Thermal Degradation Studies of Poly (Amide-Ester)s

L. H. Tagle[a]; A. Opazo[a]; D. Radic[a]; F. R. Diaz[a]

[a] Faculty of Chemistry, Catholic University of Chile, Santiago, Chile

PLEASE SCROLL DOWN FOR ARTICLE

Thermal Degradation Studies of Poly(Amide-Ester)s

L. H. TAGLE*, A. OPAZO, D. RADIC and F. R. DIAZ

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

The thermal behaviour of poly(amide-ester)s with the amide group in the side chain was studied. Polymers were sinthesized from the diphenol-amides N-(2,6-dichloro-4-nitrophenyl)-2, 2-bis(4-hydroxyphenyl)-propanamide, N-(2, 6-dichloro-4-nitrophenyl)-3,3-bis(4-hydroxyphenyl)-butanamide, and N-(2,6-dichloro-4-nitrophenyl)-4, 4-bis(4-hydroxyphenyl)-pentanamide and terephthaloyl chloride, isophthaloyl chloride and adipoyl chloride under phase-transfer conditions using several phase-transfer catalysts. The thermal decomposition temperature was influenced by both, the nature of the diacid and the length of the side chain, those derived from terephthaloyl chloride being more stable than those derived from isophthaloyl chloride and adipoyl chloride. All polymers degrade in a single-step process and the kinetics parameters were determined using the Arrhenius relationship and a computer program.

Keywords: Diphenol-amide; poly(amide-ester)s thermal degradation; dynamic thermogravimetry; kinetic parameters

INTRODUCTION

Thermogravimetry is a well known analytical tool which gives weight loss information about materials that have been exposed to a temperature. In this sense dynamic thermogravimetry has been widely used for studying the degradation process of polymeric materials and also determines the kinetics parameters, especially the activation energy associated with the entire temperature range. A non-isothermal procedure shows several advantages, such as that the kinetics parameters can be obtained from a single measure which avoids the

---

*Corresponding author. Fax: + 56-2-686-4744.

problems arising from different samples; and also that it is not necessary to raise a required temperature which could be induced to some degradation in the pre-heating period as it would be in the iso- thermal method [1].

For polymers it is of great commercial importance to know the highest permissible temperature and time of service under specified conditions because it is then possible to assess the scope of their ap- plications [2]. Normally all polymeric materials degrade under normal conditions of use and this is one of the major factors limiting their applications. In this sense several properties are affected in the deg- radation process, such as the mechanical strength, dielectric quality and aesthetic appearance. This can lead to the failure of the polymeric material when is being used and also to the foreshortening of the life time that has been recommended [3].

Previously we have studied the thermal degradation of several kinds of condensation polymers having one or two functional groups in the repeating unit, like polycarbonates and polythiocarbonates, to which we have introduced an ester group as a second functional group, showing that the thermal behaviour depends on both groups [4, 5]. When we studied polycarbonates and polythiocarbonates with an amide group (from aliphatic or aromatic amine) in the main chain, we did not observe a great difference in the thermal decomposition tem- perature, although there was an important difference in the kinetics parameters, in the sense that polymers derived from an aromatic amine degrade in a two-step process, as opposed to those derived from an aliphatic amine which degrade in a single-step process [6].

In this work we present the thermal behaviour of poly(amide-ester)s derived from diphenol-amides with an amide group in the side chain, and aromatic and aliphatic diacids, and we determined the thermal de- composition temperatures and the kinetics parameters associated with the degradation process.

EXPERIMENTAL PART

Poly(amide-ester)s were synthesized from the diphenol-amides N-(2, 6-dichloro-4-nitrophenyl)-2, 2-bis(4-hydroxyphenyl) - propanamide (I), N-(2,6-dichloro-4-nitrophenyl)-3,3-bis(4-hydroxyphenyl) - butanamide

(II), and N-(2,6-dichloro-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (III) and terephthaloyl chloride (a), isophthaloyl chloride (b) and adipoyl chloride (c) under phase-transfer conditions using several phase-transfer catalysts, according to a procedure described earlier [7].

