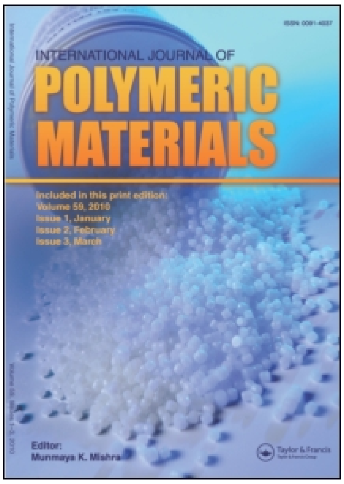

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Thermogravimetric Analysis of Polyesters Derived from 2,2-bis(4-chloroformyl-phenyl)-propane and 4,4′-Biphenyl-Dicarboxyl Chloride

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The thermal stability and the kinetic parameters of a series of polyesters were studied by non-isothermal thermogravimetry. The thermal decomposition temperatures (TDT) depend principally on the nature of the diphenols, in the sense that when the bulk of the diphenol is increased, the TDT values decrease. The kinetic parameters, determined using the Arrhenius relationship, show that these polyesters degrade by a complex mechanism or possibly two or more superimposed processes, probably due to the complex structure of both diacids and diphenols.

KEY WORDS Thermogravimetric, polyesters, chloroformyl-phenyl, propane, biphenyl-dicarboxyl chloride

INTRODUCTION

The study of the thermal decomposition of condensation polymers is hindered by the inherent complexity of the system, due to the physical state of the sample and the involved reactions, which are a set of many simultaneous single-step reactions and/or sequential reactions. Although non-isothermal thermogravimetric methods provide limited information on the nature of complex reactions, they are very useful for following the mass change of a polymeric material with changing temperature.

On the other hand, the degradation of polymers under normal conditions is a major factor limiting the use of these materials, because all polymers degrade in the environment to which they are exposed, and important properties are affected adversely. In this way, in thermogravimetric analysis, the mass changes of a sample are continuously recorded as a function of time or temperature as the sample is heated. Thermograms provide information on the sample composition and principally about the thermal stability, as well as about the relationship between the kinetic parameters and the chemical changes which occur during heating.

It is known that the properties of polyesters are affected by temperature and other factors, imparting a special importance to the temperature ranges in which they degrade. By using the thermal methods, both isothermal and non-isothermal, it is also possible to obtain reasonable kinetic data.[1]

Continuing our works on the study of the thermogravimetric behavior of polyesters,[2,3] in this paper we describe the thermal degradation of polyesters derived from two diacid chlorides, 2,2-bis(4-chloroformylphenyl)-propane and 4,4'-biphenyl-dicarboxyl chloride, and three diphenols, 2,2-bis-(4-hydroxyphenyl)-propane, 4,4'-dihydroxybiphenyl, and 1,1-bis(4-hydroxyphenyl)-4-methyl-cyclohexane. All these compounds were synthesized under phase transfer conditions,[4] and the kinetic parameters were associated with the degradation process.

EXPERIMENTAL

Polyesters were synthesized under phase transfer conditions from the diacid chlorides 2,2-bis-(4-chloroformylphenyl)-propane (**I**) and 4,4'-biphenyl-dicarboxyl chloride

