

Thermal Degradation of Polymers. XIII. Thermal Analysis Studies on *p*-N,N-Dimethylaminostyrene Homopolymers and Copolymers with Styrene in Air

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Synopsis

Homopolymers of *p*-N,N-dimethylaminostyrene and copolymers with styrene have been subjected to thermal analysis studies in air. Molecular weight and copolymer composition have been shown to influence the stability of the polymers and the shape of the TG and DSC curves obtained under dynamic conditions. Mechanisms to account for this behavior based on the antioxidant effect of the chain-bound *p*-N,N-dimethylamino substituent are discussed.

INTRODUCTION

In a previous paper,¹ we reported thermal analysis studies on *p*-N,N-dimethylaminostyrene (*p*-DAS) polymers in nitrogen. The effect of homopolymer molecular weight and copolymer composition on the glass transition temperature (T_g) was reported and compared with the behavior of polystyrene (PS). The effect of molecular weight upon the dynamic and isothermal thermogravimetric analysis curves was also described. Comparative thermal stability measurements based on procedural decomposition temperatures, 50% decomposition temperatures, and activation energies from isothermal and dynamic thermal analysis studies (TG and DSC) were also discussed.

We now report thermal analysis studies on these systems in a static air atmosphere.

EXPERIMENTAL

Materials

Homopolymers of *p*-DAS and copolymers with styrene (S) were prepared and characterized as previously described.²

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Apparatus and Procedure

Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were carried out as previously reported,¹ with air replacing the flowing nitrogen atmosphere.

DSC/Weight Loss Studies. These were made by removing the sample pan and weighing the sample on an analytical balance (± 0.0001 g).

Hot-Stage Microscope/DSC Studies. Polymer samples were removed from the DSC cell at various stages of degradation in air and visually studied. A Kofler hot-stage microscope was also used for continuous observation of samples subjected to a similar heating rate to that used in the DSC experiments (20°C/min).

RESULTS AND DISCUSSION

The *p*-N,N-dimethylaminostyrene homopolymers (PDAS 1-7) of different molecular weight and copolymers with styrene (S:*p*-DAS 8-11) of different composition were subjected to dynamic and isothermal thermogravimetric analysis (TG) studies in static air. The behavior of these systems was compared with that of polystyrene (PS) in terms of the procedural decomposition temperature (PDT), the 50% decomposition temperature (50% DT), and the percentage weight lost in 10 min at 400°C (W_{10}).

The data obtained are shown in Table I. It can be seen that the PDT values for PDAS homopolymers are molecular weight dependent, while those for PS are essentially independent of molecular weight in the range studied. The PDT values of PDAS homopolymers decrease with increasing molecular weight, initially indicating a higher stability for PDAS compared with PS. At PDAS molecular weights of $\approx 120,000$ ($[\eta]_0 = 0.42$),² the stabilities of PDAS and PS as assessed by this method become comparable.

For the lowest molecular weight sample of PDAS studied ($[\eta]_0 = 0.13$, $\bar{M}_n = 12,200$),² the PDT data suggests a stability for this sample comparable with that obtained for all samples in a nitrogen atmosphere.¹ The method of as-

TABLE I
Dynamic and Isothermal TG Data

Polymer	Sample no. ^a	$[\eta]_0^a$	PDT, °C	50% DT, °C	W_{10}
PDAS	1	0.98	260	—	5-8
	2	0.42	265	460	5-8
	3	0.33	280	—	5-8
	4	0.28	298	450	5-8
	5	0.24	310	405	5-8
	6	0.18	325	—	5-8
	7	0.13	350	400	5-8
S: <i>p</i> -DAS	8	0.24	305	390	5-8
	9	0.23	310	395	—
	10	0.23	335	405	—
PS	11	0.79	280	405	—
	12	0.28	260	365	35
	13	1.23	260	365	35

^a Reference 1.

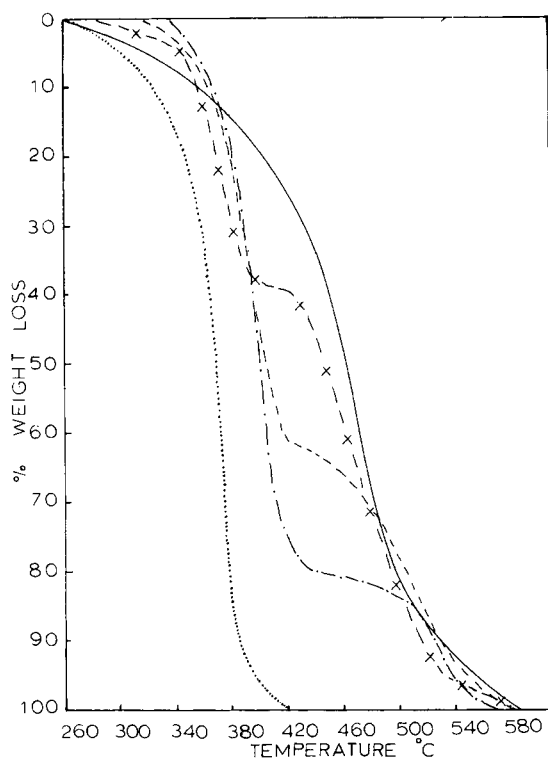


Fig. 1. TG curves for PDAS homopolymers: (—) PDAS 2; (x - - x) PDAS 4; (- - -) PDAS 5; (- · · · ·) PDAS 7; (· · · ·) PS.

assessment of thermal stability, however, dictates whether an increase in molecular weight leads to an increase or decrease in stability. Thus, 50% DT values suggest an increase in stability with increase in molecular weight, while isothermal data (W_{10}) shows only a small change in stability comparable to the change found in nitrogen.¹

Previous studies by TG on two samples of PDAS by Jones and Still³ suggested that these polymers had a much decreased PDT (230°C) in air compared to PS. This was reflected in a small (<1%) weight loss prior to the main catastrophic degradation.

A similar observation was made on samples of PDAS prepared in this study. This early weight loss was observed both in air and nitrogen atmospheres and was found to be due to entrained volatiles which could be removed by repeated precipitation or by drying the polymer to constant weight above the T_g .

