

## Thermal Degradation of Polymers. XVII. Thermal Analysis of Polyquinazolones and Related Systems

A. GHAFOR\* and R. H. STILL, *Department of Polymer and Fibre Science, UMIST, Manchester, England*

### Synopsis

The thermal characterization of a series of polyquinazolones, poly(quinazolone diones), and polybenzoxazinones by thermal analytical techniques (TG, DSC) is described. Comparative thermal stability measurements by dynamic and isothermal TG in air and N<sub>2</sub> are critically discussed. Kinetic studies by isothermal TG in air and nitrogen leading to activation energies are described. The inherent difficulties in comparative thermal stability studies on complex polymer systems are discussed in terms of their structural and compositional variables and their effect on the assessment parameters used.

### INTRODUCTION

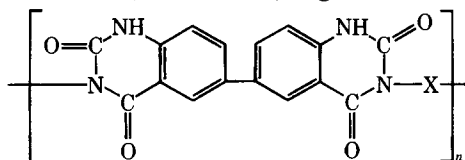
The polymers studied were prepared as binder materials for tribological application in journal bearings, and this has been reported elsewhere.<sup>1</sup> Poly(quinazolone diones), polyquinazolones, and polybenzoxazinones were chosen for study on the basis of their reported thermal stabilities, ease of preparation, and ability to be fabricated in a prepolymer state.<sup>2-6</sup> The latter was important because it enabled coatings to be prepared by spraying or casting techniques on the inside of a journal bearing bush. Such coatings could then be thermally cyclized to the partial ladder polymer.<sup>1</sup>

This paper reports the thermal characterization of these materials using dynamic and isothermal thermogravimetric analysis (TG) and DSC.

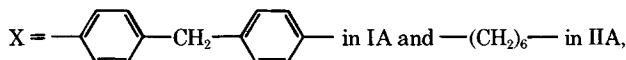
### EXPERIMENTAL

#### Materials

Two polyquinazolinediones, IA and IIA, of generalized repeating structure

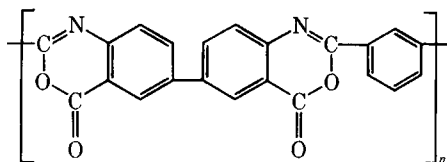


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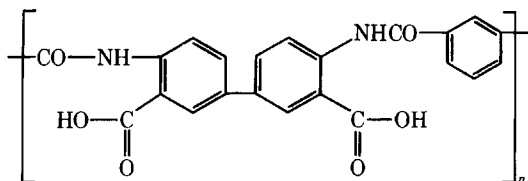
\* Present address: Peoples University of Islamabad, Islamabad, Pakistan.

were prepared from prepolymers derived from benzidinedicarboxylic acid (BDC) and diphenylmethane diisocyanate and heethylene diisocyanate as reported previously.<sup>1</sup> A polybenzoxazinone, IIIA, of generalized structure



IIIA

was prepared by cyclization of the prepolymer amido acid



prepared from BDC and isophthaloyl chloride in *N*-methylpyrrolidone solution. BDC (2.73 g) was suspended in *N*-methylpyrrolidone (80 ml) containing lithium chloride (0.424 g). This heterogeneous system was blanketed with nitrogen, and isophthaloyl chloride (2.03 g) was added to the stirred solution at such a rate to maintain the reaction medium at 5–2°C with external cooling.

An exothermic reaction took place and the solution became viscous. The solution was heated to 80°–100°C for 20 min and was then added to methanol to precipitate the polymer. A fibrous polymer was obtained which was filtered, washed with water and methanol, and dried at 30°C/2 mm of Hg. Yield, 4.85 g.