Thermogravimetric analyses were carried out in a STA 625 Polymer Laboratories thermobalance. Samples of 4–7 mg were placed in a platinum sample holder and the thermogravimetric measurements were carried out between 25 and 800°C with a heating rate of $20°C\,min^{-1}$ under N_2 flow.

RESULTS AND DISCUSSION

Poly(amide-ester)s with the following structures:

$$m = 0\ (I),\ 1\ (II),\ 2\ (III)$$
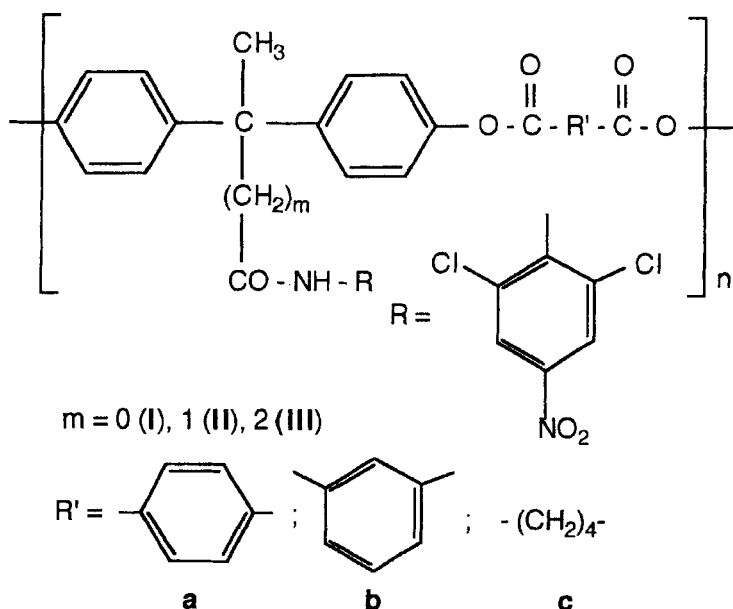
were synthesized under phase-transfer conditions using several phase-transfer catalysts in CH_2Cl_2 as solvent at 20°C, according to a procedure described previously, and were characterized by elemental analysis and IR spectroscopy. The structures were in accord with those proposed [7].

Table I shows the thermal decomposition temperatures (TDT) for the nine poly(amide-ester)s. These values were taken as the temperature at which polymers lost 10% of their weight. Figures 1 – 9 show the TG curves for the poly(amide-ester)s. All poly(amide-ester)s degrade in a single curve.

From these results it is possible to see that the thermal stability increases in respect to the nature of the ester group, and poly(amide-ester)s derived from terephthalic acid were more stable than those derived from isophthalic acid; and these more stable than those derived from adipic acid. Polymers derived from an aliphatic diacid showed the lower values of TDT. In this sense, the TDT values have a logical sequence because polymers derived from aromatic diacids were more stable than those derived from the aliphatic ones, and those derived from the more symmetrical structure as terephthalic acid were more stable than those derived from isophthalic acid.

On the other hand, if we see the influence of the diphenol-amide, there is an increase of the thermal stability when the length of the side chain is increased. If the aromatic side group is nearer to the main chain, the decomposition probably will be faster due to steric hindrance between the aromatic groups of the main chain and the chlorine atoms in the side aromatic group. If the aromatic side group is separated from the main chain by the —CH_2— groups, there will be less interaction between it and the aromatic group of the main chain, and the decomposition will occur at higher temperatures.

