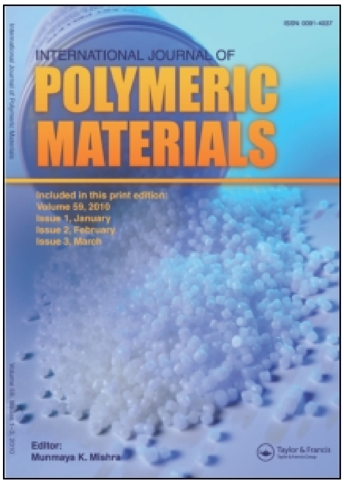

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Thermogravimetric Analysis of Poly(Ester-Carbonates) and Poly(Ester-Thiocarbonates)

L. H. Tagle[a]; F. R. Diaz[a]
[a] Organic Chemistry Department, Faculty of Chemistry, Catholic University of Chile, Santiago, Chile

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Thermogravimetric Analysis of Poly(Ester-Carbonates) and Poly(Ester-Thiocarbonates)

L. H. TAGLE and F. R. DIAZ

Organic Chemistry Department, Faculty of Chemistry, Catholic University of Chile, P.O. Box 306, Santiago, Chile

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The thermogravimetric behaviour of poly(ester-carbonates) and poly(ester-thiocarbonates) derived from the diphenol esters 4-hydroxy-phenyl-4-hydroxy-benzoate, 3-hydroxy-phenyl-4-hydroxy-benzoate, 4-hydroxy-phenyl-3-hydroxy-benzoate, and 3-hydroxy-phenyl-3-hydroxy-benzoate with phosgene and thiophosgene was studied by dynamic thermogravimetry. The thermal decomposition temperatures were determined, showing that poly(ester-carbonates) are more stable than poly(ester-thiocarbonates). The kinetics parameters, activation energy, reaction order and pre-exponential factor, were determined by using the Arrhenius relationship and a computer program.

KEY WORDS Thermogravimetry, thermal stability, poly(ester-carbonates), poly(ester-thiocarbonates), kinetics parameters.

INTRODUCTION

Dynamic thermogravimetry is a widely used tool to study the degradation of different kinds of polymers, and to elucidate the kinetics parameters associated with the thermal process. This technique presents several advantages. So, the kinetics parameters can be established over temperature range in a continuous manner; it is possible to obtain the decomposition and characteristics temperatures and the kinetics parameters with a single sample; and the problems associated with a preheating necessary for isothermal degradation, are avoided.[1]

Polymers, like all substances, may undergo a number of transformations under the effect of heat treatment. These changes are of a chemical or physical character, but the simultaneous occurrence of both types of transformation is very frequent. However, the degradation of polymers under conditions of normal use is a major factor limiting the application of these versatile materials. Without exception, all polymers degrade in the environment to which they are exposed during their life cycle. Important properties of every polymer are affected adversely as the degradation proceeds, including mechanical strength, dielectric quality and aesthetic

TABLE I

Thermal decomposition temperature (TDT) of poly(ester-carbonates) and poly(ester-thiocarbonates)

Polymer	TDT (°C)
I	374
II	330
III	402
IV	343
V	403
VI	355
VII	380
VIII	350

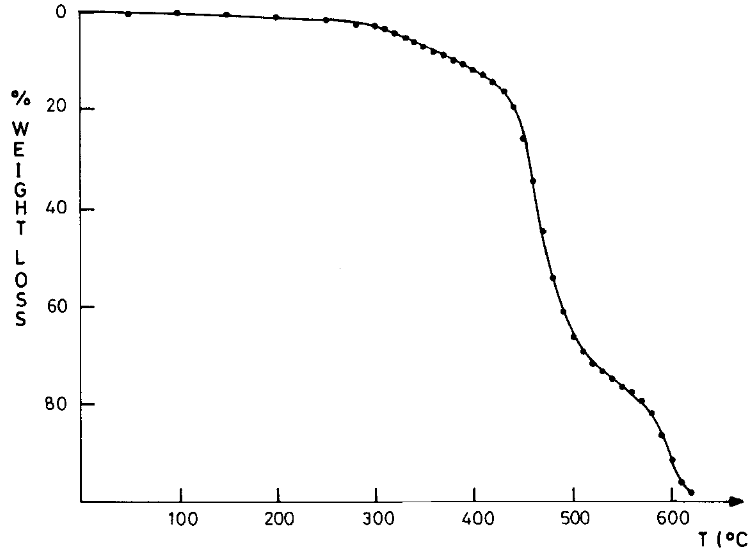


FIGURE 1 Thermogravimetric curve for poly(ester-carbonate) I.