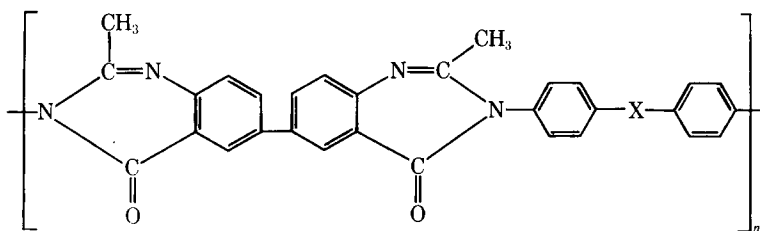
ANAL. Found: C, 64.9; H, 3.5; N, 7.0. Calcd for  $(C_{22}H_{14}N_2O_6)_n$ : C, 65.67; H, 3.51; N, 6.96; O, 23.86%.  $[\eta]_0 = 0.38$ , determined in concentrated sulfuric acid at 25°C.

DSC analysis of the prepolymer showed it to have a glass transition temperature of 240°C, but no melting endotherm was observed. Studies on a hot-stage polarizing microscope (HSPM) indicated that the sample was slightly birefringent but remained unchanged up to 320°C (the limit of the apparatus used). The DSC trace showed two other features, both endothermic processes. The first, at 250–300°C, involved significantly less energy than the second at 350°C.

Cyclization of the prepolymer amido acid precursor of IIIA was attempted by solvent casting from *N*-methylpyrrolidone yielding a brittle film after drying at 120°C for 10 min. This film was heated in a nitrogen atmosphere from room temperature to 250°C (10 min) and was maintained at this temperature for 1 hr.

ANAL. Found: C, 64.8; H, 3.7; N, 7.1; Calcd for  $(C_{22}H_{10}N_2O_4)_n$ : C, 72.13; H, 2.73; N, 7.65; O, 17.49%.

Polyquinazolones IB–IVB of generalized repeating structure



where X =  $-\text{CH}_2-$  (IB),  $-\text{O}-$  (IIB),  $-\text{SO}_2-$  (IIIB), and  $-\text{S}_2-$  (IVB), were prepared and characterized as previously reported.<sup>1</sup>

The model compounds, 2-methylbenzoxazinone and 2-acetamidobenzanilide, were prepared using known literature methods.<sup>1,7</sup>

The following commercially available high-temperature polymers (Table I) were studied for comparative purposes. The materials were cured where necessary according to the manufacturer's specification.

### Thermal-Analysis Studies

TG studies were made on a Stanton thermobalance (Model Mark II) with the furnace programmed for a heating rate of  $6^\circ\text{C}/\text{min}$  (nominal). A small platinum crucible was used with samples (10 mg). Dynamic experiments were carried out in static air and flowing white spot nitrogen at a flow rate of 200 ml/min with the gas entering at the top of the furnace. Nitrogen was passed over the sample for 30 min before commencement of the heating program to ensure that the tube furnace was free from air. Temperatures are furnace wall temperatures, and buoyancy corrections were applied.

Isothermal studies were made using the following procedure. The furnace was preheated without the sample in position with the required atmosphere passing through the furnace. Prior to operation, the furnace was quickly raised and the crucible placed in position on the rise rod and the furnace lowered and the balance switched on. To prevent air ingress when nitrogen was used as the operating atmosphere, nitrogen was blown down the furnace during this sam-

TABLE I  
Commercially Available High-Temperature Polymers

Polymer	Source
Polybenzimidazole (Imidite 2801)	Whittaker Corporation (U.S.A.)
Polybenzoxazole (PB03)	Yorkshire Chemicals
Polyimide (QX-13)	R.A.E., Farnborough
Polyimide (Kerimid 601)	Societe des Usine Chimique
Poly(phenylene sulfide) (RYTON)	Phillips Petroleum (U.K.)
Poly( <i>p</i> -hydroxybenzoic acid) (EKONOL)	Carborundum

