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EVALUATION OF THE THERMAL STABILITY OF CYCLIZED POLYMERS. I

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ABSTRACT

The thermal stability of commercially available polymers was investigated under set conditions. Some polymers show two inflections while others give a single inflection indicating the processes of cyclization and degradation. Polymers with a methyl-containing heterocyclic moeity undergo rapid decomposition while others with a carbonyl-containing heterocyclic unit are relatively more stable. In general our observations support the idea that the nature of the heterocyclic moeity and the hinge groups in the polymer chain plays a vital role in the thermal stability of these polymers.

INTRODUCTION

This paper attempts to correlate the thermal stability of polymers with their chemical structure. For comparison, a range of commercially available polymers [1–5] was evaluated using thermoanalytical techniques under identical conditions. Thermogravimetry (TG) or weight loss studies are the most suitable methods for assessing the high stability of polymer systems. The overall thermal stability [1,2] of a polymer in a given environment depends upon the polymer's structure, its molecular weight, the stereochemistry of the polymer unit, the presence or absence of crystallinity, the nature of the environment and many other factors (bond strength, activation energies, cross-linking, presence of lower molecular weight material, etc.).

In order to assess the thermal stability of polymers, many of the factors mentioned above must be simultaneously considered. Since this is virtually impossible, various investigators have devised arbitrary qualitative and quantitative methods [3], many of which involve TG. The thermal stabilities of the polymers have been assessed on the basis of the methods described below (a–d), and we report an interesting transformation when cyclic polymers are substituted with a different group.

(a) The procedural decomposition temperature (PDT), which is the temperature at which the first observable weight loss occurs in dynamic thermogravimetry (DTG).

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(b) The temperature at which 50% decomposition has occurred (50% DT) in DTG.

(c) The percentage weight loss (W_{30}) which occurs after 30 min at 400°C in isothermal TG.

(d) Comparison of overall activation energies for degradation under isothermal conditions.

DTG was carried out in air to evaluate the thermal-oxidative stability of the polymers. Dynamic TG studies in a flowing nitrogen atmosphere were made in order to assess thermal stability in the absence of oxidative initiation.

EXPERIMENTAL

For all DTG experiments a Stanton automatic thermobalance (Mark II) was employed, the furnace was programmed at a heating rate of 6°C min^{-1} (nominal) and the experiments were carried out in static air or dynamic nitrogen. The samples (10 mg) were placed in a small platinum crucible.

In studies involving dynamic nitrogen pure white spot nitrogen was passed over the sample by attaching a gas input to the top of the furnace. A flow rate of 200 ml min^{-1} (measured by an air flow meter) was employed.

Nitrogen was passed over the sample for 30 min before the heating programme was started. This ensured that the furnace tube was completely purged with nitrogen.

For comparison, a range of commercially available polymers was evaluated under the same conditions. These were:

(1) Polybenzimidazole (Imidite 2801), Whittikar Corporation, Research and Development Division, San Diego, CA.
(2) Polybenzoxazole (PBO_3), Yorkshire Chemicals Ltd., Leeds, U.K.
(3) Polyimide (QX-13), Royal Aircraft Establishment, Farnborough, U.K.
(4) Polyimide (Karamide 601), Société des Usines Chimiques, Rhone-Poulenc Départment Polymères Thermostables, Paris 8, France.
(5) PPS (Ryton), Phillips Petroleum, U.K.
(6) Ekonol, Carborundum Co. Ltd.

