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Thermogravimetric Analysis of Poly(Amide-Carbonate)s and Poly(Amide-Thiocarbonate)s

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The thermogravimetric behaviour of poly(amide-carbonate)s and poly(amide-thiocarbonate)s was studied by dynamic thermogravimetry. The thermal decomposition temperatures were determined, showing that for polymers derived from the aliphatic monomer **I** showed a very similar thermal decomposition temperature, but for those derived from the aromatic monomer **II**, the poly(amide-carbonate) showed more stability than the corresponding thiocarbonate. The kinetic parameters, activation energy, reaction order and pre-exponential factor were determined by using the Arrhenius relationship and a computer program.

Keywords: Poly(amide-carbonate); poly(amide-thiocarbonate); degradation mechanism; thermal degradation; thermogravimetry; synthesis of ...

INTRODUCTION

Dynamic thermogravimetry is a widely used tool to study the degradation of polymeric materials, in order to know the reaction order and the kinetic parameters such as activation energy. It has been pointed out that there are several advantages in using non-isothermal

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methods for studying the thermal stability of condensation polymers, such as that the kinetic parameters can be established over an entire temperature range; the information can be obtained with a single sample, which avoids the problems arising from different samples; and it is not necessary to raise to the required temperature, which could induce some degradation in the pre-heating period [1].

For all kinds of materials, and especially for polymers, their degradation under normal conditions of use is a major factor limiting the application of these versatile products. Important properties of every polymer are adversely affected as the degradation proceeds, including mechanical strength, dielectric quality and also aesthetic appearance. This often leads to the failure of polymeric materials before they attain their required service life [2].

In recent years, we have studied the synthesis and the thermal properties of several kinds of polymers [3–6], especially polycarbonates and polythiocarbonates to which we have introduced an ester group as a second functional group [7–8], showing a thermal behaviour that depends on both the carbonate or thiocarbonate group and the ester group. In this work we have studied the thermal degradation of polycarbonates and polythiocarbonates, derived from monomers that have the amide group in the main chain, which were synthesized under phase-transfer conditions [9] and determined the kinetic parameters associated with the degradation process.

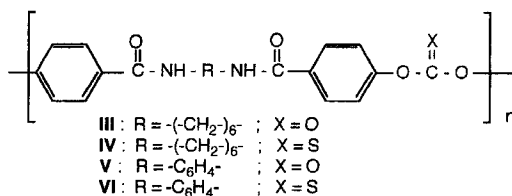
EXPERIMENTAL PART

Poly(amide-carbonate)s and poly(amide-thiocarbonate)s were synthesized under phase-transfer conditions from the diphenols 1, 6-bis(4-hydroxyphenyl-carbamoyl)-hexamethylene **I** and 1,4-bis(4-hydroxyphenyl-carbamoyl)-phenylene **II**, and phosgene or thiophosgene according to a procedure described earlier [9].

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 650°C with a heating rate of 20°C min⁻¹ under N₂ flow.

RESULTS AND DISCUSSION

Poly(amide-carbonate)s and poly(amide-thiocarbonate)s with the following structures:



were synthesized under phase-transfer conditions using several quaternary onium salts according to a procedure described earlier [9]. Polymers were characterized by elemental analysis and IR spectroscopy.

Table I shows the thermal decomposition temperatures (TDT) for the four polymers. These values were taken as the temperature at which polymers lost 10 % of their weight. Figures 1–4 show the TG curves for polymers **III** and **IV** (derived from monomer **I**) and for polymers **V** and **VI** (derived from monomer **II**), respectively. From Figures 1 and 2 it can be seen that polymers **III** and **IV** degrade in a single step, while polymers **V** and **VI** which degrade in a more complex form in at least two stages.

Polymers **III** and **IV** showed a very similar TDT, although the poly(amide-thiocarbonate) showed a slightly lower value. In this case, the influence of the aliphatic chain would probably have more importance than the nature of the functional group, carbonate or thiocarbonate.

