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Thermogravimetric analysis of polyesters derived from terephthalic, tetrachloroterephthalic and related diacids with bisphenol A

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Abstract

The thermogravimetric behaviour of polyesters derived from terephthalic, tetrachloroterephthalic and related diacids, with $-CH_2-$ and $-OCH_2-$ as spacer groups with bisphenol A as diphenol, was studied by dynamic thermogravimetry. Polyesters derived from a diacid with an entirely aromatic structure degrade at higher temperatures than those derived from aliphatic diacids owing to the flexibility of the polymeric chain. Polyesters derived from tetrachloroterephthalic acid showed a higher thermal stability than that derived from terephthalic acid, but for the aliphatic polyesters, the chlorinated form showed a lower stability than those without chlorine atoms, probably because the influence of the aliphatic character is greater. The kinetics parameters of the thermal decomposition were determined by the Arrhenius relationship; in the range considered, all the studied polyesters degrade in a single stage, but probably via complex reactions.

INTRODUCTION

Thermal analysis includes a group of analytical methods in which the properties of a substance or a polymeric material are measured as a function of temperature. Thus dynamic thermogravimetry involves a physical measurement in which the weight loss is recorded as a function of the temperature while the substance is subjected to a controlled temperature programme.

In polymer production, it is very important to determine the thermal stability of the polymeric material because this gives the temperature range over which the material can be used without degradation. The degradation of condensation polymers can occur by a random decomposition or at reactive sites in the polymeric chain, depending on the nature of the

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polymeric material, while depolymerization reactions with monomer formation are characteristic of vinylic polymers. Thus the principal degradation reactions will depend on the polymer structure and the heating conditions [1].

In the degradation of polyesters, intramolecular ester exchange and β-CH hydrogen transfer are the two processes mainly responsible for the primary steps of the thermal decomposition [2]. However, in polyesters derived from aliphatic dicarboxylic acids and diphenols, and in totally aromatic polyesters, the ester exchange process prevails in the primary thermal cleavage [3,4].

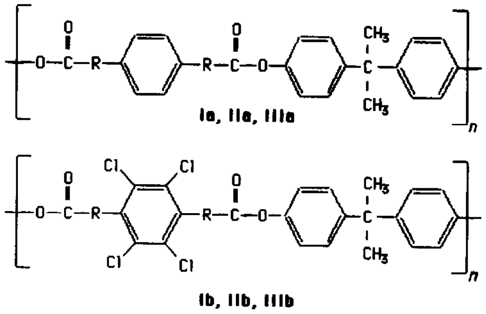
However, for chlorinated polyesters, when the chlorine content is increased, the thermal stability decreases [5], probably because the bulky chlorine atoms increase the rigidity of the polymer.

In earlier studies, we have reported the thermal stability of polythiocarbonates [6], polycarbonates [7], copoly(carbonate–thiocarbonate)s [8,9], chlorinated polycarbonates and polythiocarbonates [10] and poly(ether–ester)s [11], and have determined the thermal decomposition temperature and the kinetics parameters associated with the degradation process.

As a continuation of our work on the thermal degradation of polymers, this paper describes the thermal behaviour of polyesters derived from terephthalic and tetrachloroterephthalic acids and related diacids, with $-CH_2-$ and $-OCH_2-$ as spacer groups, with bisphenol A (2,2-bis(4-hydroxyphenyl)propane) as diphenol; the thermal decomposition temperatures (TDTs) and kinetics parameters were determined, the results obtained from polyesters with chlorine atoms being compared with those without chlorine atoms.

EXPERIMENTAL

Poly(oxycarbonyl-1,4-phenylene-carbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) **Ia**, poly(oxycarbonyl)-1,4-tetrachlorophenylene-carbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) **Ib**, poly(oxycarbonyl-methylene-1,4-phenylene-methylene-carbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) **IIa**, poly(oxycarbonyl-methylene-1,4-tetrachlorophenylene-methylene-carbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) **IIb**, poly(oxycarbonyl-methylene-oxy-1,4-phenylene-oxy-methylene-carbonyloxy-1,4-phenylene-2, 2-propyl-1,4-phenylene) **IIIa** and poly(oxycarbonylmethylene-oxy-1,4-tetrachlorophenylene-oxy-methylene-carbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) **IIIb**, were synthesized by phase-transfer catalysis from the acid dichlorides and bisphenol A using several quaternary ammonium and phosphonium salts in 1,1,2,2-tetrachloroethane as solvent. The synthesis and characterization of these polyesters have been described in previous papers [12,13].



