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# Thermogravimetric Analysis of Polycarbonates and Polythiocarbonates with Chlorine Atoms

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The thermal stability and kinetics parameters of polycarbonates and polythiocarbonates derived from diphenols with chlorine atoms in the aromatic rings were studied, showing that polycarbonates have a higher thermal stability than the polythiocarbonates. All polymers degraded in a single stage in the considered temperature range, and the kinetics parameters were determined by using the Arrhenius relationship and a computer program. Polycarbonates degraded by a zero order kinetics, while polythiocarbonates by a first order kinetic.

**KEY WORDS** Thermogravimetry, polycarbonates, polythiocarbonates, chloride

## INTRODUCTION

Dynamic thermogravimetry, with a linear temperature increase is a useful tool to study the degradation of polymeric materials. Also, with the appropriate mathematical treatment, it is possible to know in certain range of temperature the kinetics parameters as the activation energy, the reaction order and the pre-exponential factor, which in spite of its low significance, can be useful for calculating the rate of reaction and for design purposes.

In dynamic thermogravimetry, the weight loss can be determined as the temperature is increased at a definite heating rate, being the curves characteristic of each polymer, because the reactions that occur over defined ranges of temperatures are functions of the molecular structure.

In the past year we have applied dynamic thermogravimetry for the thermal analysis of several kinds of polymers, as polycarbonates, polythiocarbonates and polyesters, in order to study the influence of the structure of the monomers in the thermal decomposition temperatures, and to determine the kinetic parameters associated with the decomposition process.<sup>1–4</sup>

Continuing these works, in this paper we describe the thermogravimetric behaviour of polycarbonates and polythiocarbonates derived from diphenols with chlorine atoms in the aromatic rings. The thermal decomposition temperatures and

the kinetics parameters associated with the decomposition process were determined.

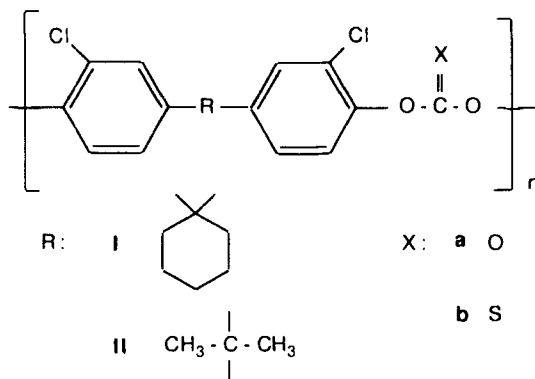
## EXPERIMENTAL

Polycarbonates and polythiocarbonates were synthesized from 1,1-bis(4-hydroxy-3-chloro-phenyl)-cyclohexane (**I**) and 2,2-bis(4-hydroxy-3-chloro-phenyl)-propane (**II**) with phosgene and thiophosgene respectively under phase transfer conditions according to a procedure described earlier.<sup>5</sup>

Thermogravimetric analysis were carried out in a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature control. Samples of 4-7 mg were placed in a platinum sample holder and the thermodegradation measurements were carried out between 25 and 650°C with a heating rate of 20°C min<sup>-1</sup> under N<sub>2</sub> flow.

## RESULTS AND DISCUSSION

Polycarbonates and polythiocarbonates with the following structure



were synthesized from the diphenols 1,1-bis(4-hydroxy-3-chloro-phenyl)-cyclohexane (**I**) and 2,2-bis(4-hydroxy-3-chloro-phenyl)-propane (**II**) and phosgene and thiophosgene respectively, under phase transfer conditions using several quaternary ammonium salts as catalysts according to a procedure described earlier, and characterized by IR and <sup>1</sup>H NMR spectroscopy and elemental analysis.<sup>5</sup>

Table I shows the thermal decomposition temperatures (TDT) for all polymers, taken when polymers lost 10% of their weight, and Figures 1-4 show the thermogravimetric curves.