On the other hand, for polymers **V** and **VI** it is possible to see a difference between the carbonate and thiocarbonate, although the

TABLE I Thermal decomposition temperatures (TDT) of poly(amide-carbonate)s and poly(amide-thiocarbonate)s

<i>Polymer</i>	<i>TDT(°C)</i>
III	307
IV	304
V	308
VI	287

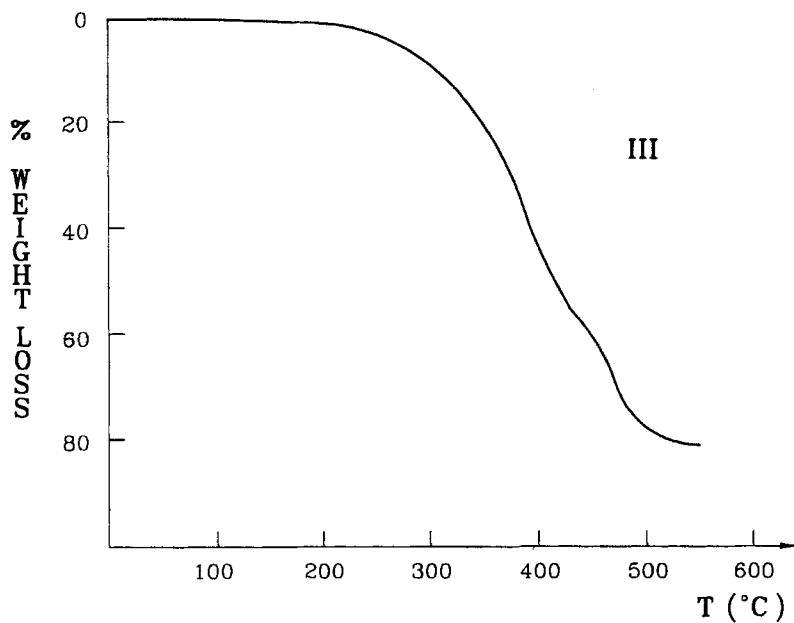


FIGURE 1 Thermogravimetric curve for poly(amide-carbonate) III.

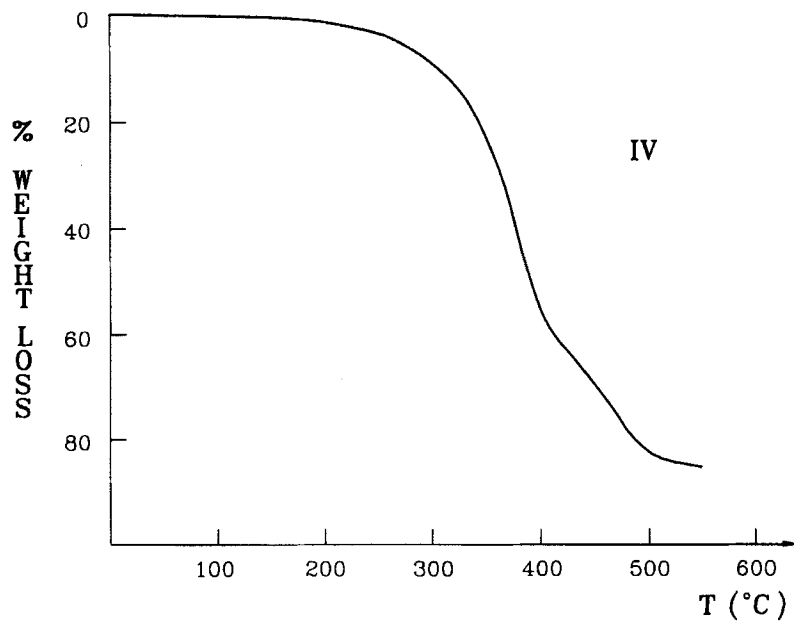


FIGURE 2 Thermogravimetric curve for poly(amide-thiocarbonate) IV.