Scheme 1. Polyesters where R is nothing in **Ia** and **Ib**, $-CH_2-$ in **IIa** and **IIb**, and $-OCH_2-$ in **IIIa** and **IIIb**.

Dynamic thermogravimetry analyses were carried out in a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature programme control. Samples (4–7 mg) were placed in a platinum sample holder and the thermal degradation measurements were carried out between 25 and 650°C at 20°C min^{-1} under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The polyesters shown in Scheme 1 were analysed by dynamic thermogravimetry. Figures 1–6 show the thermogravimetric curves for the six polyesters and Table 1 summarizes their TDTs, a TDT being taken as the temperature of 10% weight loss. The shapes of the curves are very similar

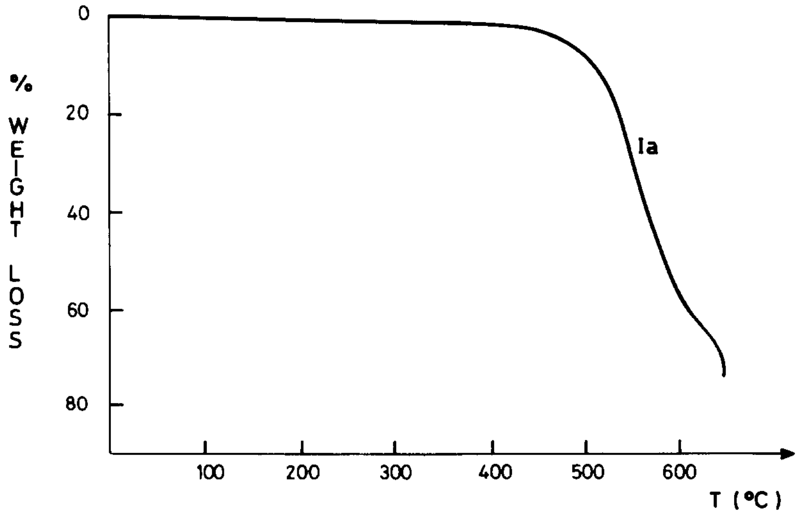


Fig. 1. Thermogravimetric curve for polyester **Ia**.

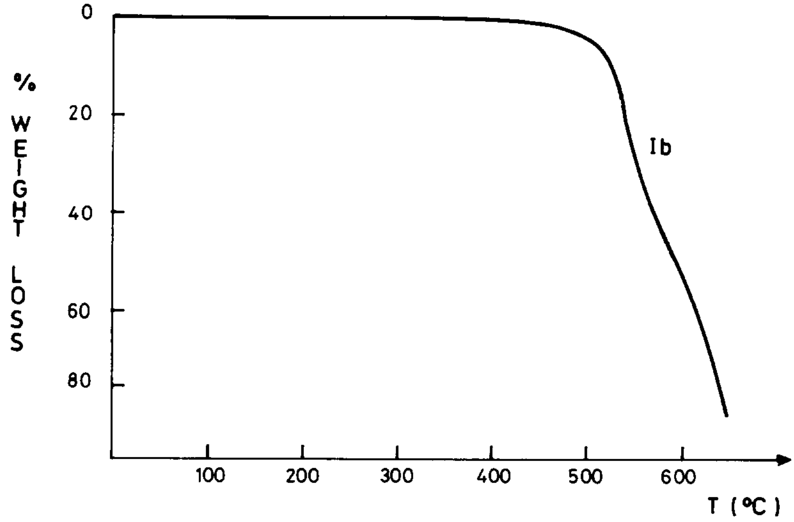


Fig. 2. Thermogravimetric curve for polyester **Ib**.

and all the polyesters degrade in a single-stage process which is characteristic of the thermal decomposition of a large number of macromolecular compounds and provides evidence that no other preferred or competitive simultaneous process occurs.

