

THERMOGRAVIMETRIC ANALYSIS OF POLYCARBONATES AND POLYTHIOPOLYCARBONATES WITH CHLORINATED AROMATIC SIDE-RINGS

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The thermal stability and kinetics parameters of polycarbonates and polythiocarbonates derived from diphenols with chlorinated aromatic side-rings were studied. The polycarbonates exhibited a higher thermal stability than the polythiocarbonates, except for polythiocarbonate Ib, which displayed similar behaviour to that of the analogous polycarbonate. The kinetic parameters of the thermal decomposition were determined by using the Arrhenius relationship and a computer program. In the considered temperature range, all the polymers degraded in a single stage with first-order kinetics.

An important property of polymeric materials is their thermal stability. This can be studied by thermogravimetric analysis, in which the weight loss is determined as the temperature is increased, and thus the temperature range in which polymers can be established.

In dynamic thermogravimetry, the weight loss can be determined as the temperature is increased at a definite heating rate, and hence it is possible to know the kinetics parameters associated with the decomposition process, and to postulate the mechanism by which the polymer decomposes. The thermogravimetric curves are characteristic for each polymer, because the reactions that occur over defined ranges of temperature are functions of the molecular structure. The weight changes result from bond rupture and formation, which lead to the formation of volatile products or more complex species [1].

In recent years, dynamic thermogravimetry has been applied in our laboratory for the thermal analysis of polycarbonates, polythiocarbonates and copoly(carbonate-thiocarbonate)s, in order to study the thermal decomposition temperatures of those polymers as a function of the structure and

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to determine the kinetic parameters associated with the decomposition process. In general, we have found that the thermal stability of polycarbonates is higher than that of polythiocarbonates [2-5].

As a continuation of our thermal studies on condensation polymers, this paper describes the thermal behaviour of polycarbonates and polythiocarbonates derived from diphenols with chlorinated aromatic side-rings. The thermal decomposition temperatures and the kinetic parameters associated with the decomposition process were determined.

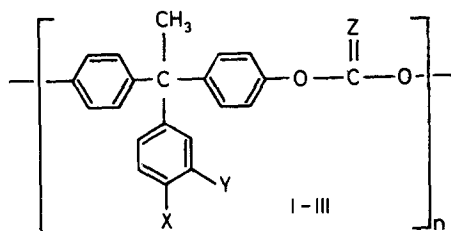
Experimental

Poly[oxycarbonyloxy-1,4-phenylene-(methyl)-(4-chlorophenyl)-methylene-1,4-phenylene], Ia, poly[oxythiocarbonyloxy-1,4-phenylene-(methyl)-(4-chlorophenyl)-methylene-1,4-phenylene], Ib, poly[oxycarbonyloxy-1,4-phenylene-(methyl)-(3-chlorophenyl)-methylene-1,4-phenylene], IIa, poly[oxythiocarbonyloxy-1,4-phenylene-(methyl)-(3-chlorophenyl)-methylene-1,4-phenylene], IIb, poly[oxycarbonyloxy-1,4-phenylene-(methyl)-(3,4-dichlorophenyl)-methylene-1,4-phenylene], IIIa, and poly[oxythiocarbonyloxy-1,4-phenylene-(methyl)-(3,4-dichlorophenyl)-methylene-1,4-phenylene], IIIb, were synthesized by phase-transfer catalysis from the diphenols and phosgene or thiophosgene, using several quaternary ammonium salts and dichloromethane as solvent. The syntheses and characterization of these polymers have been described in a previous paper [6].

Dynamic thermogravimetry analyses were carried out in a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (4-8 mg) were placed in the platinum sample holder and the thermal degradation measurements were carried out between 50 and 650° at a heating rate of 20 deg/min under a nitrogen flow.

Results and discussion

The following polycarbonates and polythiocarbonates were analyzed by dynamic thermogravimetry:



where

| | | | |
|------|---------------------|-----------------|----------------|
| Ia | $X = \text{Cl}$ | $Y = \text{H}$ | $Z = \text{O}$ |
| Ib | $X = \text{Cl}$ | $Y = \text{H}$ | $Z = \text{S}$ |
| IIa | $X = \text{H}$ | $Y = \text{Cl}$ | $Z = \text{O}$ |
| IIb | $X = \text{H}$ | $Y = \text{Cl}$ | $Z = \text{S}$ |
| IIIa | $X = Y = \text{Cl}$ | | $Z = \text{O}$ |
| IIIb | $X = Y = \text{Cl}$ | | $Z = \text{S}$ |

Figures 1-3 show the thermogravimetric curves of the studied polymers, from which the thermal decomposition temperatures (TDT) were determined at 10% weight loss. Table 1 shows the TDT values for these polymers.

