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# THERMOGRAVIMETRIC ANALYSIS OF POLYCARBONATES WITH AROMATIC SIDE GROUPS

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## ABSTRACT

The thermal stability and the kinetic parameters of three polycarbonates derived from biphenols with aromatic side groups, were studied using dynamic thermogravimetry. The kinetics data showed that for polycarbonate **I** there is a two-step decomposition, the first step being of zero order and the second of first order, indicating the possibility of two different decomposition mechanisms. Polycarbonate **II** shows a one-step decomposition which does not depend on the molecular weight. Polycarbonate **III** shows a decomposition which is dependent on the molecular weight; samples with low molecular weight show a zero-order reaction and high molecular weight species show a first-order reaction, indicating that there are two different decomposition mechanisms. The mechanism of the thermal decomposition of these polycarbonates could be similar to that reported by Davis and Golden for bisphenol A polycarbonate.

## INTRODUCTION

Thermogravimetry, a technique widely used in almost all areas of chemistry, is basically a quantitative method in that the mass change can be determined accurately. Perhaps the greatest number of applications of thermogravimetry has been in the characterization of polymeric materials. Thermogravimetric studies have also been useful not only in applied areas, but also in studies of the theoretical aspects of polymers. These applications include comparisons of relative thermal stabilities, the effect of additives on the thermal stability, studies of degradation kinetics, analysis of copolymeric systems, and many others [1].

In dynamic thermogravimetry (TG), the weight changes of a sample are continuously recorded as a function of temperature as the sample is heated. Therefore, thermograms provide information concerning the sample composition, the thermal stability and kinetic data relating to the chemical changes which occur on heating [2].

Bisphenol A polycarbonate [poly(oxycarbonyloxy-1,4-phenylene-2,2-isopropylidene-1,4-phenylene)] is one of the most versatile engineering plastics, whose thermogravimetric behaviour has been widely studied [3–15]. Davis and Golden [3,4] noticed a decrease in molecular weight when a polycarbonate was heated in a sealed and evacuated vessel, the polymer undergoing random chain scission. On the other hand, studies carried out in continuously evacuated systems show that the polycarbonate rapidly cross-linked and formed an insoluble gel [5–8]. Lee [9] emphasized the sensitivity of the carbonate group to hydrolysis and alcoholysis, and depolymerization is enhanced by the presence of acidic or basic impurities.

Davis and Golden [11–13] analyzed the most important volatile products of the polycarbonate degradation, finding that $CO_2$, phenol and bisphenol A were the major products of the decomposition, concluding that the carbonate linkage is the most reactive group in the polymer.

As a continuation of our work on the thermal degradation of polymers [16,17], we have analyzed the thermal decomposition and kinetic parameters of polycarbonates derived from biphenols with aromatic groups bonded to the central carbon atom.

## EXPERIMENTAL

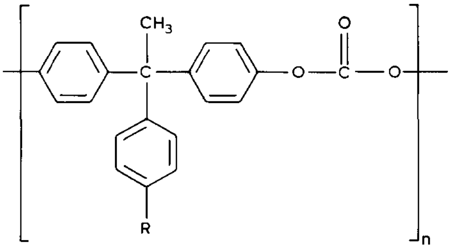
Poly[oxycarbonyloxy-1,4-phenylene-(methyl)phenylmethylene-1,4-phenylene] **I**, poly[oxycarbonyloxy-1,4-phenylene-(methyl)-(4-methyl)-(4-methylphenyl)-methylene-1,4-phenylene] **II**, and poly[oxycarbonyloxy-1,4-phenylene-(methyl)-(4-bromophenyl)methylene-1,4-phenylene] **III** were synthesized by phase-transfer catalysis from the diphenols and phosgene using several quaternary ammonium and phosphonium salts in dichloromethane as solvent. The synthesis and characterization of these polymers has been described in a previous paper [18].

Dynamic thermogravimetry analyses were carried out in a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (4–7 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 nitrogen atmosphere.

The polydispersity index and the molecular weights were determined by gel-permeation chromatography (GPC), using a Perkin-Elmer high-performance liquid chromatograph (HPLC) equipped with a 6000 lb $in.^{-2}$ pump, a Perkin-Elmer differential refractometer model LC-25, an injector of 175 $\mu$l. Three Waters Associated Ultra Styragel columns (10 Å, $10^4$ Å and $10^5$ Å) in series were used. Samples were eluted with THF and the flow rate was 1.0 ml $min^{-1}$. The columns were first calibrated with standard polystyrene samples of narrow molecular-weight distributions.