By comparing the stability of polycarbonates and polythiocarbonates, it can be seen that polycarbonates are more stable than polythiocarbonates as has been described for polycarbonates and polythiocarbonates derived from other diphenols.<sup>2,6</sup> On the other hand, for polythiocarbonates it can be seen that when the bulk

TABLE I  
Thermal decomposition temperatures (TDT) of polycarbonates and polythiocarbonates

| Polymer | TDT (°C) |
|---------|----------|
| I a     | 423      |
| I b     | 400      |
| II a    | 445      |
| II b    | 385      |

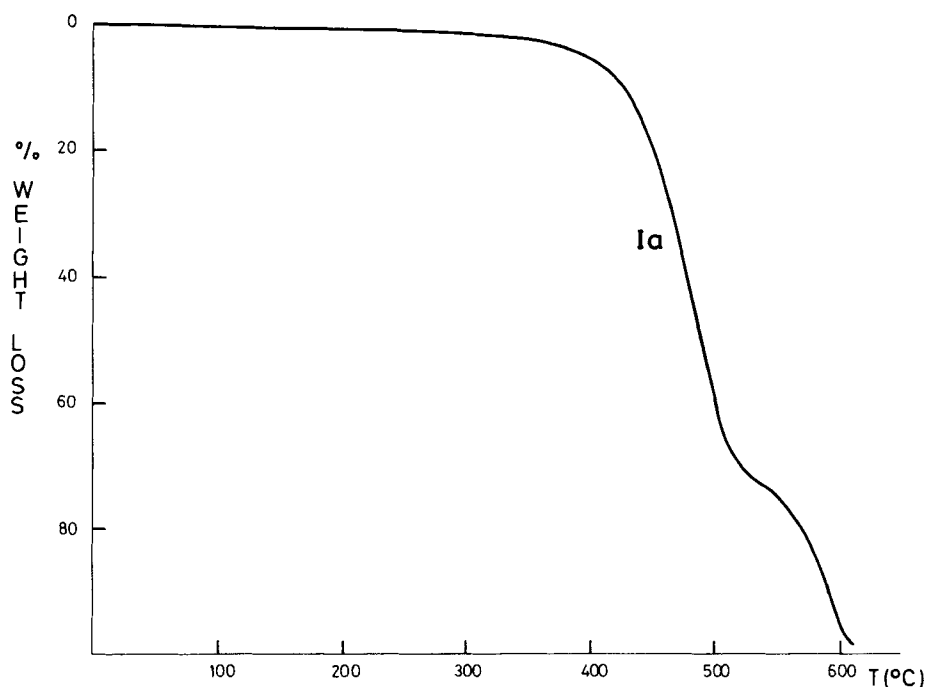


FIGURE 1 Thermogravimetric curve for polycarbonate Ia.

of  $R$  is increased, also the TDT values increased, as was described for analogous polythiocarbonates without Cl atoms, behaviour that was attributed to the steric hindrance of the side group, which appears to be responsible for the improved thermal resistance of C—C bond scission.<sup>1</sup> For polycarbonates, we observed the inverse effect, in the sense that polymer Ia was more stable than IIa that has a lower side group, which can be due to the lower molecular weight of Ia.<sup>5</sup>

It has been shown that the presence of chlorine atoms in some polymers increases the thermal stability.<sup>7</sup> When we compared the TDT values of polythiocarbonates Ib and IIb with the analogous without chlorine atoms,<sup>1</sup> there is an increase, es-