TABLE I

Thermal decomposition temperatures (TDT) of polyesters

Polyester	TDT (°C)
Ia	435
Ib	380
Ic	399
IIa	397
IIb	415
IIc	368

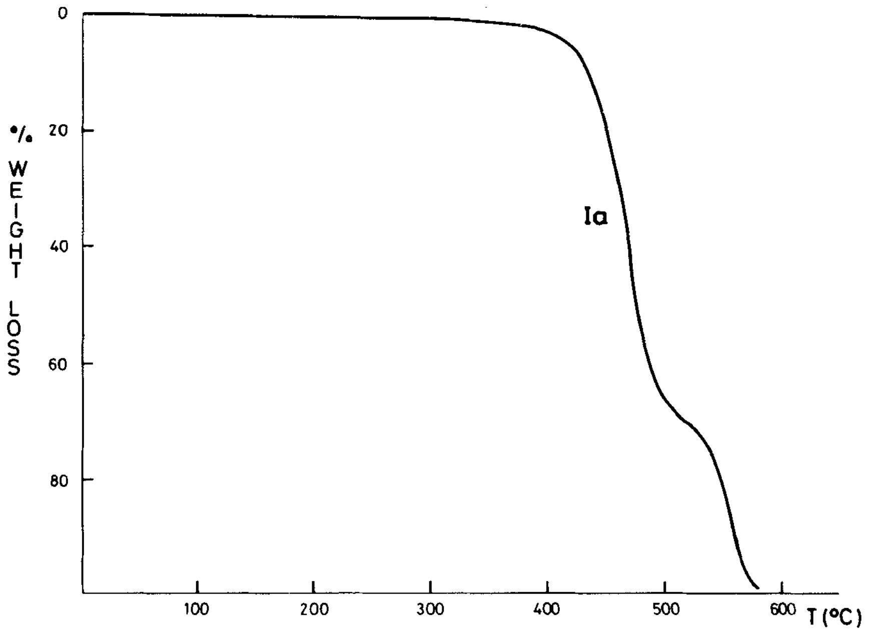


FIGURE 1 Thermogravimetric curve for polyester **Ia**.

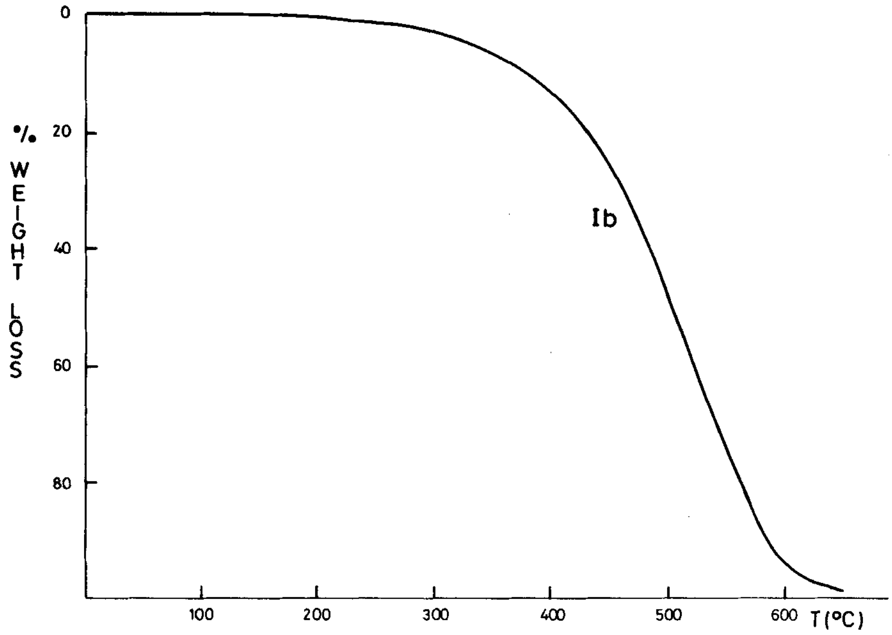


FIGURE 2 Thermogravimetric curve for polyester **Ib**.

