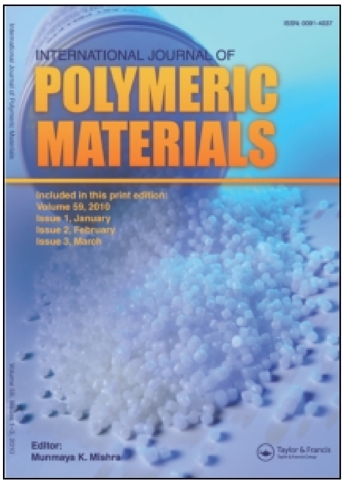

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Thermal studies of poly(carbonates) and poly(thiocarbonates) containing silicon or germanium in the main chain

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THERMAL STUDIES OF POLY(CARBONATES) AND POLY(THIOCARBONATES) CONTAINING SILICON OR GERMANIUM IN THE MAIN CHAIN

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The thermal properties of poly(carbonates) and poly(thiocarbonates) containing silicon or germanium in the main chan, derived from the diphenols bis(4-hydroxyphenyl)-dimethylsilane, bis(4-hydroxyphenyl)-dimethylgermane, bis(4-hydroxyphenyl)-diphenylsilane and bis(4-hydroxyphenyl)-diphenylgermane, and phosgene or thiophosgene, were studied by differential scanning calorimetry and dynamic thermogravimetry. Polymers containing phenyl groups bonded to the heteroatoms showed higher Tg values, and the same was valid for those with Ge in respect to Si. Poly(carbonates) showed higher Tg values than poly(thiocarbonates). The thermogravimetric curves revealed that poly(carbonates) are more stable than poly(thiocarbonates) and the same is valid for those containing Ge with respect to the silicon-containing polymers. The kinetic parameters associated with the degradation process, showed that probably there are complex degradation mechanisms, which depend on the heteroatom in the main chain, Si or Ge, and the groups bonded to it, and the nature of the functional group, carbonate or thiocarbonate.

Keywords: germanium, silicon, poly(carbonates), poly(thiocarbonates), glass transition temperature, thermal decomposition temperature, kinetics parameters

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INTRODUCTION

Polymers may undergo several transformations when they are exposed to temperature, and these changes can be of a chemical or physical character. In this sense the thermal degradation of polymers under normal conditions of use is the principal factor limiting the applications of these materials. Important properties are affected adversely as the degradation proceeds [1, 2].

On the other hand, silicon-containing polymers have been described for many years and their properties studied [3], but polymers containing germanium in the main chain in which the heteroatom is bonded to four carbon atoms have been not described. At the present time we are focussing our attention on the synthesis of condensation polymers containing Si and/or Ge in the main chain bounded to four carbon atoms. Accordingly, we have described the synthesis of poly(carbonates) and poly(thiocarbonates) [4], and poly(amides) [5] derived from diphenols and diamines respectively, containing these heteroatoms, and described their synthesis and characterization.

In this work we describe the thermal behaviour of poly(carbonates) and poly(thiocarbonates) containing Si or Ge in the main chain. So, we have determined the glass transition temperatures by DSC techniques and the thermogravimetric behaviour determined by dynamic thermogravimetry, and also the kinetic parameters associated with the thermal process. The results are discussed in light of the nature of the heteroatom, Si or Ge, and the polymeric structure, side groups bonded to the heteroatom and the nature of the functional group, carbonate or thiocarbonate.

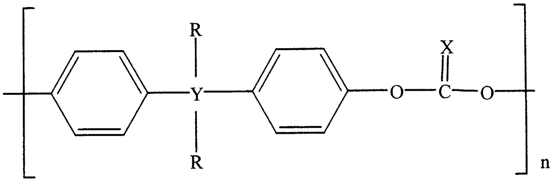
EXPERIMENTAL PART

Poly(carbonates) and poly(thiocarbonates) were synthesized from the diphenols bis(4-hydroxyphenyl)-dimethylsilane (**Ia**–**IIa**), bis(4-hydroxyphenyl)-dimethylgermane (**Ib**–**IIb**), bis(4-hydroxyphenyl)-diphenylsilane (**IIIa**–**IVa**) and bis(4-hydroxyphenyl)-diphenylgermane (**IIIb**–**IVb**), and phosgene or thiophosgene under phase transfer conditions according to a procedure described earlier [4].

