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Thermogravimetric analysis of poly(ether-ester)s derived from bisacid A-2 and related diacids and diphenols

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Abstract

The thermogravimetric behaviour of nine poly(ether-ester)s derived from three acid dichlorides and three diphenols was studied by dynamic thermogravimetry. The thermal decomposition temperatures (TDT), the temperature at which the poly(ether-ester)s lost 10% of their weight, were also determined; they are within 30 °C of each other. The kinetics parameters of the thermal decomposition were also determined. The poly(ether-ester)s in which the structures of the acid dichloride and the diphenol were the same, showed a 0 kinetic order, but when those structures were different the kinetic order was 0.5, which means that the degradation is a complex process.

INTRODUCTION

Like all substances, organic compounds, including organic macromolecular materials, 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.

The most frequent manifestation of a transformation can be observed as change in the mass of a material, and the method for observing this change in mass is dynamic thermogravimetry (TG).

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 appearance. This often leads to the failure of polymeric materials before they attain their required service life [1].

Poly(ether-ester)s are polyesters with elastomeric thermoplastic characteristics, in which the ether group has been introduced to change some of the properties, giving high electrical and stress resistance [2]. They have also been described as block copoly(ether-ester)s, in which the ether segment gives flexibility and the ester fragment crystallinity [3].

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Continuing our work on the study of the thermogravimetric behaviour of polymers, we describe here the thermal degradation of poly(ether-ester)s synthesised from bisacid A-2 and some related diacids and diphenols under phase transfer conditions [4], and the kinetics parameters associated with the degradation process.

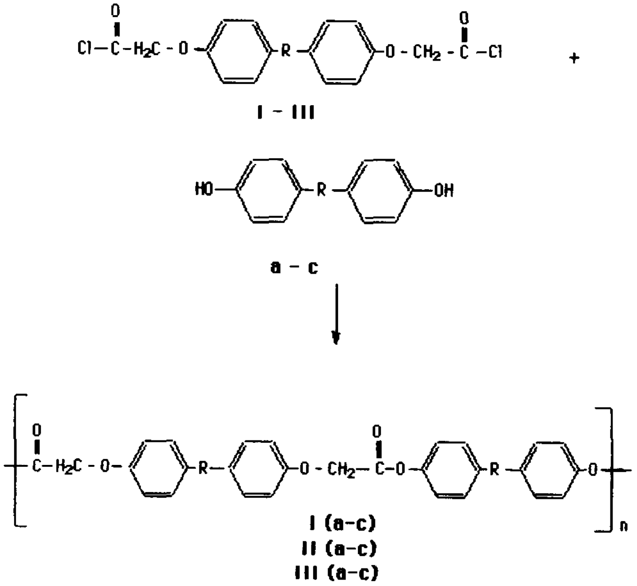
EXPERIMENTAL

The poly(ether-ester)s were synthesised under phase transfer conditions from the following acid dichlorides: α,α'-[2,2-bis-(*p*-phenyleneoxy)-propylidene]-diacetic (**I**), α,α'-[1,1-bis(*p*-phenyleneoxy)-4-methyl-cyclohexyl]-diacetic (**II**) and α,α'-bis(*p*-phenyleneoxy)-diacetic (**III**); and the diphenols: 2,2-bis(4-hydroxyphenyl)-propane (**a**), 1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane (**b**) and 4,4'-dihydroxydiphenyl (**c**), according to a procedure described earlier [4].

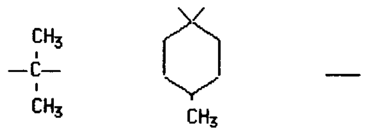
Thermogravimetry was carried out in a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature control. Samples of 4–7 mg were placed in a platinum sample holder and the thermodegradation measurements were carried out between 25 and 650 °C with a heating rate of 20 °C min^{-1} under N_2 flow.

RESULTS AND DISCUSSION

The poly(ether-ester)s were synthesised according to the reaction shown in Scheme 1 where R corresponds to the groups shown in Scheme 2, and



Scheme 1.