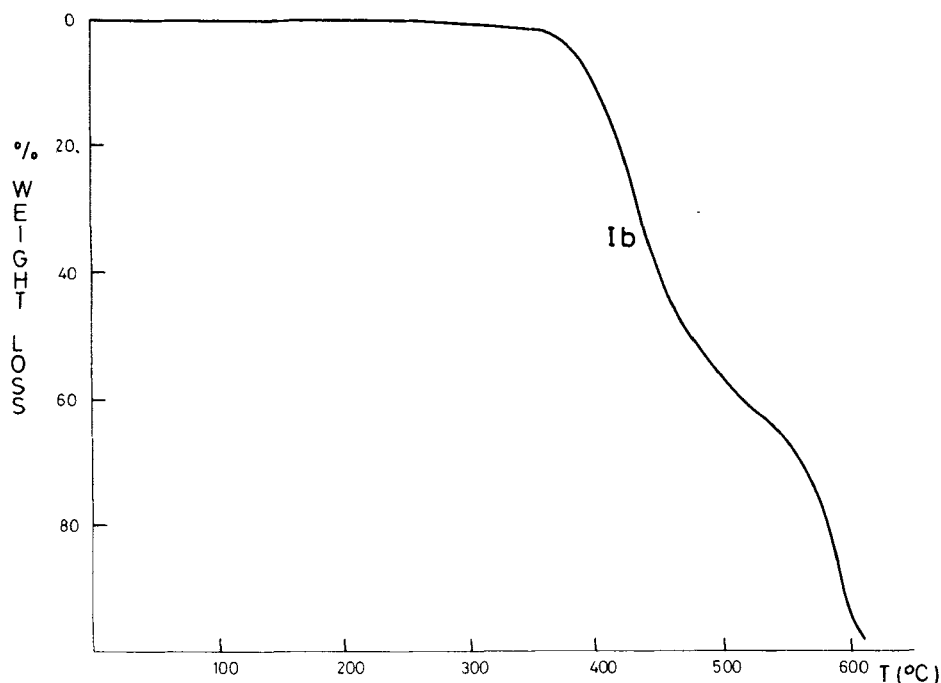


FIGURE 2 Thermogravimetric curve for polythiocarbonate **Ib**.

pecially for **IIb**, of 30°; for **Ib** the values are very similar, probably due to the low molecular weight that we always have obtained with diphenols that have a cycle as side group.

The kinetics parameters of the thermogravimetric weight loss were calculated according to the multiple linear regression method, using the kinetic equation

$$-(d\alpha/dt) = k_n(1 - \alpha)^n \quad (1)$$

where  $\alpha$  is the fraction of the sample weight at time  $t$ , and  $k_n$  the specific rate with reaction order  $n$ . The reaction rates  $-(d\alpha/dt)$  were calculated using a differential technique with the heating rate ( $20^\circ\text{C min}^{-1}$ ) incorporated directly into the temperature versus sample weight-fraction data, according to the procedure developed by Wen and Lin.<sup>8</sup> The specific rates were calculated from the Arrhenius relation

