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THERMOGRAVIMETRIC ANALYSIS OF COPOLY(CARBONATE–THIOCARBONATE)S

L.H. TAGLE and F.R. DIAZ

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)

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ABSTRACT

The thermal stability and the kinetics parameters of copoly(carbonate–thiocarbonate)s from two diphenols and for three different compositions were studied. No clear relation between the thermal decomposition temperature and the carbonate content was found for the two series of copolymers. The kinetics parameters of the thermal decomposition were determined using the Arrhenius relationship and indicated a two-step degradation process, the first step being of zero kinetic order and the second of first order. The steps were associated with two different decomposition mechanisms.

INTRODUCTION

Polymer degradation under conditions of normal use is a major factor which limits the applications of these remarkable and versatile materials. All polymers are degraded within the environment to which they are exposed during their lifecycle.

Polymers degrade by several different mechanisms depending on structure and exposure conditions. Degradation results from an irreversible change which leads eventually to failure, and the most common types of degradation occur through chemical reactions.

During degradation, changes in properties result from reactions which either reduce the size of molecules or lead to cross-linking between polymer chains to form rigid and three-dimensional structures. Usually, thermal degradation results from the combined effects of pyrolysis and thermal oxidation. Hydrolytic reaction as a result of traces of entrapped moisture may also contribute, particularly in condensation polymers [1].

On the other hand, polycarbonates, especially that derived from bisphenol A, are versatile materials, owing to an attractive combination of mechanical properties and good stability. The thermal properties of bisphenol A polycarbonate have been studied by several workers, and the thermal degrada-

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tion mechanism has been described by Davis and Golden [2–4] and Abbas [5]. They found that if the thermal degradation is carried out in a continuously evacuated system, the polycarbonate cross-links and forms an insoluble gel, produced by condensation reactions between species in which the carbonate groups are rearranged to form carboxy groups *ortho* to an ether link in the main chain. On the other hand, in polythiocarbonates this rearrangement is not possible because of the low stability of this thermolabile group, and the loss of COS is more probable [6]. Thus, polythiocarbonates have lower thermal stability than the respective polycarbonates [7,8].

In an earlier paper [8] the thermal behaviour of bisphenol A copoly(carbonate–thiocarbonate)s of three different compositions was described; it was shown that the inclusion of the thiocarbonate group reduces the thermal stability and that the copolymers degrade in a two-step process, where the steps are of different kinetic order.

In this paper, we continue work on thermal degradation of polymers and describe the thermal behaviour of copoly(carbonate–thiocarbonate)s derived from two diphenols and three mixtures of phosgene–thiophosgene which were synthesized by phase transfer catalysis, and also determined the kinetics parameters of the degradation process.

EXPERIMENTAL

Copoly(carbonate–thiocarbonate)s of three different compositions were synthesized under phase transfer conditions from 2,2-bis(4-hydroxy-phenyl)-butane (BU) and 1,1-bis(4-hydroxy-phenyl)-1-phenylethane (PE) and mixtures of phosgene and thiophosgene according to a procedure described earlier [9,10]. Copolymeric compositions were determined by IR spectroscopy (Perkin–Elmer model 1350) in $CHCl_3$ solution, using calibration curves which were obtained from mixtures of the homopolymers.

Thermogravimetry (TG) 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 thermal degradation measurements were carried out between 25 and 650 °C, with a heating rate of $20\,^{\circ}C\ min^{-1}$ under N_2 flow.