It is apparent from Figure 1 that the molecular weight of the PDAS samples also influences the degradation behavior on dynamic TG in terms of the shape of the weight loss curves obtained. The behavior observed for PS, however, is independent of molecular weight. The behavior shown by PDAS is similar to that previously reported by Still and Jones³ for *m*-aminostyrene and *m*-hydroxystyrene homopolymers and copolymers. Figure 2 shows the rate of weight loss data for these PDAS samples, and Figure 3 shows the DSC curves obtained in dynamic air for a selection of PDAS homopolymers. Both

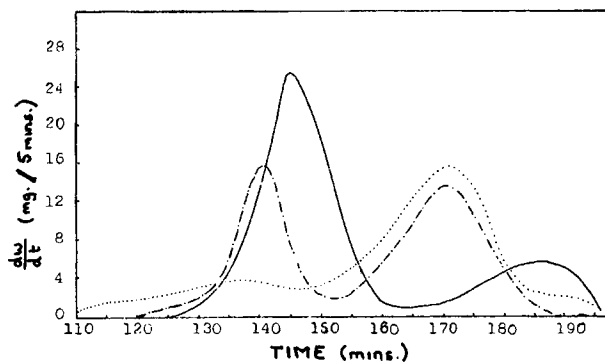


Fig. 2. Rate of weight loss curves for PDAS homopolymers: (.....) PDAS 2; (- · - · -) PDAS 4; (—) PDAS 7.

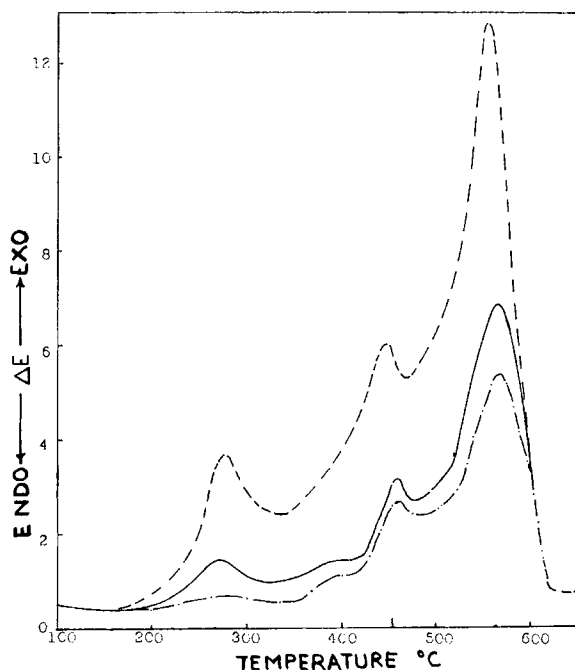


Fig. 3. DSC curves for PDAS homopolymers: (- - -) PDAS 2; (—) PDAS 3; (- · - · -) PDAS 7.

sets of data indicate the molecular weight dependence of the degradation behavior of this system under the conditions of test.

The PDT data for the S:*p*-DAS copolymers given in Table I show that they are composition dependent. The effect of composition on the overall degradation characteristics is small, as is shown for TG in Figure 4 and further confirmed by DSC in Figure 5. Two features are apparent, namely, the molecular weight effect for the 1:1 copolymer, where samples of different molecular weights were available, and the increase in PDT with increase in *p*-DAS concentration within the copolymer.

It is apparent, therefore, that any mechanism proposed to account for the behavior of the *p*-DAS polymers must explain the influence of molecular weight and copolymer composition on the PDT and the shape of the thermal

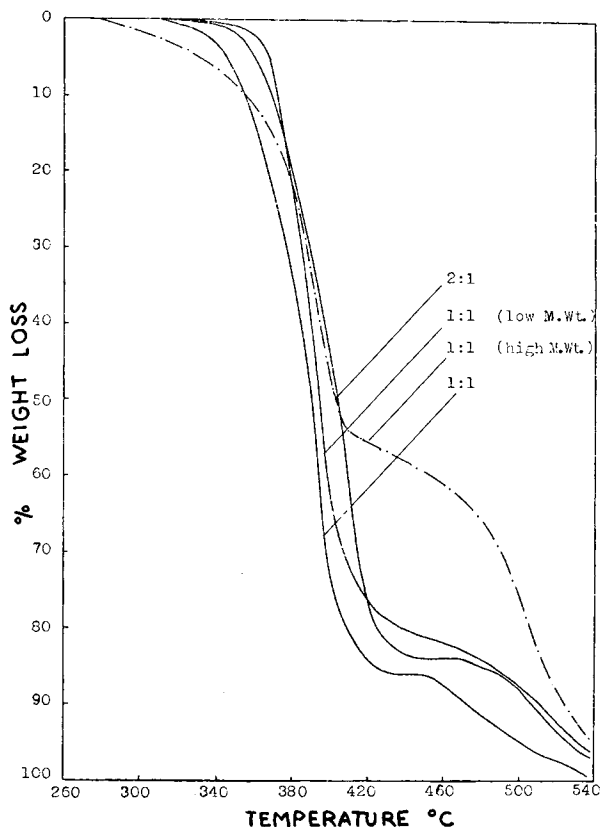
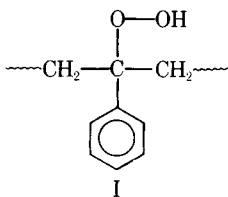


Fig. 4. TG curves for S:p-DAS copolymers.

analysis curves, both TG and DSC.

In Figure 6, the behavior of PS and the lowest molecular weight sample of PDAS (7) on dynamic TG are compared in air and nitrogen atmospheres. It can be seen that PS is more stable in nitrogen than in air. The much faster rate of volatilization of PS in air has been ascribed by Grassie⁴ and Wall⁵ to oxidative initiation of degradation. Beachell⁶ and Wall⁷ have shown that the primary product of oxygen attack on PS at temperatures below 200°C is the hydroperoxide (I):



The decomposition of this hydroperoxide has been shown to be responsible for main chain cleavage and the formation of carbonyl and hydroxyl containing degradation products.^{8,9}

The exact fate of the radicals produced in the hydroperoxide decomposition is, however, complex, and there is disagreement between various workers as to the nature of the secondary reactions.^{7,9-11}

