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THERMOGRAVIMETRIC ANALYSIS OF BISPHENOL A COPOLY(CARBONATE–THIOCARBONATE)S

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ABSTRACT

The thermal stability and kinetic parameters of three bisphenol A random copoly(carbonate–thiocarbonate)s of different compositions were investigated. The thermal degradation temperatures of the copolymers were dependent on the carbonate content of the copolymeric chain, and indicated decreased stability compared with the corresponding homopolymers. The kinetic parameters of the thermal decomposition were determined using the Arrhenius relationship. A two-step process is indicated for the degradation of the copolymers, the first step being of zero order and the second of first order. The steps are associated with two different decomposition mechanisms. The results are compared with results obtained for the homopolymers.

INTRODUCTION

In polymer and plastics science and technology, thermal methods of analysis find very wide use. In particular, dynamic TG analysis is widely used as a tool for investigating the stability of polymers, and has become prominent in applications to synthetic polymeric materials.

Dynamic TG is a popular technique because of its simplicity and because it has the advantage that only one thermogram is needed for the determination of kinetic parameters. The thermograms provide information about the sample composition as well as kinetic data relating to the chemical changes which occur on heating.

Bisphenol A polycarbonate is one of the most versatile plastics, owing to an attractive combination of mechanical properties and good stability. Bisphenol A polythiocarbonate as synthesized in phase transfer conditions [1] is a material with good thermal properties [2].

The thermal properties of bisphenol A polycarbonate have been studied by several authors, and the degradation mechanism has been described by Davis and Golden [3] and Abbas [4]. It has been shown that if thermal degradation is carried out in a continuously evacuated system, the polycarbonate crosslinks and forms an insoluble gel, produced by condensation reactions through species in which the carbonate groups are rearranged to form carboxy groups *ortho* to an ether link in the main chain. As a continuation of our work on the thermal degradation of polymers, the present paper reports on the thermal behaviour of bisphenol A copoly(carbonate–thiocarbonate)s containing random carbonate and thiocarbonate groups in the main chain. Our intention was to investigate the effect of varying carbonate group content on thermal stability and kinetic parameters, and to compare these with values obtained for the corresponding homopolymers [2–4].

EXPERIMENTAL

Copoly(carbonate–thiocarbonate)s of three different compositions were synthesized by phase transfer catalysis from 4,4′-isopropylidenediphenol (bisphenol A) and a mixture of phosgene and thiophosgene using several quaternary ammonium and phosphonium salts in dichloromethane as solvent. The synthesis and characterization of the copolymers were described in a previous paper [5]. Copolymeric composition was determined by IR spectroscopy in $CHCl_3$ solution, using a calibration curve which was obtained from mixtures of the homopolymers.

Dynamic TG analyses were carried out using a Perkin–Elmer TGS-1 thermobalance with a Perkin–Elmer UU-1 temperature program control. Samples (4–7 mg) were placed in the platinum sample holder, and the thermal degradation measurements were carried out between 25 and 650 °C with a heating rate of 20 °C min^{-1} in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Thermal decomposition temperatures

The three copoly(carbonate–thiocarbonate)s studied were coded as CO-76, CO-47, and CO-26, these numbers being the percentages of carbonate links in the polymeric chains, as determined by IR spectroscopy.

Table 1 shows the thermal decomposition temperature (TDT) values for the copolymers and bisphenol A polycarbonate (PC), which was included for comparison. The TDT value for bisphenol A polythiocarbonate (PTC) was reported in a previous paper [2]. The TDT values were taken as the temperatures at which the copolymers had lost 10% of their weight. Figure 1 shows the TG curves for the copolymers and the homopolymer PC.

These results indicate that PC decomposes in a single-step process between 400 and 600 ° C, and it has been reported [2] that PTC also decomposes in a single-step process over the same temperature range. The copoly-

TABLE 1

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

Polymer	TDT (° C)
PC	470
CO-76	326
CO-47	403
CO-26	341
PTC	410 [a]

[a] Value from ref. 2.

mers, by contrast, decompose in a two-stage process. The range of the two stages is practically the same for CO-76 and CO-26 (280–380 and 380–560° C), but different for CO-46 (350–500 and 500–580° C).

The three copolymers shows TDT values which are lower than those for the corresponding homopolymers. However, CO-46 shows a TDT value that is very similar to that reported [2] for PTC. It is surprising that copolymers with low (CO-26) and high (CO-76) carbonate content show a decreased thermal stability as compared with the homopolymers and the CO-46 copolymer, for which the thiocarbonate and carbonate content is very similar. There is no relation between TDT and carbonate content for this series. The mechanism for the degradation process is probably different for the three copolymers.