## RESULTS AND DISCUSSION

The following unfractionated poly(carbonate)s were analyzed by dynamic thermogravimetry



**Ia,b** R = -H
**IIa,b** R = $-CH_3$
**IIIa,b** R = -Br

Table 1 shows the molecular weights, inherent viscosities and the temperature for the 10% weight loss for two samples of each polycarbonate. Figure 1 shows the thermogravimetric curves for the two samples of polycarbonate **I**. The shape of both curves is very similar, but **Ia**, of higher molecular weight, shows a lower temperature for a 10% weight loss than does **Ib**, which has lower molecular weight. This fact can be ascribed to the polydispersity index, which is lower for **Ia** because this sample has more homogeneous molecules. **Ib** has a higher polydispersity index and degrades at lower temperatures than does **Ia**.

Figures 2 and 3 show the thermal-degradation curves for polycarbonates **IIa,b** and **IIIa,b**, respectively. Both figures show that the curves have the same shape for each polycarbonate, and the samples with higher molecular weight and lower polydispersity index, degrade at higher temperature.

TABLE 1

Molecular weights, inherent viscosities $\eta_{inh}$ and temperatures for a 10% weight loss for the polycarbonates

| Polycarbonate | $T^{10\%}$ (°C) | $\eta_{inh}$ [a] | $M_n \times 10^{-3}$ | $M_w \times 10^{-3}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| **Ia** | 473 | 0.14 | 5.3 | 10.0 | 1.89 |
| **Ib** | 405 | 0.34 | 6.0 | 25.2 | 4.20 |
| **IIa** | 457 | 0.14 | 0.6 | 4.6 | 7.67 |
| **IIb** | 493 | 0.38 | 4.4 | 24.2 | 5.50 |
| **IIIa** | 447 | 0.13 | 3.3 | 10.6 | 3.21 |
| **IIIb** | 507 | 0.34 | 25.1 | 67.9 | 2.71 |

[a] $dl\ g^{-1}$ in $CHCl_3$ at 25 °C ($c = 0.5\ g\ dl^{-1}$).

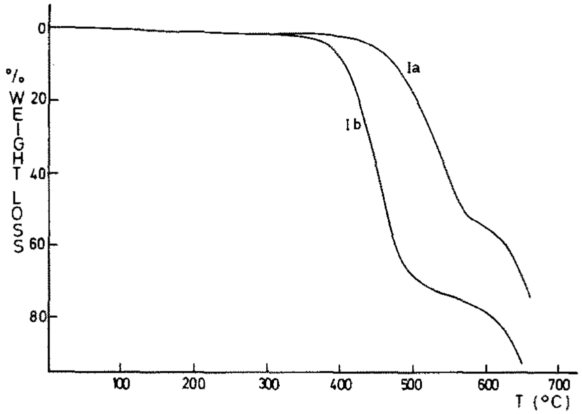


Fig. 1. Thermogravimetric curves of polycarbonate **Ia** and **Ib**.

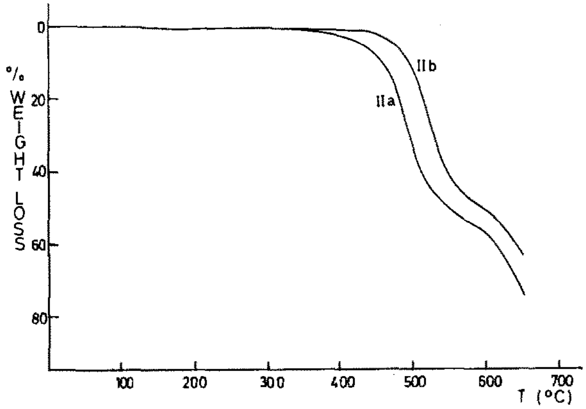


Fig. 2. Thermogravimetric curves of polycarbonate **IIa** and **IIb**.