The Tg values were obtained using a Mettler Toledo DSC 821 calorimetric system. Thermogravimetric analyses were carried out in a Mettler TA-3000 calorimetric system equiped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. Samples of 6–10 mg were placed in a platinum sample holder and the thermogravimetric measurements were carried out between 30 and 800°C with a heating rate of 20°C min^{-1} under N_2 flow.

RESULTS AND DISCUSSION

Poly(carbonates) and poly(thiocarbonates) with the following structures: 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 [4]. Polymers were characterized by IR, ^1H and ^{13}C NMR, and the structures were in accord with those proposed.



Ia: Y = Si; R = $-CH_3$ X = O
Ib: Y = Ge R = $-CH_3$ X = O
IIa: Y = Si R = $-CH_3$ X = S
IIb: Y = Ge R = $-CH_3$ X = S
IIIa: Y = Si R = $-C_6H_5$ X = O
IIIb: Y = Ge R = $-C_6H_5$ X = O
IVa: Y = Si R = $-C_6H_5$ X = S
IVb: Y = Ge R = $-C_6H_5$ X = S

Table 1 shows the Tg values obtained for poly(carbonates) and poly (thiocarbonates). Well-defined and reproducible glass transitions were observed for all polymer samples. From the results it can be seen that polymers with phenyl side groups (**III** and **IV**) showed higher Tg values than those with methyl side groups. This behaviour is due to the higher volume of the phenyl groups. It has been described for a poly(thiocarbonate) family that those containing aromatics groups in the side chain have higher Tg values. The same is true for the behaviour of poly(carbonates) [6, 7].

TABLE 1 Glass Transition Temperatures of the Poly(Carbonates) and Poly(Thiocarbonates)

Polymer	Tg (°C)
Ia	93
Ib	98
IIa	91
IIb	115
IIIa	150
IIIb	156
IVa	135
IVb	142

It is also possible to see that the Tg values of poly(thiocarbonates) are in general lower than the analogous poly(carbonates), with the only exception of the pair **Ib** and **IIb**. The steric hindrance of the poly(thiocarbonates) is lower than the poly(carbonates), which has been explained in terms of the different contribution to the partial double bond character of the CO–O and CSO groups. The difference in the Tg values between poly(carbonates) and poly(thiocarbonates) is greater in polymers with phenyl groups, due probably to the fact that both effects, the volume of the side group and the nature of the functional group, are cumulative.

On the other hand, when we compare the Tg values as a function of the nature of the heteroatom in the main chain, it was possible to see that in all cases polymers with Ge showed higher Tg values with respect to the analogous with Si. It is known that Si is larger than C, which implies larger bond lengths, lower rotational energy barriers and lower Tg values of silicon containing polymers [3]. Germanium belongs to the same family in the periodic table, but it is only slightly larger than Si [8], and Ge containing polymers should have lower Tg values. In this case polymers with Ge showed slightly larger Tg values. Probably the effect of the size is not so important to the flexibility of the polymeric chain compared to the steric hindrance of the side groups and the nature of the functional groups.

The thermal stability of the polymers was analyzed by dynamic thermogravimetry. Figures 1–8 show the thermogravimetric curves and Table 2 summarizes the thermal decomposition temperatures

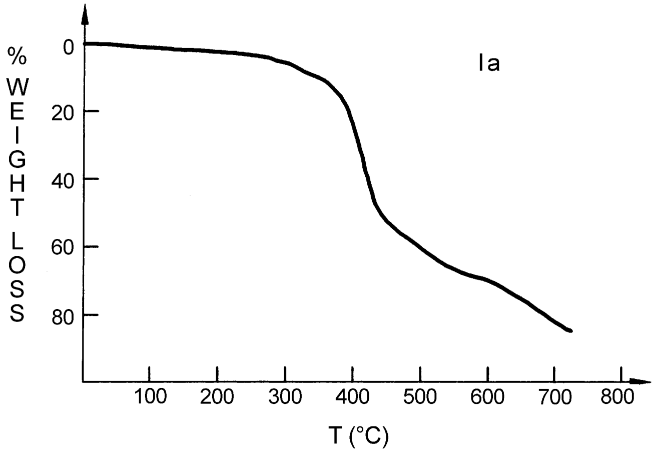


FIGURE 1 Thermogravimetric curve for poly(carbonate) **Ia**.