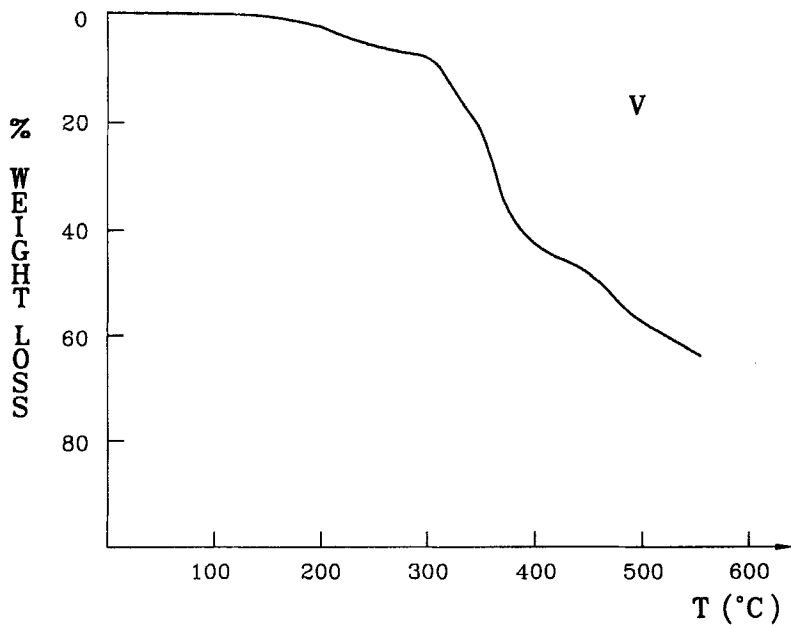


FIGURE 3 Thermogravimetric curve for poly(amide-carbonate) V.

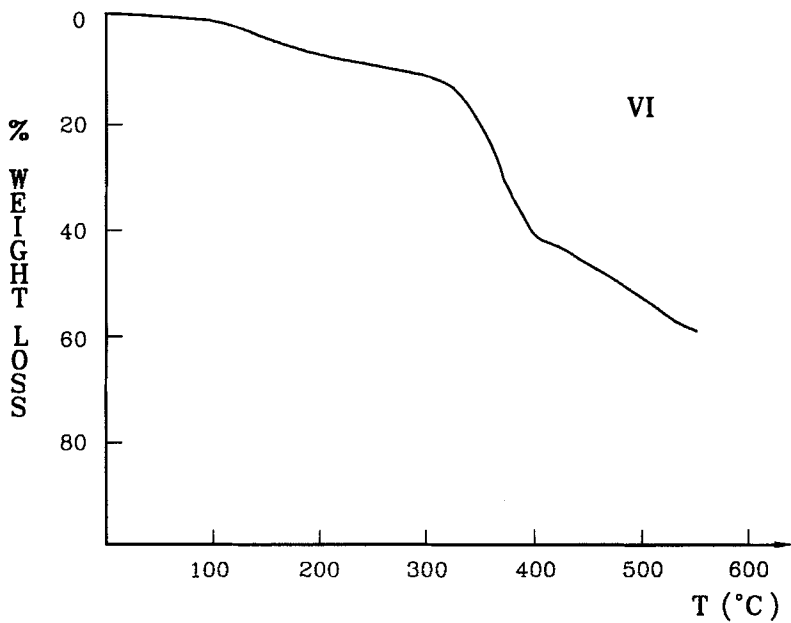


FIGURE 4 Thermogravimetric curve for poly(amide-thiocarbonate) VI.

poly(amide-carbonate) was more stable than the analogous poly-(amide-thiocarbonate), as we have shown in several other papers about thermal stability of polycarbonates and polythiocarbonates. In this case, it is possible to see the influence of the functional group, carbonate or thiocarbonate, over the aromatic ring of the terephthalic acid, which is more stable than the aliphatic chain.