RESULTS AND DISCUSSION

Table 1 gives comparative stability data for the commercially available high-temperature polymers both as supplied and cured according to the manufacturers' specifications prior to heating. The data were abstracted from thermograms obtained in air and nitrogen. In addition to the PDT and 50% DT data shown in Table 1, the complete thermograms for the polymers in Fig. 1 show that polymers 1, 2 and 3 lose weight from low temperatures in

TABLE 1

TG data (in air) for the commercial polymers and those prepared in this work

Commercial high-temperature polymers	PDT (°C)	50% DT (°C)	Polymer (cyclized)	PDT (°C)	50% DT (°C)
1. Polybenzimidazole	140(310) [a]	528(550) [a]	IA	260	492
2. Polybenzoxazole	230(360) [a]	545(550) [a]	IIA	320	520
3. Polyimide QX-13	180(380) [a]	518(580) [a]	IIIA	300	494
4. Polyimide (Karamide)	380	550	IB	305	525
5. Polyphenylene sulphide (P.P.S.)	410	580	IIB	280	520
6A. Ekonol (before plasma spraying)	340	524	IIIB	290	500
6B. Ekonol (after plasma spraying)	340	487	IVB	290	525

[a] Values in parentheses are for cured samples.

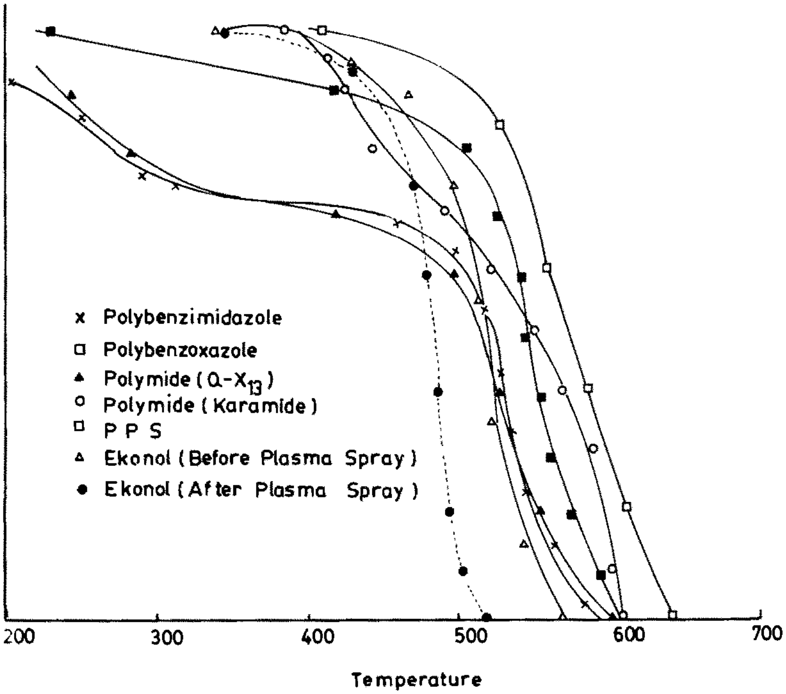


Fig. 1. TG curves of commercial polymers (1–6).