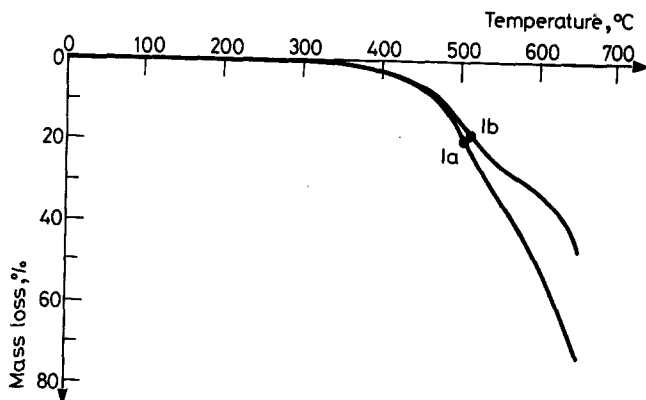


Fig. 1 Thermogravimetric curves for polycarbonate Ia and polythiocarbonate Ib

The results show that the polycarbonates are more thermally stable than the polythiocarbonates, except that polythiocarbonate Ib is slightly more stable than the respective polycarbonate, which may be due to a wider molecular weight distribution of the polycarbonate Ia, where short chains

with a major concentration of terminal groups may cause a faster degradation [7].

Table 1 Thermal decomposition temperatures (TDT) for polycarbonates and polythiocarbonates

| Polymer | TDT, °C |
|---------|---------|
| Ia | 475 |
| Ib | 483 |
| IIa | 480 |
| IIb | 435 |
| IIIa | 493 |
| IIIb | 430 |

It has been shown that the presence of chlorine atoms in some polymers increases the thermal stability [7]. This is in accordance with the TDT values obtained for these polymers as compared with the corresponding compounds without chlorine atoms, described as 385° for the polythiocarbonate [2] and 437° for the polycarbonate [3], obtained under similar conditions.

On the other hand, the chlorine atoms are responsible for an increase in the volume of the aromatic side-groups of the polymeric chains, which influences the chain rigidity and probably also the thermal stability. This effect is observed in the polycarbonates, especially when there are two chlorine atoms (IIIa).

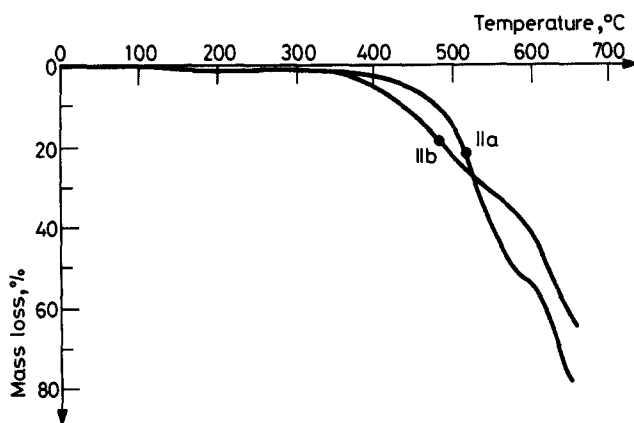


Fig. 2 Thermogravimetric curves for polycarbonate IIa and polythiocarbonate IIb

However, the opposite occurs with polythiocarbonates, where there is a decrease in thermal stability as the volume of the side-group is increased, especially when there is a chlorine atom in the meta position. The TDT values of polythiocarbonates IIb and IIIb are much lower than that of Ib. Moreover, it is probable that there are two different mechanisms for the decompositions of these polymers.

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

$$-\frac{d\alpha}{dt} = k_n (1-\alpha)^n \quad (1)$$

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 rate $-\frac{d\alpha}{dt}$ were calculated by using a differential technique with the heating rate (20 deg/min) incorporated directly in the temperature versus sample weight fraction data, according to the method developed by Wen and Lin [8]. The specific rates were calculated from the Arrhenius relation:

