lower stability of polycarbonates may also be due to the partial double bond character of –C(O)–O, which is greater than that of –C(S)–O because of the difference in electronegativity between sulphur and oxygen. This double bond character may give the polycarbonates greater rigidity and lower thermal stability, even more so if we take into account that the thermal degradation of polymers is a cooperative phenomenon [13,14].

These results, showing that polythiocarbonates have higher stability than polycarbonates of similar structure, are presumably due to different degradation mechanisms. In fact, the thermograms show that polythio-

TABLE 1

Thermal decomposition temperatures of polycarbonates and polythiocarbonates

Polymer	TDT (°C)
Ia	360
Ib	413
IIa	367
IIb	413
IIIa	368
IIIb	421
IVa	370
IVb	407

carbonates degrade in a single stage over a specific range of temperature, whereas polycarbonates degrade in two stages.

We have determined the kinetic parameters of the thermogravimetric weight loss by using the kinetic equation

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

where α is the fraction of the sample weight reacted at time t and k_n is the specific rate with 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, according to the method of Wen and Lin [22]. The specific rates k_n were obtained from the Arrhenius relation

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

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

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

A computer 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 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.

TABLE 2

Kinetic parameters for polycarbonates and polythiocarbonates

Polymer	Temperature range (°C)	n	E (kcal mol^{-1})	A (s^{-1})
Ia	300–430	0	18.54	2.99×10^{3}
	440–520	1	17.66	5.74×10^{3}
Ib	390–540	1	40.85	9.28×10^{9}
IIa	300–420	0	21.19	2.50×10^{4}
	430–510	1	10.85	3.54×10
IIb	400–550	1	45.46	2.39×10^{11}
IIIa	320–440	0	20.12	7.83×10^{3}
	450–540	1	12.17	7.34×10
IIIb	400–570	1	38.34	8.51×10^{8}
IVa	300–420	0	25.37	4.82×10^{5}
	430–520	1	12.48	1.56×10^{2}
IVb	400–520	1	56.11	8.06×10^{14}

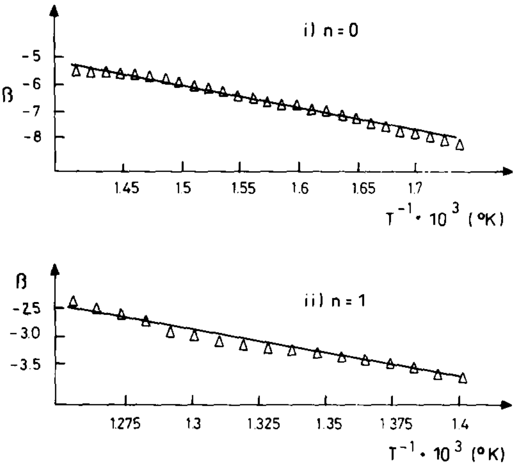


Fig. 5. Arrhenius plot for polycarbonate **Ia** degradation: (i) between 300 and 430 °C and $n = 0$; (ii) between 440 and 520 °C and $n = 1$.

Table 2 shows the values of the kinetic parameters for all the polymers studied; they were obtained from Figs. 5–12, which show good straight lines with a correlation greater than 0.99 at temperature intervals of 2.5 °C.

The results show that polycarbonates decompose in two steps, the first conforming to a zero reaction order and the second to a first-order reaction, with the temperature ranges being practically the same for all the polycarbonates. Polythiocarbonates, however, show a single-step decomposition in a range which is the same for all the polymers.

A zero-order reaction, which means that $-\mathrm{d}\alpha/\mathrm{d}t$ is constant, implies that, if the sample mass is increased, the rate of decrease in mass remains unchanged; this can happen if a constant concentration of volatile materials is maintained at the sample surface, as in a simple evaporation of preformed molecules. In the first-order case, the concentration of volatile materials depends on the residual active weight fraction [23,24].