I and **a** **II** and **b** **III** and **c**

Scheme 2.

were characterised by IR and ^{1}H-NMR spectroscopy and elemental analysis [4].

Table 1 shows the thermal decomposition temperatures (TDT) for the nine poly(ether-ester)s. These values were taken as the temperature at which the polymers lost 10% of their weight. Figures 1–3 show the TG curves for poly(ether-ester)s **I**(**a**–**c**), **II**(**a**–**c**) and **III**(**a**–**c**), respectively.

The TDT values for poly(ether-ester)s derived from **I** and **II** are very similar with only small differences. Among those polymers derived from **III**, **IIIc** shows a lower value than **IIIa** and **IIIb**, probably because this polymer was insoluble in the reaction media and in all organic solvents, and therefore the molecular weight would also be low. Even so, there is a slight increase in TDT values in the series **Ia**–**IIa**–**IIIa**, **Ib**–**IIb**–**IIIb** and **Ic**–**IIc**, in which the rigidity of the structure of the diacid is increased.

Except for **IIIc**, the TDT values are within 30 K of each other. Thus, it can be assumed that the principal influence in the thermal degradation is the $-O-CH_2-COO-$ group, which is common to all poly(ether-ester)s.

The kinetics parameters of the thermogravimetric weight lost were calculated using 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

TABLE 1

Thermal decomposition temperatures (TDT) of poly(ether-ester)s

Polymer	TDT (K)
Ia	663
Ib	668
Ic	663
IIa	673
IIb	683
IIc	683
IIIa	678
IIIb	693
IIIc	623

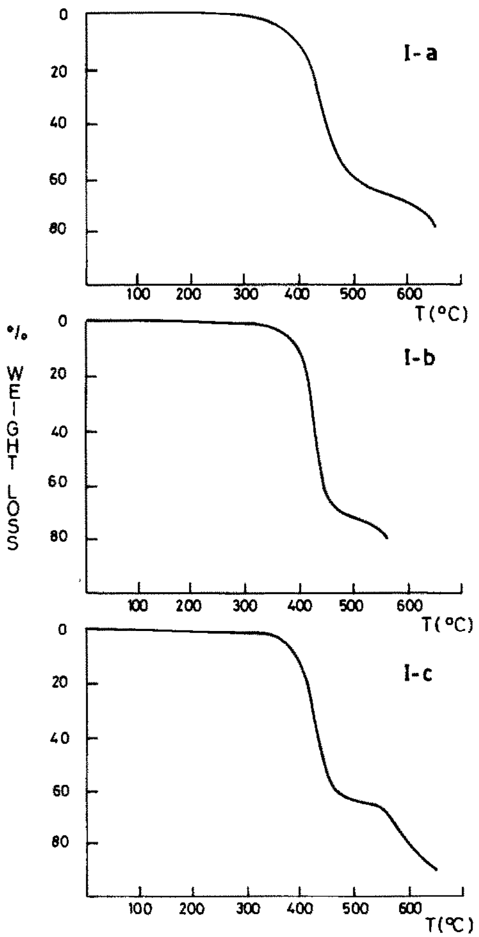


Fig. 1. Thermogravimetric curves for poly(ether-ester)s I(a–c).

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 method developed by Wen and Lin [5]. The specific rates were calculated 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 semi-logarithmic plot of β versus $1/T$, which are shown in Figs.