appearance. This often leads to the failure of polymeric materials before they attain their required service life.[2]

Poly(ester-carbonates) and poly(ester-thiocarbonates) are polymers with two functional groups in the main chain, which were synthesized from diphenols containing the ester group between the phenolic rings and phosgene and thiophosgene under phase transfer conditions, using several ammonium salts as phase transfer catalyst, and their synthesis was described previously.[3-4]

As a continuation of our work on the thermal degradation of polymers, in this paper we have studied the thermal decomposition and the kinetics parameters of these poly(ester-carbonates) and poly(ester-thiocarbonates), in which the ester group is in the main chain.

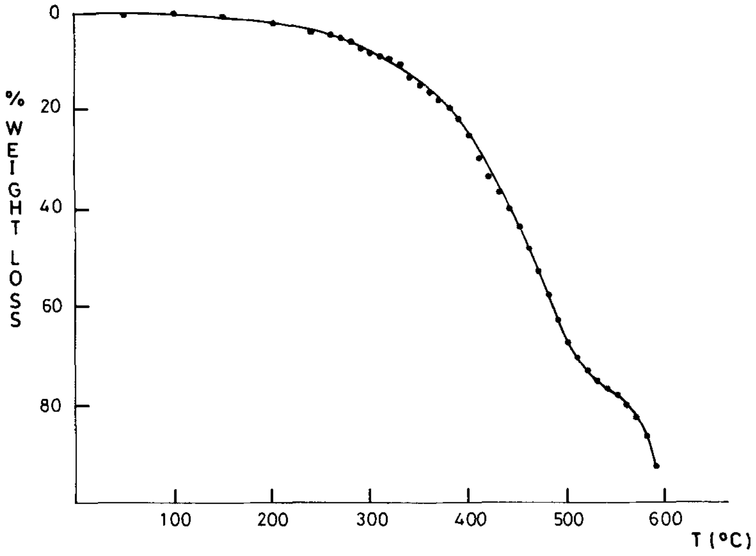


FIGURE 2 Thermogravimetric curve for poly(ester-thiocarbonate) II.

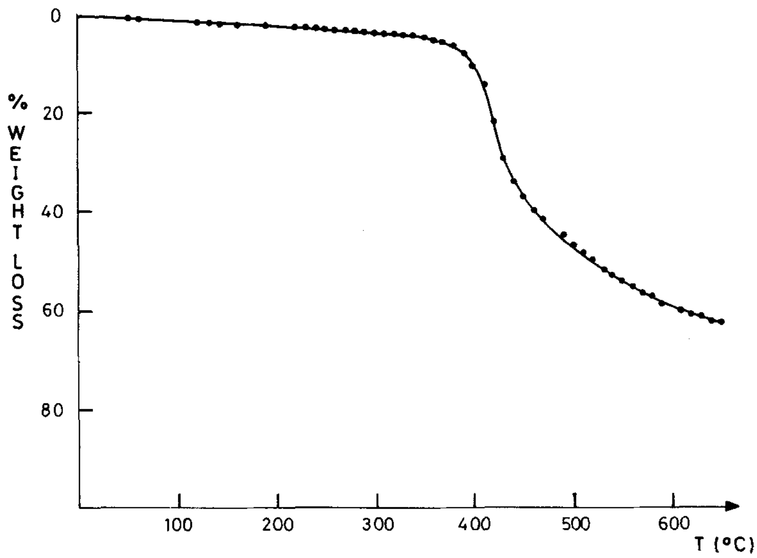


FIGURE 3 Thermogravimetric curve for poly(ester-carbonate) III.

