

Thermal Degradation of Polymers. Part XIX. The Thermal Cyclization and Characterization of Quinazolone Pre-Polymers

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Synopsis

A series of pre-polymers prepared from 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid and aromatic diacetamido compounds have been thermally cyclized and their structures have been investigated using infrared spectroscopy, combustion analysis, and weight loss techniques. The structures obtained on cyclization are discussed in terms of concurrent cyclization and decarboxylation reactions resulting in incomplete cyclization. Specific structural features due to the lability of main chain bonds at the cyclization temperatures are also discussed. Dynamic thermogravimetry and isothermal weight loss studies have been used to evaluate thermal stability and kinetic parameters. The results are discussed in terms of the overall complexity of the polymer structure and the complexity of the degradation process. It is concluded that in such systems, where the structural variations are large, it is not possible to define a meaningful stability sequence because like systems are not under comparison.

INTRODUCTION

In the previous paper¹ the preparation of pre-polymer precursors to poly-quinazolones and studies to yield optimum conditions for their cyclization were described. DTA combined with mass spectroscopic (MS) and IR studies led us to conclude that the resultant cyclized polymers had structures significantly different from those of model quinazolones. Cyclization involving cyclodehydration was shown to be accompanied by concurrent decarboxylation.

This paper reports the preparation of such cyclized polymers, their thermal and structural characterization. Thermal stability assessment by TG and DSC and kinetic studies by isothermal weight loss studies are also discussed.

EXPERIMENTAL

Materials

Quinazolone pre-polymers were prepared as previously reported.¹ Cyclization was performed in a nitrogen atmosphere and the products obtained are summarized below.

Pre-polymer *o*-DP_p was heated at 240°C for 2 hr yielding *o*-DP_c as a dark brown powder. Analysis calculated for (C₂₄H₁₆N₄O₂)_n: C, 73.5%; H, 4.1%; N, 14.3%; O, 8.1%; found: C, 73.0%; H, 4.5%; N, 14.1%.

Pre-polymer *m*-DP_p was heated for 2 hr at 300°C yielding *m*-DP_c as a dark brown powder. Analysis found: C, 75.0%; H, 5.2%; N, 15.4%.

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Pre-polymer p -DP_p was heated for 4 hr at 280°C yielding p -DP_c as a black powder. Analysis found: C, 74.0%; H, 4.6%; N, 14.6%.

Pre-polymer p -DS_p was heated for 2 hr at 300°C yielding p -DS_c as a dark brown powder. Analysis calculated for (C₃₀H₂₀N₄O₄S)_n: C, 67.7%; H, 3.8%; N, 10.5%, S, 6.0%; O, 12.0%; found: C, 68.4%; H, 4.5%; N, 10.5%; S, 5.9%.

Pre-polymer m -DS_p was heated at 300°C for 1 hr yielding m -DS_c as a dark brown powder. Analysis found: C, 68.8%; H, 4.4%; N, 10.8%; S, 6.0%.

Pre-polymer DE_p was heated at 300° for 2 hr yielding DE_c as a black powder. Analysis calculated for (C₃₀H₂₀N₄O₃)_n: C, 74.4%; H, 4.2%; N, 11.6%; O, 9.9%; found: C, 75.4%; H, 5.0%; N, 12.0%.

Pre-polymer DM_p was heated at 300°C for 1 hr yielding DM_c as a black powder. Analysis calculated for (C₃₁H₂₂N₄O₂)_n: C, 77.1%; H, 4.6%; N, 11.6%; O, 6.6%; found: C, 79.0%; H, 5.0%; N, 12.1%.

Pre-polymer DDS_p was heated at 280°C for 4 hr yielding DDS_c as a dark brown powder. Analysis calculated for (C₃₀H₂₀N₄O₂S₂)_n: C, 67.6%; H, 3.8%; N, 10.5%; S, 12.0%; O, 6.0%; found: C, 68.8%; H, 4.0%; N, 11.1%; S, 10.5%.

Pre-polymer DPY_p was heated at 280°C for 3 hr yielding DPY_c as a light brown powder. Analysis calculated for (C₂₃H₁₅N₅O₂)_n: C, 70.2%; H, 3.8%; N, 17.8%; O, 8.1%; found: C, 69.4%; H, 4.9%; N, 18.2%.

