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Thermogravimetric Analysis of Poly(ester-carbonate)s and Poly(ester-thiocarbonate)s with the Ester Group in the Side Chain

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Thermogravimetric analysis of poly(ester-carbonate)s and poly(ester-thiocarbonate)s with the ester group in the side chain, and derived from the diphenols: methyl and ethyl 2,2-bis(4-hydroxyphenyl)-propanoate, methyl and ethyl 3,3-bis(4-hydroxyphenyl)-butanoate, methyl and ethyl 4,4-bis(4-hydroxyphenyl)-pentanoate with phosgene or thiophosgene, were carried out by dynamic thermogravimetry. The thermal decomposition temperatures were determined, showing that polymers derived from the diphenols methyl and ethyl 2,2-bis(4-hydroxyphenyl)-propanoate were more stable than the others. The kinetic parameters, activation energy, reaction order and pre-exponential factor, were determined using the Arrhenius relationship.

Keywords: Poly(ester carbonate); poly(ester thiocarbonate); polyesters; thermogravimetry; thermal decomposition; kinetics of decomposition

INTRODUCTION

Dynamic thermogravimetry in which the temperature is increased as a time function, has been widely used in the degradation of condensation polymers. In these analyses it is possible to know the range in which the degradation process takes place and according to several mathematical methods, determine the kinetics parameters (activation energy, kinetic reaction order, and preexponential factor) associated with the degradation process.

Normally, the degradation of polymers under conditions of normal use is a major factor limiting their applications, and to know the conditions under which these materials can be used is one of their most important specifications. In this sense, important properties of polymers are affected adversely as a consequence of the degradation process when they are exposed to the environment [1].

Continuing our work on the studies of thermal degradation of polymers, we describe the thermal decomposition and the associated kinetic parameters of poly(ester-carbonate)s and poly(ester-thiocarbonate)s, which are polymers with two functional groups, containing the ester group in the side chain, and compared with analogous polymers in which the ester group is in the main chain between two aromatic rings. These polymers were synthesized under phase transfer conditions using quaternary ammonium salts as phase transfer catalysts, and their synthesis was described previously [2].

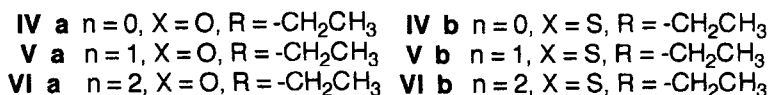
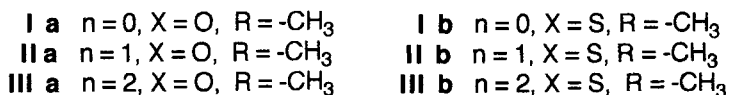
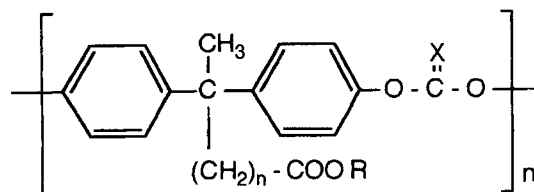
EXPERIMENTAL PART

Poly(ester-carbonate)s and poly(ester-thiocarbonate)s were synthesized under phase transfer conditions from the diphenols: methyl 2,2-bis(4-hydroxyphenyl)-propanoate (**Ia** and **Ib**), ethyl 2,2-bis(4-hydroxyphenyl)-propanoate (**IVa** and **IVb**), methyl 3,3-bis(4-hydroxyphenyl)-butanoate (**IIa** and **IIb**), ethyl 3,3-bis(4-hydroxyphenyl)-butanoate (**Va** and **Vb**), methyl 4,4-bis(4-hydroxyphenyl)-pentanoate (**IIIa** and **IIIb**), and ethyl 4,4-bis(4-hydroxyphenyl)-pentanoate (**VIa** and **VIb**), and phosgene (polymers **a**) or thiophosgene (polymers **b**), according to a procedure described previously [2].