Davis and Golden [2,3] and Abbas [4] studied the degradation of bisphenol A polycarbonate carried out in a continuously evacuated system, as

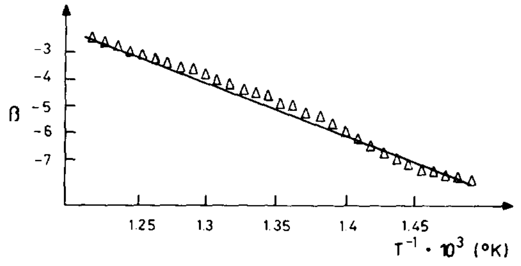


Fig. 6. Arrhenius plot for polythiocarbonate **Ib** degradation between 390–540 °C and $n = 1$.

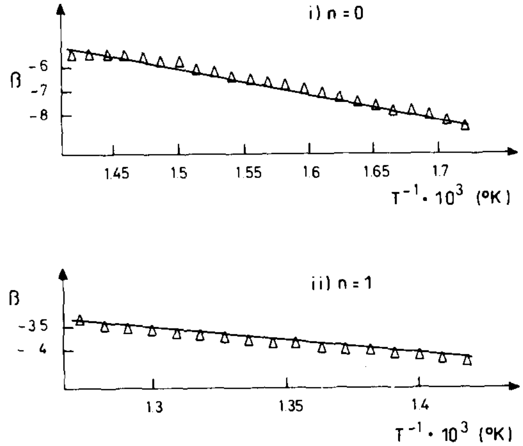


Fig. 7. Arrhenius plot for polycarbonate **IIa** degradation: (i) between 300 and 420 °C and $n = 0$; (ii) between 430 and 510 °C and $n = 1$.

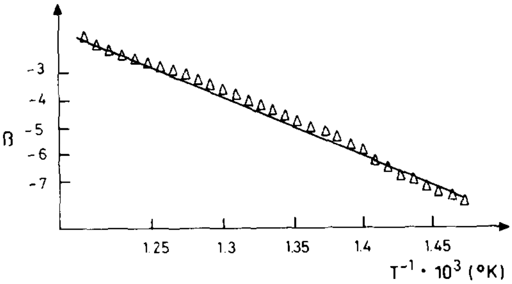


Fig. 8. Arrhenius plot for polythiocarbonate **IIb** degradation between 400 and 550 °C and $n = 1$.

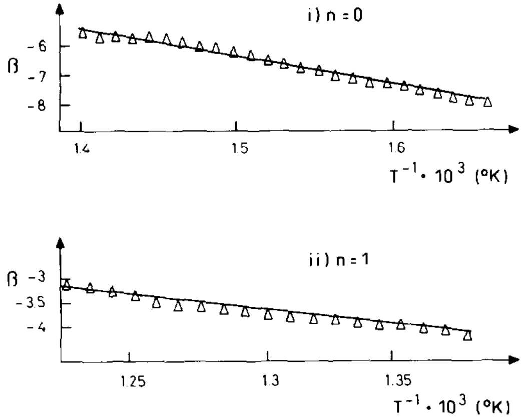


Fig. 9. Arrhenius plot for polycarbonate **IIIa** degradation: (i) between 320 and 440 °C and $n = 0$; (ii) between 450 and 540 °C and $n = 1$.

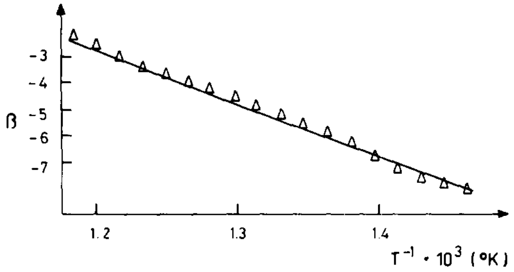


Fig. 10. Arrhenius plot for polythiocarbonate **IIIb** degradation between 400 and 570 °C and $n = 1$.