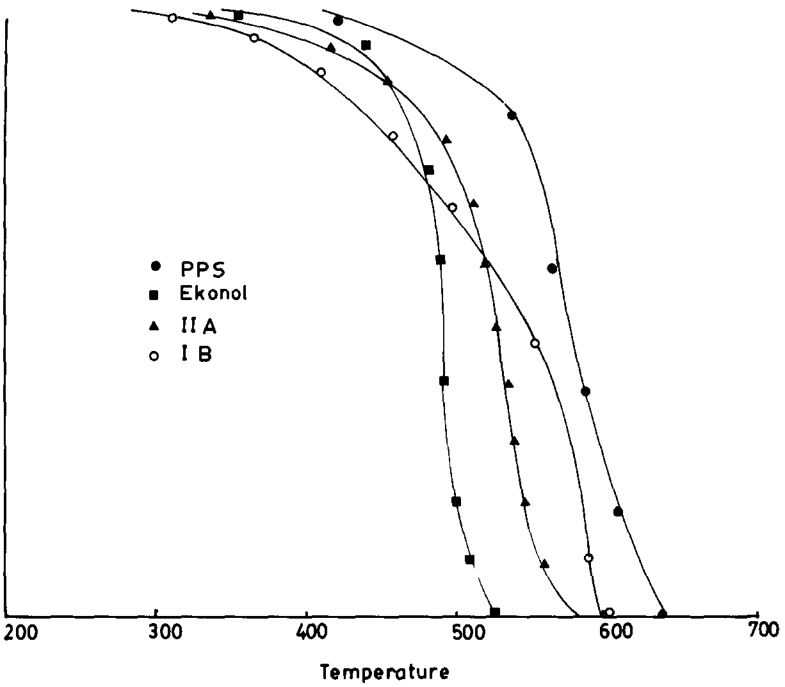


Fig. 2. TG curves showing 50% DT values of thermo-oxidative degradation in polymers of polyphenylene sulphide (PSS), ekonol, polybenzoxazole (IIA) and polyimide (IB).

an apparently two-stage process, the first of which involves "cyclization" and the second degradation. Polymers 4, 5 and 6 lose weight in one gradual process. Polymer 6 (Ekonol), unlike the other polymers, was difficult to fabricate by the spin-casting method used for preparation of bearing linings.

Attempts to coat Ekonol by plasma spraying were made and the material was assessed before and after spraying. The results indicated that the material after plasma spraying showed a slightly lower 50% DT value as compared to the untreated material. The films, however, were unsatisfactory, being soft and powdery, since plasma spraying could only be effected on flat sheets of metal.

The 50% DT data indicated that the commercial high-temperature polymers lie in the range 487–580 °C and the polymers prepared [4] in this study (IA–IIIA and IB–IVB) show 50% DT values in a similar range (492–520 °C). Figure 2 shows the thermograms for two representative polymers from the A and B series as compared with those of two commercial polymers, PPS and Ekonol. These were chosen as the two extremes showing simple behaviour, and it can be seen that the A and B polymers have an intermediate thermo-oxidative behaviour as assessed by DTG.

DTG in nitrogen was used to interpret the behaviour of these polymers during thermo-oxidative degradation (Fig. 3). DTG studies in air show the

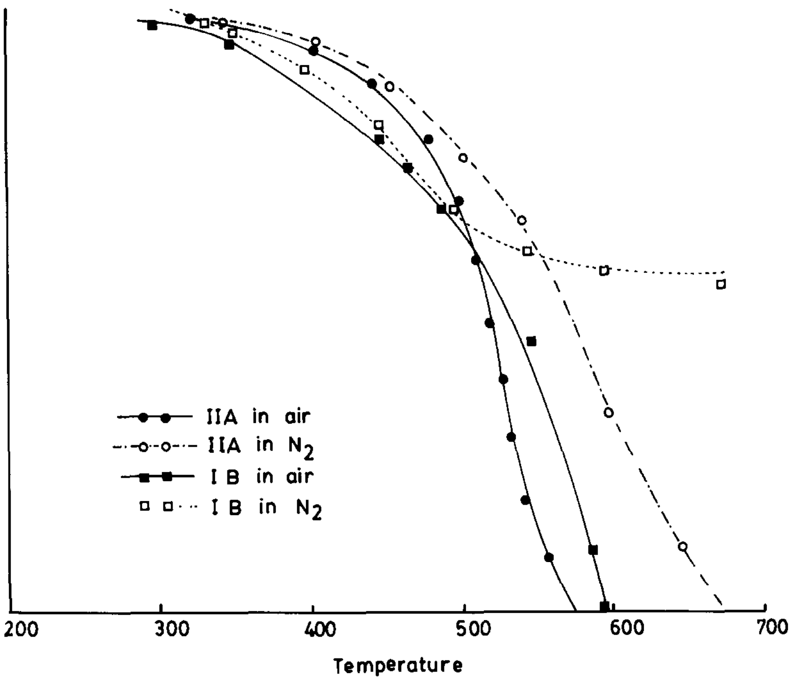
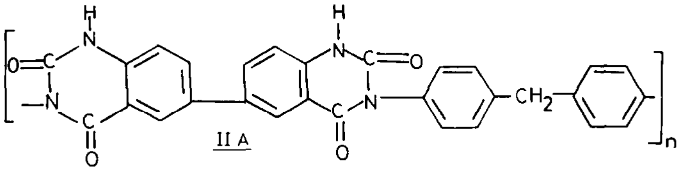
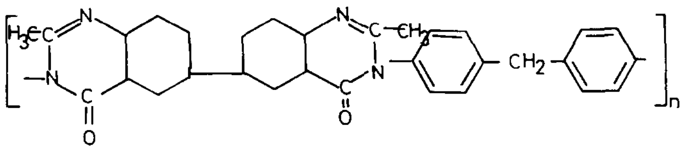