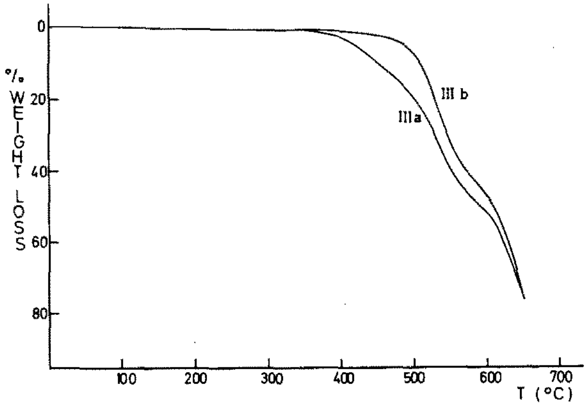


Fig. 3. Thermogravimetric curves of polycarbonate **IIIa** and **IIIb**.

By comparing the stability of the three polycarbonates, it can be seen that they follow the trend **III** > **II** > **I**, although the differences between the temperatures at which there is a 10% weight loss are not large, the difference between them being the R group in the ring bonded to the central carbon atom. In polycarbonates **II** and **III**, the R groups are bigger than in **I** which shows a higher stability. This has been described previously for the thermal stability of polythiocarbonates [16].

The kinetic parameters of the thermogravimetric weight loss were calculated by using the kinetic equation

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

where $\alpha$ is a 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 with the heating rate (20 °C $\mathrm{min}^{-1}$) incorporated directly in the data of temperature versus sample weight fraction [19]. 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

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

A computer linear multiple-regression program was developed to calculate the kinetics parameters $E$ and $A$ from a linear least-squares fit of the data in a semilogarithmic plot of $\beta$ versus $1/T$. The linearity of each plot is good, although some scatter was detected at the beginning and end of the decomposition which can be attributed to the difficulty of obtaining accurate measurements at the beginning and end of an experiment, as is frequently encountered in kinetics measurements.

As can be seen from the thermogravimetric curves shown in Fig. 1, the two samples of polycarbonate **I** showed a two-step degradation, which was confirmed by the kinetic analysis, and can be attributed to two mechanisms in the thermal decomposition, as has been described by several authors [20–22]. Polycarbonates **II** and **III** degrade in a single-step in the range considered.

Table 2 shows the kinetic parameters obtained for the polycarbonate samples, derived from Figs. 4–7. For the samples of polycarbonate **I**, the degradation occurs in two steps. The first step obeys zero-order kinetics and the second first-order kinetics. A zero reaction order, 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 [23].

TABLE 2

Kinetics parameters for polycarbonates

| Polycarbonate | Temp. range (°C) | $n$ | $E$ (kcal $\mathrm{mol}^{-1}$) | $A$ ($\mathrm{sec}^{-1}$) |
|---|---|---|---|---|
| **Ia** | 400–580 | 0 | 20.42 | $6.99\times10^{2}$ |
| | 580–630 | 1 | 16.91 | $1.74\times10^{2}$ |
| **Ib** | 370–480 | 0 | 25.04 | $8.53\times10^{4}$ |
| | 510–580 | 1 | 25.30 | $3.73\times10^{5}$ |
| **IIa** | 450–590 | 1 | 44.47 | $1.77\times10^{10}$ |
| **IIb** | 450–620 | 1 | 44.30 | $4.13\times10^{9}$ |
| **IIIa** | 400–570 | 0 | 15.17 | $3.21\times10^{1}$ |
| **IIIb** | 480–600 | 1 | 50.72 | $1.70\times10^{11}$ |

According to the mechanism proposed by Davis and Golden [13] and Abbas [15] for bisphenol A polycarbonate degradation carried out in a continuously evacuated system, the first step in 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 (especially condensation) and then crosslinks to form an insoluble gel with loss of $CO_2$, which is the major product, indicating that the carbonate linkage is the most reactive group in the polymer.