EXPERIMENTAL PART

Poly(ester-carbonates) and poly(ester-thiocarbonates) were synthesized under phase transfer conditions from phosgene and thiophosgene and the diphenol ester 4-hydroxy-phenyl-4-hydroxy-benzoate (I and II), 3-hydroxy-phenyl-4-hydroxy-benzoate (III and IV), 4-hydroxy-phenyl-3-hydroxy-benzoate (V and VI), and 3-hy-

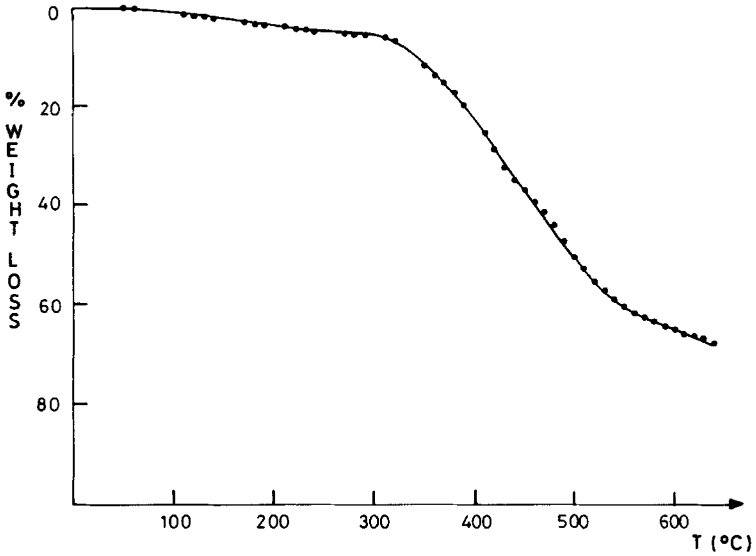


FIGURE 4 Thermogravimetric curve for poly(ester-thiocarbonate) IV.

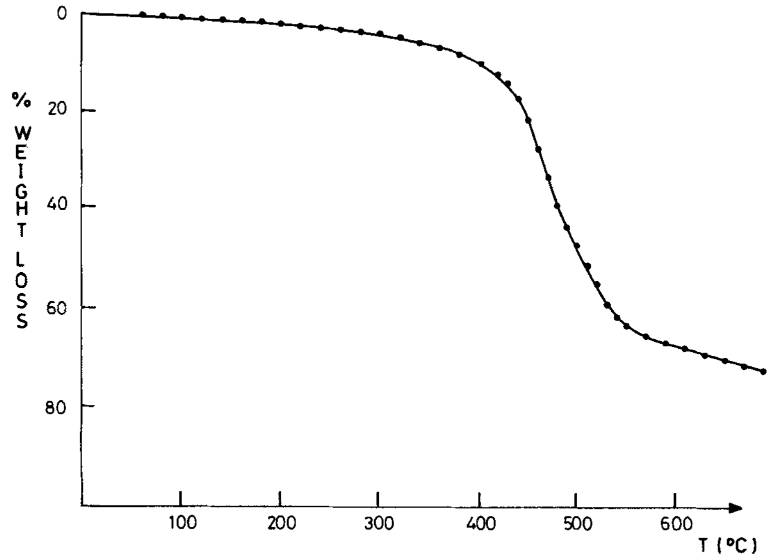


FIGURE 5 Thermogravimetric curve for poly(ester-carbonate) V.

droxy-phenyl-3-hydroxy-benzoate (VII and VIII), according to a procedure described earlier.[3-4]

Thermogravimetric analysis were carried out in a Mettler TG 50 thermobalance, and the thermogravimetric measurements were carried out between 50 and 690°C with a heating rate of 20°C min^{-1} under N_2 flow.