Fig. 3. TG curves showing thermo-oxidative degradation in polymers of polybenzoxazole (IIA) and polyimide (IB).

extreme behaviour of the polymers prepared in this study [4]. IIA behaves similarly in air and nitrogen; PDT (in air) = 320 °C, PDT (in nitrogen) = 340 °C, 50% DT (in air) = 520 °C, 50% DT (in nitrogen) = 576 °C. IB, in contrast, has a more rapid decomposition in air than nitrogen showing its high susceptibility to oxidatively initiated degradation. This can be explained on the basis of the chemical structures of IIA and IB. Apart from the same methylene hinge group occurring in both structures, polymer IB consists of a methyl group in the heterocyclic unit. It is more easily bonded by oxygen compared to the carbonyl group in IIA.



II A

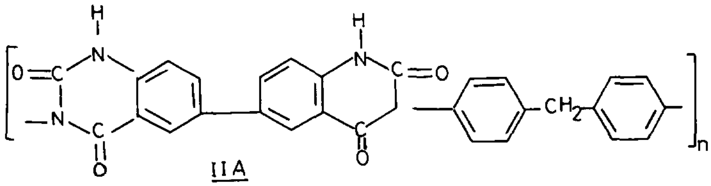


I B

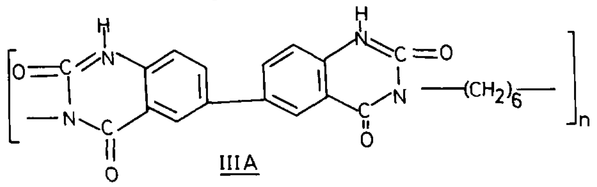
TABLE 2

TG data (in nitrogen) of the polymers prepared in this work

	IA	IIA	IIIA	IB	IIB	IIIB	IVB
PDT	325	340	340	300	330	320	320
50% DT (°C)	670	576	514	40% DT at 750°C	30% DT at 750°C	40% DT at 750°C	50% DT at 700°C



IIA



IIIA

On the basis of 50% DT, TG data in nitrogen (Table 2) indicated the order of stability: IA > IIA > IIIA and IIB > IB ≈ IIIB > IV. 50% DT data in air suggested the order of stability: IIA > IA ≈ IIIA and IB ≈ IIB ≈ IVB > IIIB.

The increase in stability (in air) of IIA as compared to IIIA is understandable on the basis of its aromatic structure, with alternate heterocyclic units in the main chain.

In IIIA the heterocyclic units are linked with aliphatic (hexamethylene) groups which are less stable to thermo-oxidative degradation. IA is less stable than IIA due to the presence of a less thermally stable heterocyclic unit in its structure.

The stability order of polyquinazolones (IB–IVB) may be explained in terms of the nature of the hinge groups in the polymer chain. It was found that the order of stability in air for these groups was as follows: $-CH_2- \approx -O- > -S-S > -SO_2-$, while in nitrogen the order was: $-O- > -CH_2- \approx -SO_2- > -S-S-$.

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