Polymer Characterization

This was effected by DTA/DSC, IR, and thermogravimetry (TG) by the methods reported previously.¹

Thermal Stability Studies

Dynamic and isothermal studies in flowing air and nitrogen were made using a Stanton thermobalance (Model TR02) and the crucible and conditions reported previously.¹

Kinetic Studies

Weight loss curves were obtained at temperatures of 400°, 425°, 450°, and 475°C for 40 min in nitrogen and for 70 min in air.

Cyclization Studies Under Non-Optimized Conditions

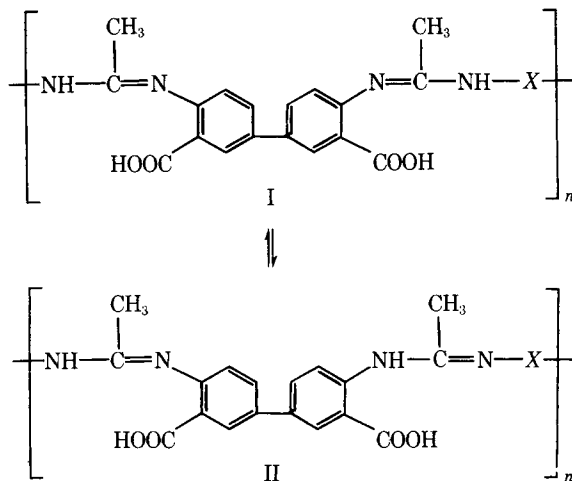
Pre-polymer DM_c (0.5 g) was cyclized under a vacuum of 0.02 Torr. The pre-polymer was subjected to a cyclization procedure similar to that of Sillion² by heating the pre-polymer for ½ hr at 280°C, then 1 hr at 300°C, 2 hr at 350°C, and finally for ½ hr at 400°C. The percentage weight loss was found to be 31% and the combustion analysis figures obtained were analysis found: C, 80.2%; H, 4.9%; N, 11.1%. The pre-polymer was also subjected to Kurihara's³ cyclization procedure by heating under similar conditions with omission of the 400°C heating cycle. The percentage weight loss was then 26.5% and the combustion analysis figures obtained were analysis found: C, 79.5%; H, 4.7%; N, 11.3%.

DM_c cyclized under the conditions optimized previously¹ gave the following combustion analysis figures: Analysis calculated for (C₃₁H₂₂N₄O₂)_n: C, 77.1%;

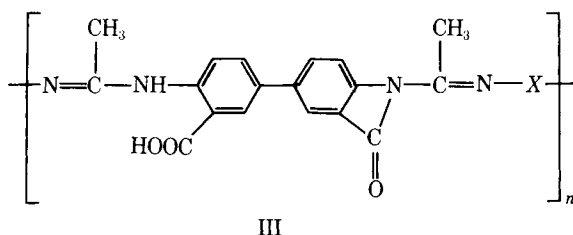
H, 4.6%; N, 11.6%; O, 6.6%; found: C, 79.0%; H, 5.0%; N, 12.1%. The percentage weight loss was 12.0%.

DISCUSSION

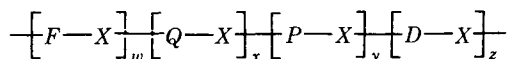
The pre-polymer systems which were cyclized exhibit tautomerism and the tautomeric equilibrium involves structures of types I and II



On cyclization tautomer I would yield the stable six-membered quinazolone ring system. Cyclization could also occur via tautomer II, leading to the less stable four-membered ring system, III, as a possible structural defect



Microanalysis results for the cyclized polymers prepared under the conditions optimized previously, however, confirm the DTA-MS and isothermal weight loss-evolved gas analysis and IR studies¹ which indicated concurrent loss of carbon dioxide and water from such systems on cyclization. The data presented in Table I, together with the previous studies and the analysis figures suggests that the structures deviate significantly from that of a true poly quinazolone and would be better represented by a copolymer of the type



where *F*, *Q*, *P*, and *D* represent the repeating unit of the polymer, in the four-

TABLE I
Isothermal Weight Loss Studies at Optimized Cyclization Conditions

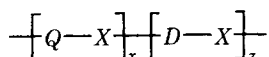
Polymer code	Cyclization conditions temperature (°C)/time (hr)	% weight loss	% weight loss for 2H ₂ O	% weight loss for 2H ₂ O + 2CO ₂
<i>o</i> -DP _c	240/2	10.5	8.4	14.5
<i>m</i> -DP _c	300/2	13.5	8.4	14.5
<i>p</i> -DP _c	280/4	13.0	8.4	14.5
<i>p</i> -DS _c	300/2	14.0	6.3	10.9
<i>m</i> -DS _c	300/1	11.0	6.3	10.9
DE _c	300/2	14.5	6.9	11.9
DM _c	300/1	12.0	7.0	12.0
DDS _c	280/4	14.5	6.8	10.9
DPY _c	280/3	15.0	8.4	14.4

membered ring form, quinazolone ring form, pre-polymer form, and decarboxylated form, respectively, and X the "hinge grouping" derived from the diacetamido unit.