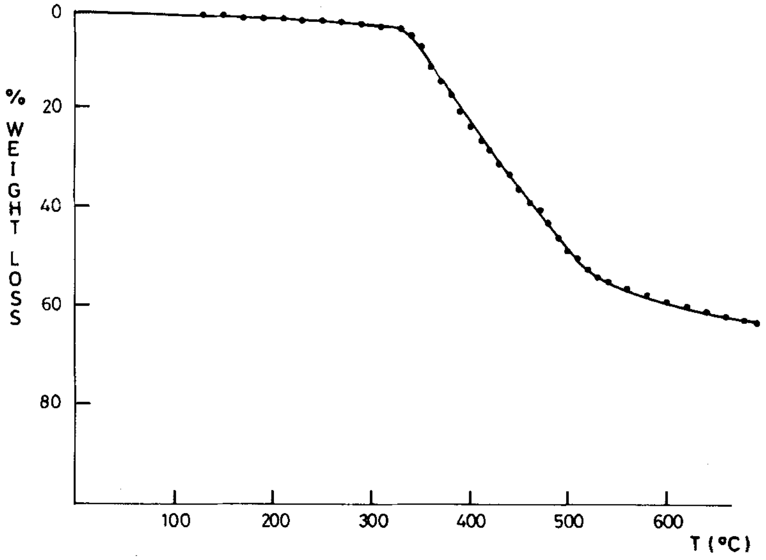
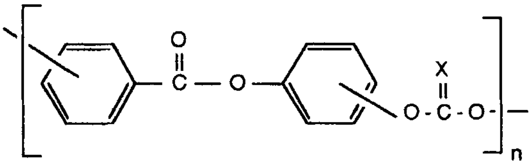


FIGURE 6 Thermogravimetric curve for poly(ester-thiocarbonate) VI.

RESULTS AND DISCUSSION

Poly(ester-carbonates) and poly(ester-thiocarbonates) with the following structure



where I: para, para, X=O, II: para, para, X=S, III: para, meta, X=O, IV: para, meta, X=S, V: meta, para, X=O, VI: meta, para, X=S, VII: meta, meta, X=O, VIII: meta, meta, X=S were synthesized under phase transfer conditions from the respective diphenol-esters and phosgene or thiophosgene, using several cuaternary ammonium salts as catalysts and dichloromethane as solvent, according to a procedure described earlier, and characterized by the usual methods.[3-4]

Table I shows the thermal decomposition temperatures (TDT) for all polymers, taken when polymers lost 10% of their weight, and Figures 1–8 show the thermogravimetric curves. By comparing the thermal stability of poly(ester-carbonates) and poly(ester-thiocarbonates), it can be seen that poly(ester-carbonates) are more stable than poly(ester-thiocarbonates) as has been described for polycarbonates and polythiocarbonates derived from several diphenols.[5-7]

On the other hand, if we compare polymers derived from *p*-hydroxy-benzoic acid with polymers derived from *m*-hydroxy-benzoic acid, there is not a logic sequence in the sense that polymers derived from para structures would be more stable than those derived from meta structures. In both, poly(ester-carbonates)

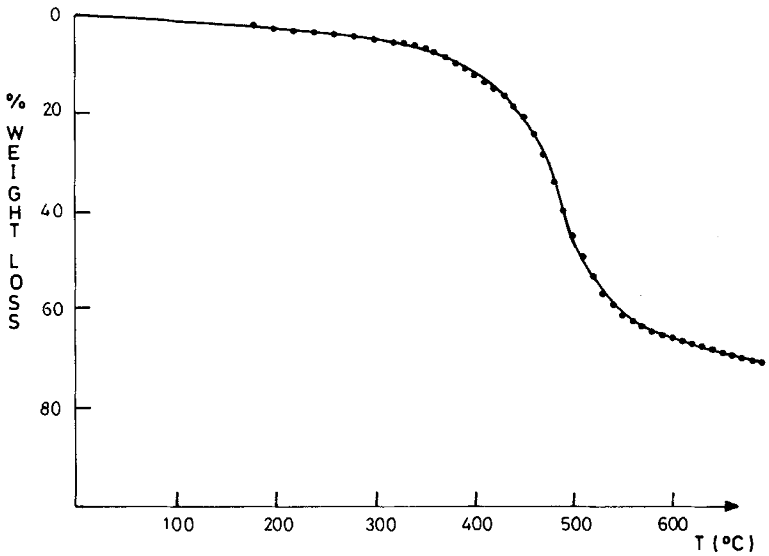


FIGURE 7 Thermogravimetric curve for poly(ester-carbonate) VII.