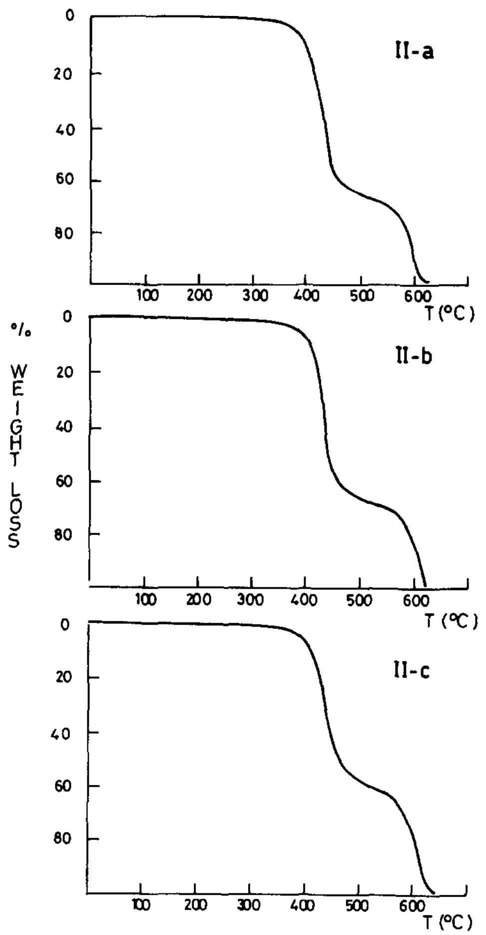


Fig. 2. Thermogravimetric curves for poly(ether-ester)s **II(a–c)**.

4–6. The linearity of each plot was good (> 0.995), although 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, as is frequently encountered in kinetics measurements.

Table 2 shows the kinetics parameters E and A determined for the nine poly(ether-ester)s, the temperature ranges and the reaction order n.

Poly(ether-ester)s in which the structures of the diacid and the diphenol were the same (**Ia**, **IIb** and **IIIc**) showed a kinetic order of 0 and low values of E and A; but when those structures were different, the kinetic order was 0.5 and the values of E and A were higher.

A zero kinetic order means that $-\mathrm{d}\alpha/\mathrm{d}T$ is constant, which implies that when the mass of sample is increased, the rate of loss of mass is

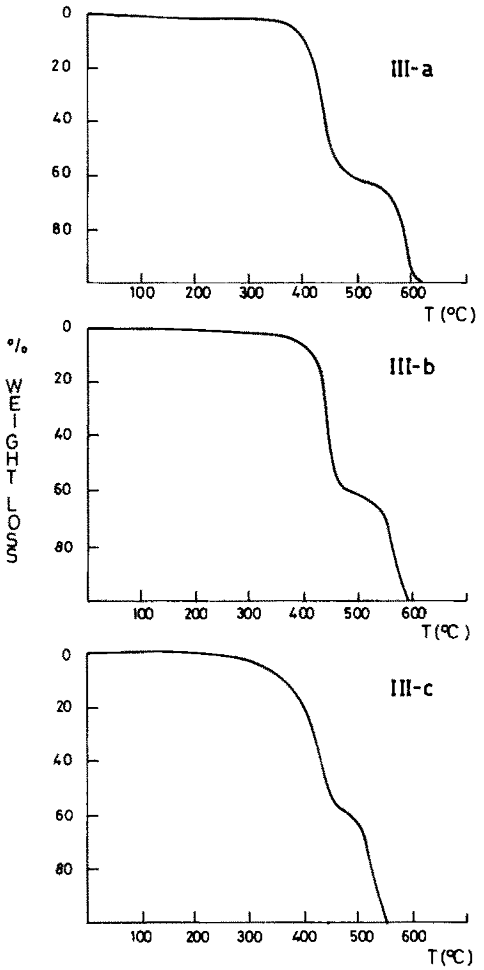


Fig. 3. Thermogravimetric curves for poly(ether-ester)s III(a–c).

constant. This can happen if the concentration of volatile material at the surface of the sample is constant, as in a simple evaporation [6].

On the other hand, a 0.5 kinetic order means that the degradation is a complex process, or may be two or more superimposed processes. Surprisingly, this kinetic order was found in poly(ether-ester)s in which both structures, diacid and diphenol, were different. It is possible that these polymers degrade by a complex mechanism with the participation of both structures, and with a higher activation energy.