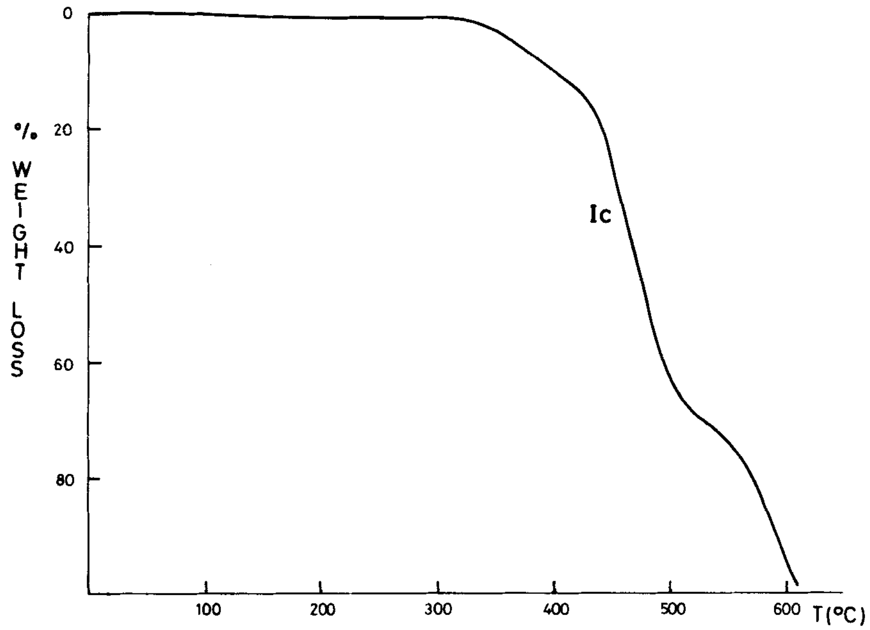


FIGURE 3 Thermogravimetric curve for polyester **Ic**.

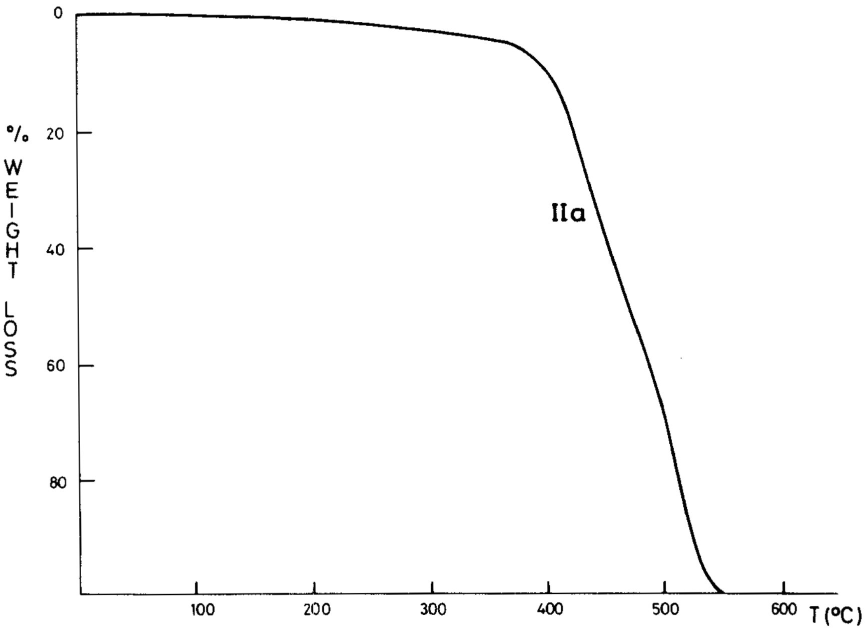


FIGURE 4 Thermogravimetric curve for polyester **IIa**.

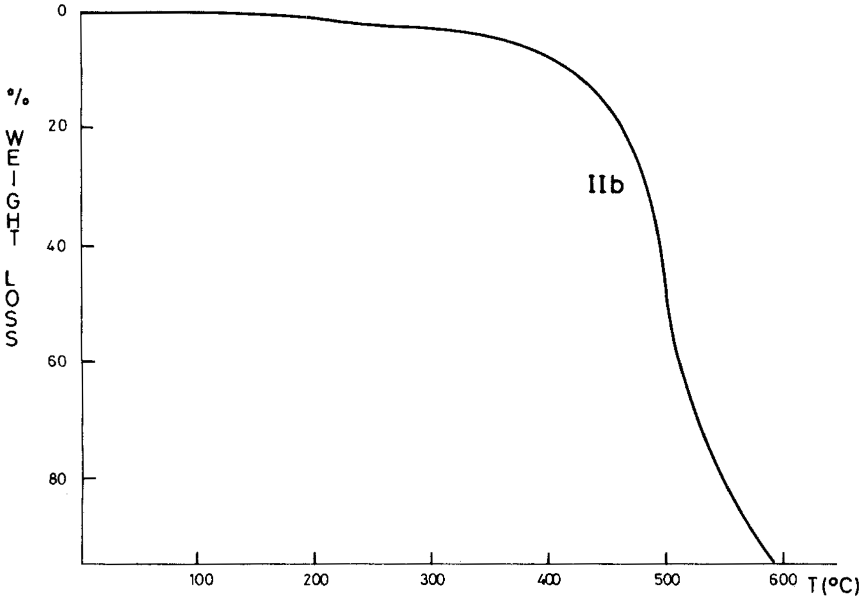


FIGURE 5 Thermogravimetric curve for polyester **IIb**.