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

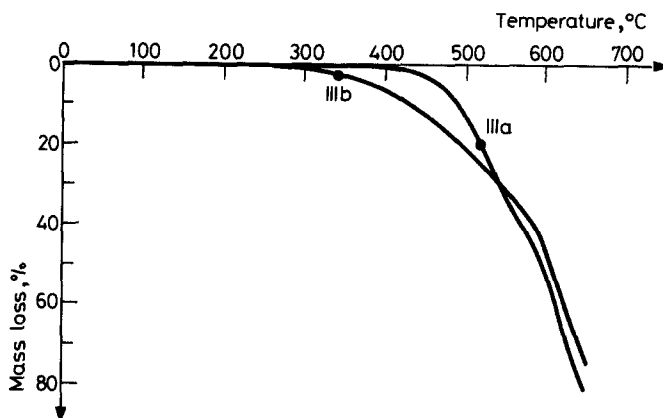


Fig. 3 Thermogravimetric curves for polycarbonate IIIa and polythiocarbonate IIIb

where E is the activation energy, A the preexponential factor, T the absolute temperature and R the gas constant. Equations (1) and (2) were combined and used in logarithmic form:

$$\beta = \ln \left[-\frac{\frac{d\alpha}{dT}}{3(1-\alpha)^n} \right] = \ln A - \frac{E}{RT} \quad (3)$$

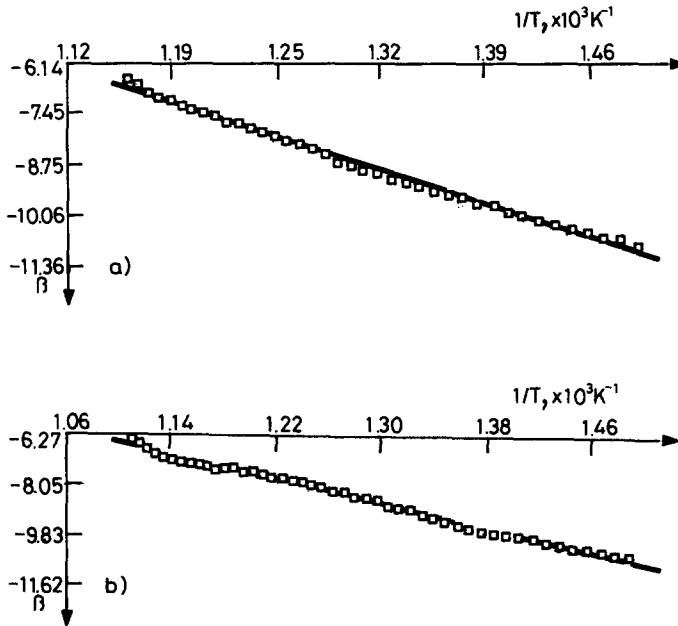


Fig. 4 Arrhenius plot for the degradation of: a) polycarbonate Ia, and b) polythiocarbonate Ib

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from a linear least-squares fit of the data in a semilogarithmic plot of β vs. $1/T$. Such plots are shown in Figs 4-6. The linearity of each plot was good ($>.995$), although some scatter was detected at the beginning and end of the 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 2 lists the values of the kinetic parameters obtained for the polycarbonates and polythiocarbonates. In the considered range, all the polymers degrade in one stage and according to a first-order kinetic process, which means that there is a volatile material concentration in the sample surface that depends on the active residual fraction [5].

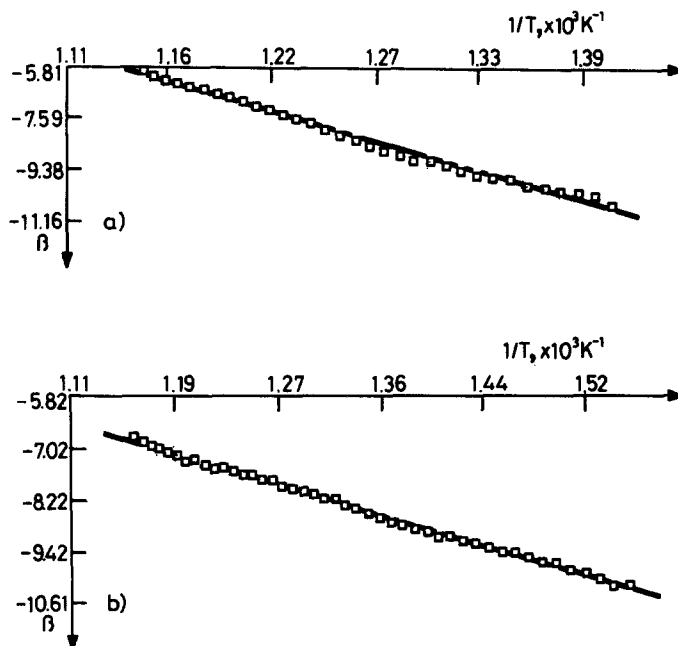


Fig. 5 Arrhenius plot for the degradation of: a) polycarbonate IIa, and b) polythiocarbonate IIb