RESULTS AND DISCUSSION

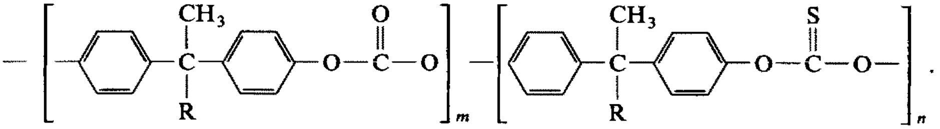
Copoly(carbonate–thiocarbonate)s from 2,2-bis(4-hydroxy-phenyl)butane were coded as COBU-75, COBU-50 and COBU-25, and those from 1,1-bis(4-hydroxy-phenyl)-1-phenylethane as COPE-75, COPE-50 and COPE-25,

TABLE 1

Thermal decomposition temperatures (TDT) of copoly(carbonate–thiocarbonate)s

Copolymer	TDT (°C)
COBU-75	460
COBU-50	397
COBU-25	400
COPE-75	412
COPE-50	350
COPE-25	440

according to the following structures:



BU R = $-CH_2-CH_3$
PE R = $-C_6H_5$

where the numbers give the percentage of carbonate groups in the copolymeric chains, as determined from IR spectroscopy using a calibration curve based on the C=O band at 1780 cm^{-1} for mixtures of the homopolymers.

Table 1 shows the thermal decomposition temperature (TDT) values for the copolymers. These values were taken at the temperature at which the copolymers had lost 10% of their weight. Figures 1 and 2 show the TG curves for COBU and COPE copolymers respectively. As can be seen, all the copolymers decompose in a two-stage process.

There is no clear relationship between TDT and carbonate content for the two series of copolymers. A similar finding was reported for copoly(carbonate–thiocarbonate)s of the same composition derived from bisphenol A [8]. The copoly(carbonate–thiocarbonate)s with 50% carbonate content both show lower thermal stability. It has been found that polycarbonates are more stable than polythiocarbonates, principally because the functional group is more reactive in the latter [4,11]. In fact, when polycarbonates are heated, the carbonate groups rearrange to a carboxylic group *ortho* to the main chain and then react with other chains to form an insoluble gel [4], with the result that the molecular weight and the TDT values increase. This rearrangement is not possible in polythiocarbonates because the –C(S)OH group is not stable, and the loss of COS is more probable [6].

Thus copoly(carbonate–thiocarbonate)s with a high carbonate content should be more stable, as is seen with COBU-75. On the other hand, COBU-50 and COBU-25 show very similar TDT values.

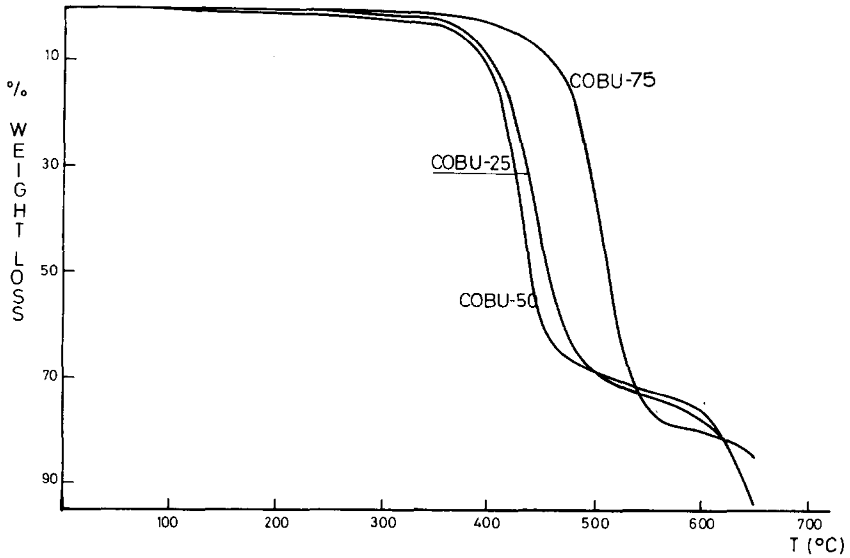


Fig. 1. TG curves for COBU-75, COBU-50 and COBU-25.

For the COPE copolymers, COPE-25, which has a low carbonate content, was the most stable. It is probable that, for these copoly(carbonate–thiocarbonate)s, there is a different mechanism for the degradation process. Furthermore, we do not know the sequence of groups in the chain, nor the influence of the aromatic rings bonded to the central carbon atom.