The thermogravimetric analyses were carried out in a Mettler TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. The thermal degradation measurements were performed between 50 and 600°C at 20°C min⁻¹ under nitrogen flow.

RESULTS AND DISCUSSION

The following poly(ester-carbonate)s and poly(ester-thiocarbonate)s were synthesized under phase transfer conditions using several



quaternary ammonium salts as catalysts, and characterized by IR spectroscopy and elemental analysis. The results were described previously [2].

Table I shows the thermal decomposition temperatures (TDT) for all the polymers, and represent the temperature at which polymers lost 10% of their mass, which were taken from graphics of weight loss versus temperature. By comparing the thermal stability of poly (ester-carbonate)s and poly (ester-thiocarbonate)s, it can be seen that is not possible to find a relationship between the thermal stability of the polycarbonates with the corresponding polythiocarbonates. Likewise, there was no influence of the methyl or ethyl group bonded to the

TABLE I Thermal decomposition temperatures (TDT) of poly (ester-carbonate)s and poly (ester-thiocarbonate)s

| Polymer | TDT ($^{\circ}C$) |
|--------------|---------------------|
| I a | 302 |
| II a | 266 |
| III a | 240 |
| IV a | 335 |
| V a | 228 |
| VI a | 225 |
| I b | 362 |
| II b | 240 |
| III b | 267 |
| IV b | 362 |
| V b | 298 |
| VI b | 210 |

ester one. But when the comparison is with the length of the side chain, it is possible to see in the four groups, that polymers derived from the acid 2,2-bis(4-hydroxyphenyl)-propanoic, with the shorter side chain, are more stable than those derived from the other acids. In other papers we described that in general, polycarbonates are more stable than polythiocarbonates [3–5], but in these polymers the principal influence is the length of the side chain.

There are two reasons to explain this. The first is the solubility. Independent of the fact that all polymers were insoluble in the reaction media, polymers derived from the acid 2,2-bis(4-hydroxyphenyl)-propanoic were more soluble in solvents as N,N-dimethylformamide or phenol/1,1,2,2-tetrachloroethane mixture than the others, being polymers **VIa** and **VIb** insoluble in all solvents, which led to obtain only low molecular weight polymers. The second is the greater rigidity than the polymers should probably have derived from the acid 2,2-bis(4-hydroxyphenyl)-propanoic, with respect to those derived from the other acids with a longer side chain. Polymers derived from the acid 4,4-bis(4-hydroxyphenyl)-pentanoic ($n = 2$) showed the less thermal stability.

Both factors are responsible for the fact that when the side chain is increased, the thermal stability decreases in the four groups of polymers, independently of their nature, polycarbonate or polythiocarbonate, or the group bonded to the ester one.

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

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

where α is the fraction of the sample weight at time t , and k_n the specific rate with kinetic reaction order n . The reaction rates $-(dx/dt)$ 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 [6]. 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

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

A lineal multiple-regression computer program was developed to calculate the kinetics parameters E and A from a linear least-squares fit of the data in a semi-logarithmic plot of β versus $1/T$, which are shown in Figures 1–12. The figures show good straight lines with a correlation greater than .99 at intervals of 10°C . Table II shows the values of the kinetics parameters, the kinetic reaction order and the temperature range in which they were calculated.

All polymers decomposed in one step, and the best fit was obtained for three values of n : 0, 0.5, and 1. A zero kinetic reaction order implies that $-(d\alpha/dt)$ is constant and consequently if the sample mass is increased, the rate of decrease in mass remains constant, which happens if a constant concentration of volatile materials is maintained constant at the sample surface, as in a simple evaporation of performed molecules [7]. On the other hand, the first order kinetic implies that there is a volatile material concentration in the sample surface that depends on the active residual fraction [8]. A 0.5 kinetic reaction order probably means that the degradation is a complex process, or may consist of two or more superimposed process [9–10].