Kinetic parameters

To explain the behaviour of the copolymers, a study was made of the kinetics of their thermal degradation. Thus, the thermal decomposition

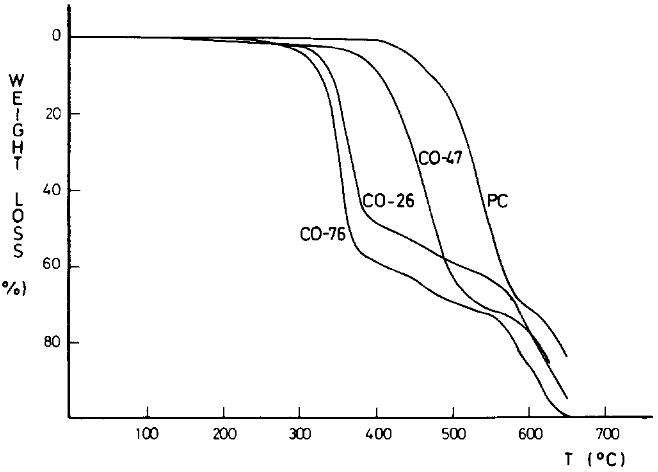

Fig. 1. TG curves for CO-76, CO-47, CO-26 and PC.

TABLE 2

Kinetic parameters for copoly(carbonate–thiocarbonate)s

Polymer	E (kcal mol^{-1})	A (s^{-1})	n	Range (° C)
PC	34.7	8.70×10^6	1	400–600
CO-76	24.1	6.51×10^5	0	280–380
	8.5	7.11	1	380–560
CO-47	20.3	2.51×10^3	0	350–500
	23.2	6.10×10^4	1	500–580
CO-26	28.8	2.03×10^7	0	300–380
	7.3	1.89	1	380–560
PTC [a]	32.3	1.78×10^8	1	350–500

[a] Values from ref. 2.

kinetics of the TG weight loss data were attributed to 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 calculated using a differential technique and directly incorporating the heating rate (20 ° C min^{-1}) into the data of temperature versus sample weight fraction [6]. The specific rates k_n were obtained from the Arrhenius relation

$$k_n = A \exp(-E/RT) \tag{2}$$

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

$$\beta = \ln[-(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n] = \ln A - E/RT \tag{3}$$

A 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 versus $1/T$.

Table 2 shows the values of the kinetic parameters for each of the ranges considered, as obtained from Figs. 2–4. As can be seen, good straight lines (correlation > 0.99) were obtained for the three copolymers at temperature intervals of 25 ° C, although some scatter at the beginning and end of each decomposition range was detected. This scatter can be attributed to the difficulty of obtaining accurate measurements at the beginning and end of an experiment, as is frequently encountered in kinetic measurements of polymers.

The results show that the three copolymers decompose in two steps, the first of which obeys a zero reaction order, and the second of which obeys a first order kinetic. The temperature ranges at which the two decomposition steps occur are the same for CO-76 and CO-26, but for CO-47 the first step is bigger. By contrast, PC shows a single-step decomposition across the

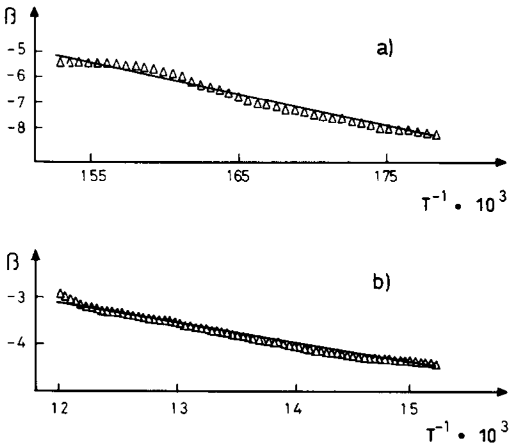

Fig. 2. Arrhenius plot for degradation of CO-76: (a) 280–380 ° C, $n = 0$; (b) 380–560 ° C, $n = 1$.

whole range (Fig. 5), and an activation energy very similar to that reported in the literature as having been obtained by TG methods [4,7].