The aromatic polyesters **Ia** and **Ib** have the highest thermal stability, which shows an important decrease for the aliphatic polyesters, probably

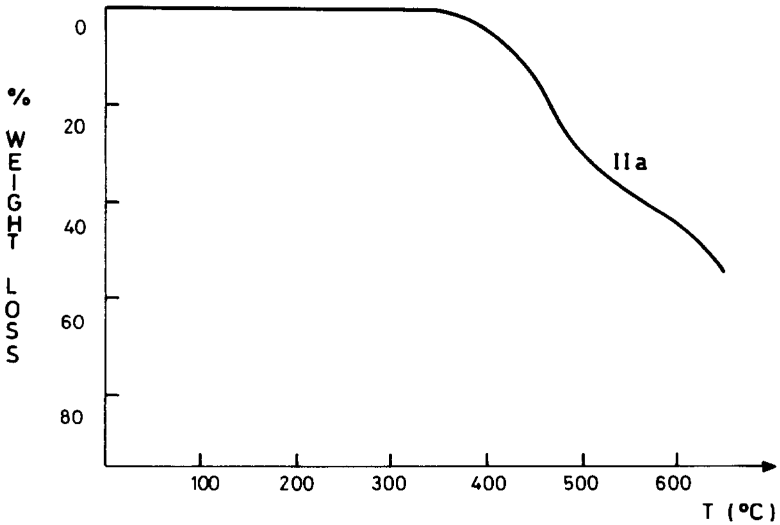


Fig. 3. Thermogravimetric curve for polyester **IIa**.

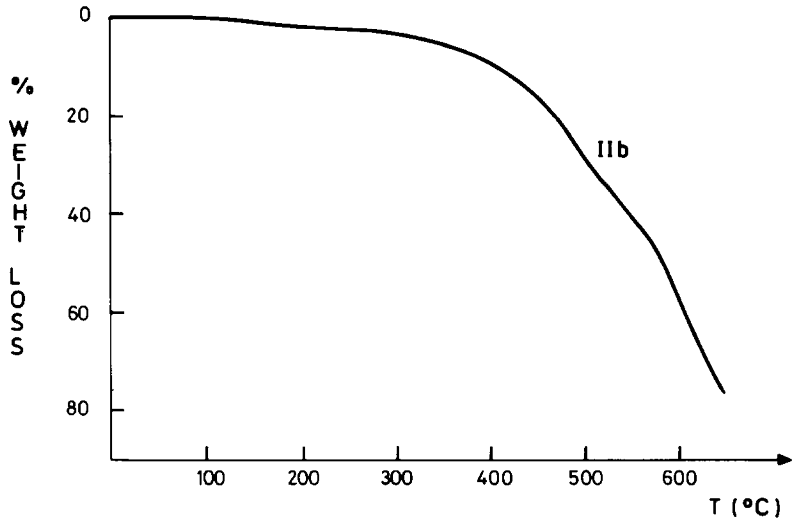


Fig. 4. Thermogravimetric curve for polyester **IIb**.

owing to the higher flexibility of the polymeric chain as a consequence of the presence of the spacer groups $-CH_2-$ and $-OCH_2-$ between the aromatic ring and the ester group.

The chlorinated aromatic polyester **Ib** showed a higher thermal stability than **Ia** which does not contain chlorine atoms in its structure. However, the aliphatic polyesters **IIa** and **IIIa** without chlorine atoms, showed a lower thermal stability than the chlorinated polyesters **IIb** and **IIIb**, which

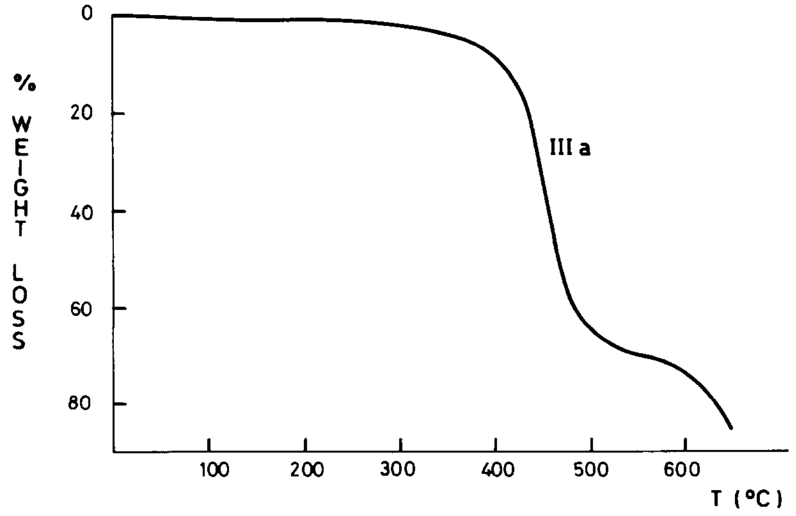


Fig. 5. Thermogravimetric curve for polyester **IIIa**.

