

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

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Synopsis

Homopolymers of *m*-N,N-dimethylaminostyrene and *p*-N,N-diethylaminostyrene and their 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 in the case of polymers containing *m*-N,N-dimethylaminostyrene. Polymers containing *p*-N,N-diethylaminostyrene show TG and DSC curves essentially independent of molecular weight and copolymer composition. The behavior of the two systems is discussed in terms of the antioxidant effect of the chain-bound N,N-dialkylamino substituents and their secondary reactions.

EXPERIMENTAL

Materials. As prepared and reported in parts XI¹ and XII² of this series.

Differential Scanning Calorimetry (DSC). A Du Pont 900 thermal analyzer equipped with a DSC cell capable of operation from ambient to 600°C was used. The sample (≈6 mg) was located in an uncrimped aluminum pan (7 mm in diameter) without a covering lid, and an empty pan acted as the inert reference. A heating rate of 20°/min (nominal) was used together with a flow rate of 400 ml/min of air.

Dynamic TG Studies. A Du Pont 900 thermal analyzer with a 950 thermogravimetric analysis attachment was used programmed for a heating rate of 8°C/min (nominal) in static air. Approximately 10 mg of material was employed in each experiment, and samples were contained in aluminum crucibles. The maximum safe operating temperature for the unit employed in these studies was 550°C, and all runs were terminated at 530°C.

Isothermal TG Studies. The 950 TG attachment was employed in its isothermal mode using the following procedure. The furnace was heated to the required temperature in the operational position, and the apparatus was allowed to come to thermal equilibrium with air passing through the quartz

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TABLE I
TG Data for PDEAS Degradation in Air

Polymer ^a	Intrinsic Viscosity ^a [η] ₀	Temperature, °C; for specified % weight loss			
		0 ^b	10	50 ^c	75
PDEAS 1	0.55	276	412	437	452
PDEAS 2	0.39	285	410	436	450
PDEAS 3	0.31	280	405	435	449
PDEAS 4	0.22	300	398	426	443
PDEAS 5	0.18	353	399	430	445
PS 10	0.28	271	324	370	388

^a Reference 1.

^b Procedural decomposition temperature (PDT).

^c Fifty per cent decomposition temperature (50% DT).

tube. The furnace was then rolled away from the tube and the sample/crucible added to the rise rod. The furnace was then placed over the sample and the weight loss recorded for periods up to 90 min. Sample sizes of ≈ 10 mg and an air flow rate of 250 ml/min were used.

RESULTS AND DISCUSSION

In Tables I and II are reported the degradation parameters obtained by dynamic TG in a static air atmosphere for *p*-N,N-diethylaminostyrene homopolymers (PDEAS 1–5) and *m*-N,N-dimethylaminostyrene homopolymers (PmDAS 1–4) of different molecular weights. In the case of PDEAS, it can be seen that the PDT is molecular weight dependent (Table I), but the thermogram shape is unaffected by molecular weight (Fig. 1, where the two most extreme molecular weight samples are shown for clarity).

In addition, the DSC traces (Fig. 2) for PDEAS samples of different molecular weight but similar sample weights confirm the TG behavior; no molecular weight effect is apparent.

PmDAS similarly shows a molecular weight effect upon PDT (Table II), and in this case the thermogram shape is also molecular weight dependent (Fig. 3). DSC curves for similar sample weights of the different molecular

TABLE II
TG Data for PmDAS Degradation in Air

Polymer ^a	Intrinsic Viscosity ^a [η] ₀	Temperature, °C; for specified % weight loss			
		0 ^b	10	50 ^c	75
PmDAS 1	0.83	261	410	454	530 ^d
PmDAS 2	0.35	271	421	454	513 ^d
PmDAS 3	0.31	343	427	451	472
PmDAS 4	0.15	367	416	439	453
PS 10	0.28	271	324	370	388

^a Reference 2.

^b PDT.

^c 50% DT.

^d 65% weight loss, see Fig. 3.