The values of *w*, *x*, *y*, and *z* in these systems are not easily elucidated because of the small differences in combustion analysis data associated with the various model structures which can be proposed. Further, because of the difficulties associated with combustion and the insolubility and infusibility of these materials they are not readily amenable to study by other methods.

The weight loss evidence presented in Table I, together with previous studies, suggest that the major structural defect in these systems will be due to decarboxylated units, although IR analysis showed that in these systems cyclization was incomplete.

In general, it would appear that these systems approximate to a copolymer having the structure



For most systems studied *x* = *z* = 1 but it must be stressed that the combustion analysis data do not differ to a large extent for the various model structures. Thus the structural interpretation is highly dependent on the accuracy of this data but the results do confirm that the structures deviate significantly from that of the fully cyclized quinazolone.

The systems *o*-DP_c and DDS_c show significant deviation from this generalized structure due to specific structural features. Thus the ease of cyclization of *o*-DP_p described earlier¹ leads to a lower cyclization temperature and less decarboxylation and its structure approaches that of the poly quinazolone. The behavior of the DDS_c system is described later, but reference to its analysis figures indicates that sulphur is lost from this system. Studies by combined DTA/MS indicated concurrent loss of water, carbon dioxide and hydrogen sulphide at the cyclization temperature.

The conditions used for cyclization to the pre-polymer systems described in this study are significantly less harsh than those reported by Kurihara et al.³ and Sillion et al.² in their preparation of poly(quinazolone) systems.

DM_c prepared under these conditions gives the TG curves A and B (Fig. 1) which may be compared with C prepared under the conditions optimized in this study. Sillion et al.² report that PDT in nitrogen for a poly(quinazolone) possessing a *m*-phenylene hinge grouping to be 400°C and that the weight loss reached 10% towards 480°C. These are similar to the values obtained for DM_c cyclized under Sillion's conditions. a similar PDT to that reported by Kurihara and Hagiwara³ for the diphenyl ether linkage was obtained from polymer DM_c (Fig. 1) cyclized under their heating program.

This indicates that the polyquinazolones prepared in this study, although of low molecular weights, exhibit comparable thermal stability to those reported previously^{2,3} after cyclization at temperatures in the range 300°–400°C. The weight losses recorded under these conditions are considerably in excess of the theoretical for water loss and cannot be accounted for on the basis of volatilization of low molecular weight species, decarboxylation and water loss due to further cyclization. The cyclization conditions cause considerable decomposition of the polymers prepared in this study and chain scission and/or crosslinking reactions may result in a modification of the polyquinazolone to a more stable structure. This explains why DM_c was difficult to pulverize which prevented their infrared spectroscopic analysis. The small differences in analysis figures for the three methods of cyclization failed to indicate the type of structure formed as a result of this "post curing."

In the studies by Sillion et al.² and Kurihara et al.³ no weight loss studies were

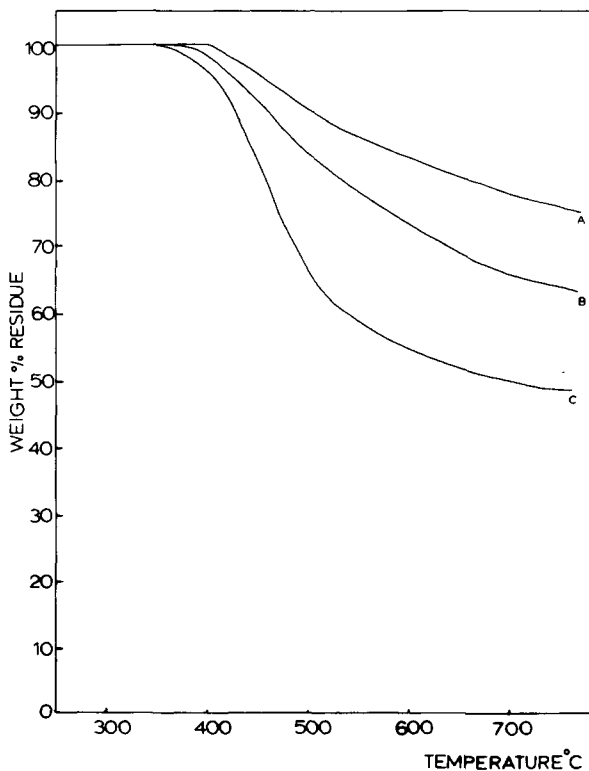


Fig. 1. TG curves for DM_c in nitrogen. Curve A, Kurihara's method of cyclization; curve B, Sillion's method of cyclization; curve C, cyclized under conditions optimized in this study.