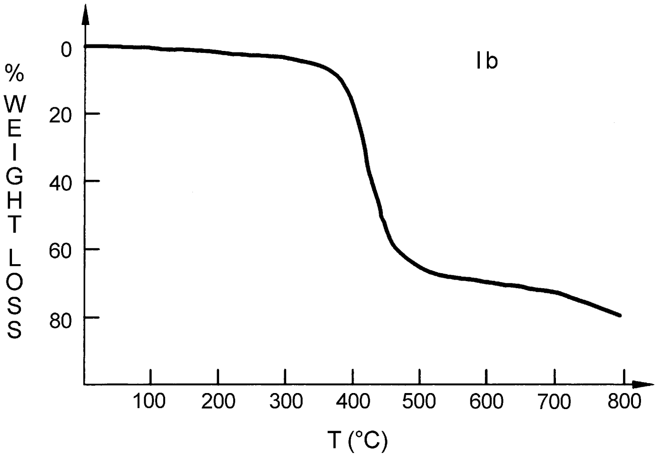


FIGURE 2 Thermogravimetric curve for poly(carbonate) **Ib**.

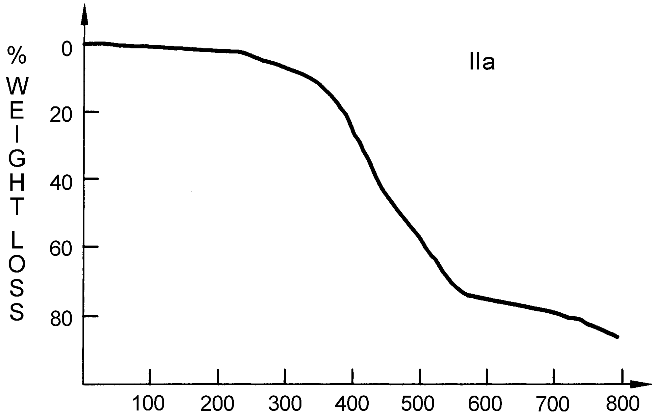


FIGURE 3 Thermogravimetric curve for poly(thiocarbonate) **IIa**.

(TDT) for all the polymers. The data are reported as the temperature at 10% weight loss.

From the TDT values it is possible to see that polymers with Ge in the main chain were more stable than those with Si. The relationship between electronegativity, bond polarity and thermal stability of heteroatom polymers has been described [9]. In fact, due to the different electronegativity of the elements in polymers with heteroatoms as Si or Ge, the bond polarity can result in reduced thermal stability [8]. In this case, the bond SiC, due to the difference of electronegativity, has a

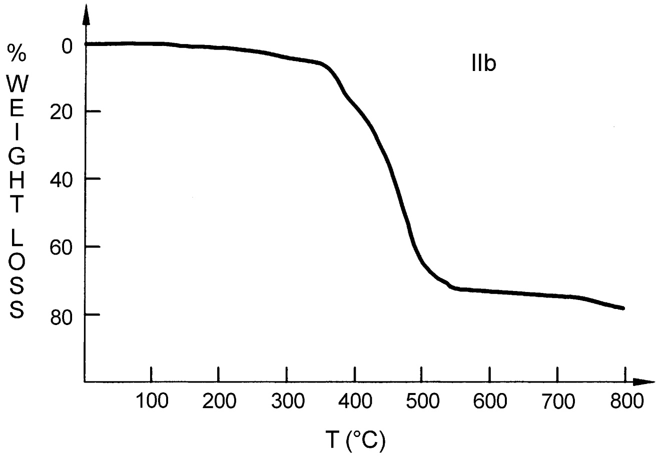


FIGURE 4 Thermogravimetric curve for poly(thiocarbonate) **IIb**.