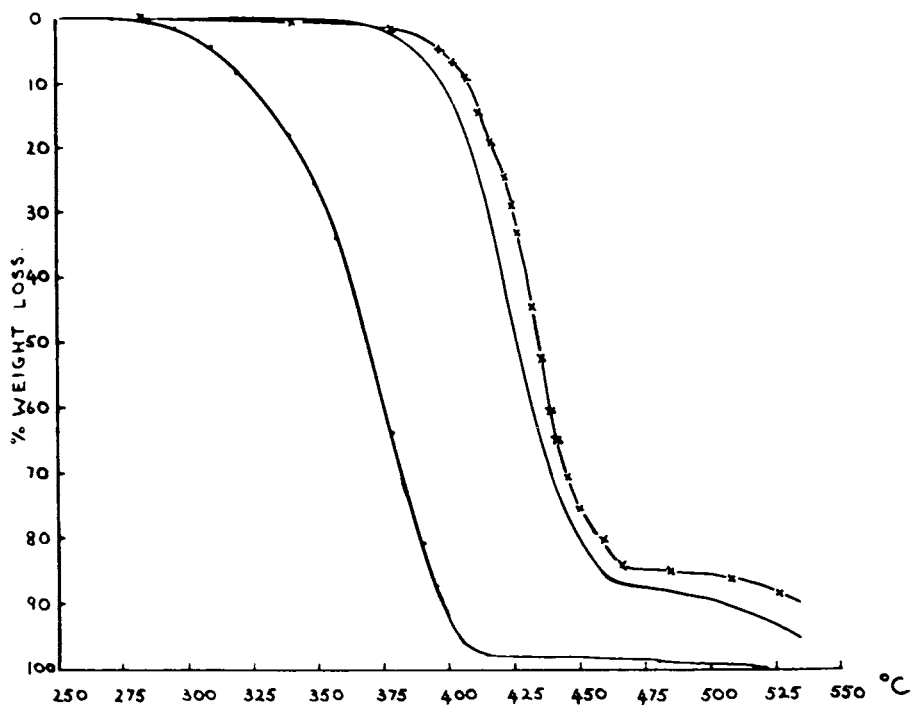


Fig. 1. TG traces for PS and PDEAS homopolymers in air: (—●—) PS; (—) PDEAS 1; (—x—) PDEAS 5.

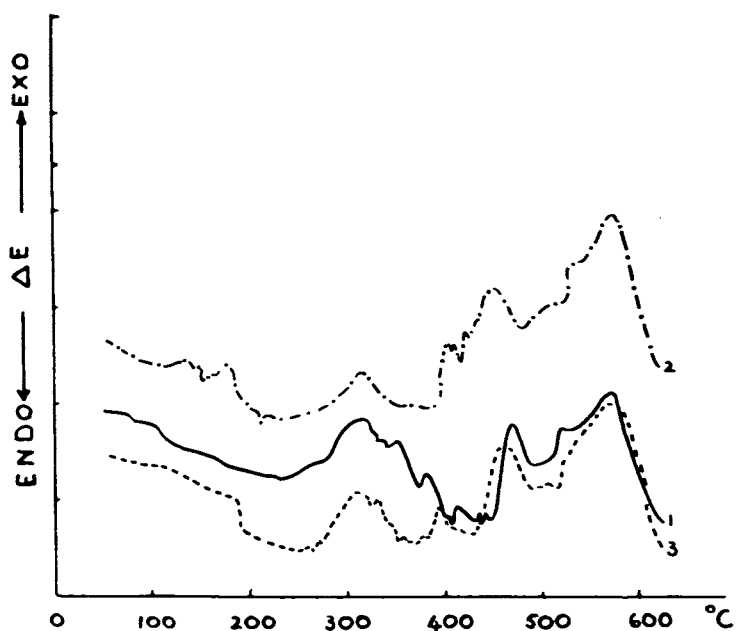


Fig. 2. DSC traces for PDEAS homopolymers in air: (1) PDEAS 1, 7.4 mg; (2) PDEAS 2, 6.75 mg; (3) PDEAS 3, 6.70 mg.

TABLE III
TG Data for PDEAS, PmDAS and PS in a Flowing Nitrogen Atmosphere^a

Polymer	Temperature, °C, for specified % weight loss			
	0 ^b	10	50 ^c	75
PDEAS 1	353	397	417	428
PDEAS 5	353	398	423	434
PmDAS 1	338	393	426	439
PmDAS 4	340	402	434	447
PS 10	314	394	421	431
PS 11	357	402	422	430

^a Reported in full in references 1 and 2.

^b PDT.

^c 50% DT.

weight samples of PmDAS (Fig. 4) confirm the molecular weight dependence of this system. This dependence of PDT on molecular weight has been observed previously by Still and co-workers¹⁻⁴ for polystyrene and hydroxy, amino, and substituted aminostyrene polymers and by Malhotra and co-workers⁵ for polystyrene in nitrogen.

The molecular weight dependence of the TG and DSC thermograms in air has also been reported previously by Still and co-workers for amino, hydroxy, and substituted aminostyrene polymers.^{3,4}