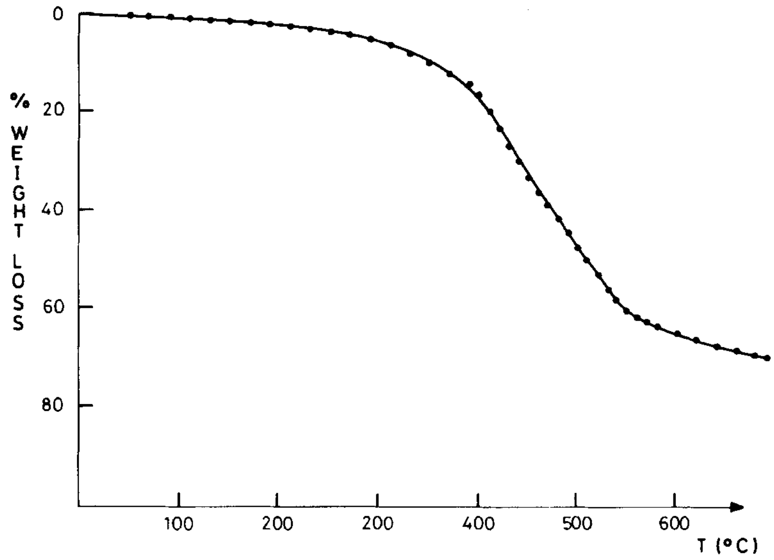


FIGURE 8 Thermogravimetric curve for poly(ester-thiocarbonate) VIII.

and poly(ester-thiocarbonates), the differences of stability are low, and we can not to obtain more conclusions about the influence of the structure of the repeating unit. Furthermore, polymers were insoluble in the reaction media, and therefore the molecular weights probably are low, which is an important factor in thermal stability of polymers.

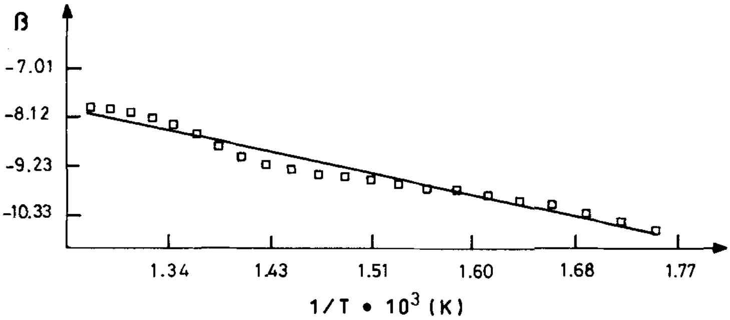


FIGURE 9 Arrhenius plot for the degradation of poly(ester-carbonate) I.

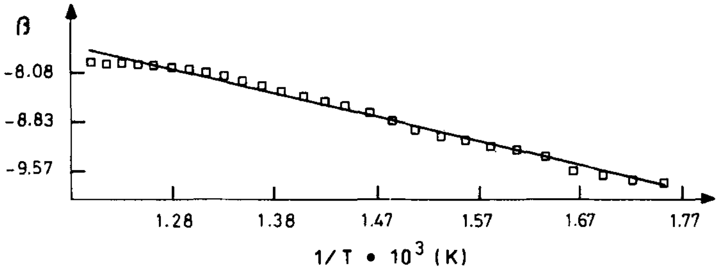


FIGURE 10 Arrhenius plot for the degradation of poly(ester-thiocarbonate) II.