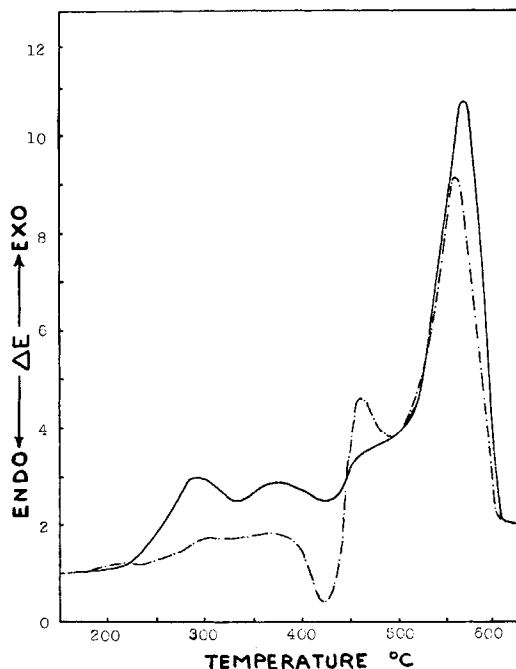
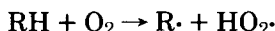


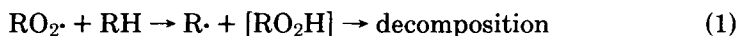
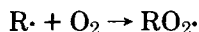
Fig. 5. DSC curves for S:p-DAS copolymers: (---) S:p-DAS 8, 9, 10; (—) S:p-DAS 11.

At temperatures above 200°C, the existence of hydroperoxides is thought to be unlikely by Smiley^{9,12} and Reich and Stivala¹³ on the basis that cumene hydroperoxide, a model for the PS system, decomposes rapidly at 150°C.

It is thought that at these temperatures, attack by oxygen occurs without appreciable hydroperoxide formation:



On dynamic thermal analysis, as the temperature is increased from ambient, the propagation steps in the auto-oxidation mechanism proposed by Bolland et al.^{14,15} then become important:



Thus, depending on the temperature, the hydroperoxides will break down as previously described, and a proportion of the polymer radicals will undergo unzipping and hydrogen transfer reactions to give monomer and associated products.

Termination of the auto-oxidative chain will occur by combination of radicals. The complexity of the degradation mechanism in air is apparent from Jellinek's work⁸ who has found 14 volatile components on degradation of isotactic PS between 250° and 280°C. These include benzaldehyde, acetophenone, benzophenone, benzyl alcohol, benzoic acid, and styrene.

To prevent oxidative initiation of degradation, antioxidants such as phenols and amines and metal dithiocarbamates are incorporated into commercial polymers during manufacture. Phenolic and amine antioxidants con-

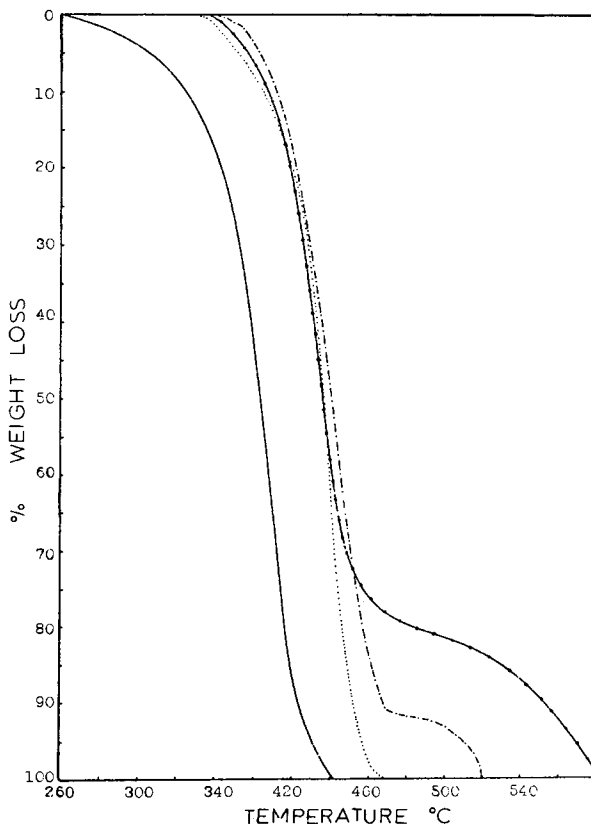


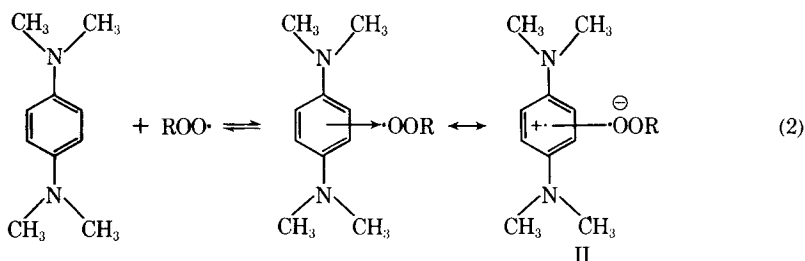
Fig. 6. TG curves for PS and PDAS 7 in air and nitrogen: (—) PS (air); (.....) PS (N₂); (-.-.-.) PDAS (air); (- - - -) PDAS (N₂).

taining mono- and unsubstituted amino groupings act by reacting with the peroxy radical in the following manner:

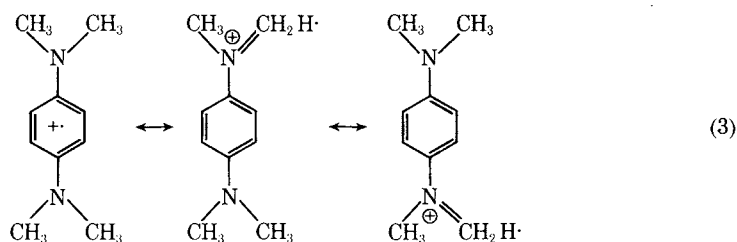


where AH is the amino or phenolic antioxidant containing a transferable hydrogen and A· is a radical less reactive than the peroxy radical and is usually resonance stabilized.