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

$$-(d\alpha/dt) = k_n(1 - \alpha)n \qquad (1)$$

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 $-(d\alpha/dt)$

TABLE I   Thermal decomposition temperatures (TDT) of poly(amide-ester)s

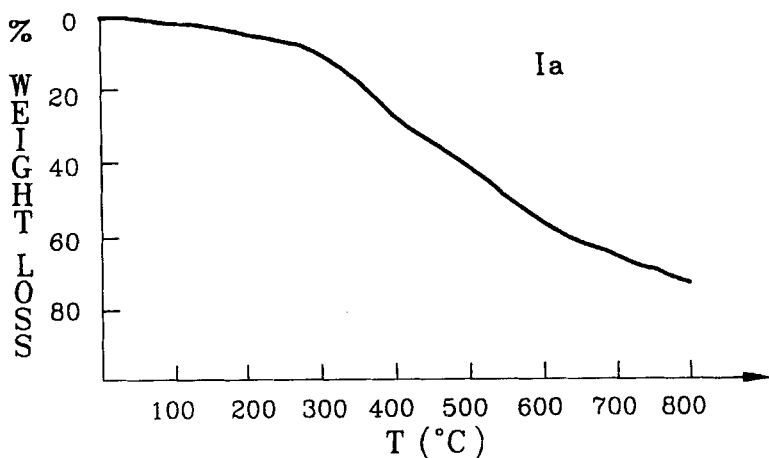| Polymer	TDT (°C)		
	a	*b*	*c*
I	295	292	260
II	313	305	283
III	330	315	293

FIGURE 1   Thermogravimetric curve for poly(amide-ester) **Ia**.

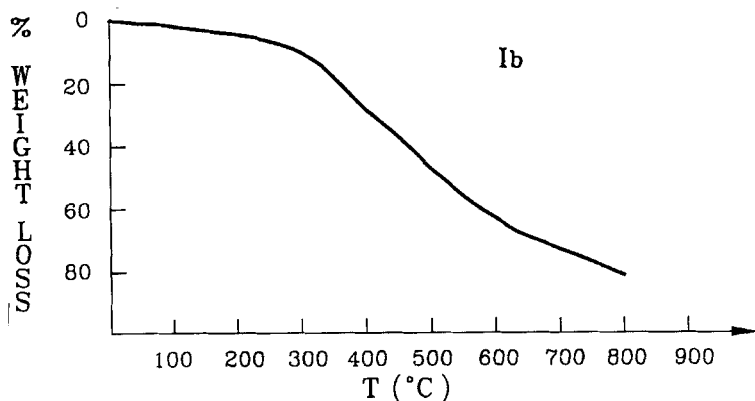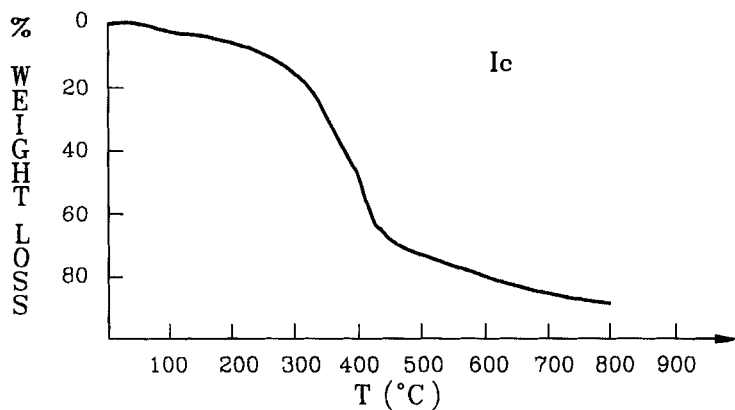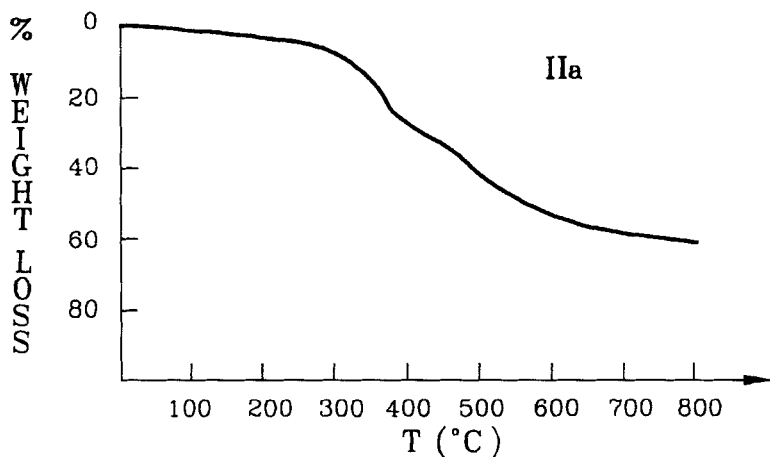

FIGURE 2   Thermogravimetric curve for poly(amide-ester) **Ib**.