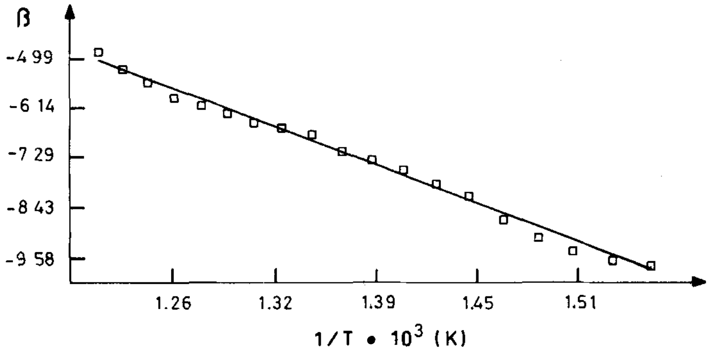


FIGURE 11 Arrhenius plot for the degradation of poly(ester-carbonate) III.

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

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

where α 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°C min^{-1}) incorporated directly into the temperature versus sample weight-fraction data, according to the procedure developed by Wen and Lin.[8] The specific rates were calculated from the Arrhenius relation

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

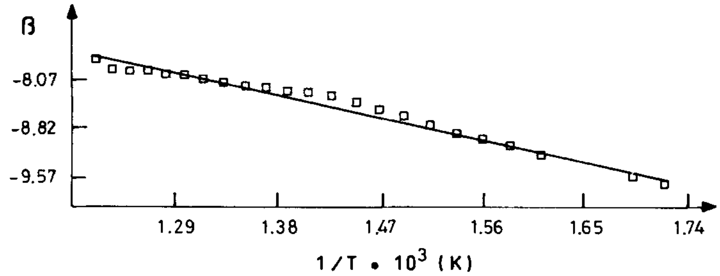


FIGURE 12 Arrhenius plot for the degradation of poly(ester-thiocarbonate) IV.

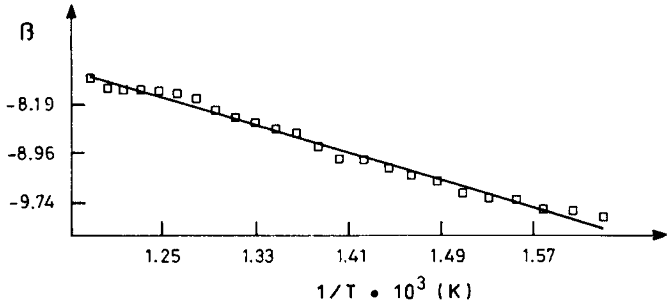


FIGURE 13 Arrhenius plot for the degradation of poly(ester-carbonate) V.

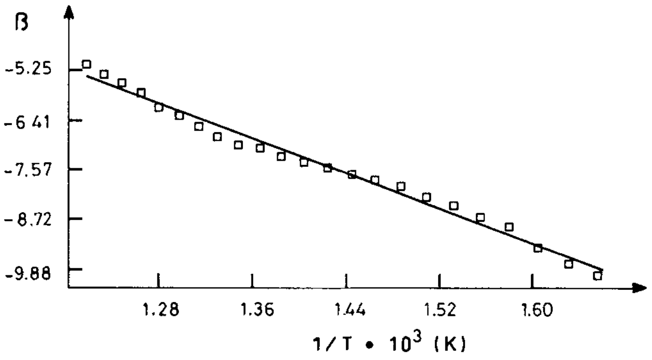


FIGURE 14 Arrhenius plot for the degradation of poly(ester-thiocarbonate) VI.

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

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

A computer, lineal multiple-regression 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 9–16. The figures show good straight lines with a correlation greater than .99 at intervals of 10°C.

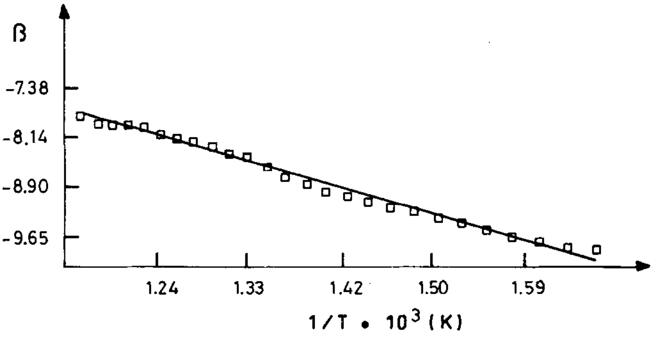


FIGURE 15 Arrhenius plot for the degradation of poly(ester-carbonate) VII.