Alkylation of phenols destroys their antioxidant action, but complete N-alkylation of aromatic amines only reduces their effect. Pedersen¹⁶ has reported that tetramethyl-*p*-phenylenediamine is 36% as efficient as the powerful antioxidant N,N'-di(*sec*-butyl)-*p*-phenylenediamine. Since it has no labile hydrogen, the deactivating mechanism can only involve electron transfer from the nitrogen atom:

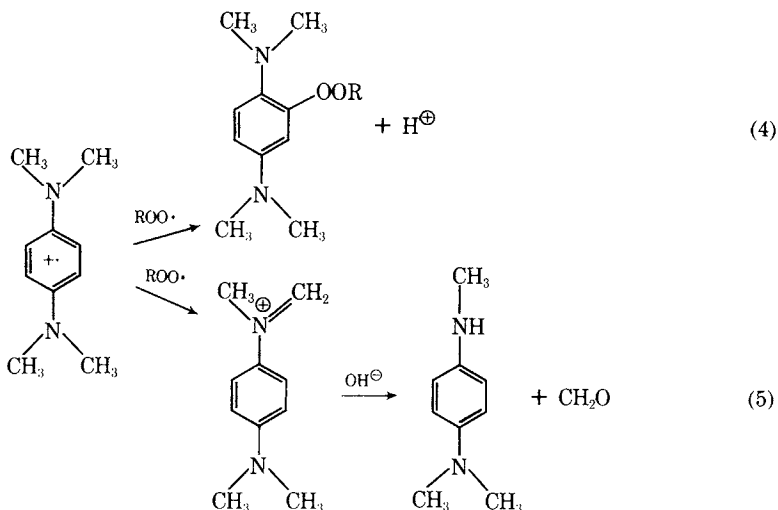


The Wurster radical ion (II) is stabilized by hyperconjugation [eq. (3)]



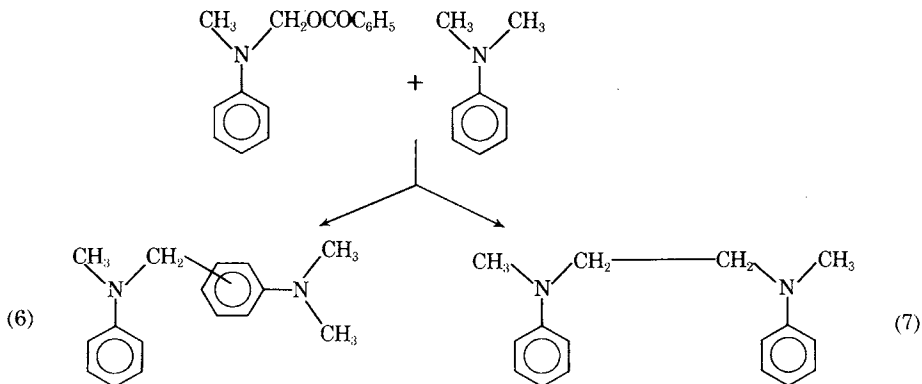
as has been shown by esr studies,¹⁷ and physical evidence of its formation under auto-oxidative conditions has been provided by Boozer et al.¹⁸

Scott¹⁷ has suggested that further reaction of this system with the peroxy radical involves the hydrogens or the nuclear carbon atoms, eqs. (4) and (5):



Loss of alkyl groups in the oxidation of amines is well known, and the complex II above is similar to that proposed by Horner¹⁹ to explain the dealkylation of dimethylaniline with benzoyl peroxide.

Recently, Hrabak and Coupek²⁰ have shown that the primary products of reaction between benzoyl peroxide and a tertiary amine can condense either with the initial amine, or with each other, to yield benzoic acid and dehydrogenated oligomers of the original amine according to the following schematic equation:



If the behavior of PDAS 7 in Figure 6 is now considered, there would appear to be a "built-in" antioxidant action in this system, probably with the formation of a Wurster radical ion similar to II, since the weight loss curves are identical to approximately 80% volatilization and the oxidative initiation of degradation observed for PS is absent in this system.

Further confirmation of this behavior is afforded by the data presented in Figure 7 for isothermal studies on PS and PDAS 7 in air and nitrogen atmospheres at 400°C.

As the molecular weight of PDAS increases, the "efficiency" of the antioxidant action appears to decrease and the difference between the weight loss curves for dynamic TG studies in air and nitrogen becomes more exaggerated.

On isothermal TG in the temperature range of 360–420°C, all the samples behave similarly irrespective of molecular weight until 65% volatilization has occurred, when the rate of weight loss in air decreases rapidly. This suggests that the molecular weight dependence of PDT and the shape of the dynamic TG curves is due to some process occurring prior to weight loss and certainly below 360°C.

In an attempt to elucidate the nature of reactions occurring prior to, and during, weight loss, PDAS samples were subjected to further TG and DSC studies. PDAS samples 4 and 7 were degraded on the thermobalance and samples were removed at temperatures consistent with the weight losses A, B, and C (temperatures 1, 2, and 3) shown in the idealized TG curve for PDAS (Fig. 8).

The samples were quench cooled in a nitrogen atmosphere and subjected to combustion analysis, as shown in Table II.

During the B stage of weight loss, extensive carbonization occurs with an increase in carbon content and a decrease in hydrogen content. In the first stage, A, the higher molecular weight sample shows a degree of carbonization which is not apparent for the low molecular weight sample, again emphasizing the molecular weight dependence.

Figures 3 and 9 show the behavior observed on DSC for selected PDAS samples and PS. The behavior of PS is more complex than that reported previously,^{3,21,22,23} but this may be ascribed to differences in technique and

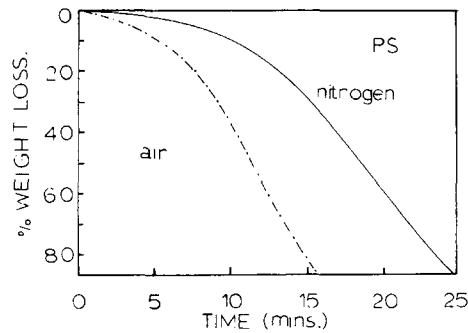
TABLE II
Combustion Analysis Data for PDAS Samples Subjected to Dynamic TG to
Temperature Specified

Polymer	Temperature, °C	% Volatilized	%O, ^a	%C, ^b	%H, ^b	%N, ^b	Stage of weight loss ^c
PDAS 4	ambient	0	0	82.06	8.94	9.55	—
	390	35	4.8	83.20	7.30	9.50	1
	440	46	9.2	85.70	4.72	9.70	2
	550	95	18.6	82.06	2.33	12.80	3
PDAS 7	ambient	0	0	82.83	8.92	9.35	—
	410	70	5.7	82.03	8.90	9.17	1
	500	85	12.5	85.60	2.61	11.80	2

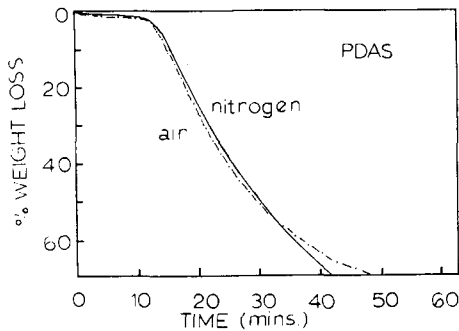
^a Calculated by difference and expressed as a percentage of the residue.