made and the IR spectra in the latter case showed NH absorption, suggesting that cyclization was incomplete. Further to this Sillion et al.² indicate that in their preparations the polyquinazolone is accompanied by the diimide. On the basis of our findings, the thermal stability, combustion analysis figures, and IR spectroscopy data available on these systems and possibly other heat resistant polymers, should be assessed with caution especially if thermal or chemical cyclization procedures are involved.

Thermal Stability Studies

The thermal stability studies were made by dynamic and isothermal studies and stability has been assessed by dynamic TG in terms of (i) the procedural decomposition temperature (PDT) defined as the temperature at which the first observable weight loss occurs, (ii) the temperature at which 40% weight loss has occurred (40% DT), and (iii) the temperature at which 50% weight loss has occurred (50% DT). Isothermal studies yielded the parameters W_{30} the percentage weight loss after 30 min at 400°C and t_{50} the time required for 50% weight loss at 450°C. In addition the activation energies for degradation were evaluated under isothermal conditions as a function of degree of conversion.

Typical dynamic TG curves obtained in air and nitrogen for the systems under study are shown in Figure 2. From such curves the data shown in Table II was evaluated. Isothermal studies yielded the data recorded in Table III. Activation

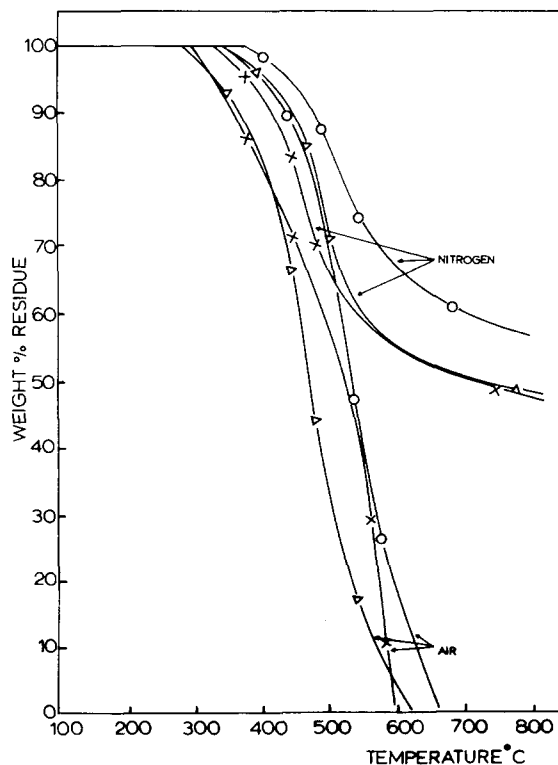


Fig. 2. TG curves for representative cyclized polymers in air and nitrogen. —○—, p -DP_c; —×—, p -DS_c; —△—, DM_c.

TABLE II
Thermal Stability Indices from Dynamic TG

Polymer code	Nitrogen			Air		
	PDT°C	40% DT°C	50% DT°C	PDT°C	40% DT°C	50% DT°C
<i>o</i> -DP _c	280	470	630	210	430	450
<i>m</i> -DP _c	320	500	660	295	510	520
<i>p</i> -DP _c	380	700	a	350	530	545
<i>p</i> -DS _c	340	540	700	300	490	530
<i>m</i> -DS _c	320	500	700	250	450	490
DE _c	340	575	720	320	460	500
DM _c	355	540	710	290	460	470
DDS _c	370	650	a	330	515	550
DPY _c	360	600	a	210	520	530

^a The polymers did not reach 50% weight loss.