On the other hand, when the samples were heated to the temperature at which a 10% weight loss occurred, the remaining polycarbonate, **Ia**, was

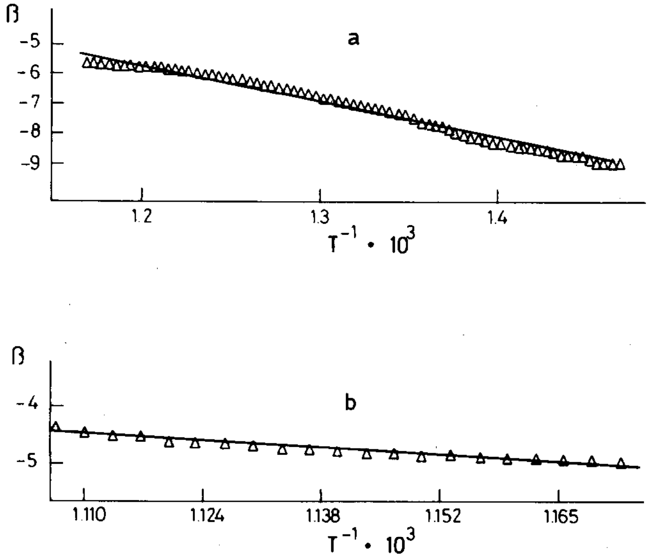


Fig. 4. Arrhenius plot for the degradation of polycarbonate **Ia**: (a) $n = 0$; (b) $n = 1$.

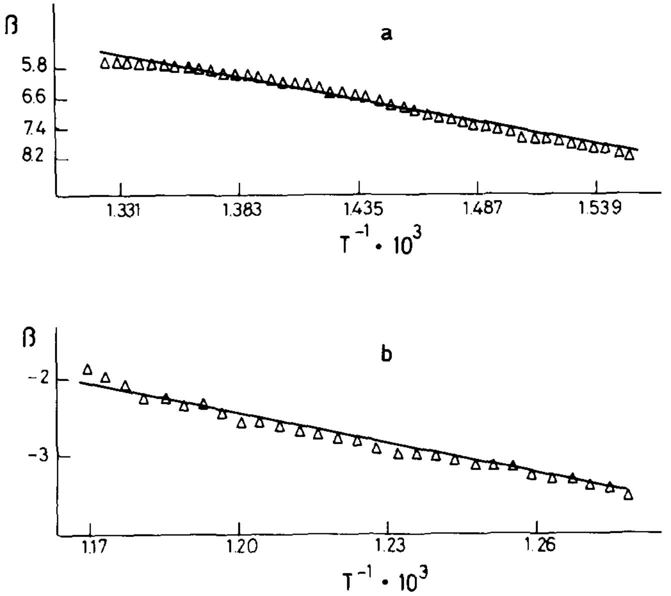


Fig. 5. Arrhenius plot for the degradation of polycarbonate **Ib**: (a) $n = 0$; (b) $n = 1$.

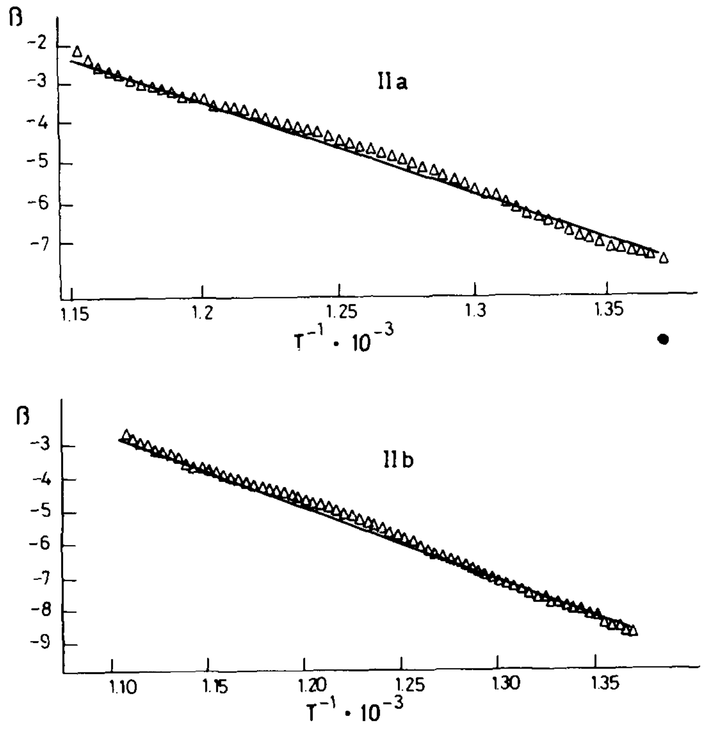


Fig. 6. Arrhenius plot for the degradation of polycarbonates **IIa** and **IIb**.