$$k_n = A \exp(-E/RT) \quad (2)$$

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

$$\beta = \ln[-(d\alpha/dT)/3(1 - \alpha)^n] = \ln A - E/RT \quad (3)$$

A computer lineal multiple-regression program was developed to calculate the

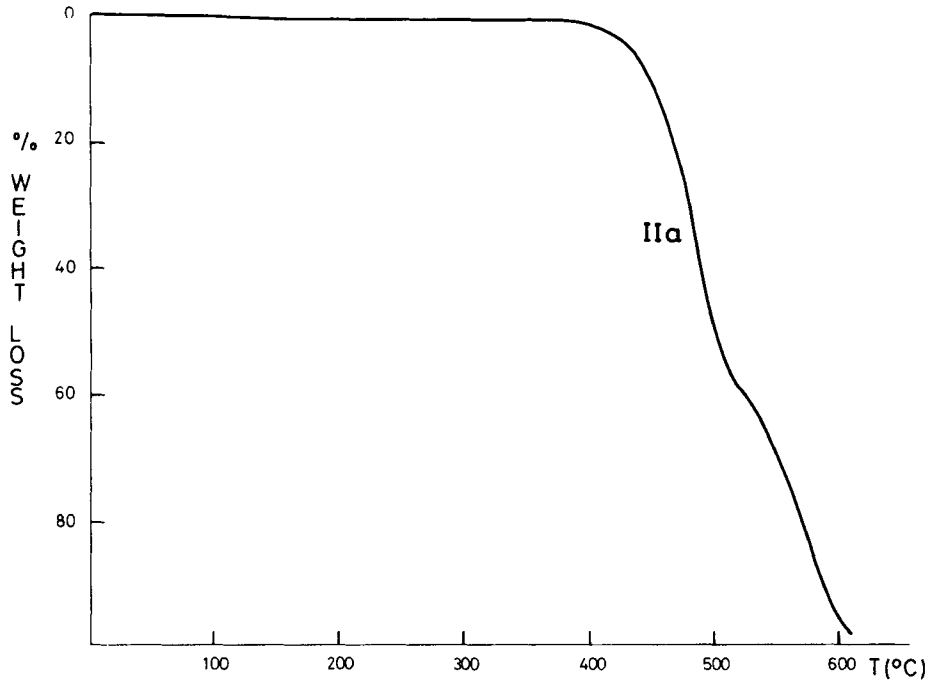


FIGURE 3 Thermogravimetric curve for polycarbonate IIa.

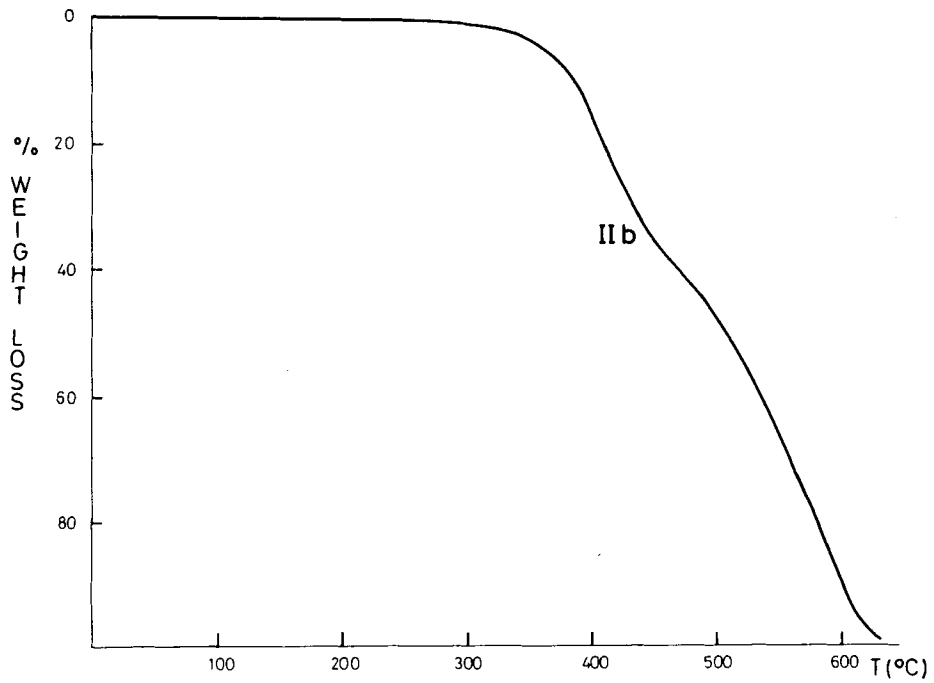


FIGURE 4 Thermogravimetric curve for polythiocarbonate IIb.

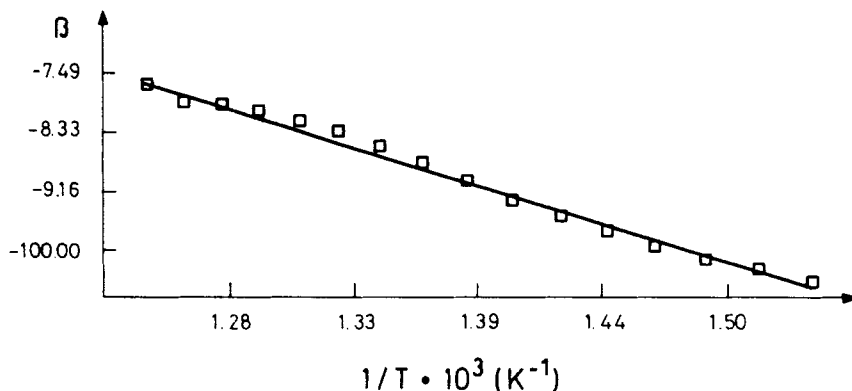


FIGURE 5 Arrhenius plot for the degradation of polycarbonate Ia.