TABLE III
Thermal Stability Indices from Isothermal Weight Loss Studies

Polymer code	Nitrogen		Air	
	W ₃₀ (%)	t ₅₀ (min)	W ₃₀ (%)	t ₅₀ (min)
<i>o</i> -DP _c	32.0	32.1	40.0	20.5
<i>m</i> -DP _c	26.0	85.3	27.5	46.0
<i>p</i> -DP _c	13.5	140.0	15.0	68.0
<i>p</i> -DS _c	34.0	36.5	35.0	21.0
<i>m</i> -DS _c	40.0	34.5	41.5	16.5
DE _c	20.0	108.5	22.0	47.5
DM _c	22.5	102.0	25.0	40.8
DDS _c	20.0	107.5	22.0	60.5
DPY _c	19.0	110.0	24.0	31.5

TABLE IV
Activation Energies Calculated from Isothermal Weight Loss Studies

Polymer code	E (KJ mole ⁻¹) in nitrogen					E (KJ mole ⁻¹) in air				
	20%	30%	40%	50%	60%	20%	30%	40%	50%	60%
<i>o</i> -DP _c	120.5	137.4	162.5	—	—	89.9	108.0	116.9	151.1	—
<i>m</i> -DP _c	169.3	226/—	263.8	—	—	122.6	143.2	168.0	—	—
<i>p</i> -DP _c	226.8	277.7	—	—	—	140.3	166.3	—	—	—
<i>p</i> -DS _c	103.7	168.0	202.9	254.5	—	101.2	126.0	181.0	201.6	—
<i>m</i> -DS _c	116.8	124.7	130.2	—	—	95.8	116.8	133.1	183.1	—
DE _c	221.8	213.2	241.3	—	—	105.4	133.6	136.9	158.1	184.8
DM _c	154.1	265.4	—	—	—	125.2	151.6	188.2	—	—
DDS _c	184.0	326.6	—	—	—	134.0	210.1	—	—	—
DPY _c	225.1	257.0	—	—	—	62.6	69.3	64.3	97.4	—

energies determined at various percentage decomposition by the method of MacCallum^{4,5} are given in Table IV for all systems studied. The order of reaction was also shown to vary with temperature and percentage conversion. It is apparent that these systems show complex degradation behavior which results in part from the structural features discussed earlier.

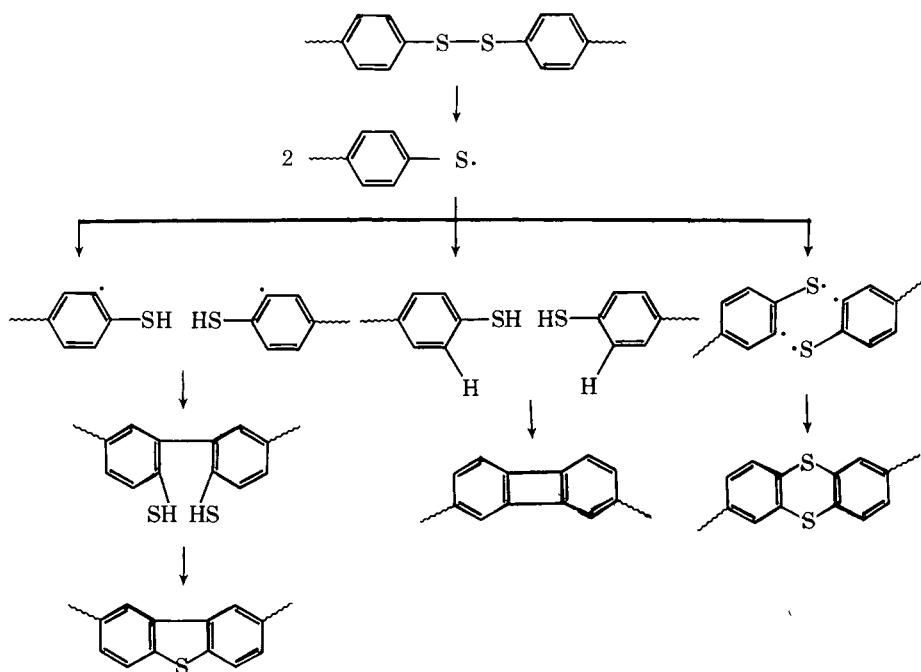
Stability sequences derived from the different assessment methods are given in Table V, the most stable system being denoted by the number 1.

In the ideal case where each system could be represented by the fully cyclized

quinazolone unit $\{Q - X\}_n$ the only variable structural feature determining stability should be the hinge grouping X . However it is apparent that such a correlation is not valid in these systems since other major structural variations occur. Thus, on the basis of hinge group stability, the system containing the labile S—S link should exhibit a much inferior stability. However, the loss of hydrogen sulphide from these systems, together with the low amounts of sulphur present in the cyclized polymer, suggests that rupture of the S—S link occurs at the cyclization temperature to yield a more stable system.