^b Expressed as a percentage of total CHN content.

^c Stage of removal Fig. 8.



(a)



(b)

Fig. 7. Isothermal TG curves for (a) PDAS and (b) PS in air and nitrogen at 400°C.

apparatus sensitivity. The PDAS homopolymers (Fig. 3) are characterized by three major exotherms, A, B, and C, having peak maxima at approximately 270°, 450°, and 560°C, respectively.

Increasing the PDAS molecular weight increases the size of the exotherms obtained from samples of the same weight, again indicating the molecular weight dependence of the system. Comparison of data obtained for the percentage residue prior to each of the exotherms (Table III) shows that they correspond to the three stages of weight loss in the TG curves (Figs. 7 and 8).

If PDAS 7 is deliberately oxidized by exposure to air/diffused sunlight, the DSC trace shown in Figure 10 is obtained, whence it can be seen that all the exotherms are increased in size and the oxidized sample exhibits behavior which closely resembles that of untreated PDAS 2. This behavior is also observed if the samples are subjected to dynamic TG (Fig. 11). IR examination of this oxidized sample reveals a high concentration of hydroperoxide groups.

TABLE III
Weight Losses During DSC

Polymer	% Volatilized at given temperature,		
	330 °C	425 °C	480 °C
PDAS 1	3.8	25	54.4
2	1.8	27.3	74.6
3	1.1	33.7	85.0
PS	4.8	80.4	99.6

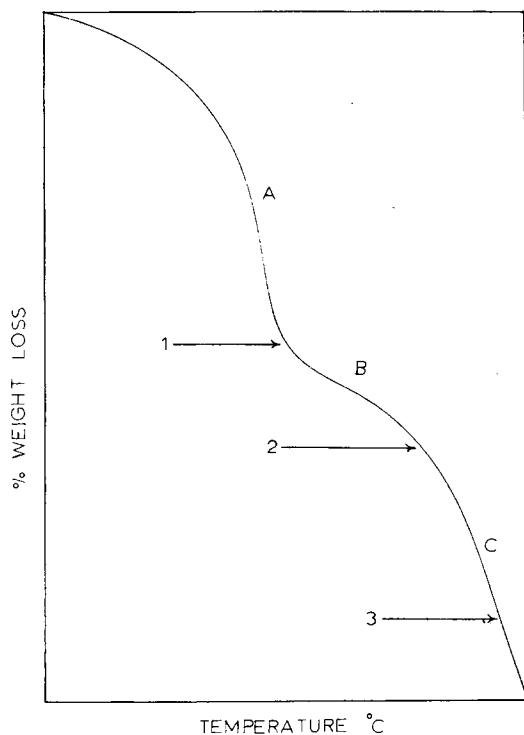


Fig. 8. Idealized TG curve for PDAS.

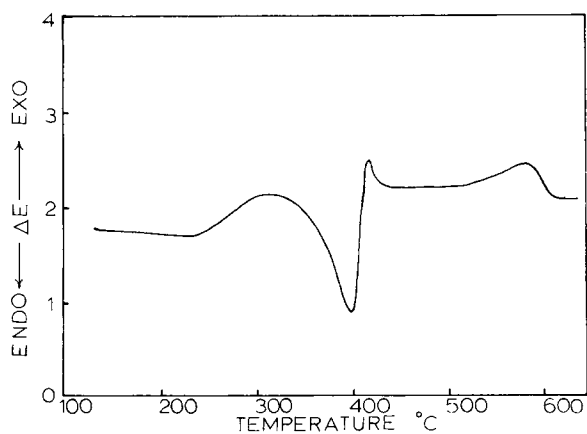


Fig. 9. DSC curve in air for PS.

The existence of hydroperoxides of the type previously discussed for PS beyond 180°C, the onset of the first exotherm A on the DSC trace, is doubtful. Further, since an increase in the concentration of hydroperoxides in the samples causes an increase in the size of exotherm A, it is probable that it is associated with secondary reactions following the decomposition of the hydroperoxide.

PDAS 7, the lowest molecular weight sample studied, shows only a small exotherm A, suggesting a greater antioxidant "efficiency" in this system leading to less propagation of oxidation and secondary reactions.

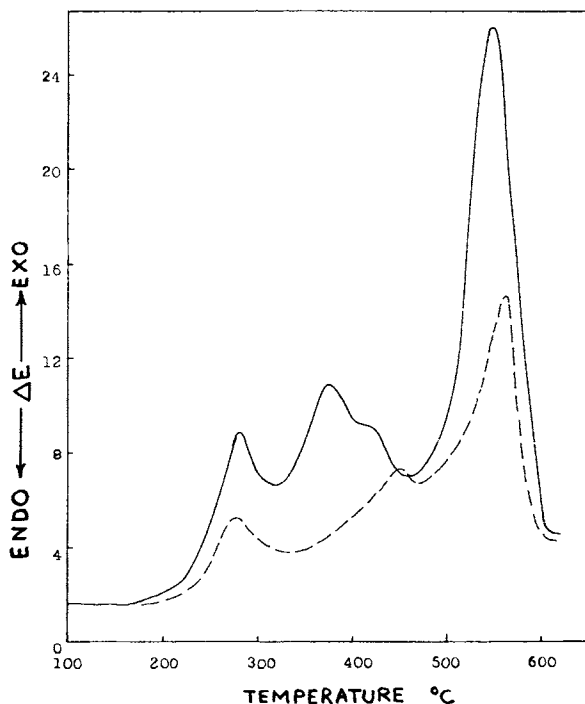


Fig. 10. Effect of preoxidation on the DSC trace for PDAS in air: (---) PDAS 7 untreated; (—) PDAS 7 preoxidized in air/sunlight for six weeks.

The intermediate exotherm B corresponds to the intermediate slow rate of weight loss on the TG curve (Figs. 1 and 8) and the combustion analysis data (Table II) suggest that it is caused by carbonization of the polymer.