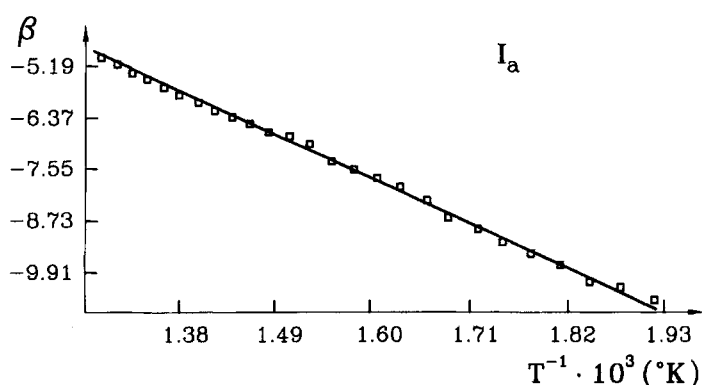


FIGURE 1 Arrhenius plot for the degradation of poly (ester-carbonate) **Ia**.

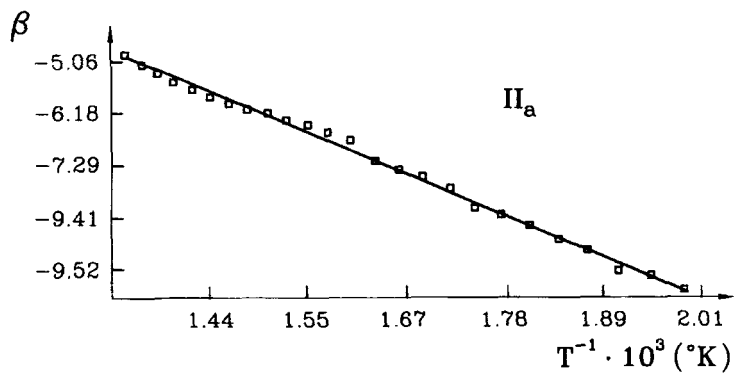
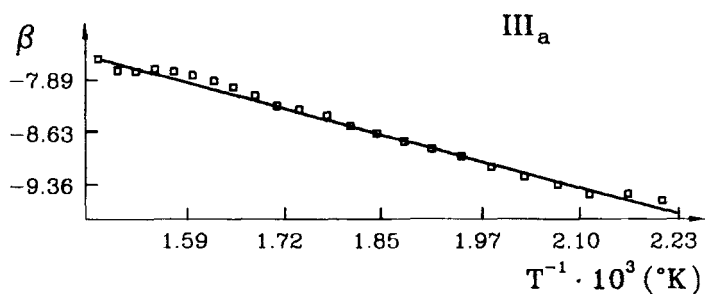
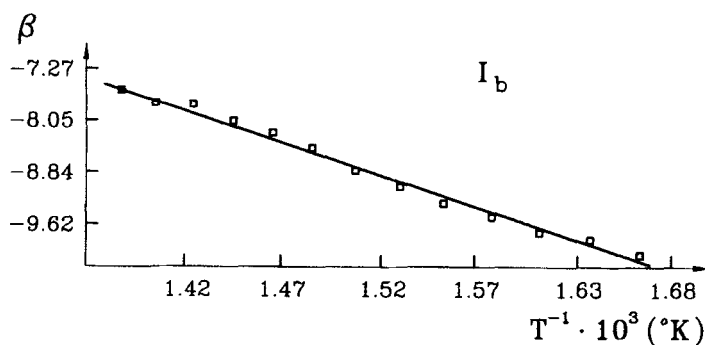
FIGURE 2 Arrhenius plot for the degradation of poly(ester-carbonate) II_a.FIGURE 3 Arrhenius plot for the degradation of poly(ester-carbonate) III_a.

FIGURE 4 Arrhenius plot for the degradation of poly(ester-thiocarbonate) Ib.