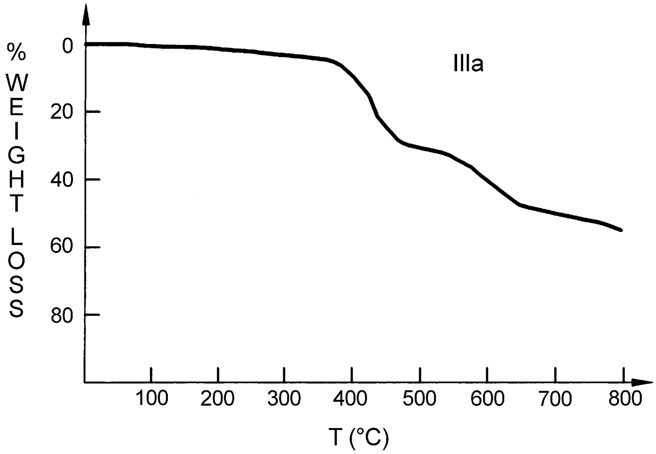


FIGURE 5 Thermogravimetric curve for poly(carbonate) **IIIa**.

slightly higher polarity than the GeC bond. Also the GeC bond is stronger than SiC because the former has a higher bond enthalpy [8]. Both situations would explain that polymers with the same structure with Ge have higher thermal stability than those with Si. The effect of the heteroatom size is more important in polymers with methyl groups bonded to the heteroatom than in those with phenyl groups, probably due to the steric hindrance and the volume of the phenyl groups.

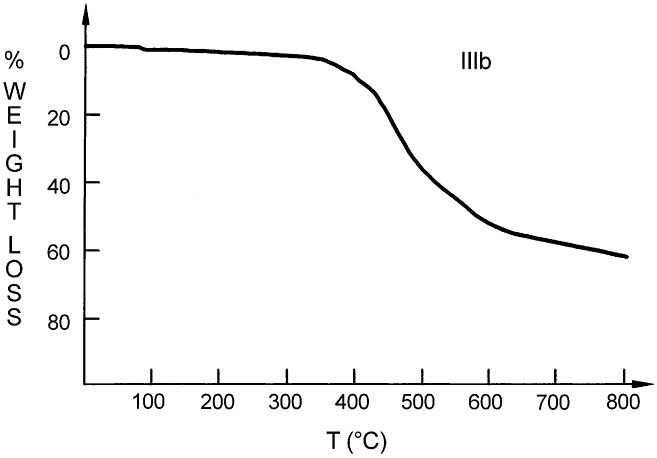


FIGURE 6 Thermogravimetric curve for poly(carbonate) **IIIb**.

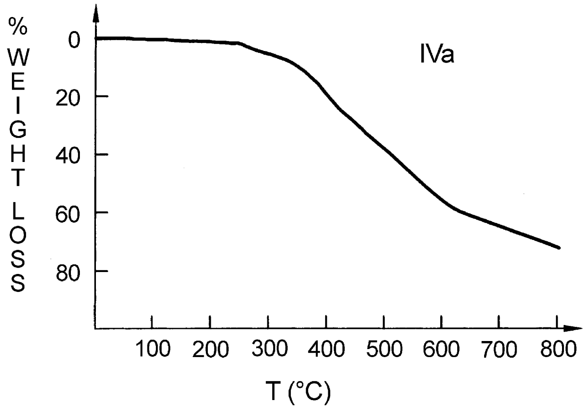


FIGURE 7 Thermogravimetric curve for poly(thiocarbonate) **IVa**.

On the other hand, poly(carbonates) showed higher thermal stability than the respective poly(thiocarbonates). This behaviour has been reported for poly(carbonates) and poly(thiocarbonates) derived from different diphenols [10–13].

Polymers with phenyl groups bonded to the heteroatom showed higher TDT values than the analogous with methyl groups, with the exception of polymers **IIb** and **IVb**, both poly(thiocarbonates) with Ge, being more stable than with methyl groups bonded to the Ge atom. In this case it can be seen that when the bulk of the side group is

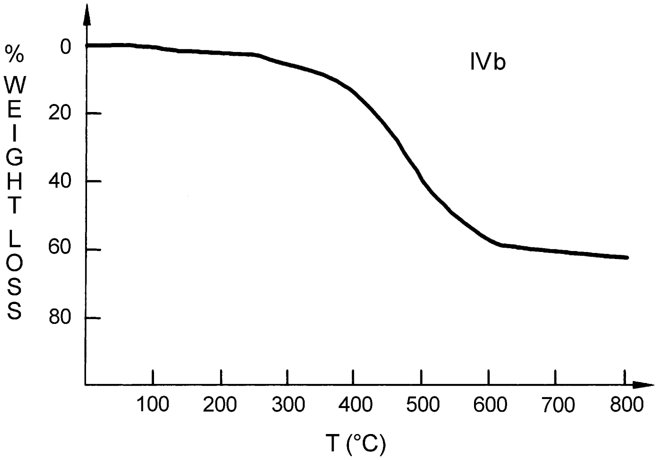


FIGURE 8 Thermogravimetric curve for poly(thiocarbonate) **IVb**.