Davis and Golden [9, 10] studied the thermal decomposition of bisphenol *A* polycarbonate, and suggested a mechanism similar to that for these polycarbonates. When bisphenol *A* polycarbonate is degraded in a continuously evacuated system such as this, the first step in the mechanism is the rearrangement of the carbonate group to form a pendant carboxy group ortho to an ether link in the main chain, which undergoes other reactions (principally condensations) and then crosslinks with other polymeric chains to form an insoluble gel with the loss of CO_2 , which is the major product, indicating that the carbonate group is the most reactive group in the polycarbonate [9-11]. The experimental conditions used in this work were similar to

those used by Davis and Golden, and it is probable that the mechanism is similar.

Table 2 Kinetics parameters of the thermal decomposition of polycarbonates and polythiocarbonates

| Polymer | Range, °C | n , | E , kcal/mol | A , sec ⁻¹ |
|---------|-----------|-------|----------------|-------------------------|
| Ia | 400-630 | 1 | 26.80 | 7.34×10^3 |
| Ib | 400-590 | 1 | 22.09 | 3.54×10^2 |
| IIa | 370-590 | 1 | 36.26 | 3.36×10^6 |
| IIb | 440-600 | 1 | 17.70 | 3.59×10^2 |
| IIIa | 330-590 | 1 | 35.27 | 1.19×10^6 |
| IIIb | 430-590 | 1 | 13.55 | 1.64 |

In polythiocarbonates, rearrangement of the thiocarbonate group is not possible because of the low stability of the -COSH group, and therefore the loss of COS and the formation of an ether linkage in the main chain are more probable [12].

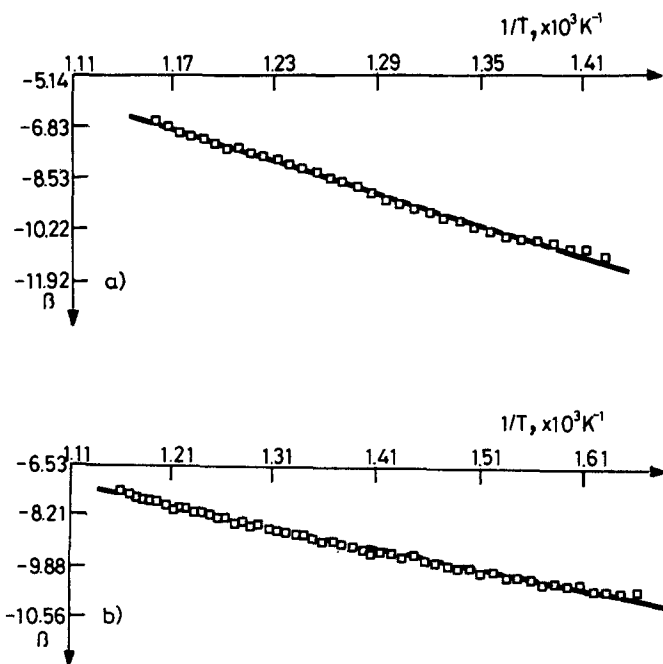


Fig. 6 Arrhenius plot for the degradation of: a) polycarbonate IIIa, and b) polythiocarbonate IIIb

It is not likely that the chlorine atoms in the aromatic side-group participate in the mechanism of thermal degradation.

For the polycarbonates, the E values increase as the volume of the side-chain is increased, and the same is observed for the TDT values. For the polythiocarbonates, both E and TDT decrease as the volume of the side-chain is increased. It is probable that, in spite of both types of polymers undergoing first-order reactions, the mechanisms by which they degrade are different and very complex.

Finally, it is necessary to consider that degradation reactions in polymers are often complex, involving several stages of reaction, which may not be separated in the given temperature range. Assumptions about the reaction order and the constancy of the activation energy over a particular temperature range may therefore 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].

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Zusammenfassung — Es wurde die thermische Stabilität und die kinetischen Parameter von aus Diphenolen mit chlorierten aromatischen Nebenringen abgeleiteten Polycarbonate und Polythiocarbonate untersucht. Polycarbonate zeigen eine höhere thermische Stabilität als Polythiocarbonate. Eine Ausnahme bildet das Polythiocarbonat Ib, das in seinem Verhalten den Polycarbonaten gleicht. Mittels der Arrheniusschen Gleichung und einem Rechnerprogramm wurden die kinetischen Parameter der thermischen Zersetzung ermittelt. Im untersuchten Temperaturbereich zersetzen sich alle Polymere in einer einstufigen Reaktion erster Ordnung.