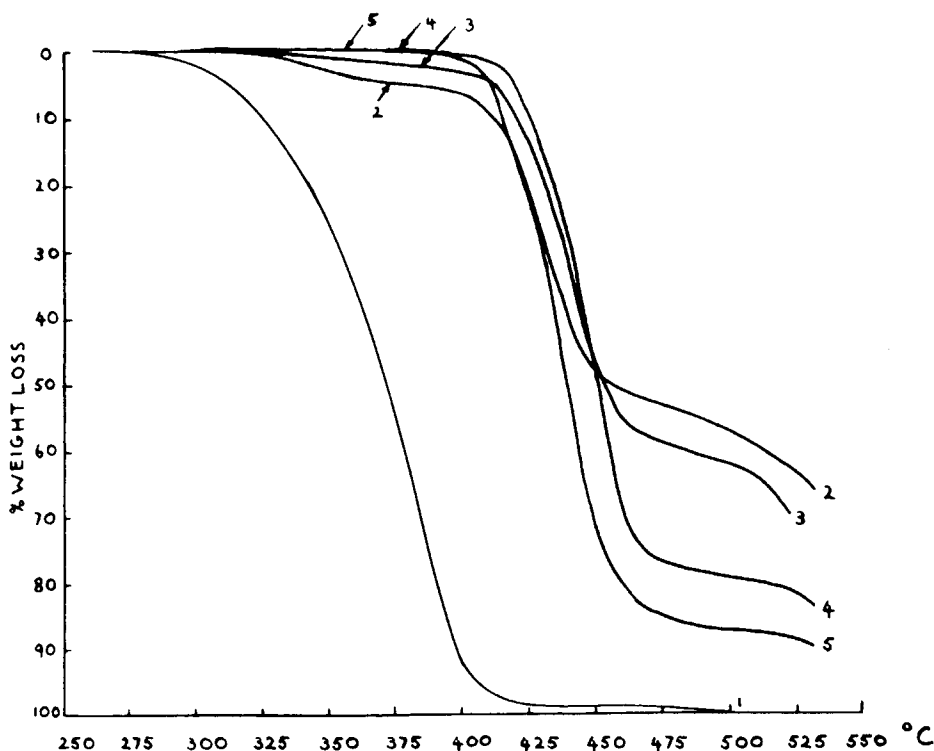


Fig. 3. TG traces for PS and PmDAS homopolymers in air: (1) PS; (2) PmDAS 1; (3) PmDAS 2; (4) PmDAS 3; (5) PmDAS 4.

The comparative data for a selection of these polymers in a flowing nitrogen atmosphere are given in Table III. This table shows that in nitrogen the three polymers behave essentially in the same manner. Further to this, it shows the suppression of the oxidative initiation of degradation observed for PS (Tables I and II).

The behavior of PDEAS and of PmDAS in air and in nitrogen is essentially similar, and it is apparent that the oxidative initiation of degradation observed for PS is suppressed in these systems (Figs. 1, 3, and 5). The apparently slightly lower stability of PmDAS and PDEAS in nitrogen as compared with air may be due to an artifact of the assessment system used. This arises because of the greater rate of volatilization of the degradation products by a flowing nitrogen atmosphere as compared to static air.

The DSC curves in air Figures 2 and 4 for the two systems are markedly different. The behavior of PmDAS is similar to that observed previously by Still and Whitehead⁴ for the isomeric poly(*p*-N,N-dimethylaminostyrene) homopolymer system (PDAS). Its behavior was discussed in detail previously,⁴ and the three exothermic peaks at peak maxima approximately 250°, 450°, and 560°C were shown to be due to secondary reaction of hydroperoxides (plus carbonization which was molecular weight dependent), carboniza-

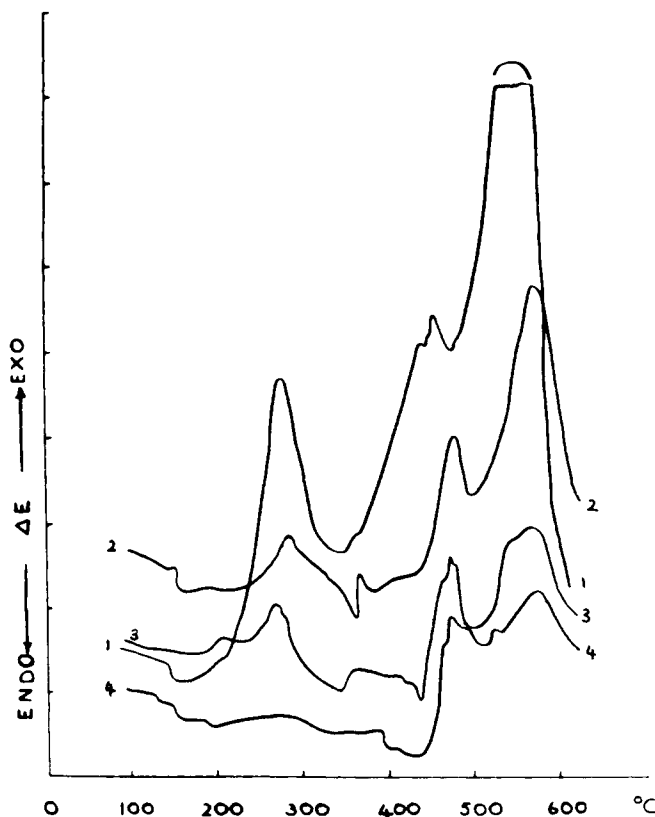


Fig. 4. DSC traces for PmDAS homopolymers in air: (1) PmDAS 1, sample weight 6.90 mg; (2) PmDAS 2, sample weight 7.00 mg; (3) PmDAS 3, sample weight 5.30 mg; (4) PmDAS 4, sample weight 6.50 mg.