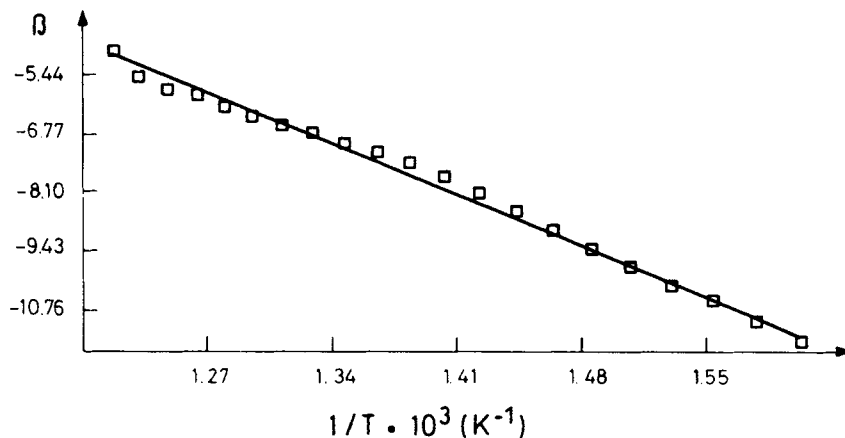


FIGURE 6 Arrhenius plot for the degradation of polythiocarbonate Ib.

kinetics parameters  $E$  and  $A$  from a linear least-squares fit of the data in semi-logarithmic plots of  $\beta$  versus  $1/T$ , which are shown in Figures 5–8. The figures show good straight lines with a correlation greater than 0.99 at intervals of  $10^\circ\text{C}$ . Table II shows the values of the kinetics parameters, the reaction order and the temperature range in which were calculated.

Polythiocarbonates decompose in one step with a first reaction order, which implies that the rate of the mass loss depends on the concentration of volatile materials. On the other hand, polycarbonates also decompose in one step, but with a zero reaction order. A zero reaction order means that  $-(dx/dt)$  is constant, and implies that if the sample mass is increased, the rate of decrease in mass remains constant, which can happen if a constant concentration of volatile materials is maintained at the sample surface, as in simple evaporation of preformed molecules.<sup>9</sup> It has been described that polythiocarbonates degrade according to a first order kinetic,<sup>1–3,6</sup> but polycarbonates can degrade according to a zero kinetic order or to a first kinetic order, which depends on the molecular weight and the polydispersity index,<sup>10</sup> according to the mechanism proposed by Davis and Golden and Abbas.<sup>11–13</sup>