Common to all the systems studied is the C exotherm at peak maximum 550°C. It is the dominating feature of the PDAS homopolymer and the *S:p*-DAS copolymer traces (Figs. 3 and 5). With PS, however, it is only a minor feature of the overall degradation. Studies were made on the percentage residue prior to the C exotherm and the magnitude of the C exotherm for samples of constant weight, and the data are presented in Table IV. In addition, visual examination of the samples prior to the C exotherm were made (Table V).

From the data presented in Tables IV and V, it is evident that the C exotherm is associated with "burning off" of the residue. The relatively small C

TABLE IV
The C Exotherm

Polymer	% Residue in air at 480 °C	Mass of C exotherm, mg ^a	Peak mass
			% residue
PDAS 3	45.6	265	5.8
PDAS 5	25.4	140	5.5
PDAS 7	15.4	82	5.3
PS	0.9	4.5	5.0

^a Weight of peak cut from paper.

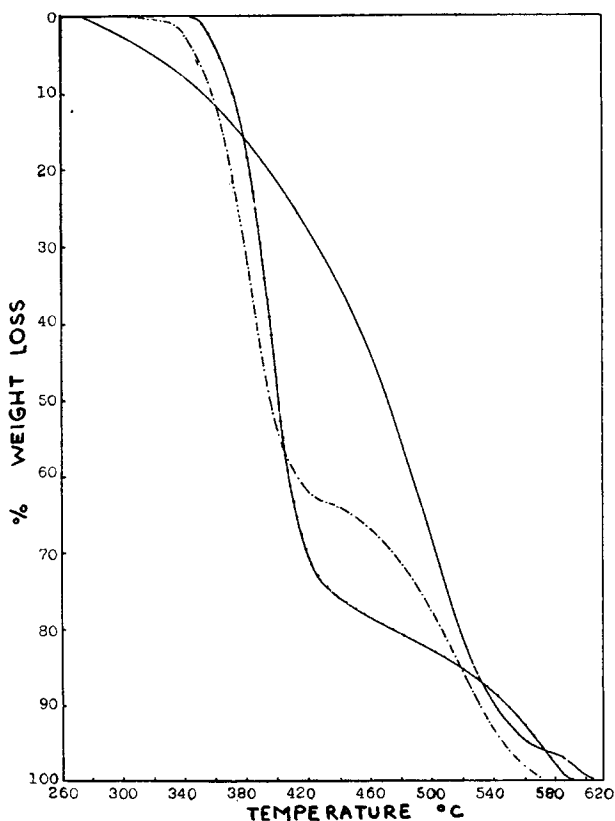


Fig. 11. Effect of preoxidation on the TG curve for PDAS in air: (-·-·-) PDAS 7 untreated; (· · · ·) PDAS 7 preoxidized for three weeks; (—) PDAS 7 preoxidized for six weeks.

exotherm in the case of PS may be explained since PS shows little tendency to yield a carbonaceous residue in air or nitrogen. Further examination of the residue from PDAS at 480°C showed that (a) on reheating in air to 600°C, an exotherm was obtained; (b) no weight loss (>0.5%) occurs on heat-

TABLE V
Physical Appearance of Polymer Samples During DSC in Air After Heating to Specified Temperature and Cooling in Nitrogen

Polymer sample	Ambient	330 °C	430 °C	480 °C
PDAS 2	white fibrous material	yellow fibrous material	dark brown fibrous material	black fibrous material
PDAS 4	white fibrous material	yellow glass with fibres at extremities	brown glass with fibres at extremities	black carbonaceous material
PDAS 7	white fibrous material	yellow glass	yellow/brown glass	black carbonaceous material
PS	white fibrous material or powder	colorless transparent glass	yellow transparent glass with brown spots	brown residue (trace)

ing the residue to 850°C in nitrogen (no depolymerization); (c) combustion analysis indicates an increased carbon content (81% → 90%) and a decreased hydrogen content (9% → 1.0%) in the residue.

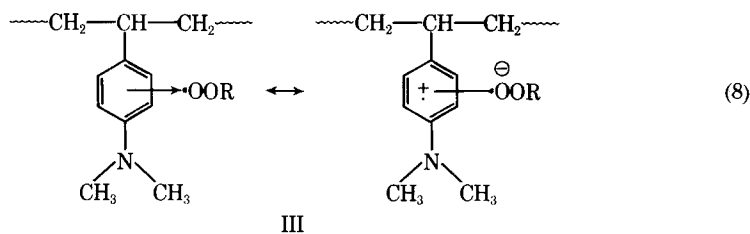
These observations indicate that the C exotherm is produced in the case of PDAS samples by combustion of a highly carbonized material produced in an earlier stage of degradation.

The weight of the residues (Table IV) shows that the C exotherm corresponds to the third stage of weight loss in the TG curves (Fig. 8). A molecular weight effect is again observable with the C exotherm with higher molecular weight samples yielding higher proportions of carbonized residue.

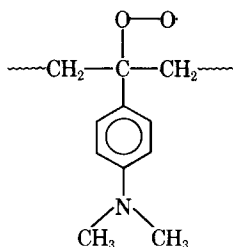
The DSC traces of the low molecular weight *S:p*-DAS copolymers 8, 9, and 10 change little with copolymer composition and show a small endotherm prior to the second exotherm B (Fig. 5). Comparison of PDAS and *S:p*-DAS copolymers with PS (Figs. 3, 5, and 9) suggests that this endotherm is related to thermal degradation processes (unzipping and transfer reactions of radicals produced on chain cleavage caused by hydroperoxide decomposition reactions) producing monomer and related volatiles.

While the reactions occurring during the various stages of weight loss and the exo- and endothermic processes observed on DSC during the degradation of PS and *p*-DAS homopolymers and copolymers have been discussed. The effect of molecular weight and copolymer composition on the stability and carbonization behavior has yet to be explained.