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 form the Arrhenius relation

$$k_n = A \exp(-E/RT) \qquad (2)$$

FIGURE 3   Thermogravimetric curve for poly(amide-ester) **Ic**.

FIGURE 4   Thermogravimetric curve for poly(amide-ester) **IIa**.

where E is the activation energy, A the pre-exponential factor, T the absolute temperature, and R the gas constant. Eqs. (1) and (2) were combined and used in logarithmic form

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

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from linear least-squares fit of
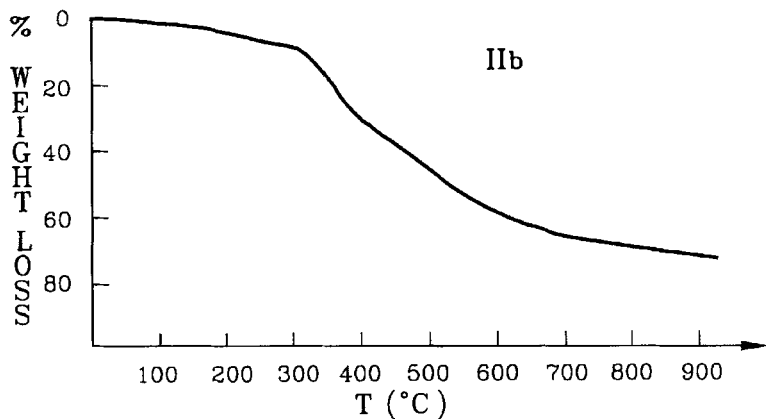
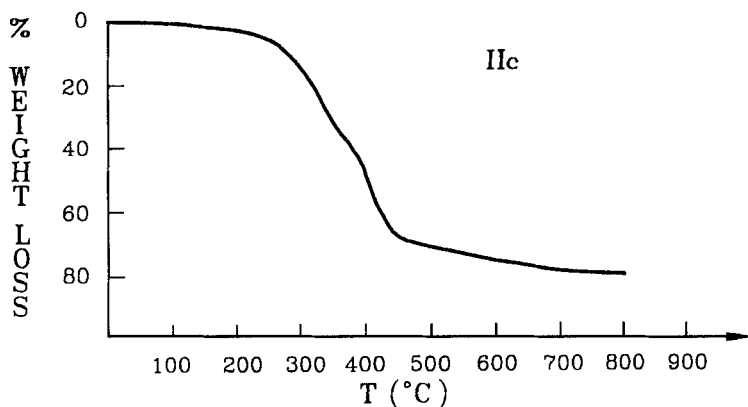FIGURE 5   Thermogravimetric curve for poly(amide-ester) **IIb**.

FIGURE 6   Thermogravimetric curve for poly(amide-ester) **IIc**.

the data in a semilogarithmic plot of β *vs.* $1/T$. Figures 10–18 show those graphics and the results are summarized in Table II. The linearity of the plots was > .995, although some scatter was detected at the beginning and end of each decomposition, which can be attributed to the difficulty of making accurate measurements at the beginning and end of an experiment, as is frequently encountered in kinetic measurements.