II_b

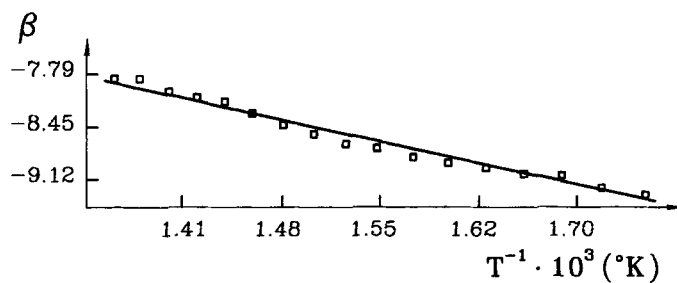


FIGURE 5 Arrhenius plot for the degradation of poly(ester-thiocarbonate) II_b.

III_b

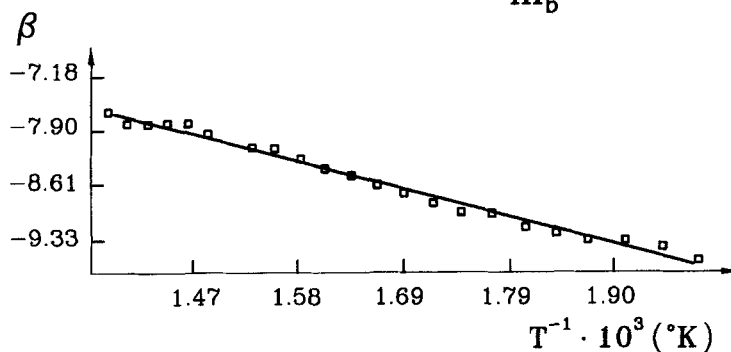


FIGURE 6 Arrhenius plot for the degradation of poly(ester-thiocarbonate) III_b.

IV_a

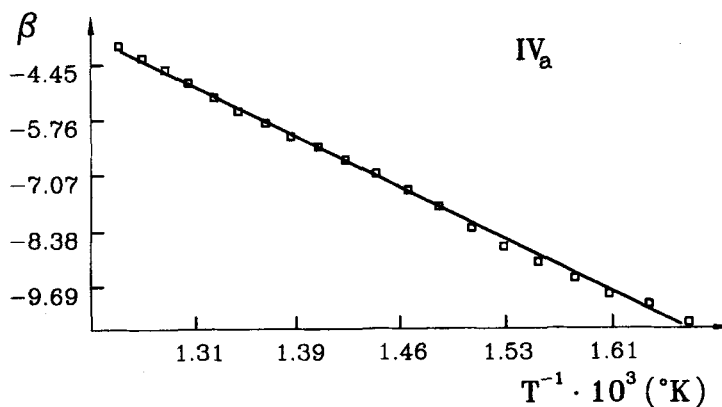


FIGURE 7 Arrhenius plot for the degradation of poly(ester-carbonate) IV_a.

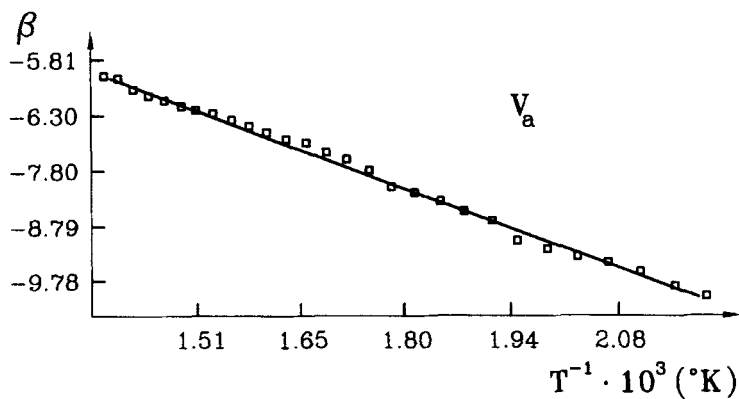


FIGURE 8 Arrhenius plot for the degradation of poly(ester-carbonate) Va.