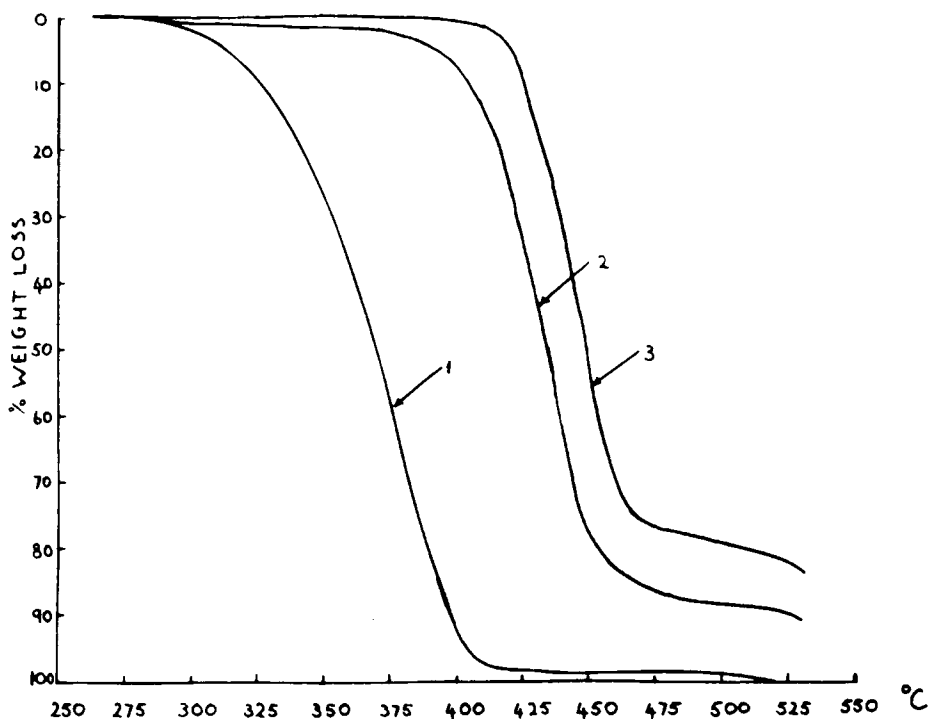


Fig. 5. TG traces for PS, PDEAS, and PmDAS homopolymers: (1) PS $[\eta]_0 = 0.28$; (2) PDEAS $[\eta]_0 = 0.32$; (3) PmDAS $[\eta]_0 = 0.31$.

tion, and burning off of the carbonaceous residue, respectively. In the case of PmDAS, similar reactions to those proposed for PDAS⁴ may account for the DSC and TG behavior.

The molecular weight effect for PDAS was ascribed to changes in chain mobility as a result of major differences in the T_g with increasing molecular weight. This influences the course of reaction between the antioxidant N,N-dimethylamino substituent and peroxy radicals and their secondary reactions.⁴

It is apparent in the case of PmDAS, where the T_g is considerably lower and changes little with molecular weight (PmDAS has a T_g of 86°C at M_n 38.65×10^4 and 80°C at M_n 1.821×10^4 , compared with that for PDAS⁶ of 143°C at M_n 52.00×10^4 and 125°C at M_n 24.2×10^4), that this is not the decisive factor in controlling the shape of the thermogram. Secondary reactions^{4,7,8} of (a) the peroxidic groupings with (b) the Wurster radical ion intermediate formed by the antioxidant reaction of the N,N-dialkylamino substituents,^{9,10} and (c) the unreacted N,N-dialkylamino units at the surface of the polymer sample appear to play the dominant role in determining the thermogram shape. The availability of such groupings at the surface will, of course, be dependent on both the T_g and the melt viscosity.

In the case of PDAS, the high and low molecular weight samples showed differences in behavior when heated on a hot-stage microscope at a similar rate to that used for the DSC studies.⁴ The low molecular weight sample changed from the "fibrous state" to a "melt" and remained liquid at 360°C.

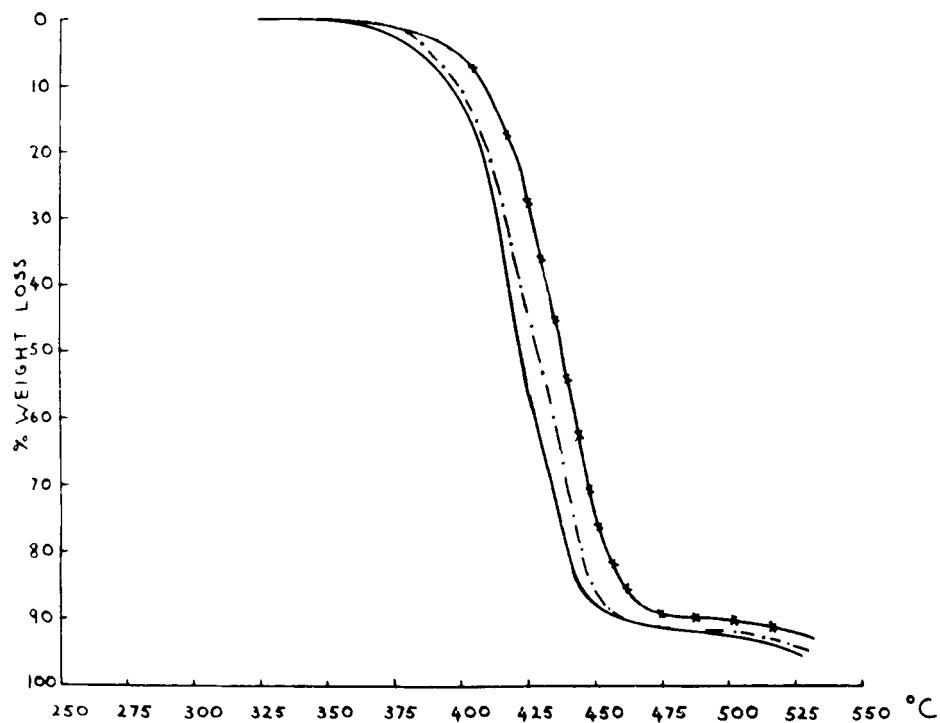


Fig. 6. TG traces for *S:p*-DEAS copolymers in air: (—) *S:p*-DEAS 6; (---) *S:p*-DEAS 7; (-x-x-) *S:p*-DEAS 8.