Table II shows the kinetics parameters obtained for the degradation process in the considered range. Poly(amide-ester)s derived from
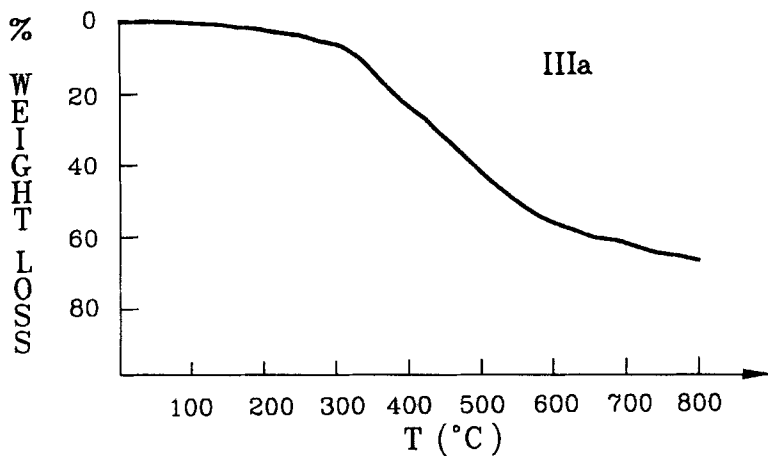
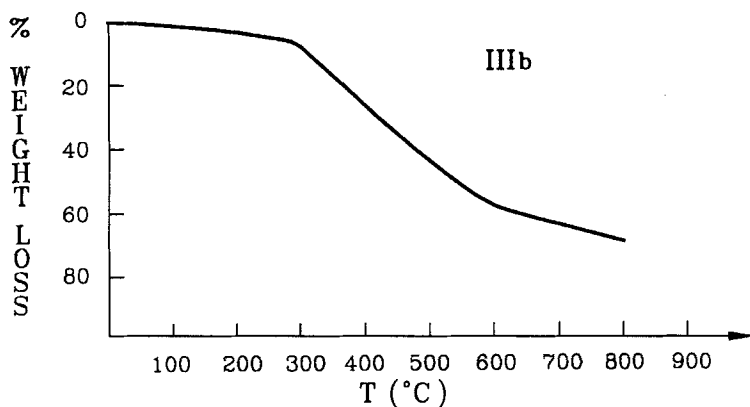FIGURE 7   Thermogravimetric curve for poly(amide-ester) **IIIa**.

FIGURE 8   Thermogravimetric curve for poly(amide-ester) **IIIb**.

aromatic diacids showed a single-step degradation of 0.25 reaction order. A 0.25 reaction order implies that the degradation is probably a complex process or may consist of two or more superimposed processes. Rather than the single curves showed in the Figures 10 – 18, it is probable that there was a complex degradation process, which could be influenced by both the main and the side chains. This behaviour have been described in the degradation process of poly(carbonate)s
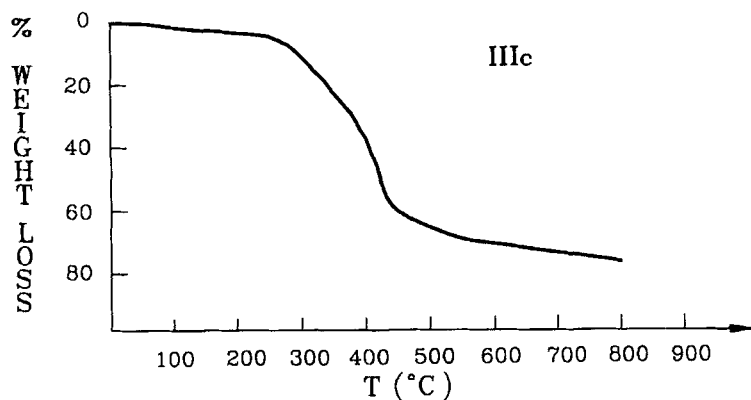
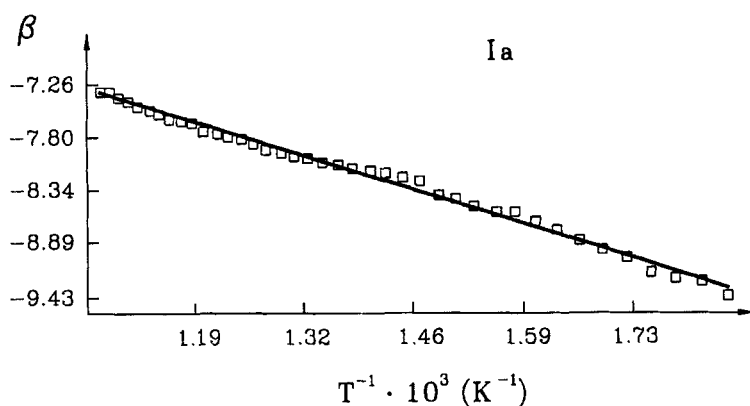FIGURE 9   Thermogravimetric curve for poly(amide-ester) **IIIc**.

FIGURE 10   Arrhenius plot for the degradation of poly(amide-ester) **Ia**.

and poly(thiocarbonate)s containing also an ester or an amide group, in the main or in the side chain [4–6].