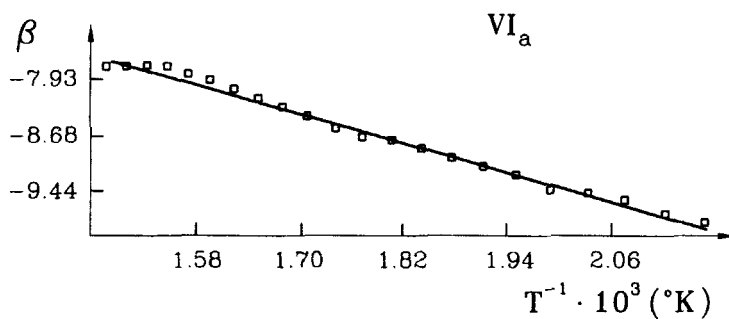


FIGURE 9 Arrhenius plot for the degradation of poly(ester-carbonate) VIa.

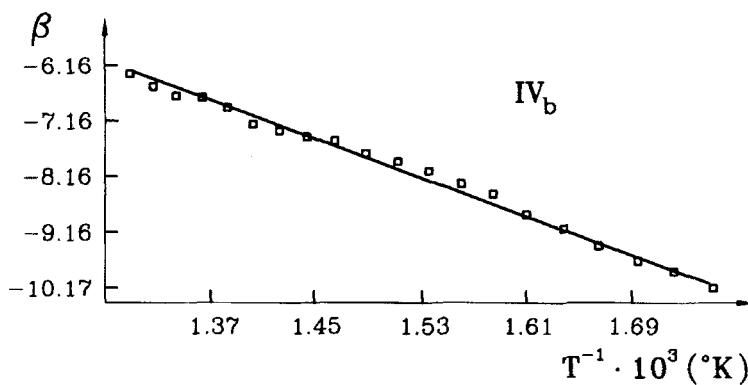


FIGURE 10 Arrhenius plot for the degradation of poly(ester-thiocarbonate) IVb.

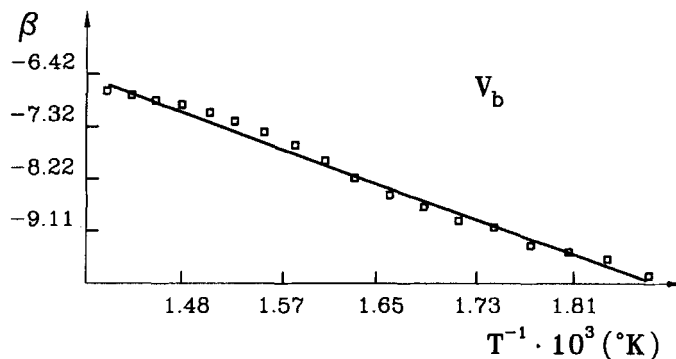


FIGURE 11 Arrhenius plot for the degradation of poly (ester-thiocarbonate) Vb.

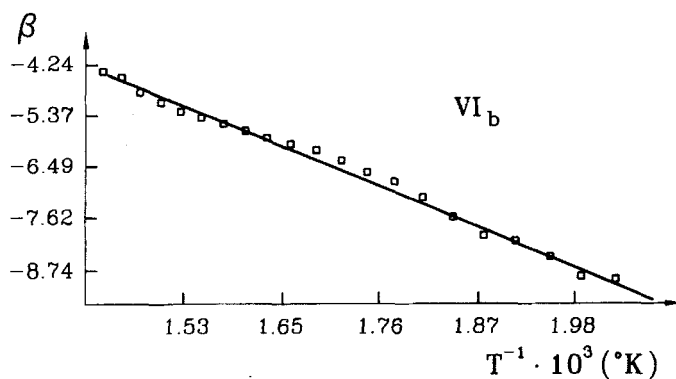


FIGURE 12 Arrhenius plot for the degradation of poly (ester-thiocarbonate) VIb.