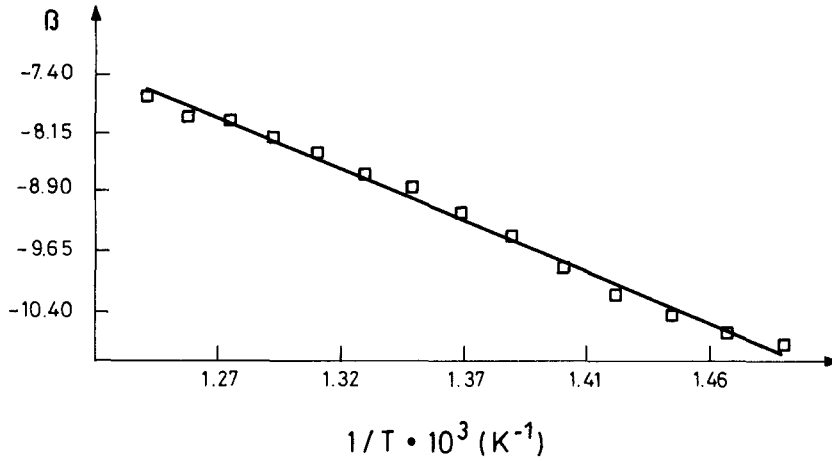
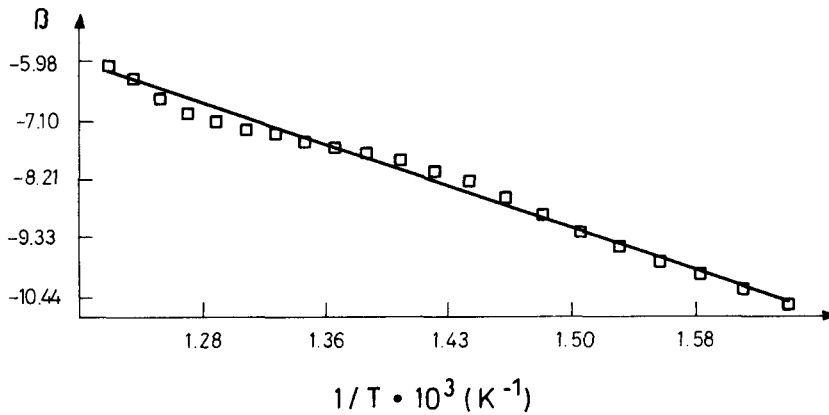
FIGURE 7 Arrhenius plot for the degradation of polycarbonate **IIa**.FIGURE 8 Arrhenius plot for the degradation of polythiocarbonate **IIb**.

TABLE II

Kinetic parameters of the thermal decomposition of polycarbonates and polythiocarbonates

| Polymer     | Range (°C) | n | E (kcal/mol) | A (seg <sup>-1</sup> ) |
|-------------|------------|---|--------------|------------------------|
| <b>I a</b>  | 380 - 523  | 0 | 21.19        | $3.12 \times 10^2$     |
| <b>I b</b>  | 350 - 550  | 1 | 32.91        | $4.21 \times 10^6$     |
| <b>II a</b> | 400 - 530  | 0 | 28.40        | $2.97 \times 10^4$     |
| <b>II b</b> | 340 - 540  | 1 | 22.50        | $2.56 \times 10^3$     |



The experimental conditions used in the degradation process were similar to that used by Davis and Golden for the degradation of the bisphenol A polycarbonate: a continuously evacuated system,<sup>11,12</sup> in which the first step of the mechanism is the rearrangement of the carbonate group to form a pendant carboxy group ortho to an ether link in the main chain, which undergoes other reactions (principally condensations) and then crosslinks with other polymeric chains to form an insoluble gel with the loss of CO<sub>2</sub>, which is the major product, indicating that the carbonate group is the most reactive group in the polycarbonate. Then, when the temperature is increased, the insoluble gel is degraded to a little volatile molecules. It is probably that the mechanism for the degradation of these polycarbonates was similar to that described by Davis and Golden.

In polythiocarbonates, the rearrangement of the thiocarbonate group is not possible because of the low stability of the —COSH group, and therefore the loss of COS and the formation of an ether linkage in the main chain are more probable.

It has been described that the kinetics parameters have a limited significance for complex reactions as those that occur in thermal degradation of condensation polymers, because the physical state of the sample is far from the ideal and may change during the reaction. On the other hand, it is necessary to consider that the degradation process can be composed by several superimposed stages that can not be separated in clear ranges of temperature.<sup>14</sup> Moreover, the kinetic treatment of thermal degradation assumes that the residual weight of the sample may be handled as if it was a concentration, which is of doubtful validity.<sup>15</sup>

So, in this case it is impossible to know if the observed weight loss is related to the conversion or if it depends on the volatility of the reaction products already produced at low temperatures, because only in the first case are thermal stability measurements and kinetic evaluations justifiable. The obtained kinetic parameters from a single thermogravimetric curve, are typical only for the experimental conditions described previously.<sup>16</sup>

Finally, it is possible to point out that thermogravimetric analysis is an important tool which permits to know the temperature ranges in which a polymeric material can be used, and also to know the influence of the structure of the monomers on the thermal stability.

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