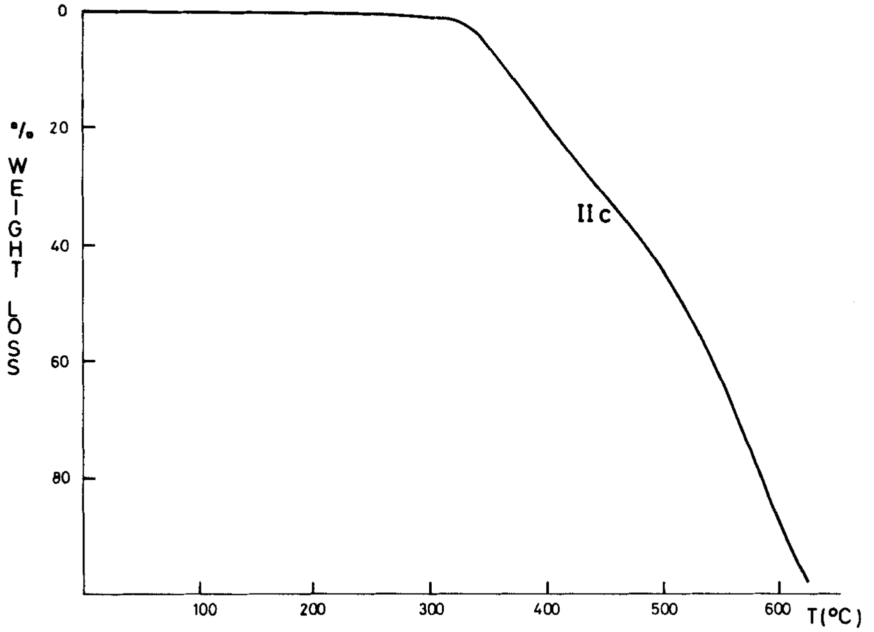


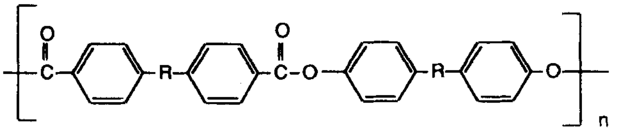
FIGURE 6 Thermogravimetric curve for polyester **IIc**.

(**II**), and the diphenols 2,2-bis-(4-hydroxyphenyl)-propane (**a**), 4,4′-dihydroxy-biphenyl (**b**), and 1,1-bis(4-hydroxyphenyl)-4-methyl-cyclohexane (**c**), according to a procedure described previously.[4]

The thermogravimetric analyses 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 50 and 650°C with a heating rate of 20°C min^{-1} under nitrogen flow.

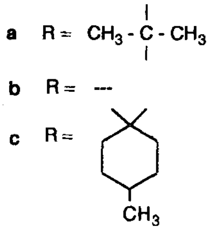
RESULTS AND DISCUSSION

The following polyesters:



I (a-c)
II (a-c)

where



were synthesized under phase transfer conditions using several quaternary ammonium and phosphonium salts as catalysts, then characterized by IR and ^{1}H NMR spectroscopy and elemental analysis.[4]

Table I shows the thermal decomposition temperatures (TDT) for the six polyesters. These values represent the temperature at which the polyesters lost 10% of their mass, and Figures 1–6 show the thermogravimetric curves.

For the polyesters derived from diacid chloride **I**, the TDT values decrease when the volume of the diphenol is increased because the polymeric chain is more flexible. The exception is polyester **Ib**, which has no group between the phenol rings.

Since polyester **Ib** has the more rigid diphenol one might predict it to have the high value of TDT, but on the contrary it is observed to have the lower value. This polyester was insoluble in the reaction media and in all organic solvents, and therefore the molecular weight should be low.