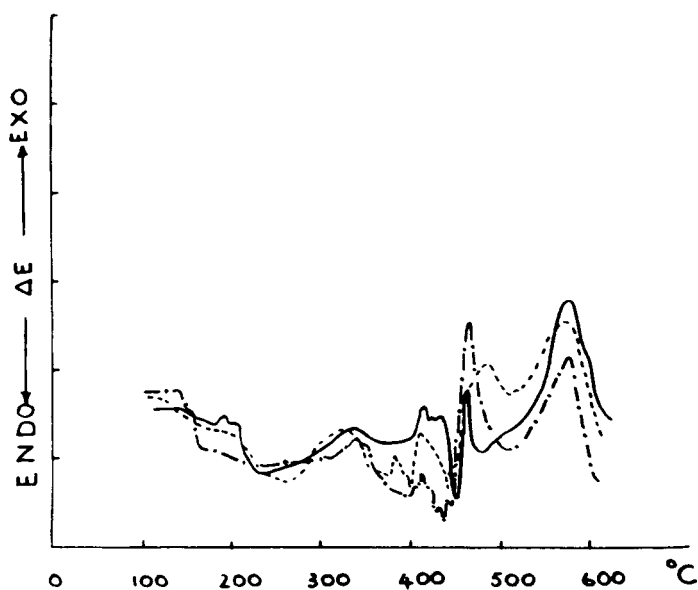


Fig. 7. DSC traces for *S:p*-DEAS copolymers in air: (-·-·-) *S:p*-DEAS 6, sample weight 6.40 mg; (---) *S:p*-DEAS 7, sample weight 6.55 mg; (—) *S:p*-DEAS 8, sample weight 6.60 mg.

TABLE IV
TG Data for S:p-DEAS Copolymer Degradation in Air

Polymer ^a	S:p-DEAS molar ratio	Intrinsic Viscosity [η] ₀	Temperature, °C, for specified % weight loss			
			0 ^b	10	50 ^c	75
S:p-DEAS 6	2.20:1	0.52	324	398	423	435
S:p-DEAS 7	1.11:1	0.45	329	398	426	442
S:p-DEAS 8	0.62:1	0.43	340	410	436	452
S:p-DEAS 9	1.79:1	0.93	314	402	429	444

^a Reference 1

^b PDT.

^c 50% DT.

The higher molecular weight sample showed only a colour change (white to brown) with no change in appearance from the "fibrous state" on heating to 360°C. PmDAS samples show similar behavior.

The thermograms observed for PDEAS are not molecular weight dependent (Figs. 1 and 2), and two important features are observed. The overall pattern of degradation on TG appears to follow a similar course to that for PS except that it is displaced to higher temperatures. The DSC curves show three exotherms similar to those observed for PmDAS and PDAS, but of much reduced magnitude, suggesting that secondary reactions leading to car-

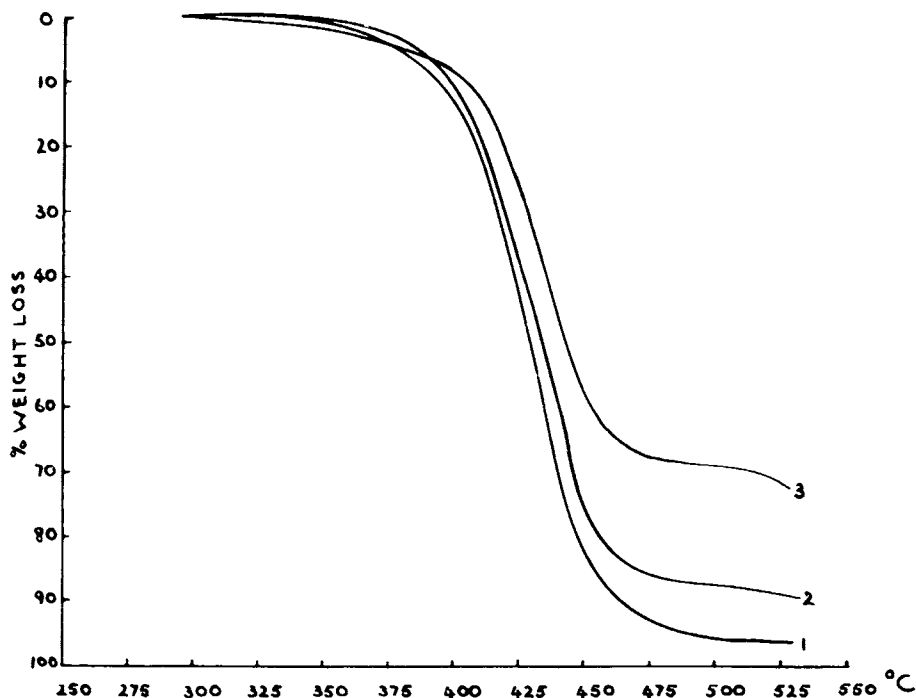


Fig. 8. TG traces for S:m-DAS copolymers in air: (1) S:m-DAS 5; (2) S:m-DAS 6; (3) S:m-DAS 7.

TABLE V
TG Data for *S:m*-DAS Copolymer Degradation in Air

Polymer ^a	<i>S:m</i> -DAS molar ratio	Intrinsic Viscosity [η] ₀	Temperature °C for specified % weight loss			
			0 ^b	10	50 ^c	75
<i>S:m</i> -DAS 5	2.43:1	0.42	314	394	430	445
<i>S:m</i> -DAS 6	1.56:1	0.48	314	398	435	450
<i>S:m</i> -DAS 7	0.56:1	0.55	276	406	441	462 ^d

^a Reference 2,

^b PDT,

^c 50% DT,

^d For 65% weight loss.