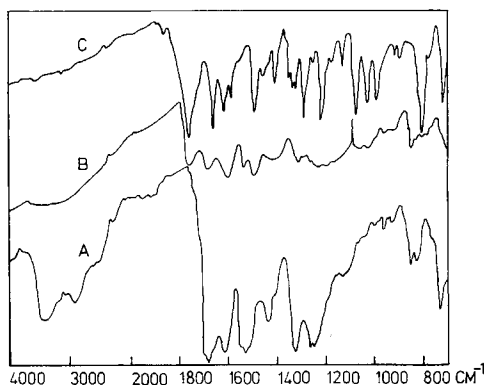


Fig. 1. IR Spectra: A, poly(amido acid) precursor to polybenzoxazinone (IIIA); B, polybenzoxazinone (IIIA); C, 2-methylbenzoxazinone.

ple-loading operation. Nitrogen and air were used in these studies at a flow rate of 200 ml/min.

DSC studies were made on a du Pont 900 thermal analyzer equipped with a DSC cell. The samples ( $\approx 6$  mg) were contained in open aluminum pans, and an empty pan acted as the inert reference material. Studies were made at a heating rate of 20°C/min (nominal).

### Hot-Stage Microscopy (HSPM)

Studies were made using a Kofler hot-stage microscope at a similar heating rate to that used in the DSC studies.

### Infrared Spectroscopy

Spectra were run on 1% suspensions in potassium bromide discs using a Unicam SP200 spectrophotometer.

## DISCUSSION

The preparation and characterization of the precursors to the poly(quinazoline diones) IA and IIA and the polyquinazolones IB–IVB have been reported previously together with their tribological evaluation.<sup>1</sup> The polybenzoxazinone IIIA was unsuitable for tribological studies due to the brittle nature of its films. The preparation of the polyamide acid precursor to the polybenzoxazinone IIIA proceeded smoothly and combustion analysis data and the IR spectra A (Fig. 1) are in accord with the proposed structure and are similar to those reported by Yoda.<sup>5</sup>

The DSC behavior recorded may be ascribed to cyclization (cyclodehydration) at 250–300°C) as shown by IR spectroscopy on sample heated to this temperature in the DSC cell (spectrum identical with spectrum B (Fig. 1), followed by degradation at temperatures in excess of 350°C.

The cyclization process yielded polymer IIIA whose combustion analysis data and IR spectrum B (Fig. 1) indicate that cyclization is not complete. The model

TABLE II  
 PDT and 50% DT Values in Air

Polymer (cyclized)	PDT, °C	50% DT, °C	C.H.T.P.	PDT, °C	50% DT, °C
IA	320	520	1. polybenzimidazole	310	550
IIA	300	494	2. polybenzoxazole	360	550
IIIA	260	492	3. polyimide QX-13	380	580
IB	305	525	4. polyimide (Kerimid)	380	550
IIB	280	520	5. poly(phenylene sul- fide)	410	580
IIIB	290	500	6. poly( <i>p</i> -hydroxy- benzoic acid)	340	524
IVB	290	525			

 TABLE III  
 $W_{30}$  Values from Isothermal TG in Air

Polymer	IA	IIA	IIIA	IB	IIB	IIIB	IVB
$W_{30}$	31	61	52	28	31	42	30

compound 2-methylbenzoxazinone has a spectrum C (Fig. 1) similar, but not identical with that of polymer IIIA. Spectrum B (Fig. 1) is, however, in accord with that obtained by Kurihara and Hagiwara,<sup>6</sup> for similar polybenzoxazinones. However, the incomplete combustion analysis figures, the presence of an ash (<0.5%), and the carbonyl absorption band at 1680  $\text{cm}^{-1}$  in the cyclized polymer spectrum suggest that uncyclized amide units are present.

### Thermal-Analysis Studies

These were made on the cyclized polymers in an attempt to evaluate comparative thermal stabilities. Thermal stability in this context has been assessed by dynamic TG, in terms of the procedural decomposition temperature (PDT), the temperature at which weight loss becomes observable, and the temperature at which 50% decomposition as measured by weight loss had occurred (50% DT).

Isothermal TG studies gave the percentage weight lost after 30 min at 400°C ( $W_{30}$ ), the time for 50% decomposition (50% D) at various isothermal temperatures; kinetic studies yielded activation energies.