Polyesters **IIa** and **IIc** show the same trend, in the sense that when the bulk of the diphenolate is increased, the TDT value decreases. However, **IIb** shows the higher TDT value. This polyester was insoluble in the reaction media and in all organic solvents, and therefore the molecular weight is expected to be low. On the other hand, in polyester **IIb** both the diacid chloride and diphenolate have a very rigid structure, which explains the large TDT value of 415°C.

The thermal stability of these polyesters depends primarily on the nature of the diphenols, but when both parts of the repeating unit have a high rigidity, as in polyester **IIb**, the thermal stability is increased.

It is possible that the molecular weight also influences the process. In fact, all the samples had similar values of η_{inh}, except **Ib** and **IIb**, which were insoluble in the reaction media and precipitated during the polymerization step. It is thus impossible to determine the influence of the molecular weight, although it probably will be minor due to the steric nature of the polymeric chains.

The kinetic process can be represented by the equation:

$$-(d\alpha/dt) = k_a f(\alpha) \tag{1}$$

where α represents the conversion of the reactant at time t, $f(\alpha)$ is the conversion factor of α, and k_a is the rate constant. For a true reacting system, $f(\alpha)$ is a function of time and k_a is a function of the temperature. The temperature dependence of the rate constant is assumed to have the Arrhenius form:

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

where A is the pre-exponential factor, E the activation energy and R the gas

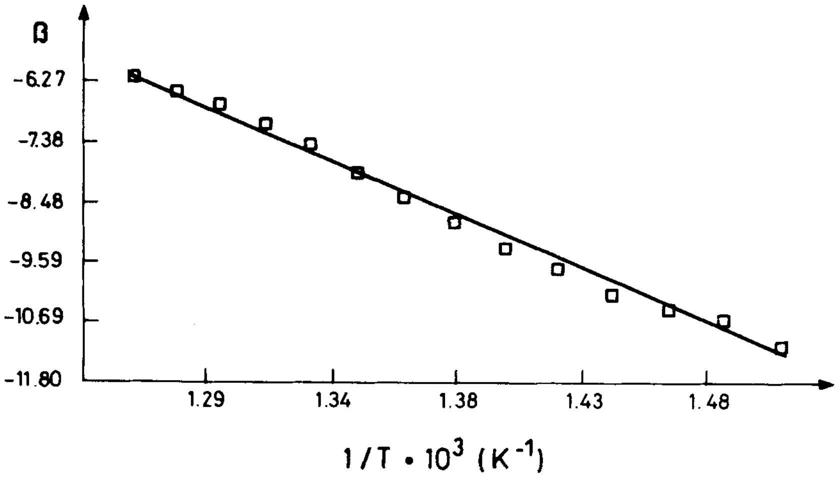


FIGURE 7 Arrhenius plot for the degradation of polyester **Ia**.

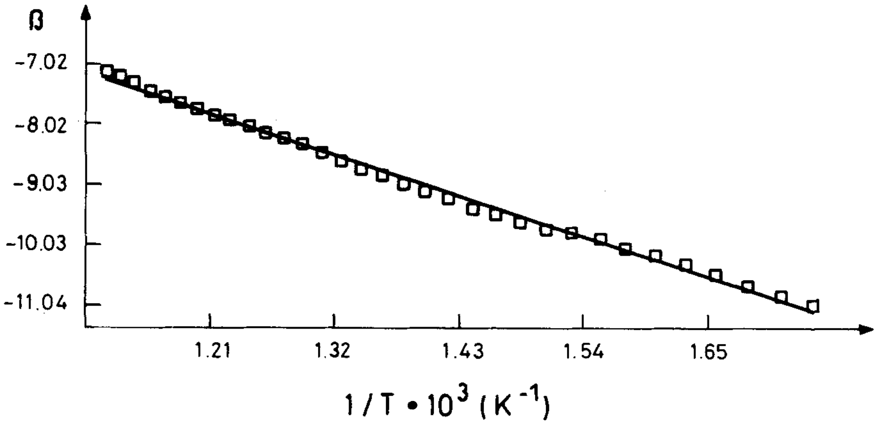


FIGURE 8 Arrhenius plot for the degradation of polyester **Ib**.

constant. In this work we used the simplest and the most frequently used model for $f(\alpha)$ in the analysis of non-isothermal data:

$$f(\alpha) = (1 - \alpha)^n \tag{3}$$

where n is the reaction order.