It has been pointed out that for several complex reactions, the kinetic order has no significance, and that some divergences in *E* values are of limited significance; this is due principally to the physical state of the sample being far from ideal and possibly changing during the reaction. Also, it is necessary to consider that the degradation process in condensa-

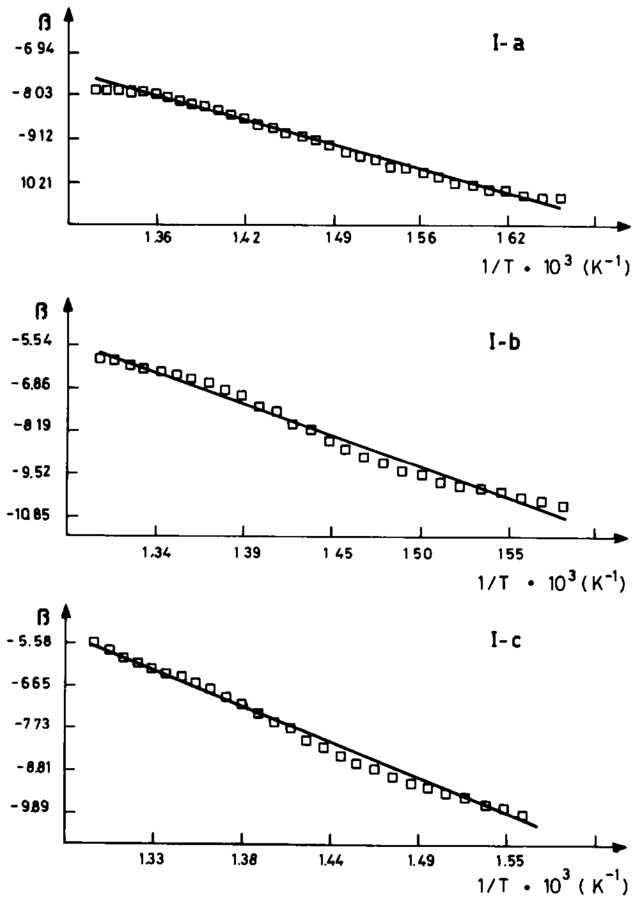


Fig. 4. Arrhenius plot for degradation of poly(ether-ester)s **I(a–c)**.

TABLE 2

Kinetics parameters of the thermal decomposition of poly(ether-ester)s

Polymer	Range (K)	n	E (kcal mol^{-1})	A (sec^{-1})
Ia	603–763	0	17.97	7.36×10^{-1}
Ib	633–763	0.5	38.56	5.64×10^{19}
Ic	633–773	0.5	34.45	7.56×10^{16}
IIa	633–773	0.5	37.44	5.98×10^{18}
IIb	643–733	0	24.48	1.56×10^{4}
IIc	643–773	0.5	38.39	1.63×10^{19}
IIIa	653–773	0.5	39.78	1.97×10^{20}
IIIb	663–773	0.5	48.39	1.15×10^{26}
IIIc	563–733	0	12.97	4.06

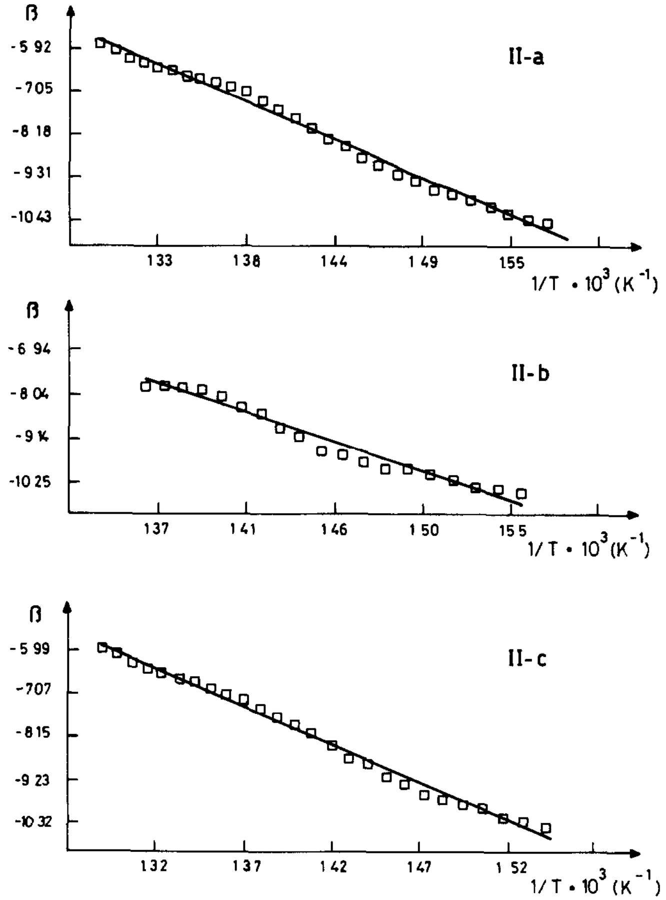


Fig. 5. Arrhenius plot for degradation of poly(ether-ester)s **II(a–c)**.