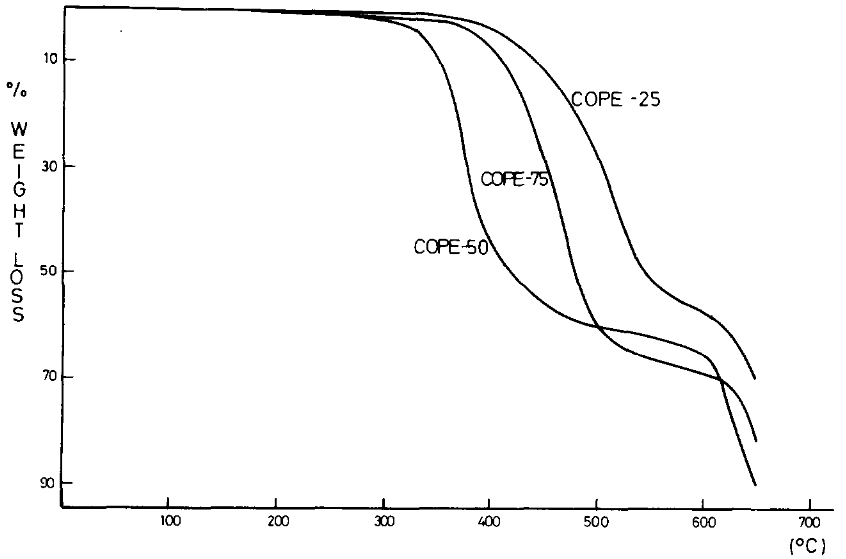


Fig. 2. TG curves for COPE-75, COPE-50 and COPE-25.

The kinetics of the thermal degradation were also studied. The thermal decomposition kinetics of the TG weight loss data can be attributed to the equation

$$-(\mathrm{d}\alpha/\mathrm{d}t) = k_n(1-\alpha)^n \qquad (1)$$

where α is the fraction of the sample 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 calculated using a differential technique and directly incorporating the heating rate (20 °C min^{-1}) into the temperature vs. sample weight fraction data, according to the method of Wen and Lin [12]. The specific rates k_n were calculated from the Arrhenius relation

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

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

$$\beta = \ln\left[-(\mathrm{d}\alpha/\mathrm{d}T)/3(1-\alpha)^n\right] = \ln A - E/RT \qquad (3)$$

A linear multiple regression program was developed to calculate the kinetics parameters A and E from a least-squares fit of the data in a semilogarithmic plot of β vs. $1/T$.

Table 2 summarizes the values of E and A for each of the ranges considered, and Figs 3–8 show the plots of β vs. $1/T$. Good straight lines were obtained for the copolymers, although some scatter at the beginning and end of each decomposition was detected.

TABLE 2

Kinetics parameters for copoly(carbonate–thiocarbonate)s

Copolymer	Range (°C)	n	E (kcal mol^{-1})	A (s^{-1})
COBU-75	410–550	0	25.6	2.99×10^3
	550–620	1	24.4	1.88×10^4
COBU-50	360–460	0	27.2	6.39×10^4
	470–580	1	19.9	4.86×10^2
COBU-25	380–490	0	22.8	1.88×10^3
	500–580	1	16.3	1.17×10^2
COPE-75	360–510	0	21.3	4.79×10^2
	510–610	1	15.1	4.27×10
COPE-50	320–450	0	38.1	2.58×10^9
	450–580	1	5.1	0.05
COPE-25	390–560	0	17.3	1.66×10
	560–620	1	13.2	3.57