A zero-order reaction, which means that $-\mathrm{d}\alpha/\mathrm{d}t$ is constant, implies that if the sample mass 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 the simple evaporation of preformed molecules [8,9]. On the other hand, in the case of a first-order reaction, the concentration of volatile materials at the surface of the sample depends on the residual active weight fraction [9].

These results would seem to indicate that the replacement of one oxygen atom of the carbonate group by a sulphur atom leads to two different

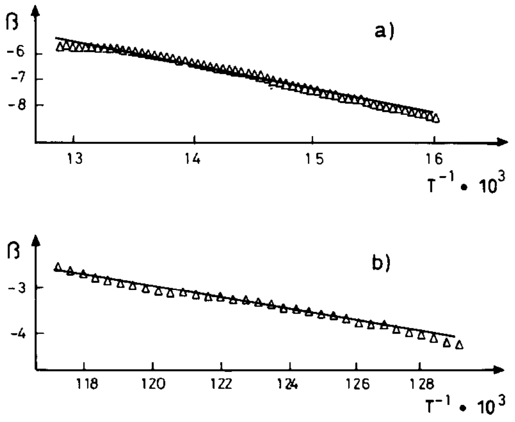

Fig. 3. Arrhenius plot for degradation of CO-47 (a) 350–500 ° C, $n = 0$; (b) 500–580 ° C, $n = 1$.

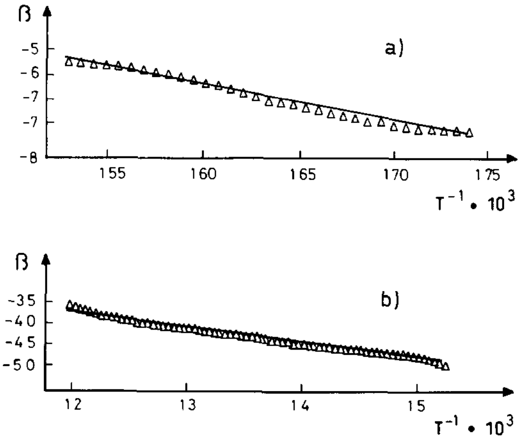

Fig. 4. Arrhenius plot for degradation of CO-26: (a) 300–380 °C, $n = 0$; (b) 380–560 °C, $n = 1$.

mechanisms in the decomposition of the copolymer as compared with the corresponding homopolymer. This is possible because copolymers have –OC(O)O– and –OC(S)O– groups, which behave differently with changes in temperature. Davis and Golden [3] have studied the thermal degradation of the polycarbonate, and suggested a mechanism which is based on the rearrangement of the carbonate group to form a pendant carboxy group *ortho* to an ether link in the main chain, which would undergo a series of subsequent reactions. These reactions include the formation of CO_2 and gelation of the polymer. With the thiocarbonate group, rearrangement of this thermolabile group is difficult, and it is likely that COS formation and the ether link in the main chain would be more important [10].

Thus, the first stage in the thermal degradation of the copolymers probably occurs through rearrangement of the carbonate group, breaking of the thiocarbonate group and gelation of the polymeric chains, according to the mechanism proposed by Davis and Golden, through the pendant carboxylic group in *ortho* position [3], with the temperature and magnitude of the reactions being dependent on the composition of the copolymer it should be

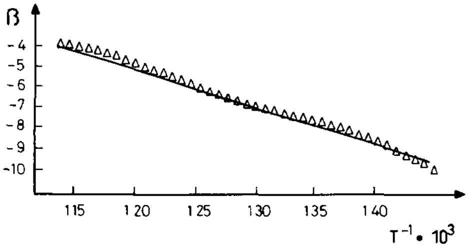

Fig. 5. Arrhenius plot for degradation of PC: 400–600 °C, $n = 1$.

noted that when the copolymers were heated until the TDT was reached, the residue obtained in each case was insoluble in $CHCl_3$, which would seem to confirm the formation of crosslinked molecules. The second stage of thermal degradation would then be decomposition of the crosslinked molecules.

The activation energy for the copolymers cannot be correlated with the copolymeric composition because there is apparently no relation between the mechanism and the carbonate content. It is likely that the two types of group, carbonate and thiocarbonate, undergo degradation independently, especially since they are assumed to occur in random order in the copolymeric chain.

CONCLUSIONS

We can conclude that inclusion of the thiocarbonate group in a polymeric chain of polycarbonates to form copoly(carbonate–thiocarbonate)s changes the mechanism of thermal degradation into a two-step process, as compared with the thermal degradation of the corresponding homopolymers, which occurs in a single step.

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