TABLE 2 Thermal Decomposition Temperatures (TDT) and Kinetics Parameters of the Thermal Decomposition of Poly(Carbonates) and Poly(Thiocarbonates)

Polymer	TDT (°C)	n	E (kcal/mol)	Range (°C)	A (seg^{-1})
Ia	344	0	10.5	274–454	5.96×10^{-1}
Ib	380	0.5	25.1	324–504	3.30×10^{4}
IIa	323	0	7.0	234–574	2.96×10^{-2}
IIb	370	0	12.4	344–524	1.25
IIIa-1	400	0	15.5	364–464	1.89×10^{1}
IIIa-2		0	3.5	544–644	2.41×10^{-3}
IIIb	405	0.5	13.9	344–624	2.89
IVa	350	0.5	9.0	254–624	1.45×10^{-1}
IVb	355	0	6.6	254–604	1.94×10^{-2}

increased, the TDT values also increase, behaviour that can be attributed to the steric hindrance of the side group, which appears to be responsible for the improved thermal resistance. The same behaviour was described in other poly(thiocarbonates) with groups with different bulkiness as side chains [14], and for poly(amides) derived from acid dichlorides in which the Si atom is bonded to methyl and phenyl groups [15].

The kinetic parameters for the thermogravimetric weight loss were calculated according to the multiple linear regression method, using the kinetic equation:

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

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°C min^{-1}) incorporated directly into the temperature *versus* sample weight-fraction data, according to the procedure developed by Wen and Lin [16]. 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

$$\beta = \mathrm{Ln}[-(d\alpha/dT)/3(1-\alpha)^n] = \mathrm{Ln}\,A - E/Rt \tag{3}$$

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from linear least-squares fit of

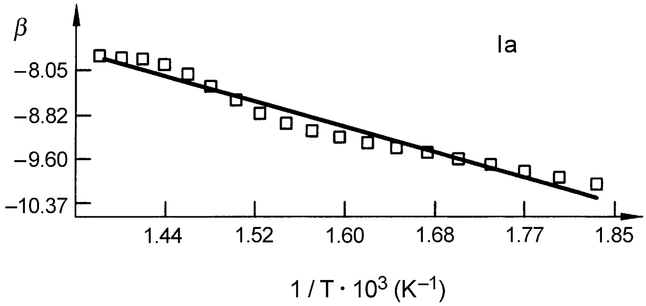


FIGURE 9 Arrhenius plot for the degradation of poly(carbonate) **Ia**.

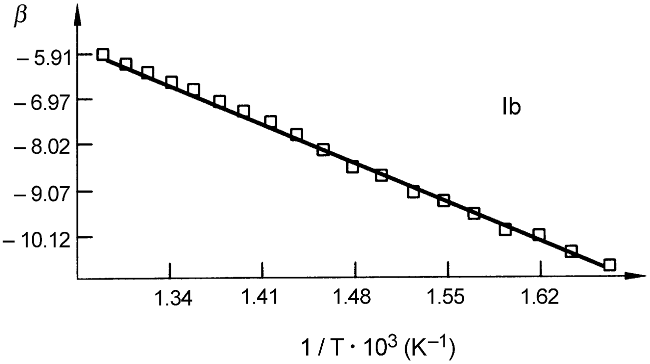


FIGURE 10 Arrhenius plot for the degradation of poly(carbonate) **Ib**.

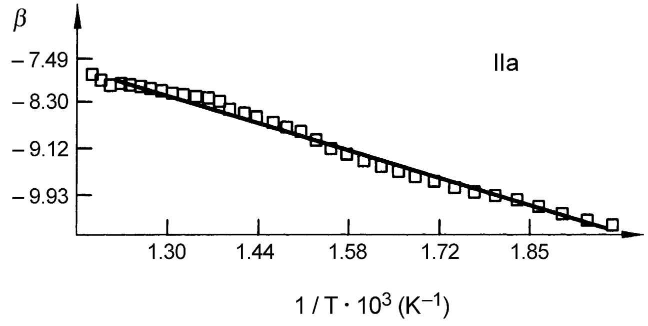


FIGURE 11 Arrhenius plot for the degradation of poly(thiocarbonate) **IIa**.