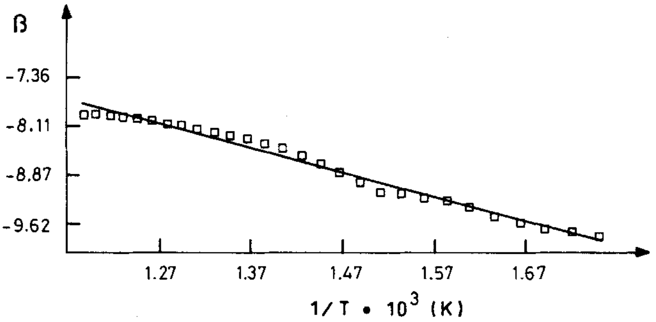


FIGURE 16 Arrhenius plot for the degradation of poly(ester-thiocarbonate) VIII.

TABLE II

Kinetics parameters of the thermal decomposition of poly(ester-carbonates and poly(ester-thiocarbonates)

Polymer	Range (°C)	n	E (kcal/mol)	A (seg^{-1})
I	300 - 510	0	11.95	7.55×10^{-1}
II	300 - 560	0	8.20	6.82×10^{-2}
III	370 - 550	1	29.53	5.31×10^{5}
IV	310 - 550	0	7.86	5.92×10^{-2}
V	340 - 570	0	11.49	4.46×10^{-1}
VI	330 - 550	1	21.40	2.55×10^{3}
VII	330 - 580	0	9.66	1.35×10^{-1}
VIII	300 - 570	0	8.05	5.53×10^{-2}

Table II shows the values of the kinetics parameters, the reaction order and the temperature range in which were calculated.

All polymers decompose in one step with and the best fit were obtained for $n = 0$, except polymers II and VI for which the best fit was for $n = 1$. A zero reaction order means that $-(d\alpha/dt)$ 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 constant at the sample surface, as in a sample evaporation of performed molecules.[9] 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.[10] These differences in the reaction order would be attributed to different decomposition mechanism, due to the position of the aromatic rings.

If we compare these results with those obtained for polycarbonates and polythiocarbonates with other kind of groups between the aromatic rings,[5,7,11] it is possible to point out that there are several results. In fact, we have not found a relationship between the kinetic reaction order and the polymer structure. Polycarbonates and polythiocarbonates degrade according to a zero or first kinetic order, without take into account the nature of the groups bounded to the aromatic rings. Furthermore, we also studied the thermal degradation of polyesters, and the results were similar: polymers degrade according to a zero or first kinetic order, independently of the polymer structure.[6,12] Probably there are several superimposed degradation mechanisms which depend from both, the functional group and the polymer structure.

Except polymers V and VI which have the higher activation energies, the *E* values were very similar, but some differences are observed between poly(ester-carbonates) and poly(ester-thiocarbonates). These differences can be interpreted in terms of the differences of the structure between the polymers, due principally to the position of the aromatic rings, that could play an important role in the degradation process. Anderson and Freeman[13] and Rudin[14] suggested that the differences in activation energy and reaction order could be due to two different reaction mechanism; one would be dominant in a lower temperature range and the other in a higher range.

On the other hand, it has been described for complex reactions as those that occur in thermal degradation of condensation polymers, the kinetic order and *E* values have limited significance, due to the fact that the physical state of the sample is far from ideal and may change during the reaction. Furthermore, the degradation process in polymers as these that contain two functional groups, can be composed of several stages that can not be separated in clear range of temperature.[15] So, assumptions about the reaction order and constancy of the activation energy over a particular temperature range may therefore be questionable. Moreover, the kinetic treatment of thermal degradation assume that the residual weight of the sample may be handled as if it was a concentration, which is of doubtful validity.[16]

In spite of those considerations, thermal degradation is a good tool to analyze the influence of the unit repeating structure in the thermal stability of these polymers, and to determine the temperature range in which they can be used, and the activation energy associated with the total degradation process.

Acknowledgments

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