The results obtained for poly(amide-ester)s derived from adipic acid (**Ic, IIc, IIIc**) also showed a single-step degradation but of zero reaction order. The degradation range considered for these poly(amide-ester)s was less than that for the aromatic ones. A zero reaction order implies that $-(d\alpha/dt)$ is constant, which means that when the mass of a sample is increased, the rate of loss of mass is constant. This can happen if the concentration of volatile material at the surface is
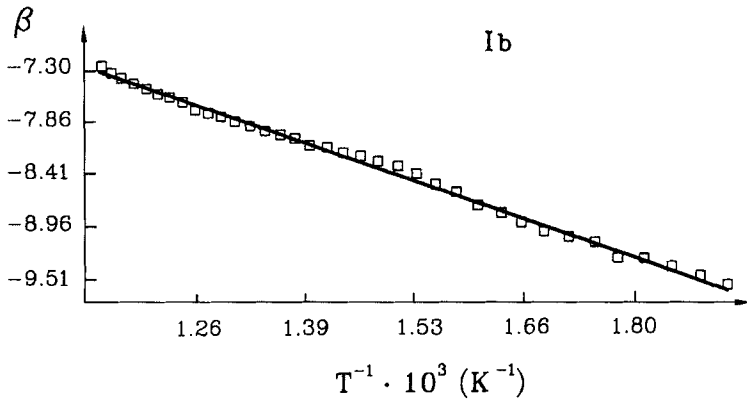
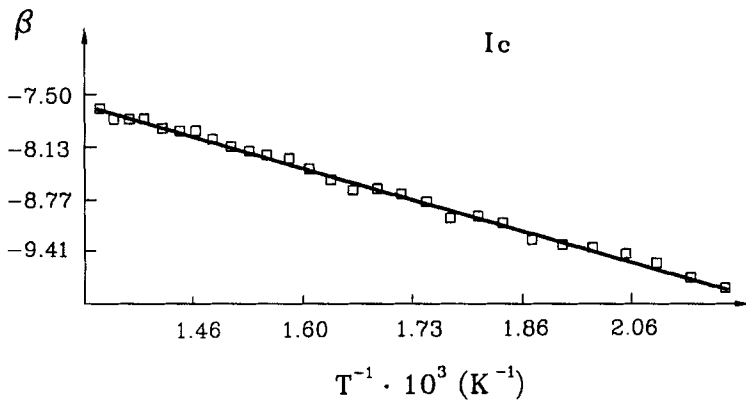FIGURE 11   Arrhenius plot for the degradation of poly(amide-ester) **Ib**.

FIGURE 12   Arrhenius plot for the degradation of poly(amide-ester) **Ic**.

constant, as in a simple evaporation [9]. Nevertheless, it is probable
that the degradation of these poly(amide-ester)s also is a complex
process, in which both functional group and the aromatics rings have
participation.

If we assume a first-order reaction, a non-linearity plot is obtained,
which has been described as a change in the degradation mechanism
and also as a change in the activation energy [10]. In this work the
reaction order for each process was obtained when the linearity over
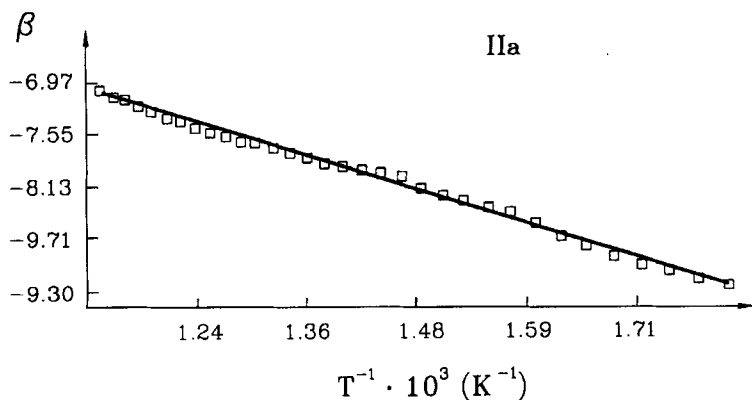the entire decomposition range was achieved, and the activation