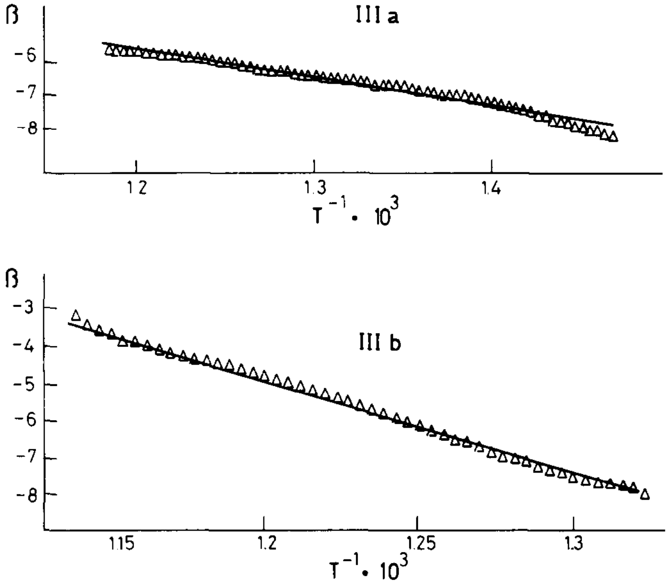


Fig. 7. Arrhenius plot for the degradation of polycarbonates **IIIa** and **IIIb**.

insoluble in $CH_2Cl_2$; **Ib** was soluble in this solvent, being the sample that degrades at low temperature. It is possible that in this sample the crosslinked species is soluble because of the high polydispersity index, or, more probably, that these crosslinked species are not formed in the first step, which would explain the low decomposition temperature in comparison with **Ia**. With **Ib**, the crosslinked species increase the molecular weight and, therefore, the temperature at which decomposition occurs. In the second step, the decomposition of the crosslinked species could dominate, because it is the decomposition-rate dependent species of the polymer mass.

The activation energy values, $E$, for the decomposition of polycarbonate **I** are higher in the samples with high molecular weight.

The two samples of polycarbonate **II** showed a very similar decomposition in one step over the whole of the range considered, having the same reaction order and activation energies. These samples, when heated to the temperature of 10% weight loss, were insoluble in $CH_2Cl_2$, which means that there was a crosslinking reaction according to the mechanism proposed by Golden and Davis [13]. These crosslinked species degrade with first-order kinetics. Moreover, sample **IIa**, which has a low molecular weight and a high polydispersity index, degrades at a higher temperature than does **IIb**, which has a higher molecular weight but a lower polydispersity index. The molecular weight and the polydispersity index do not appear to influence the degradation of this polycarbonate.

The two samples of polycarbonate **III** showed two different reaction orders. Sample **IIIa** degrades with zero-order kinetics and **IIIb** with first-order kinetics, but both decomposed in a single step in the range considered, probably as a consequence of the different molecular weights. Consequently there are two mechanisms of degradation.

However, when the samples were heated to the temperature at which there was a 10% weight loss, both samples were insoluble in $CH_2Cl_2$, due to the formation of crosslinked species, according to the mechanism proposed by Golden and Davis [13]. In sample **IIIa**, of low molecular weight, the decomposition rate was independent of the polymeric mass and probably due to the low molecular weight, the crosslinked species either decomposed during its formation or the preformed molecules evaporated [24]. On the other hand, sample **IIIb** has a higher molecular weight, and the crosslinked species are formed between longer polymeric chains, which degrade at higher temperatures.

The thermogravimetric analysis of polycarbonate **I** can be compared with the analogous thiocarbonate reported previously [16]. The temperature reported for a 10% weight loss for the polythiocarbonate was 385 ° C, and the kinetics showed a first-order reaction for the whole of the temperature range considered here (370–520 ° C), probably due to a different mechanism with the participation of the sulfur atom.

## CONCLUSIONS

It can be concluded that the thermal decomposition of polycarbonates with aromatic side groups would have a similar mechanism to that proposed by Golden and Davis for bisphenol A polycarbonate, in which the carbonate groups rearrange to carboxylic groups *ortho* to an ether linkage, and then crosslink. The R groups bonded to the aromatic side ring have little influence in the thermal stability and the decomposition mechanism, but were not evaluated. More investigations are necessary to clarify these aspects.

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