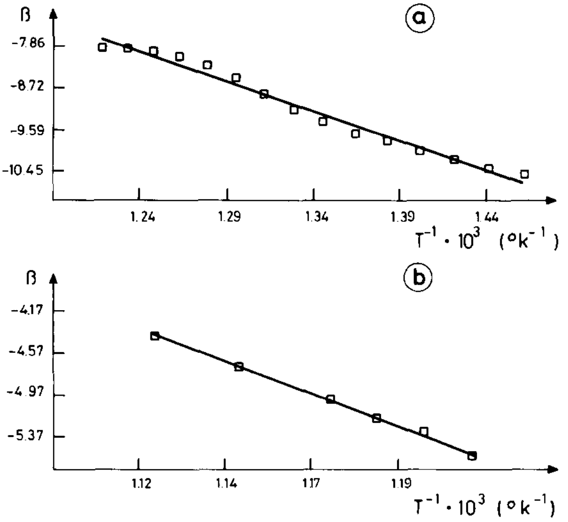


Fig. 3. Arrhenius plot for degradation of COBU-75: (a) 410–550 °C, $n=0$; (b) 550–620 °C, $n=1$.

The results show that all copolymers degrade in two steps, the first which obeys a zero kinetic order, whereas the second obeys a first kinetic order. The same behaviour was reported for copoly(carbonate–thiocarbonate)s derived from bisphenol A.

A zero kinetic order means that $-\mathrm{d}\alpha/\mathrm{d}T$ is constant, which implies that when the sample weight is increased the rate of decrease in mass remains unchanged. This can happen if a constant concentration of volatile materials is maintained at the sample surface, as in a simple evaporation of preformed

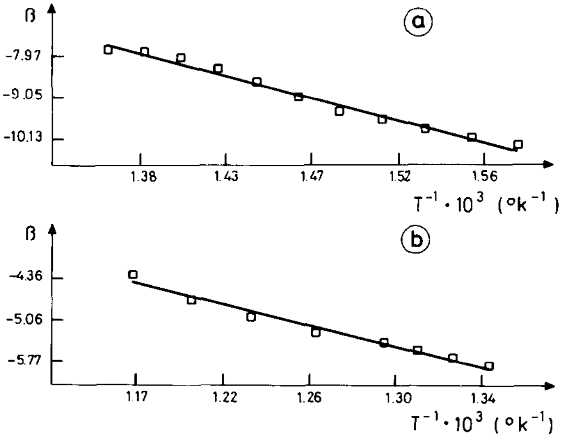


Fig. 4. Arrhenius plot for degradation of COBU-50: (a) 360–460 °C, $n=0$; (b) 470–580 °C, $n=1$.

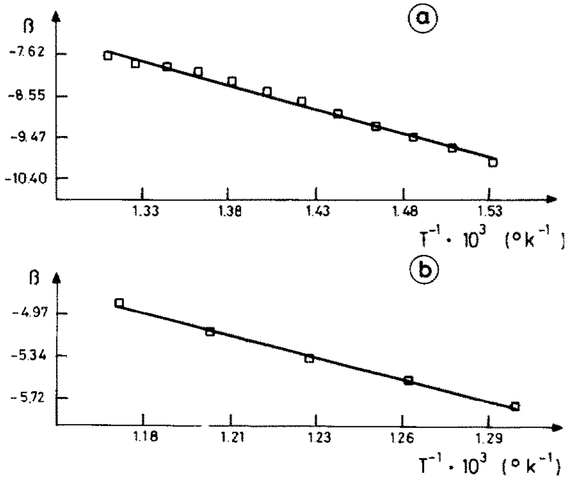


Fig. 5. Arrhenius plot for degradation of COBU-25: (a) 380–490 °C, $n = 0$; (b) 500–580 °C, $n = 1$.

molecules [13]. In the case of first-order kinetics the concentration of volatile molecules at the sample surface depends on the residual active weight fraction.

It has been found that, for many complex reactions, the kinetic order has no meaning [14], especially in copolymers as described here, which have two functional groups that behave differently on heating.