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 mass-fraction data, according to the method developed by Wen and Lin.[5] Equations (1), (2), and (3) were combined and used in logarithmic form:

$$\beta = \ln[-v(d\alpha/dT)/(1 - \alpha)^n] = \ln A - E/RT \tag{4}$$

where v is the heating rate (20°C min^{-1}). A computerized linear multiple-regression

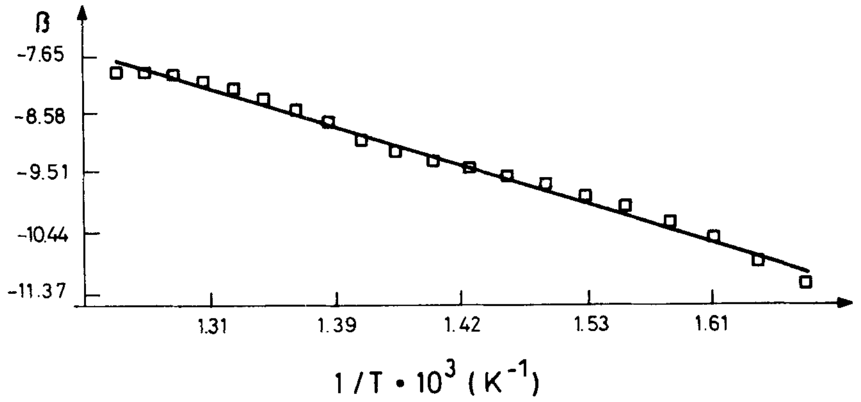


FIGURE 9 Arrhenius plot for the degradation of polyester **Ic**.

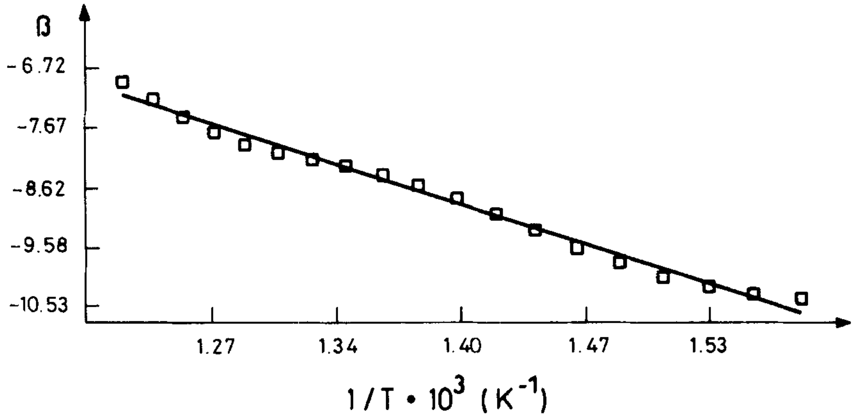


FIGURE 10 Arrhenius plot for the degradation of polyester **IIa**.

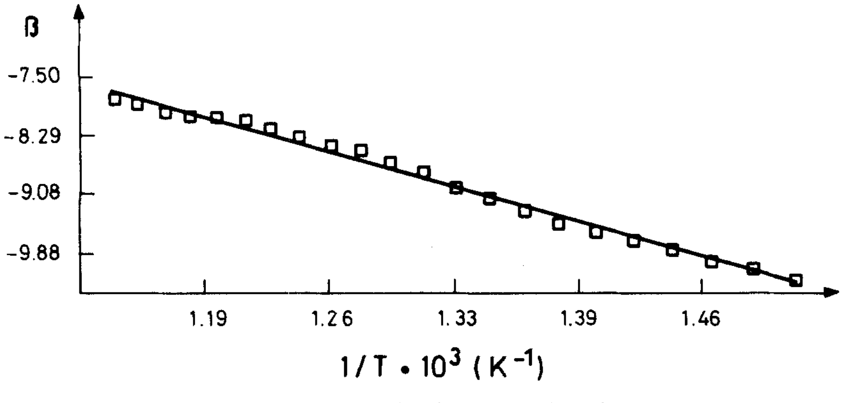


FIGURE 11 Arrhenius plot for the degradation of polyester **IIb**.