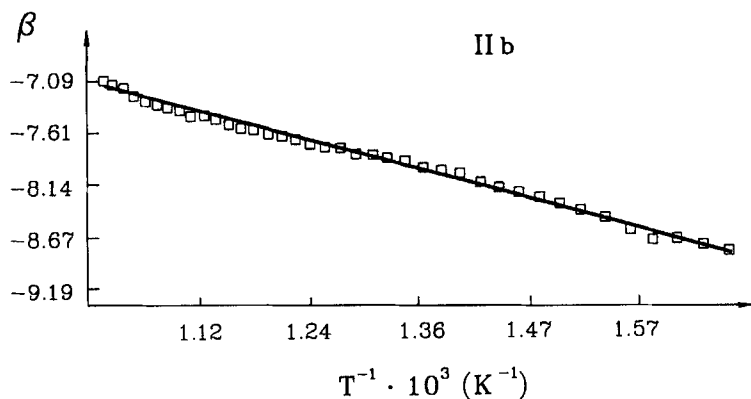FIGURE 13   Arrhenius plot for the degradation of poly(amide-ester) **IIa**.

FIGURE 14   Arrhenius plot for the degradation of poly(amide-ester) **IIb**.

energy was calculated from the slope of the graphics β vs. $1/T$ from the Eq. (3), and corresponds to a constant value in this range, without considering changes in the degradation mechanism.

The degradation process of these condensation polymers should be a very complex process due to the great number of different groups in the repeating unit, and consequently there will be several reactions during the degradation, which can be of both the inter- and intramolecular types. Furthermore in this case in which there are two functional groups the degradation process can be composed of several stages that cannot be separated in a clear range of temperature [11].
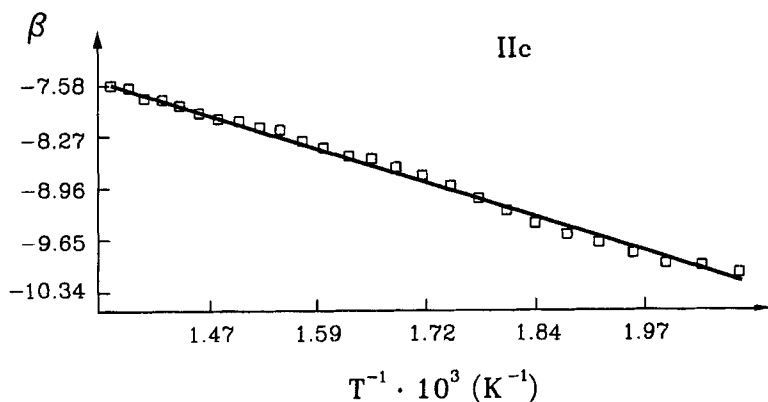
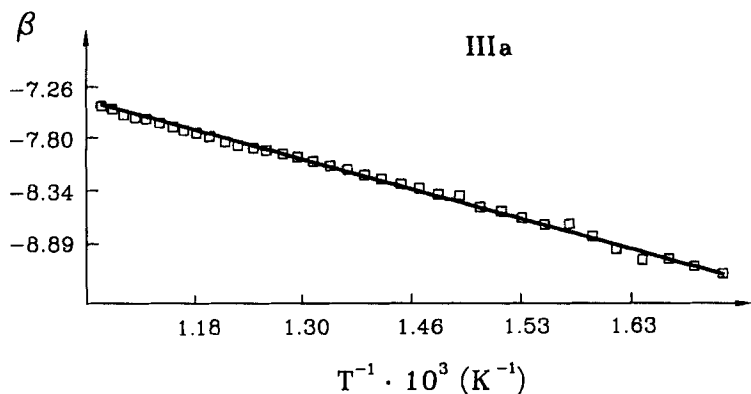FIGURE 15 Arrhenius plot for the degradation of poly(amide-ester) **IIc**.

FIGURE 16 Arrhenius plot for the degradation of poly(amide-ester) **IIIa**.

Therefore, assumptions concerning reaction order and the constancy of the activation energy over a temperature range may be questionable. Moreover, kinetic treatment assumes that the residual weight of the sample can be handled as a concentration, which is of doubtful validity [12].