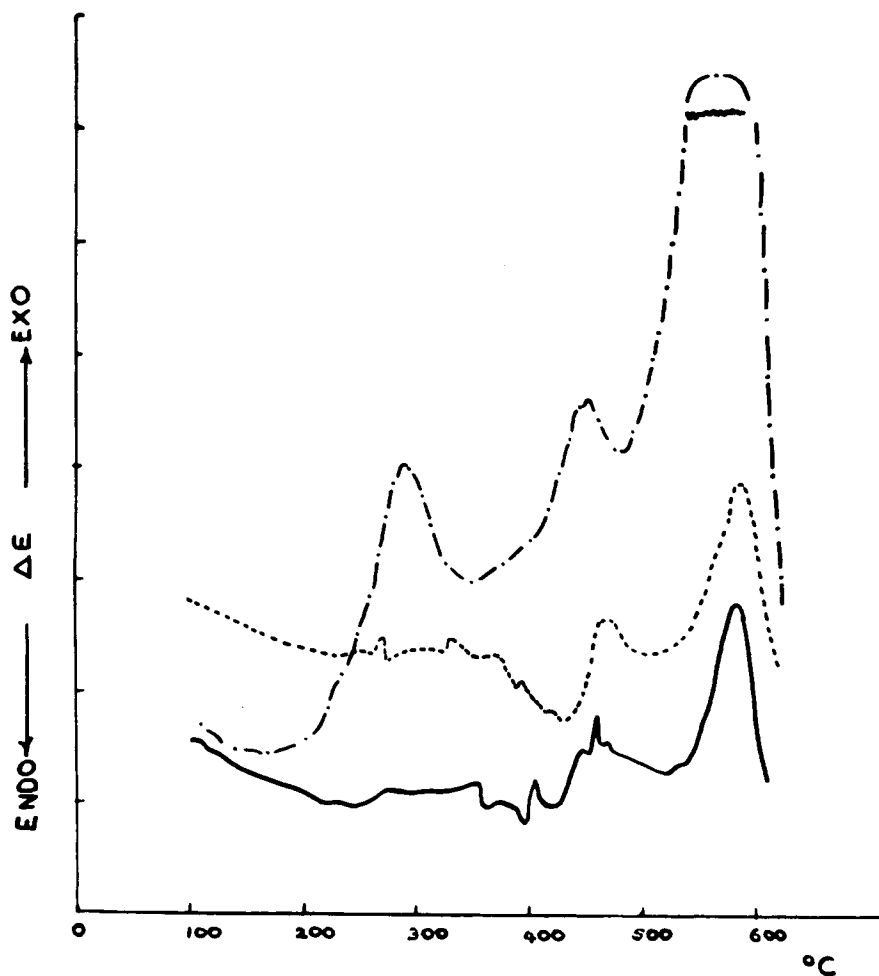


Fig. 9. DSC traces for *S:m*-DAS copolymers in air: (—) *S:m*-DAS 5, sample weight 6.10 mg; (---) *S:m*-DAS 6, sample weight 6.65 mg; (- · - · -) *S:m*-DAS 7, sample weight 7.40 mg.

TABLE VI
 Isothermal TG Data for the Degradation of PMDAS 1, PDEAS 1, and PS (10) in Air

Tem- pera- ture, °C	Time, mins, for specified % weight loss											
	PmDAS 1				PDEAS 1				PS 10			
	0	20	50	75	0	20	50	75	0	20	50	75
367	5	58	—	—	28	63	—	—	0.7	1.5	3.0	4.8
396	1.1	3.4	33	—	2.5	4.5	6.3	22	0.6	1.1	1.8	2.6
422	1.0	1.8	3.5	59	1.0	1.9	3.5	6.6	—	—	—	—
443	0.4	0.7	0.9	6.9	0.7	1.0	1.1	1.5	—	—	—	—