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

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

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 $-(d\alpha/dt)$ were calculated using a differential technique with the heating rate ($20^\circ\text{C min}^{-1}$) incorporated directly into the temperature *versus* sample weight-fraction data, according to the procedure developed by Wen and Lin [10]. The specific rates were calculated from the Arrhenius relation

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

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

$$\beta = \ln[-(d\alpha/dT)/3(1 - \alpha)^n] = \ln A - E/RT \quad (3)$$

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from linear least-squares fit of the data in a semilogarithmic plot of β *vs.* $1/T$. Figures 5–8 show those graphics and the results are summarized in Table II. The linearity of the plots was > 0.995 , 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 kinetic parameters obtained for the degradation process in the considered range. The results obtained for polymers **III** and **IV** derived from monomer **I** are very similar, showing a single-step

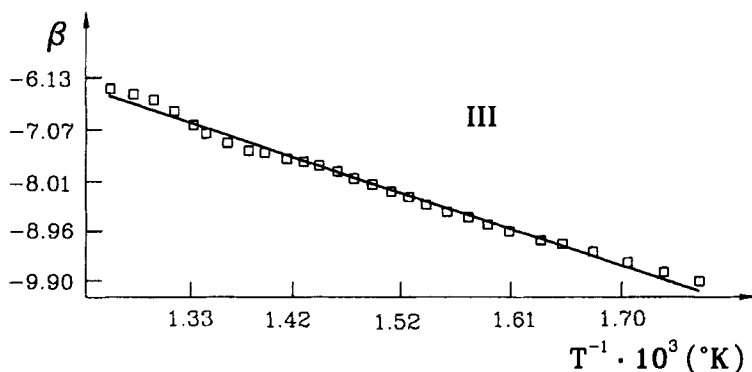


FIGURE 5 Arrhenius plot for the degradation of poly(amide-carbonate) III.

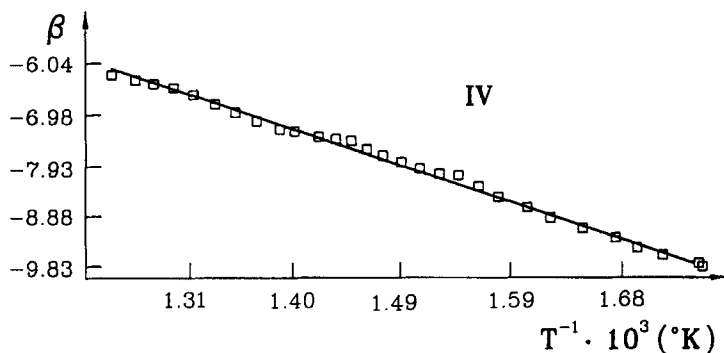


FIGURE 6 Arrhenius plot for the degradation of poly(amide-thiocarbonate) IV.

degradation of 0.5 reaction order. A 0.5 reaction order implies that the degradation is probably a complex process or may consist of two or more superimposed processes. Rather than the simple degradation curve showed in Figures 1 and 2, it is probably that there was a complex degradation process, which could be influenced by both the functional groups and the aliphatic chains. This behaviour has been described in the degradation process of poly(ester-carbonate)s and poly(ester-thiocarbonate)s [8].

The results obtained for polymers V and VI derived from monomer II showed a two-step degradation process, as can be seen clearly from the Figures 3 and 4 respectively, both of zero reaction order.

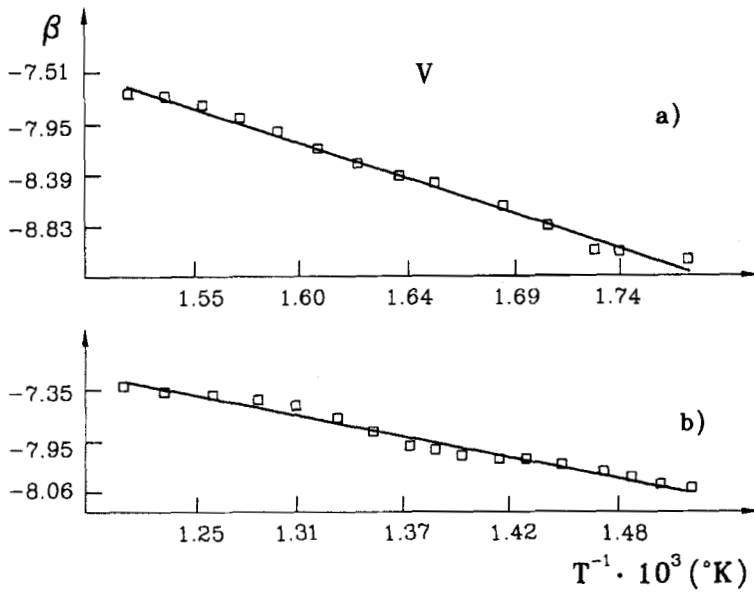


FIGURE 7 Arrhenius plot for the degradation of poly(amide-carbonate) V.