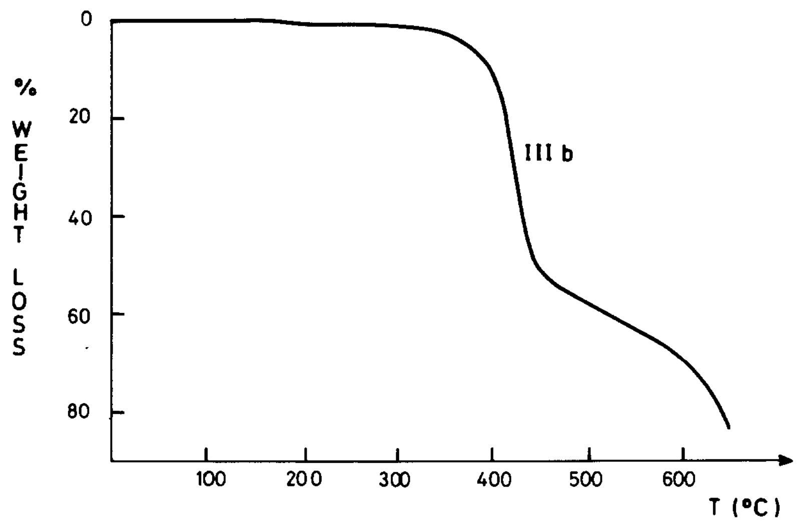


Fig. 6. Thermogravimetric curve for polyester **IIIb**.

indicates that the influence of the aliphatic character is greater than that of the chlorine content.

If we compare the polyesters of the **a** series, there are significant decreases in the TDT values when the spacer groups are incorporated between the aromatic ring and the ester group. The same behaviour was observed for the polyesters of the **b** series, with chlorine atoms in the aromatic ring of the ester group.

The thermal decomposition kinetics of the thermogravimetric weight loss data were attributed to the kinetic equation

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

where α is the 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 min^{-1})

TABLE 1

Thermal decomposition temperatures of polyesters

Polyester	TDT (°C)
Ia	512
Ib	527
IIa	435
IIb	410
IIIa	412
IIIb	401

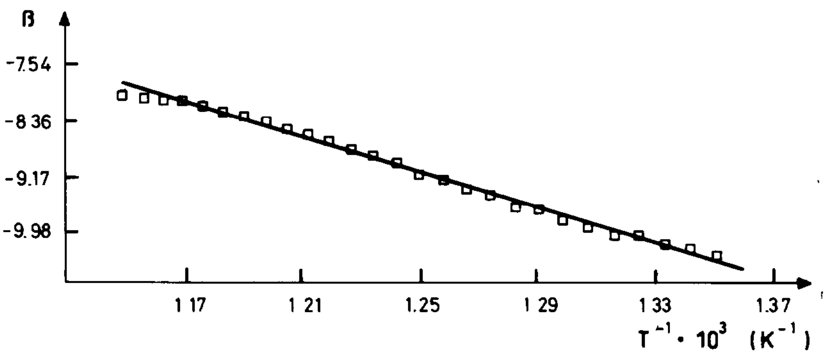


Fig. 7. Arrhenius plot for the degradation of polyester **Ia**.

incorporated directly in the data of temperature versus sample weight fraction, according to the method developed by Wen and Lin [14]. 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

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

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 β versus $1/T$. The Arrhenius plots for the thermal degradation of the polyesters are shown in Figs. 7–12. The linearity (greater than 0.995) of each plot is good, although some scatter is