Model compound studies have shown that organic di- and polysulphides undergo thermolytic cleavage at temperatures above 140°C ⁶ and diphenyl disulphides decompose to give the reactive sulphenyl radical and form the thio and thianthrene.⁷ Further to this, diaryl disulphides have been reported⁸ to give a monosulphide and a trisulphide on heating at 280°C .

In the present work, the thermal cyclization of DDS_p was effected at a temperature in excess of that required to bring about homolytic scission of the S—S bond. The abnormally high stability of DDS_p indicates that structural modification occurs which, by analogy to simple disulphides, could result from reactions of the following type



Such reactions in the polymer would yield a ladder polymer of improved stability. Similarly a mono(sulphide) system should also be more stable though not as resistant as the ladder units.

As expected, the system based on *p*-phenylene is apparently the most stable in both air and nitrogen. The lack of stability of the *o*-phenylene system similarly is not unexpected due to its reduced symmetry and resonance stabilization as compared with the *p*-phenylene system, and the low molecular weight obtained because of preparative difficulties. The stability order *p*-phenylene >

TABLE V
 Stability Sequences in Air and Nitrogen

Atmo- sphere	Parameter	Polymer code								
		<i>p</i> -DP _c	DPY _c	DDS _c	DM _c	DE _c	<i>p</i> -DS _c	<i>m</i> -DS _c	<i>m</i> -DP _c	<i>o</i> -DP _c
Air	PDT ^a	1	7	2	4	3	4	4	4	7
	40% DT ^a	1	2	2	5	5	3	6	3	7
	W ₃₀ ^b	1	4	2	5	2	7	8	5	8
	t ₅₀ ^b	1	6	2	5	3	7	8	3	8
Nitrogen	PDT ^a	1	1	1	4	5	5	8	5	9
	40% DT ^a	1	3	2	5	4	5	7	7	9
	W ₃₀ ^b	1	2	2	5	2	7	9	6	8
	t ₅₀ ^b	1	2	3	5	3	7	7	6	7

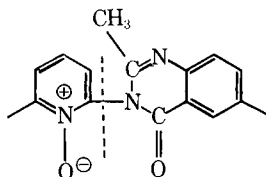
^a TG studies.

^b Isothermal weight loss studies.

m-phenylene > *o*-phenylene is similar to those obtained by other workers, notably Wright⁹ and Volpe.¹⁰

It is of interest that the introduction of the hetero-atom into the benzene ring as in the 2,6-pyridine system gives good thermal stability in nitrogen but poor stability in air. The unexpectedly low order of stability in air coupled with the unique shape of the isothermal weight loss curves and its very low PDT suggested that the pyridine moiety must be reacting with oxygen, giving a product which degrades in a different manner to that of the other polymers. This is supported by the relatively small change in activation energy evaluated by isothermal weight loss for the first 30% of volatilization (Table IV). Such behavior is similar to that observed by Wright and co-workers¹¹ on the perfluoropolypyridine system, which was shown to be more stable than polytetrafluoroethylene in nitrogen, and less stable in air as measured by weight loss studies. No mechanistic interpretation of this observation was, however, reported.

Pyridine can be easily oxidized to form the pyridine-*N*-oxide¹² and this led us to suspect that a similar reaction may occur in the polymer at elevated temperatures in an oxidizing environment. The formation of the *N*-oxide in the polymer could yield "weak links" at the points joining the pyridine nucleus to the quinazolone ring



The cleavage of such bonds could yield either stabilized radicals or ions and volatile fragments whose weight loss could be monitored by thermogravimetric analysis.

Attempts were made to establish the validity of the hypothesis by infrared spectroscopy. The characteristic absorption of the N—O bond at 1260–1270 cm⁻¹ (ref. 13) was not observed on samples heated in air from 200°–300°C. However, it is possible that the concentration may be below the limits of detection

by ir analysis and a transitory existence of the *N*-oxide at these temperatures cannot be ruled out.

Kinetic Studies

No attempt has been made to evaluate stability orders from the data presented in Table IV because of the complex nature of degradation process for each individual system.

Bearing in mind the differences in preparative conditions and the resulting structural features the data presented is in general agreement with previous observations by Still and Ghafoor¹⁴ on similar systems.

CONCLUSIONS

This paper shows that in addition to the procedural variables associated with thermal analysis, the structural features of the systems under study can play an overriding role in what is observed. In such cases therefore results of thermal studies must be interpreted with caution, unless detailed structural analysis is available to confirm that like systems are under comparison.

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