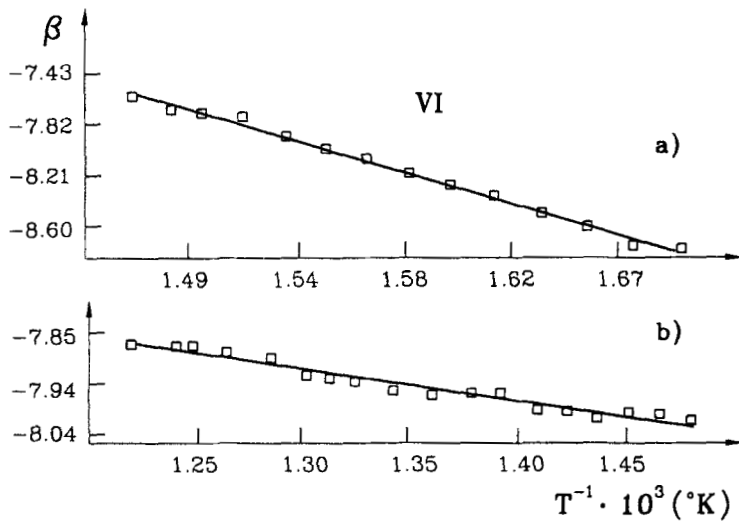


FIGURE 8 Arrhenius plot for the degradation of poly(amide-thiocarbonate) VI.

TABLE II Kinetic parameters of the thermal decomposition of poly(amide-carbonate)s and poly(amide-thiocarbonate)s

Polymer	Range (°C)	<i>n</i>	<i>E</i> (kcal/mol)	<i>A</i> (seg ⁻¹)
III	290–522	0.5	13.83	1.10×10^1
IV	298–533	0.5	14.30	1.85×10^1
V	291–385	0	13.10	1.15×10^1
	385–549	0	1.57	1.05×10^{-3}
VI	317–408	0	10.95	1.72
	401–550	0	1.26	8.36×10^{-4}

A zero reaction order implies that $-(d\alpha/dt)$ is constant, which means that when the mass of sample is increased, the rate of loss of mass is constant. This can happen if the concentration of volatile material at the surface of the sample is constant, as in a simple evaporation [11].

If the results obtained for polymers derived from monomer I are compared with those derived from monomer II, it is possible to point out that there are probably two different degradation mechanisms, in which the nature of the *R* group of the amines, aliphatic or aromatic, have great influence. On the other hand, we have not found a relationship between the kinetic parameters, especially reaction order, and the polymer structure. We have described degradation studies of polycarbonates and polythiocarbonates which degrade according to a zero, one or 0.5 kinetic order, independently of the nature of the groups bonded to the phenolic aromatic rings. The same situation has been described for the degradation of poly(ester-carbonate)s and poly(ester-thiocarbonate)s [8].

The thermal degradation of condensation polymers can be a very complex process due to the great number of different parts present in the repeating unit. This shows as a consequence, the probable presence of several reactions during the degradation, which can be of both the inter- and intra-molecular types. Also, the degradation process in polymers such as these that contain two functional groups can be composed of several stages that cannot be separated in a clear temperature range [12].

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 were a concentration, which is of doubtful validity [13].

Regardless of, the difficulties of interpreting the results of kinetic studies in the degradation of condensation polymers, the thermal behaviour allows us to know the temperature range in which they can be used, as well as the kinetic parameters, such as the activation energy corresponding to the complete process.

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