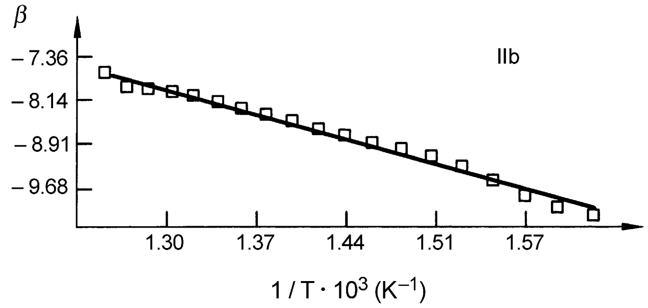


FIGURE 12 Arrhenius plot for the degradation of poly(thiocarbonate) **IIb**.

the data in a semilogarithmic plot of β *versus* 1/T. Figures 9–16 show those graphics and the results are summarized in Table 2. 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.

All polymers degrade in one single step with the exception of the poly(carbonate) **IIIa** in which it was possible to see two clear stages. The best fits were obtained for $n = 0$ or 0.5. A zero order reaction means that $-(d\alpha/dt)$ is constant, and implies that if the sample mass is increased, the rate of decrease in mass remains constant, which can happen if a constant concentration of volatile materials in maintained at the sample surface, as in a simple evaporation of preformed molecules [17].

When we assume a first-order reaction, a non-linearity plot was obtained, which has been described as a change in the degradation

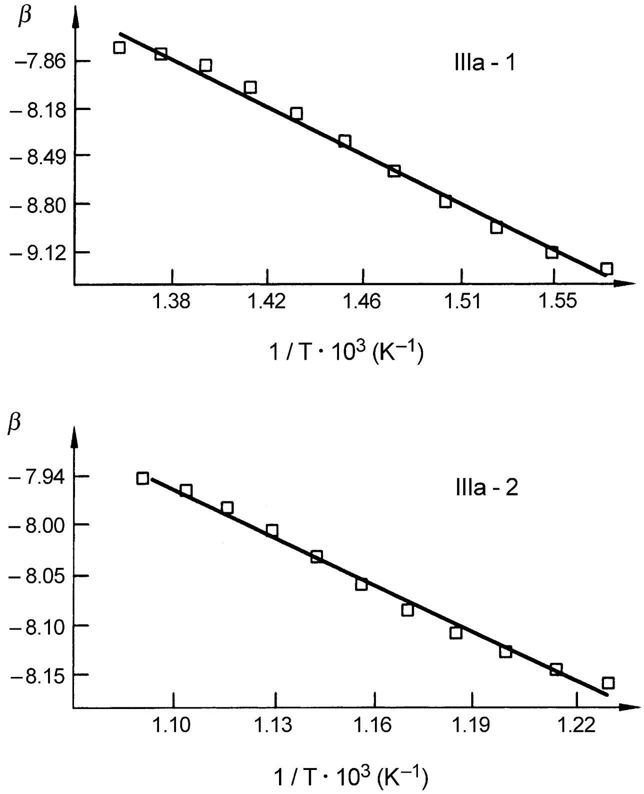


FIGURE 13 Arrhenius plot for the degradation of poly(carbonate) **IIIa**.

mechanism and also as a change in the energy [18]. In this work the reaction order for the degradation process was obtained when the linearity over the entire decomposition range was achieved and the activation energy was calculated from Eq. (3) having its value constant over the range considered.

However, it is probable that the degradation process of these polymers is very complex, in which the functional groups, the heteroatom and the side groups have participation, and the differences in the reaction order would be attributed to different decomposition mechanisms. The same is valid for the poly(carbonate) **IIIa** which degrades in two steps.