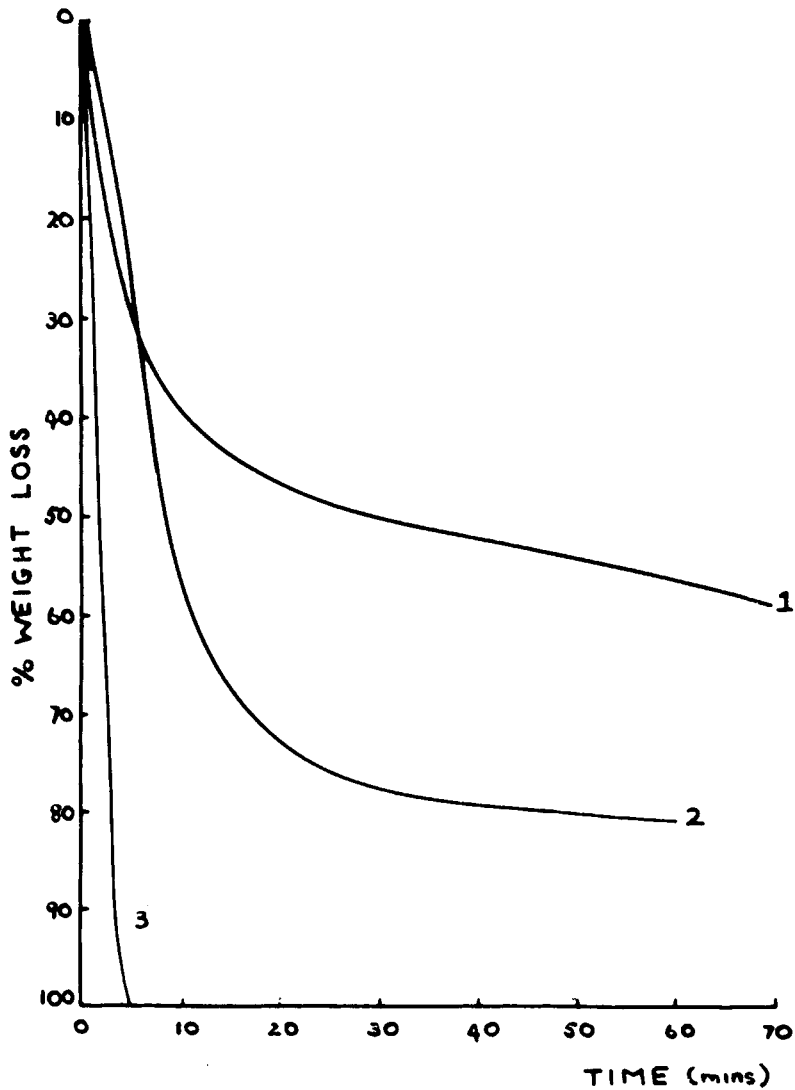
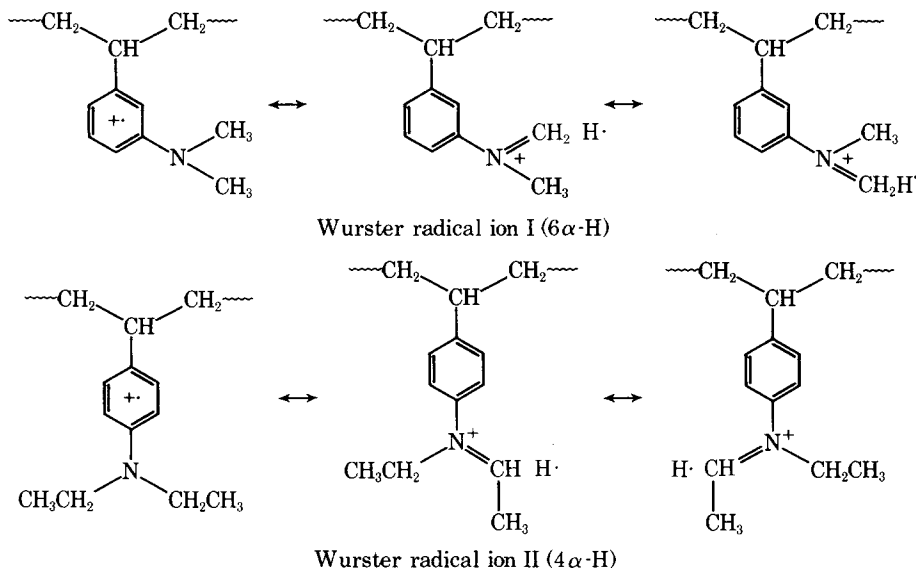


Fig. 10. Isothermal TG traces for PS, PmDAS, and PDEAS at 396°C in air: (1) PmDAS 1; (2) PDEAS 1; (3) PS 10.

bonization and the burning off of a residue are much reduced in this system. Observations on the hot-stage microscope confirm this behavior since both high and low molecular weight samples were converted into a "melt" and remained liquid to 360°C. The TG curves (Fig. 1) similarly show the formation of approximately 10% carbonaceous residue at 525°C. It would, therefore, appear that the PDEAS system is not such an efficient antioxidant as PmDAS or PDAS, and this leads to less secondary reactions of the Wurster radical intermediate produced from PDEAS on reaction with a peroxy radical. Consideration of the Wurster radical ions I and II produced from



PmDAS and PDEAS, shows that they are not of the same stability due to differences in hyperconjugative stabilization⁷ afforded by the α hydrogen atoms of the *N,N*-dialkyl substituents.

Thus, the formation of I would be more favored for PmDAS leading to secondary reactions giving rise to a carbonaceous residue similar to those reported for PDAS.⁴ In the case of PDEAS, although some formation of II would occur, the degradation process with main-chain cleavage similar to that which occurs with PS would predominate. This would lead to less secondary reactions and a reduced tendency towards the formation of a carbonaceous residue.

In Tables IV and V, the degradation parameters obtained by dynamic TG in static air for the styrene:*p*-diethylaminostyrene (S:*p*-DEAS) and the styrene:*m*-dimethylaminostyrene (S:*m*-DAS) copolymers are reported.

The overall degradation behavior of S:*p*-DEAS polymers on TG (Table IV and Fig. 6) and DSC (Fig. 7) is essentially independent of copolymer composition in the range studied. The behavior is similar to that of PDEAS homopolymers (Fig. 1 and Table I). The PDT varies having the lowest value for the copolymer containing the highest percentage of styrene. The displacement of the thermograms to higher temperatures than observed for PS is indicative of some suppression of the oxidative initiation of degradation observed with PS.