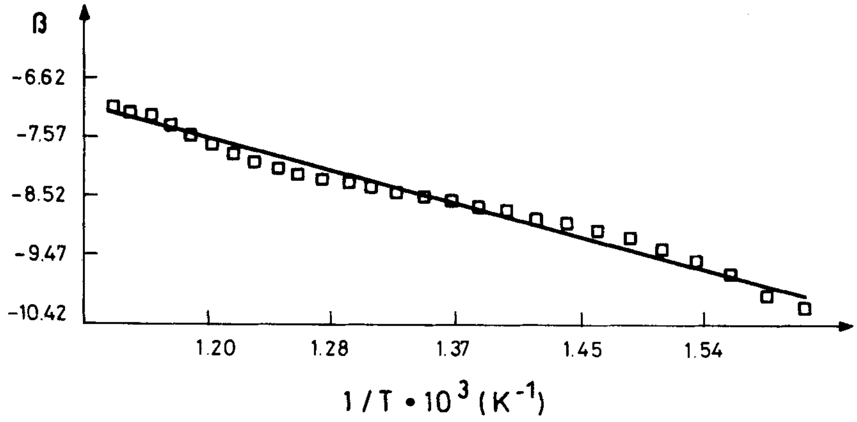


FIGURE 12 Arrhenius plot for the degradation of polyester **IIc**.

TABLE II

Kinetic parameters of the thermal decomposition of polyesters

Polyester	Range (°C)	*n*	*E* (kcal/mol)	A (sec^{-1})
Ia	390–520	0.5	42.45	1.22×10^9
Ib	300–620	0.25	12.76	1.02
Ic	330–520	0	17.15	2.62×10^1
IIa	360–540	0.25	20.57	2.98×10^2
IIb	390–600	0.25	14.71	2.41
IIc	350–610	0.5	12.64	1.12

program was developed to calculate the kinetic parameters *E* and *A* from a linear least-squares fit of the data in semi-logarithmic plots of β versus $1/T$, which are shown in Figures 7–12. The linearity of each plot was good (>.99); some scatter was detected at the beginning and end of the decomposition, which can be attributed to the difficulty in obtaining accurate measurements at the beginning and end of an experiment, a frequent problem in kinetics measurements.

Table II shows the kinetic parameters *E* and *A* determined for the polyesters, as well as the temperature range and the reaction order *n*.

The *n* values for all the polyesters except **Ic** were either 0.25 or 0.5, which means that the degradation is a complex process, or may consist of two or more superimposed processes. In a previous paper[2] we studied the thermal degradation of some poly(ether-ester)s derived from the same diphenols and similar diacids but with the oxymethylene group between the aromatic rings and the carboxilic group. In that work polyesters in which both structures were different had an *n* value of 0.5, indicative of a complex degradation process. On the other hand, when both structures were similar, the *n* value was zero.

In this work it is likely that all polymers studied degrade by one complex mechanism or a composite mechanism of superimposed processes, especially considering the complex structure of both the diacids and diphenols. However, it has been argued that it is difficult to determine the reaction order based only on the limited information obtained from thermal analysis.[6]

On the other hand, the E values described in Table II only represent the activation energy for the global process, and as was described, when the reaction temperature range decreases, E increases. With a decrease in E, the reaction becomes less temperature sensitive, occuring over a broad temperature range. Also, an increase in E is generally accompanied by an increase in the pre-exponential factor A.[6]

It has also been pointed out that for the decomposition of condensation polymers, which implies several complex reactions, the kinetic order has no significance, and that some disparity in the E values is of limited significance, due mainly to the far from ideal physical state of the sample. Moreover, the kinetic treatment of thermal degradation is based on the questionable assumption[7-8] that the residual mass of the sample may be considered as a concentration.

In spite of the above kinetic considerations, thermogravimetric analysis of these polyesters leads to the conclusion that their thermal stability is influenced by both the structure of the diacid and especially of the diphenol, in the sense that when the volume of the diphenol is increased, the TDT values decrease because the chain is more flexible.

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