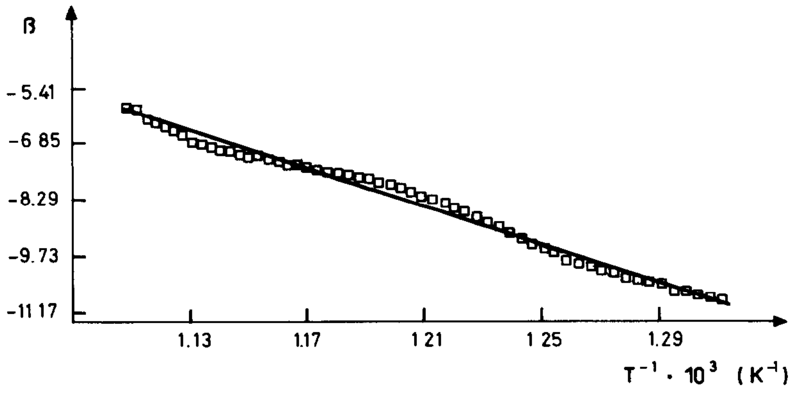


Fig. 8. Arrhenius plot for the degradation of polyester **Ib**.

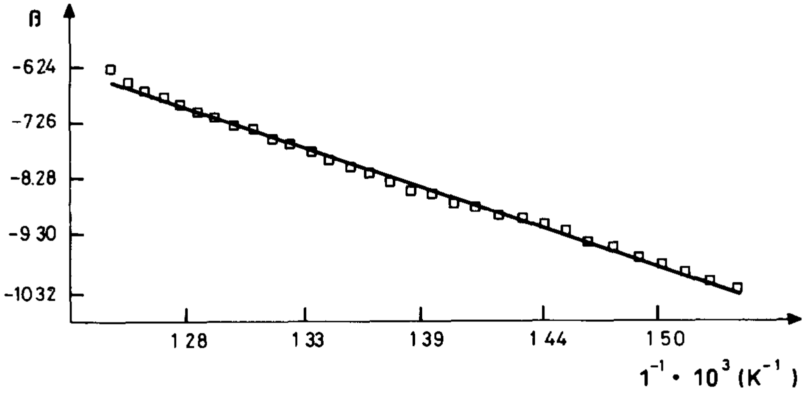


Fig. 9. Arrhenius plot for the degradation of polyester **IIa**.

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, as is frequently encountered in kinetics measurements.

Table 2 shows the kinetics data obtained according to the above method and the temperature range used to calculate the parameters.

Polyesters **Ia** and **IIb** showed a zero reaction order, which means that $d\alpha/dt$ is constant and implies that if the sample mass is increased the rate of decrease in mass remains unchanged, as in a simple evaporation, because the concentration of volatile substances at the surface of the sample remains constant. The shape of the sample means that the diffusion and evaporation of the volatile products from the surface are the factors that control the degradation rate [15].

Polyesters **IIa** and **IIIa**, however, showed a 0.5 reaction order, which implies a complex degradation process in which two or more processes can

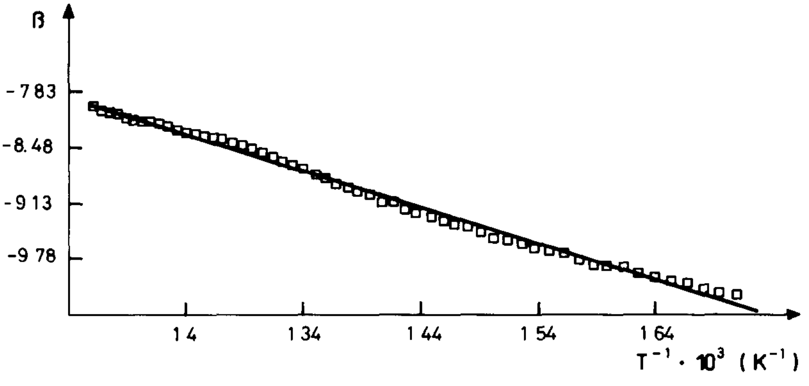


Fig. 10. Arrhenius plot for the degradation of polyester **IIb**.