tion polymers may be very complex, and be composed of several stages that cannot be separated in clear ranges of temperature [7].

Therefore, assumptions concerning reaction order and the constancy of the activation energy over a particular temperature range may be questionable. Moreover, the kinetic treatment of thermal degradation assumes that the residual weight of the sample may be handled as if it was a concentration, which is of doubtful validity [8].

Despite this, the thermal degradation of these poly(ether-ester)s depends on whether the structures of the diacid and the diphenol are the same or different, as different degradation mechanisms are involved.

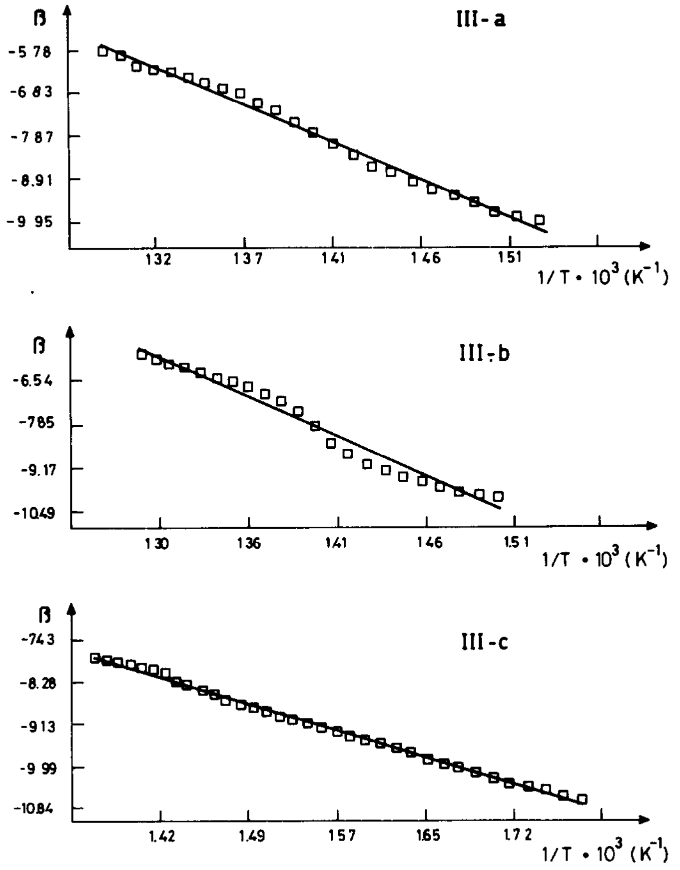


Fig. 6. Arrhenius plot for degradation of poly(ether-ester)s **III(a–c)**.

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REFERENCES

1 W.L. Hawkins, Polymer Degradation and Stabilization, Springer-Verlag, Berlin, 1984.
2 Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edn., Vol. 8, Wiley, New York, 1978, p. 636.
3 A. Noshay and J.E. McGrath, Block Copolymers, Academic Press, New York, 1977, p. 313.
4 L.H. Tagle, F.R. Diaz and M.A. Vargas, Acta Polymerica, 42 (1991) 398.
5 W.V. Wen and J.W. Lin, J. Appl. Polym. Sci., 22 (1978) 2285.
6 G.G. Cameron and A. Rudin, J. Polym. Sci., Polym. Phys. Ed., 19 (1981) 179.
7 J.R. MacCallum, Br. Polym. J., 11 (1979) 120.
8 I.C. McNeill, in G. Allen (Ed.), Comprehensive Polymer Science, Vol. 6, Pergamon, London, 1989, p. 456.