The increased stability of PDAS 7 relative to PS in air was explained in terms of a "built-in" antioxidant action of the dimethylamino substituent with the intermediate formation of a Wurster radical ion intermediate (III):



where ROO· is



However, since this reaction involves either intra- or intermolecular transfer, the effectiveness of this inhibition reaction will depend upon the mobility of the molecules. Oxidation is primarily a surface reaction and is limited by the depth and rate of diffusion of oxygen into the polymer. Comparison of PDAS 2 and 7 in air on a hot-stage microscope showed differences in behavior similar to that reported in Table IV. PDAS 7 changed from the "fibrous

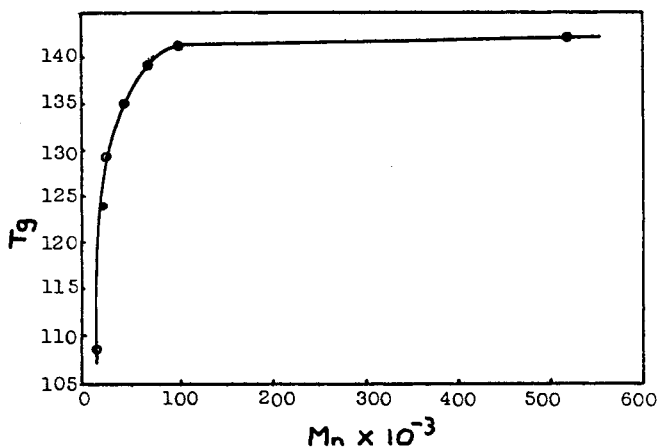


Fig. 12. Effect of molecular weight on T_g for PDAS homopolymers.

state" to a "melt" between 148° and 165°C and remained liquid at 360°C. PDAS 2, however, showed only a color change (white → brown) with no change in physical appearance from the "fibrous state" on heating to 360°C.

In a previous paper,¹ the change in glass transition temperature with molecular weight and copolymer composition was discussed. It can be seen from Figures 12 and 13 that the PDT/molecular weight and T_g /molecular weight graphs closely resemble one another.

The dependence of the PDT and the change in the TG curves for poly(*m*-aminostyrene) was ascribed to differences in the melt viscosity of samples by Still and Jones¹ leading to a reduced antioxidant effect with high molecular weight samples.

However, with the PDAS samples, the observations on the hot-stage microscope, the close resemblance of T_g and PDT changes with molecular weight, and the isothermal TG observations (no molecular weight effect) suggests that it is not only the comparative melt viscosity which is important but the temperature at which mobility begins, i.e., the T_g . This is perhaps more apparent with the high molecular weight samples. At molecular weights of the order of 100,000, further changes in molecular weight produce little change in PDT, T_g , and the shape of the TG and DSC curves. This occurs even though such changes are likely to produce an increase in melt viscosity.

The earlier the mobility of the polymer chain begins (the lower the T_g), the earlier the reaction of the "built-in" antioxidant groups in PDAS with the peroxy radicals will occur.

In the case of the copolymers, an increase in the concentration of the "antioxidant comonomer" will tend to lead to an increased antioxidant efficiency. This effect, however, would be offset by an increase in the glass transition temperature with reduced chain mobility as shown in Table VI, which would lead to a decrease in the overall antioxidant efficiency. As a consequence, the overall effect is a balance between these two effects.

The mechanism of the antioxidant effect and the carbonization reaction must be similar to that proposed by Scott¹⁷ to explain the antioxidant action of tetramethyl-*p*-phenylenediamine, eqs (4) and (5). If this scheme is ap-

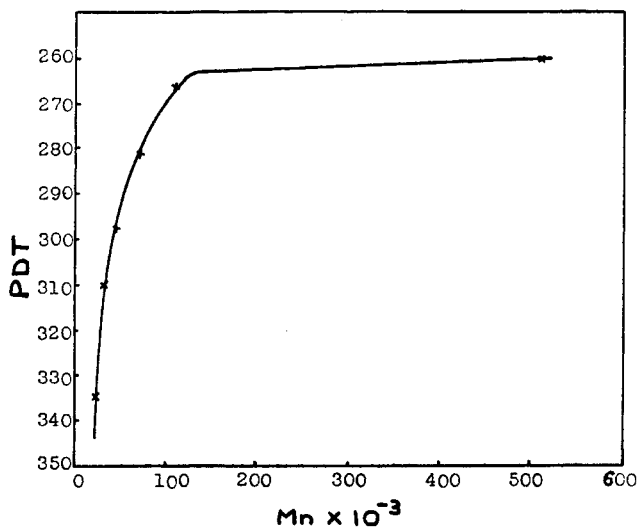


Fig. 13. Effect of molecular weight on PDT for PDAS homopolymers.

plied to PDAS initially, the Wurster radical ion III is formed as in eq. (8). Further reaction of this species by reactions similar to those in eq. (4) and (5) would give

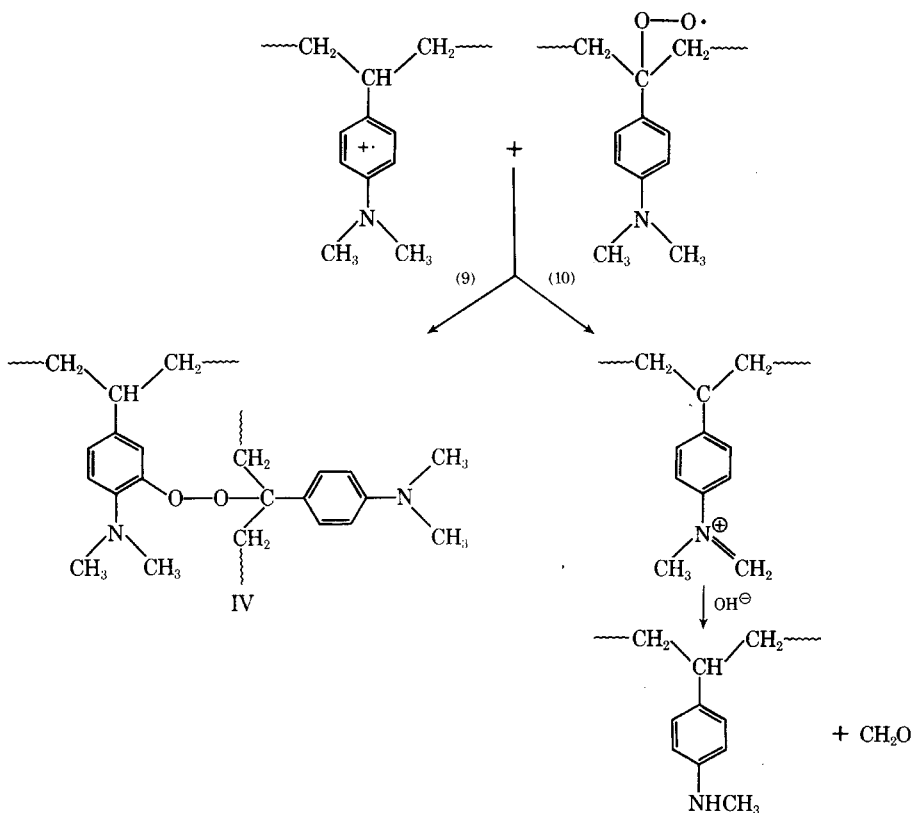
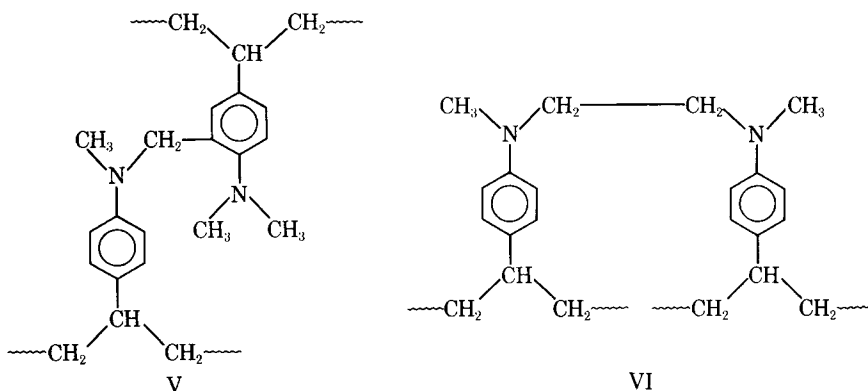