Also, the wide divergence in values of activation energy suggests that this parameter is of limited value, principally because the physical state of the sample is far from ideal (usually a solid) and may change as the reaction proceeds. On the other hand, reaction degradations are often complex in

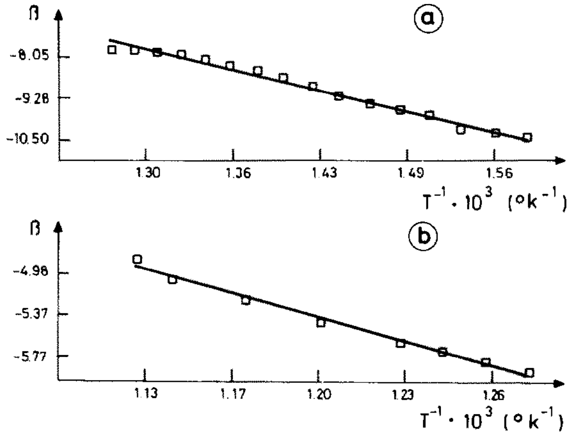


Fig. 6. Arrhenius plot for degradation of COPE-75: (a) 360–510 °C, $n = 0$; (b) 510–610 °C, $n = 1$.

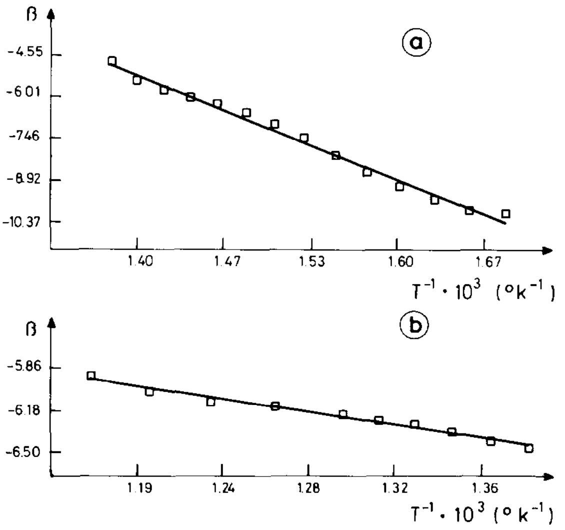


Fig. 7. Arrhenius plot for degradation of COPE-50: (a) 320–450 °C, $n = 0$; (b) 450–580 °C, $n = 1$.

polymers, and usually involve several reaction stages which cannot be well separated over a clear temperature range. Thus, assumptions about reaction order and constancy of kinetics parameters over a particular temperature range may be questionable. Also, the kinetics treatments of thermal degradation assume that the residual weight of the sample may be handled as if it were a concentration, which is of doubtful validity [15].

Even so, it is probable that the first stage in the thermal degradation of the copolymers occurs through rearrangement of the carbonate group,

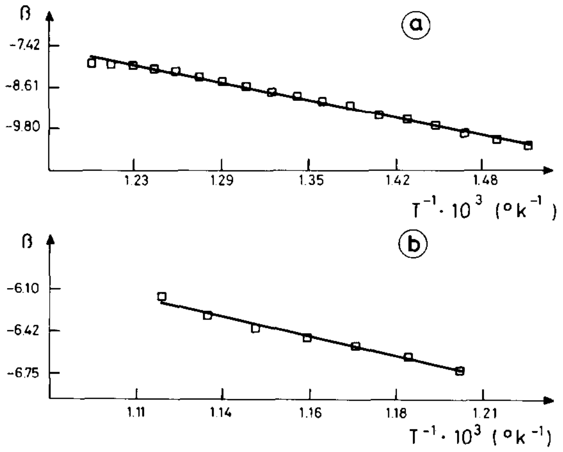


Fig. 8. Arrhenius plot for degradation of COPE-25: (a) 390–560 °C, $n = 0$; (b) 560–620 °C, $n = 1$.

breaking of the thiocarbonate group and gelation of the polymeric chains through the pendant carboxylic group in the *ortho* position, with the temperature and magnitude of the reaction being dependent on the composition of the copolymer. The second stage of the thermal degradation would then be decomposition of the cross-linked molecules.

CONCLUSIONS

It may be concluded that the thermal behaviour of these copolymers is similar to that described for bisphenol A, consisting of thermal decomposition in two stages which are of different kinetic order. Moreover, the inclusion of the thiocarbonate group in copolymers would reduce the thermal stability and it is probable that such copolymers have two different mechanisms of degradation.

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