The range considered for the degradation process of polymers with methyl groups bonded to the heteroatom was 180°C, with the exception of poly(carbonate) **IIa**, but in polymers with phenyl groups bonded to the heteroatom it was 280°C for polycarbonates **IIIa** and **IIIb**, and

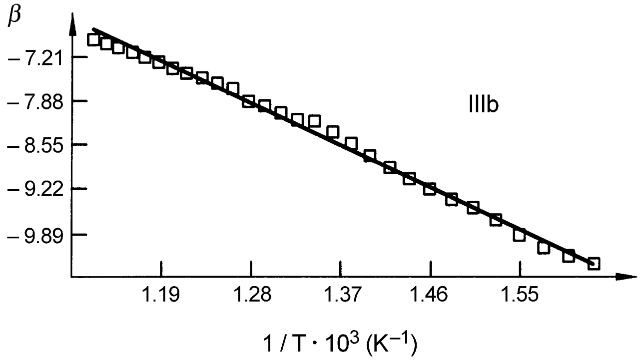


FIGURE 14 Arrhenius plot for the degradation of poly(carbonate) **IIIb**.

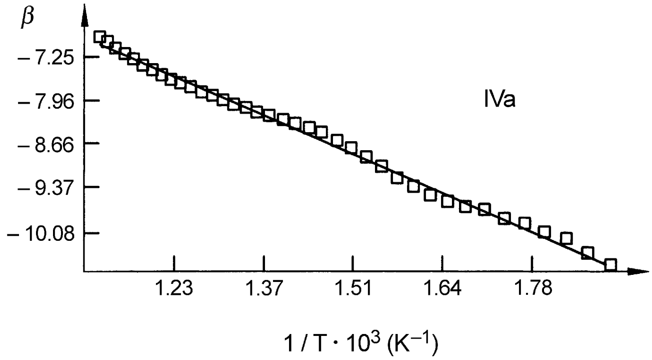


FIGURE 15 Arrhenius plot for the degradation of poly(thiocarbonate) **IVa**.

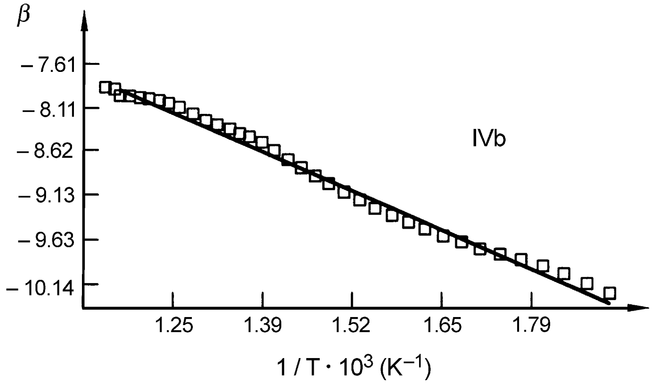


FIGURE 16 Arrhenius plot for the degradation of poly(thiocarbonate) **IVb**.

370 or 350°C for poly(thiocarbonates) **IVa** and **IVb**. These differences could also be indicative of different degradation mechanism, depending on the above structural factors.

When the results are compared with those obtained by us for poly(carbonates) and poly(thiocarbonates) with other kind of aliphatic or aromatic groups bonded to the central carbon atom of the diphenol, it is possible to see that there are several results [10–14]. In fact, we have not found a relationship between the diphenol structure, groups bonded to the central carbon atom, and the kinetic parameters, specially the kinetic reaction order. Poly(carbonates) and poly(thiocarbonates) can degrade according to first, zero or fractional kinetic order without taking into account the kind of side groups. Similar results were obtained in the thermal degradation of poly(esters) [11, 19] and poly(amido-esters) [20–23]. Polymers in this work have the additional factor of the presence of a heteroatom such as Si or Ge in the main chain.

Probably there are several superimposed degradation mechanisms which depend on the functional groups, the side groups and the presence and nature of the heteroatom in the main chain. None of the activation energy values showed a relationship with the nature of the polymer. In this sense some authors have suggested that the differences in activation energy and reaction order can also be due to a different reaction mechanism in the degradation process [24, 25].

The thermal degradation process in a solid state for condensation polymers is a very complex process and also complex reactions can occur, and consequently, the kinetic parameters have limited significance. The solid state of the sample is far from the ideal and can change in the course of the degradation process. Also in this kind of condensation polymers the degradation process can be composed of two or more superimposed process than can not be separated in a clear range of temperatures and it is difficult to suppose a constancy of the kinetic parameters over the temperature range [18, 26].

In spite of the above considerations, the thermal degradation is a very important tool to know the influence of the polymer structure on the thermal stability, and also to know the temperature at which the polymers can be used and the activation energy associated with the total degradation process.

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