TABLE II Kinetics parameters of the thermal decomposition of poly (ester-carbonate)s and poly (ester-thiocarbonate)s

| Polymer | Range (°C) | <i>n</i> | <i>E</i> (kcal/mol) | <i>A</i> (seg ⁻¹) |
|---------|------------|----------|---------------------|-------------------------------|
| Ia | 250-500 | 1 | 18.66 | 1.57×10^3 |
| IIa | 230-470 | 1 | 16.21 | 4.70×10^3 |
| IIIa | 180-400 | 0 | 5.93 | 4.58×10^{-2} |
| IVa | 300-490 | 0.5 | 18.13 | 3.40×10^2 |
| Va | 180-450 | 0.5 | 10.01 | 2.63 |
| VIa | 190-400 | 0 | 7.02 | 9.78×10^{-2} |
| Ib | 330-450 | 0 | 19.06 | 3.20×10^2 |
| IIb | 300-460 | 0 | 7.78 | 8.37×10^{-2} |
| IIIb | 230-450 | 0 | 6.80 | 5.72×10^{-2} |
| IVb | 330-520 | 1 | 33.83 | 4.08×10^7 |
| Vb | 260-430 | 0.5 | 15.78 | 1.22×10^2 |
| VIb | 210-420 | 1 | 16.24 | 1.84×10^3 |

In both series, poly (ester-carbonate)s and poly (ester-thiocarbonate)s, it is possible to observe that the three possibilities are present, and there is no relationship between the kinetic reaction order and the polymer structure. The differences in the kinetic reaction order would be attributed to a different decomposition mechanism, or perhaps more precisely, to one very complex, or two or more superimposed degradation mechanism, which depends not only on the polymeric structure (carbonate or thiocarbonate, the length of the side chain, and the group bonded to the ester one), but also on the molecular weight [11].

In other works [4, 11–12], it has been described that the degradation process for poly (carbonate)s and poly (thiocarbonate)s occurs according to a zero or first kinetic order, without taking into account the nature of the groups bonded to the aromatic rings. On the other hand, when we studied the degradation process of polyesters with the ester group in the main chain [4, 12], we also described two kinetic reaction orders, which were attributed to several superimposed degradation mechanisms, depending on both the functional group and the polymer structure. Finally, the same results were found when the thermal degradation of poly (ester-carbonate)s and poly (ester-thiocarbonate)s was studied [11], observing a zero or first kinetic order independently of the kind of polymer and the position of the aromatic rings.

The trend of the E values is the same as that obtained for the TDT values. Poly (ester-carbonate)s and poly (ester-thiocarbonate)s derived from the methyl or ethyl 2,2-bis (4-hydroxyphenyl)-propanoate (**Ia**, **Ib**, **IVa** and **IVb**) showed the highest values of activation energy, which can be interpreted in terms of the greater rigidity of the structure and of the greater stability that they presented. Also, the E values have been interpreted as average energy for all the complex processes, which occur in the thermal decomposition of polycondensation polymers [13].

It has been described that in the degradation of polycondensation polymers, both values, E and the kinetic orders, have a limited significance, due to the fact that the degradation process in polymers with two functional groups, can probably be composed by several stages that cannot be separated in a clear range of temperature [14]. For this reason, assumptions about the activation energy over a particular and wide range of temperatures, may be questionable. On the other hand, we assume that the kinetic treatment of the degradation process may be handled as a simple concentration, which is of doubtful validity [15].

In spite of the above considerations, thermal degradation studies are good tools for studying the influence of the unit repeating structure in the thermal stability of condensation polymers. It is also possible to determine the range in which the polymer can be used and the activation energy associated with the total degradation process.

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