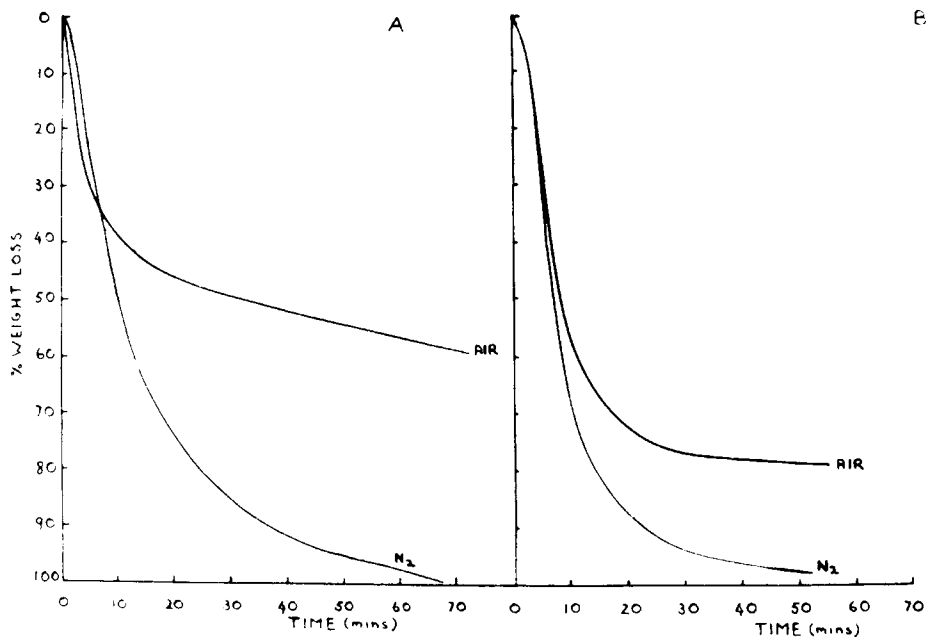


Fig. 11. Isothermal TG traces for PmDAS and PDEAS in air and nitrogen at 396°C: (A) PmDAS 1; (B) PDEAS 1.

In the case of the *S:p*-DEAS copolymer 9, the lowering of the PDT with this system is again indicative of a possible molecular weight effect in the system. The DSC traces for the *S:p*-DEAS copolymers (Fig. 7) show behavior indicating that secondary reactions of the *N,N*-diethylaminostyrene units with peroxy radicals and Wurster radical ion II lead to a low percentage of carbonaceous residue. This is shown by the small exotherm at peak maximum 560°C and the low residue obtained on TG to 530°C (Fig. 6).

The degradation behavior of the *S:m*-DAS copolymers again differs from the corresponding systems containing *p*-DEAS. (Table V, Figs. 8 and 9). The behavior on TG is shown in Fig. 8, and it can be seen that the thermograms are composition dependent and that the residue obtained at 530°C increases with increasing *m*-DAS content in the copolymer system. This behavior is again confirmed on DSC (Fig. 9) where it can be seen that the magnitude of the exotherm at peak maximum of approximately 560°C increases in magnitude with increasing *m*-DAS concentration within the polymer. This behavior again indicates the burning off of a carbonaceous char formed by the secondary reactions of the peroxy radicals with the Wurster radical ion I and the unreacted *m*-DAS units within the chain. As the concentration of styrene increases, the percentage of units available to participate in the antioxidant reaction and subsequent secondary reactions is decreased, and consequently there is an overall higher percentage weight loss prior to burning off of the residue.

The PDT's are higher than for PS, and the value for the *S:m*-DAS copolymer 7 containing the highest concentration of *m*-DAS of the systems studied

is in accord with that expected for a PmDAS sample of similar molecular weight.

The data obtained on isothermal TG studies in air for representative samples of PmDAS, PDEAS, and PS are given in Table VI, and the behavior of the three systems at 396°C is compared in Figure 10, where it can be seen that the basic features shown on dynamic TG and DSC are again observed. If the PmDAS and PDEAS systems are compared in air and nitrogen at 396°C (Fig 11), then the relative effect of the secondary reactions of the two N,N-dialkylamino substituents in air can be seen. In the case of *m*-DAS, the effect is greater than for *p*-DEAS. A total absence of any stabilizing (antioxidant) effect is seen for PS which degrades at a much faster rate in air than in nitrogen.

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References

1. S. Oprea and R. H. Still, *J. Appl. Polym. Sci.*, **20**, 639 (1976).
2. S. Oprea and R. H. Still, *J. Appl. Polym. Sci.*, **20**, 651 (1976).
3. R. H. Still, P. B. Jones, and A. L. Mansell, *J. Appl. Polym. Sci.*, **13**, 401, (1969).
4. R. H. Still and A. Whitehead, *J. Appl. Polym. Sci.*, **20**, 661 (1976).
5. S. L. Malhotra, J. Hesse, and L. P. Blanchard, *Polymer*, **16**(2), 81 (1975).
6. R. H. Still and A. Whitehead, *J. Appl. Polym. Sci.*, **20**, 627 (1976).
7. G. Scott, *Atmospheric Oxidation and Anti-Oxidants*, Elsevier, London, 1965.
8. F. Hrabak and J. Coupek, *Makromol. Chem.*, **145**, 289 (1971).
9. L. Horner, *J. Polym. Sci.*, **18**, 438 (1955).
10. C. E. Boozer and G. S. Hammond, *J. Amer. Chem. Soc.*, **76**, 3861 (1954).

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