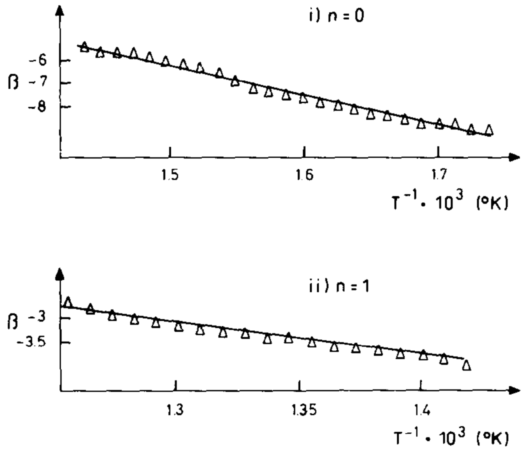


Fig. 11. Arrhenius plot for polycarbonate **IVa** degradation: (i) between 300 and 420 °C and $n = 0$; (ii) between 430 and 520 °C and $n = 1$.

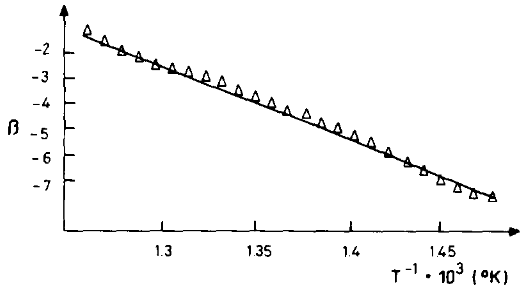


Fig. 12. Arrhenius plot for polythiocarbonate **IVb** degradation between 400 and 520 °C and $n = 1$.

in this work, and they proposed a mechanism in which the first step is the rearrangement of the carbonate group to form a pendent carboxy group *ortho* to an ether link in the main chain. This undergoes several reactions, such as the loss of CO_2 or, especially, condensation to produce cross-linked polymers, which form an insoluble gel, also with loss of CO_2. The major product of the decomposition is CO_2, indicating that the carbonate group is the most reactive group in the polymer.

Thus, it is probable that the first step in polycarbonate degradation occurs through the rearrangement of the carbonate group to a carboxy group in the *ortho* position, and the gelation of the polymer with loss of CO_2; the second step would be the breakdown of this cross-linked polymer.

The above mechanism is not wholly valid in polythiocarbonate decomposition. The possibility of rearrangement of the thermolabile thiocarbonate group is slight, and it is probable that COS formation and ether linkage in the main chain would be more important. In other polymers with –O–C(O)–S– and –S–C(O)–S– groups, but not the thiocarbonyl –C(S)– group, it has been reported that thermal degradation occurs through the decomposition of the thiocarbonate group, with evolution of CO, CO_2 and COS, and the formation of a thioether group [7,8].

In the polythiocarbonates with the –O–C(S)–O– group, there is no rearrangement of the thiocarbonyl group, and the decomposition will occur principally through the scission of the thiocarbonyl group, COS evolution and formation of an ether linkage in the main chain; subsequently, through a more complex mechanism, cross-linked polymers will be produced that degrade at higher temperatures.

Furthermore, when polycarbonates and polythiocarbonates are heated to the thermal decomposition temperature, they all form an insoluble gel; this would be indicative of a cross-linked polymer according to the mechanism proposed by Davis and Golden [2,3].

As was described for polythiocarbonates without methyl groups in the main rings [15], in polythiocarbonates with two aliphatic side-groups (**Ib** and **IIb**), the activation energy values increase as the bulk of one chain increases. As the values are higher than those reported for the analogous polythiocarbonates without methyl groups, the influence of the methyl groups on the thermal decomposition is confirmed.

CONCLUSIONS

It can be concluded that the thermal decomposition of polycarbonates and polythiocarbonates with methyl groups in the aromatic rings of the main chain, and various R groups as side chains, involves different mechanisms, and takes place in two steps for polycarbonates and in one step for polythiocarbonates. The degradation of polycarbonates appears to be similar to that proposed by Davis and Golden, in which the carbonate groups rearrange to a carboxylic group *ortho* to an ether linkage and cross-linking then occurs. In contrast, in polythiocarbonates the rearrangement of the thiocarbonate group is difficult; polythiocarbonates probably decompose to form COS and an ether linkage in the main chain, and then become cross-linked to a more complex species.

The R groups have little influence on the TDT values, which are very similar for each type of polymer, probably due to the influence of the methyl groups in the aromatic rings in the *ortho* position to the carbonate or thiocarbonate group, which are the most reactive groups in the polymers.

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