The data obtained from dynamic TG studies were compared with those obtained from the commercial high-temperature polymers (Table II).

The PDT and 50% DT data show that the polymers synthesized in this study had generally lower values than the commercial samples, suggesting inferior thermal stability. Since their application involved fabrication via the soluble precursor stage, this loss in stability was not considered to be sufficiently detrimental to prevent their tribological evaluation.

In order to further characterize these materials, isothermal TG studies were carried out at 400°C in air, which yielded the data presented in Table III. This suggests an order of stability for the A series of polymers of IA > IIIA > IIA, while PDT and 50% DT values suggest that IA > IIA > IIIA and IA > IIA ~ IIIA, respectively.

TABLE IV  
 Stability Orders for Polyimides

Order	Author	Reference
$-\text{O}->-\text{S}->-\text{CH}_2-$	Bower and Frost	8
$-\text{O}->-\text{CH}_2-$	Scroog et al.	9
$-\text{O}->-\text{CH}_2->-\text{SO}_2-$	Nishizaki	10
$-\text{S}->-\text{SO}_2->-\text{CH}_2->-\text{O}-$	Dine-Hart and Wright	11

Similarly, the B series of polymers also show a different stability order dependent on the mode of assessment used. Thus, 50% DT and  $W_{30}$  data indicate that  $\text{IB} \sim \text{IIB} \sim \text{IVB} > \text{IIIB}$ , while PDT values indicate that  $\text{IB} > \text{IVB} \sim \text{IIIB} > \text{IIB}$ . Isothermal studies at temperatures between 375° and 450°C indicate that  $\text{IB} > \text{IVB} > \text{IIB} > \text{IIIB}$  on the basis 50% D values.

This lack of correlation indicates the difficulties inherent in comparative thermal stability studies even within the same work. In this work, the difficulties arise both from the mode of assessment used and the nature of the materials being assessed. Thus, in the A series of polymers, differences in chemical structure should play a major role in determining stability. These, however, may be masked by features such as incomplete cyclization, and the entrainment of monomers and oligomeric materials which affect the assessment parameters to different extents. In the B series, the polymers should have essentially the same repeating structure and differ only in the nature of the hinge grouping X. However, this is an oversimplification; the materials studied are not inherently the same, since they can differ in terms of the extent of cyclization to the quinoxalzone structure. This can lead to different numbers of potential sites for scission and hence weight loss from within these systems. In addition, the percentage "impurity" level (oligomeric and monomeric species) will also differ.

Such differences may then be reflected in the PDT values obtained where low values may be associated with weight losses due to volatilization of "impurities" from the system. Thus, more realistic values are likely to be obtained from 50% DT and 50% D values which will be less affected by these factors than PDT or  $W_{30}$  data.

The thermal oxidative stability of the B series of polymers on the basis of 50% D values should be related to the "hinge group" stability. The order suggested from such data is  $\text{IB} > \text{IVB} > \text{IIB} > \text{IIIB}$ , that is,  $-\text{CH}_2- > -\text{S}_2- > -\text{O}- > -\text{SO}_2-$ , assuming that the systems have similar "impurity" levels, degrees of cyclization, and loss of pendent groups.

These results may be compared with published data on a family of polyimides which differ in structure in terms of their hinge groupings. Thus, for systems prepared from similar diamines to those used in this study, the stability orders reported in the literature are as shown in Table IV. The apparent lack of correlation between workers has been discussed<sup>11</sup> and has been ascribed to the different preparative conditions used, the environmental conditions during degradation, and the methods used for assessment.

In view of this, and our comments above, it is not surprising that the results obtained in this study do not correlate unequivocally with the work by other workers (Table IV). Studies on these polymers were also made in nitrogen by

TABLE V  
Stability Data from Dynamic TG in Nitrogen

Polymer	IA	IIA	IIIA	IB	IIB	IIIB	IVB
PDT, °C	340	340	325	300	330	320	320
50% DT	576	514	670	<sup>a</sup>	<sup>b</sup>	<sup>b</sup>	700

<sup>a</sup> Stable char formed after 40% weight loss.