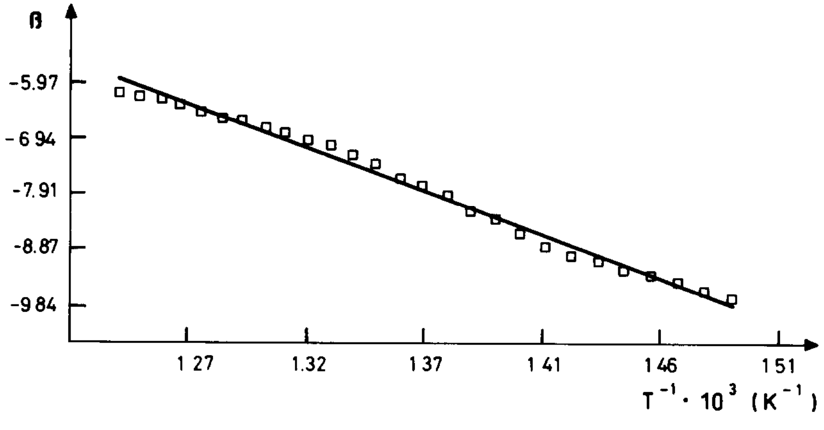


Fig. 11. Arrhenius plot for the degradation of polyester **IIIa**.

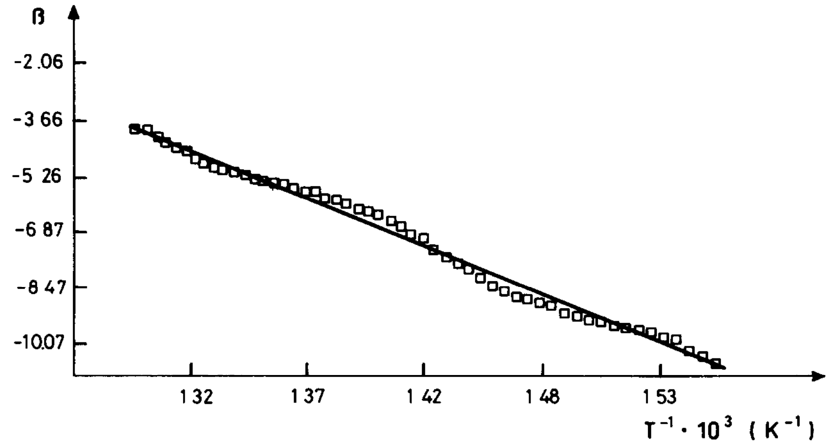


Fig. 12. Arrhenius plot for the degradation of polyester **IIIb**.

TABLE 2

Kinetics parameters for polyesters

Polyester	Temp. range (°C)	n	E (kcal mol^{-1})	A (sec^{-1})
Ia	470–600	0	27.2	2.84×10^{3}
Ib	490–630	1	51.1	6.55×10^{9}
IIa	380–530	0.5	27.9	6.31×10^{4}
IIb	310–490	0	8.9	6.10×10^{-2}
IIIa	400–530	0.5	33.8	4.81×10^{6}
IIIb	370–500	1	53.6	3.29×10^{13}

be superimposed, especially in condensation polymers such as these, and which cannot be clearly separated in temperature. This reaction order was observed in polyesters with the $-CH_2COO-$ and $-OCH_2COO-$ groups, which can participate in the degradation process and produce complex mechanisms with the participation of all the groups of the molecule [11].

If we analyse the reaction order of the degradation process, there is no logical sequence in the results obtained for the different polyesters. It has been pointed out that for complex reactions such as those that occur in the thermal degradation of condensation polymers, the kinetic order and E values have a limited significance, mainly because the physical state of the sample is far from ideal and may change during the reaction or degradation process. Also, it is important to remember that the degradation process, especially in polyesters and chlorinated polyesters, can be composed of several stages that cannot be clearly separated by temperature [16]. Therefore, assumptions concerning the reaction order and the constancy of activation energy over a temperature range may be questionable. Moreover, the kinetic treatment of the thermal degradation assumes that the residual weight of the sample may be handled as if it was a concentration, which is of doubful validity [17].

Nevertheless, thermal degradation is a very useful tool for analysing the thermal stability of these polyesters and for determining the temperature range in which they can be used, as well as for assessing the influence of the diacid structure (aliphatic or aromatic) and the presence of chlorine atoms bonded to the aromatic ring. In addition, the kinetics parameters associated with the total degradation process can be determined.

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