TABLE VI
Glass Transition and Procedural Decomposition Temperatures for
S:*p*-DAS Copolymers

Polymer no.	Molar ratio S: <i>p</i> -DAS	$[\eta]_0$	$T_g, ^\circ\text{C}$	PDT, $^\circ\text{C}$
8	2:1	0.24	107	305
9	1:1	0.23	111	310
10	0.5:1	0.23	119	335
11	1:1	0.79	126	280

In addition to this, further crosslinking by a reaction pathway similar to that proposed by Hrabak and Coupek²¹ for reaction of dimethylaniline with benzoyl peroxide, eqs. (6) and (7), is possible. With PDAS, this would result in the formation of structures such as V and VI by inter- or intramolecular re-action:



On slowly programming the temperature from ambient in air as in the dynamic TG experiment, the samples of PDAS with low molecular weight will favor the formation of the radical ion III. The probability of further reaction of the radical ion with the peroxy radical will be reduced by the mobility of the chains. Initially, both the radical ions and the peroxy radicals will be concentrated on the surface, but chain mobility will result in their replacement at the surface by unreacted aromatic dimethylamino groupings. Only when a high concentration of these radical ions has built up within the polymer bulk will the further reaction to give crosslinked systems of the type IV, V, and VI occur to give a more rigid system favoring carbonization.

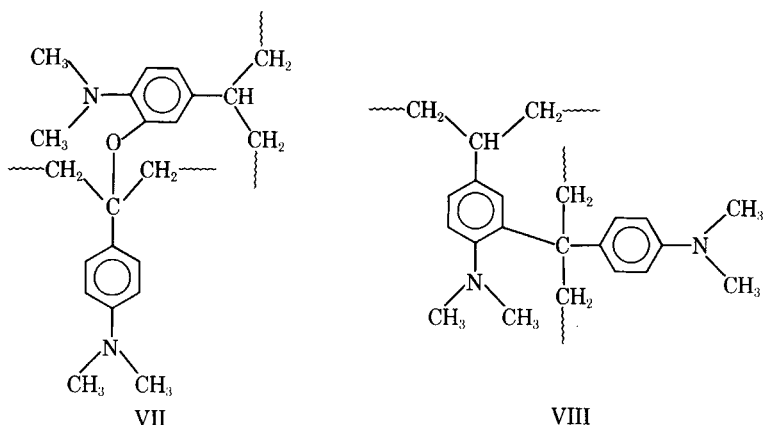
TABLE VII
Carbon Yield from PDAS

Pretreatment temperature in air, $^\circ\text{C}$	% Residue in nitrogen at 1000°C	
	PDAS 2	PDAS 7
Ambient	2.3	1.0
325	10.5	1.2
425	40.0	8.0
480	98.0	99.0

With the high molecular weight samples, a localized concentration of peroxy radicals and radical ions will build up on the surface prior to the onset of chain mobility, and further reaction will occur on the surface.

This is the probable explanation of the observation that PDAS 1 and 2 do not yield "melts" in air but do so in a nitrogen atmosphere. Crosslinking then tends to occur from the outside inward, instead of homogeneously as in the case of the low molecular weight samples.

The crosslinked structure IV would not be expected to be thermally stable, and reaction by scission of the peroxy link or by hydrogen abstraction followed by nuclear substitution could lead to structures of the type VII and VIII:



Further reactions of species such as V, VI, and VII, and VIII could lead to cyclization and aromatization.

Crosslinking via the antioxidant mechanism consequently occurs before the T_g for PDAS 2 but only during weight loss for PDAS 7. Combustion analysis of the residue confirms this behavior.

In a similar way, the degradation characteristics of the intermediate molecular weight samples can be explained in terms of a hybrid of the low and high molecular weight behavior.

The appearance of PDAS 1 at the C stage of weight loss is very similar to the carbon fiber from polyacrylonitrile. Pretreatment of PDAS in air at temperatures between 300° and 500°C also effectively crosslinks the polymer, and heating to 1000° in nitrogen yields a high carbon content material. The carbon yields at different pretreatment conditions are shown in Table VII. The higher the initial molecular weight and pretreatment temperature, the greater is the carbon yield.

Elemental analysis of the "carbon fiber" from PDAS 1 gave C, 90.8%; H, 1.24%; N, 7.97%. The original polymer gave C, 81.58%; H, 8.90%; N, 9.52%.

Observation made during degradation of PDAS in air are very similar to those found for poly(trivinylbenzene) (PTVB) by Winslow and Matreyek²⁴ who found that before weight loss exceeded 1–2%, PTVB turned dark, indicating development of extensive conjugated unsaturation.

In PDAS, crosslinking as a result of oxidation produces a pseudo-PTVB system which is very susceptible to carbonization. IR investigation of the

carbonaceous product reveals a very broad absorption band at 1600–1200 cm^{-1} , indicative of an aromatic C—C out-of-plane deformation and in agreement with an aromatized structure. The IR of the carbonized residue compares favorably with the IR spectrum of Ovalene and 1,2,3,4,6,7-tribenzophenazine, although the resolution of the absorptions of the carbonized material is poor.

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