In spite of the difficulties of interpreting the results of the kinetics parameters of the degradation of these condensation polymers, the thermal behaviour allows us to know the temperature range in which they degrade and can be used, as well as the activation energy associated with the complete process.
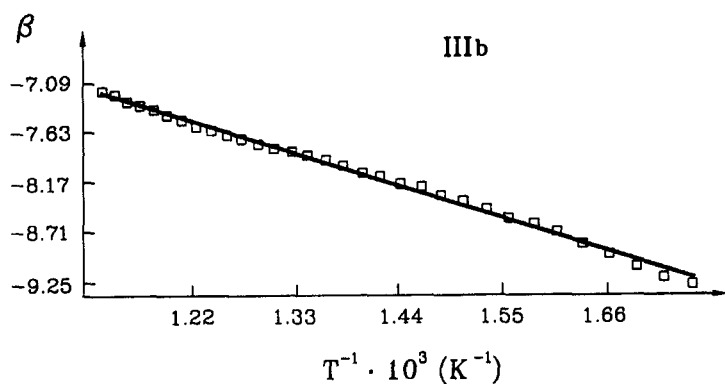
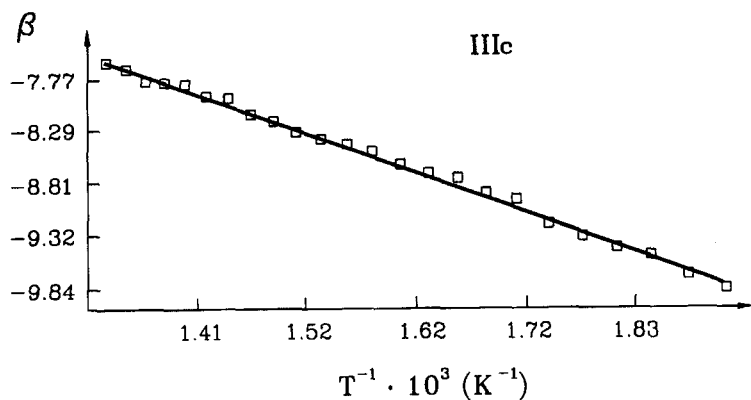FIGURE 17   Arrhenius plot for the degradation of poly(amide-ester) **IIIb**.

FIGURE 18   Arrhenius plot for the degradation of poly(amide-ester) **IIIc**.

TABLE II   Kinetic parameters of the thermal decomposition of poly(amide-ester)s

Polymer	Range (°C)	n	E (kcal/mol)	A (seg⁻¹)
Ia	270–660	0.25	5.46	1.31×10^{-2}
Ib	250–600	0.25	6.27	2.60×10^{-2}
Ic	200–470	0	6.13	3.12×10^{-2}
IIa	280–600	0.25	7.26	5.88×10^{-2}
IIb	320–700	0.25	5.72	1.60×10^{-2}
IIc	210–460	0	7.90	12.42×10^{-2}
IIIa	300–650	0.25	7.24	4.41×10^{-2}
IIIb	300–610	0.25	6.81	3.83×10^{-2}
IIIc	250–480	0	7.83	9.97×10^{-2}

Acknowledgement

References

[1] Carrasco, F. (1993). *Thermochim. Acta*, **213**, 115.
[2] Dobkowski, Z. and Rudnik, E. (1997). *J. Thermal Anal.*, **48**, 1393.
[3] Hawkins, W. L. (1984). "Polymer Degradation and Stalibization", Springer-Verlag, Berlin.
[4] Tagle, L. H. and Diaz, F. R. (1998). *Inter. J. Polym. Mat.*, **40**, 17
[5] Tagle, L. H. and Diaz, F. R. (1995). *Inter. J. Polym. Mat.*, **28**, 187.
[6] Tagle, L. H., Diaz, F. R. and Godoy, A., *Inter. J. Polym. Mat.* (in press).
[7] Tagle, L. H., Diaz, F. R., Cerda, G., Oyarzo, M. and Peñafiel, G. (1998). *Polym. Bull.*, **40**, 35.
[8] Wen, W. Y. and Lin, J. W. (1978). *J. Appl. Polym. Sci.*, **22**, 2285.
[9] Cameron, G. G. and Rudin, R. (1981). *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 179.
[10] MacCallum, J. R. (1979). *British Poly. J.*, **11**, 120.
[11] McNeill. I. C. (1989). "Comprehensive Polymer Science", Ed., Allen, G., **6**, Pergamon. London.