<sup>b</sup> Stable char formed after 30% weight loss.

TABLE VI  
Stability Parameters from Isothermal TG in Nitrogen

Polymer	IA	IIA	IIIA	IB	IIB	IIIB	IVB
$W_{30}$	28	37	31	32	18	39	27

dynamic and isothermal TG leading to the stability parameters shown in Tables V and VI. These studies suggest a stability order for the A series of IA ~ IIA > IIIA, while 50% DT values suggest IIIA > IA > IIA. For the B series, PDT values suggest essentially a similar order of stability, while 50% DT values suggest IIB > IB ~ IIIB > IVB, that is, —O— > —CH<sub>2</sub> ~ SO<sub>2</sub> > —S—S—.

The data in Table VI together with 50% D values in the temperature range of 375–450°C suggest for the A series IA > IIIA > IIA, while for the B series,  $W_{30}$  and 50% D values suggest IIB > IVB > IB > IIIB, that is, —O— > —S—S— > —CH<sub>2</sub>— > —SO<sub>2</sub>—.

The expected order of stability in nitrogen of the “hinge groups” may be predicted in terms of the bond strengths involved in linking the hinge groupings or within the hinge group itself.<sup>12</sup> Thus, —O— > —CH<sub>2</sub>— > —SO<sub>2</sub>— > —S—S—. The results are, of course, subject to the limitations discussed previously, but are in general accord with that predicted except for the —S—S— containing system. The anomalous position of this system may arise from crosslinking reactions resulting from scission of the weak disulfide link to give thiyl radicals and their subsequent reactions.

### Kinetic Studies

These were made using isothermal TG in air and nitrogen. Weight loss studies in air indicate that at least three phases of weight loss occurred. Thus, a rapid initial weight loss (0–5%) was observed followed by a period of low weight loss which was followed by a period of high rate of weight loss over the range of 20–80% decomposition.

In nitrogen, a similar initial rapid weight loss occurred followed by a period of low weight loss (5–20%), which was followed by a region of higher weight loss (20–40%) at which point stabilization occurred. In air and nitrogen, the activation energy data obtained from a plot of  $-\log_e K$  versus the reciprocal of the absolute temperature are shown. The initial ( $E_i$ ) and final ( $E_f$ ) activation energy values were derived from the two processes of weight loss following the 0–5% weight losses due to entrained material. The stability orders obtained for these systems again do not correlate with the previous data.

Thus, for the A series of polymers, IIIA ~ IIA > IA in air from  $E_f$ , while IIIA

TABLE VII  
Activation Energies in Air and Nitrogen<sup>a</sup>

Polymer	$E_i$ , kcal/mole		$E_f$ , kcal/mole	
	Air	Nitrogen	Air	Nitrogen
IA	21.4	34.0	42.0	52.0
IIA	24.0	39.6	52.0	52.4
IIIA	26.4	54.5	47.7	67.0
IB	27.0	45.3	40.0	61.2
IIB	25.0	32.0	39.2	69.1
IIIB	22.0	29.1	45.1	56.0
IVB	29.0	46.1	47.0	65.6

<sup>a</sup>  $E_i$  = Initial activation energy;  $E_f$  = final activation energy.

> IIA ~ IA in nitrogen. In the B series, IB ~ IVB > IIB > IIIB from  $E_f$  in air, while in nitrogen,  $E_i$  yields IVB ~ IB > IIB > IIIB and  $E_f$  yields IIB ~ IVB >> IB > IIIB.

Thus, the data presented in this paper stress the difficulties associated with comparative thermal stability measurements even within a series of similar polymers showing complex behavior.

The data further confirm the need for caution in comparison of data from different sources and confirm the relevance of standardized reporting procedures for thermal analysis as recommended by the International Confederation for Thermal Analysis (ICTA).<sup>13,14</sup>

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