

Thermal Degradation of Polymers. II

Further Thermogravimetric and Differential Thermal Analysis Studies of Atactic Poly(*m*-aminostyrene) Homopolymers, Copolymers, and Related Polymers

R. H. STILL, P. B. JONES, and A. L. MANSELL, *Department of Chemistry and Biology, Hatfield College of Technology, Hatfield, Hertfordshire, England*

Synopsis

Thermogravimetric and differential thermal analysis have been employed to study the effect on the thermal degradation pattern in static air of the molecular weight of poly(*m*-aminostyrene) homopolymers and copolymers with styrene. Related substituted styrene polymers and copolymers with styrene have also been studied in order to assess the effect of introduction of amino, substituted amino, and hydroxy groupings into a polystyrene main chain. The effect of these groupings on the thermal stability of the polymers as compared with polystyrene suggests that the inherent antioxidant characteristics of the substituent grouping plays the major role in stabilization. A molecular weight effect has been shown to be operative for *m*-aminostyrene, *p*-*N,N*-dimethylaminostyrene, and *m*-hydroxystyrene polymers. This manifests itself in terms of different thermograms rather than by significantly influencing the procedural decomposition temperatures, although a trend is seen.

INTRODUCTION

In a previous paper^{1*} we studied the effect of introducing both the amino and acetamido groupings into styrene in the meta position and showed that the resultant polymers had a higher thermal stability in static air than polystyrene, as measured by thermogravimetric analysis.

We showed with the then available samples that there was no molecular weight effect and that a copolymer of *m*-aminostyrene and styrene (2 mols of styrene to 1 mol of *m*-aminostyrene) had a thermal stability similar to that of polystyrene.

We now report studies with a series of poly(*m*-aminostyrenes) of significantly different molecular weights and copolymers with styrene having a variety of compositions. In addition we have made studies of other ring-substituted polystyrenes: poly(*m*-hydroxystyrene), poly(?-aminostyrene), poly(*p*-*N,N*-dimethylaminostyrene), and copolymers with styrene.

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EXPERIMENTAL

Materials

The monomer *m*-aminostyrene was synthesized as previously reported²⁻⁴ with a modification at the dehydration stage, which afforded a twofold increase in yield.⁵ The monomer was homopolymerized in bulk under nitrogen with α, α' -azobisisobutyronitrile as initiator at concentrations of 0.2–1.0% on the monomer weight. This yielded poly(*m*-aminostyrenes) numbers 1–9, of atactic stereochemical configuration and different molecular weights. Characterization was effected by determination of their intrinsic viscosities in aniline at 25°C by the procedure described earlier.

The data presented in Table I shows the polymers to have sensibly different molecular weights.

TABLE I

Sample No.	Initiator, %	Intrinsic viscosity $[\eta]_0$
1	0.2	0.64
2	0.25	0.54
3	0.40	0.49
4	0.50	0.45
5	0.75	0.37
6	1.0	0.31
7 ^a	0.2	0.80
8 ^a	0.30	1.22
9 ^a	0.35	0.45

^a Polymerized under different temperature conditions.

Copolymerization of styrene and *m*-aminostyrene in various molar ratios under similar conditions with an initiator concentration of 0.4% on the total monomer weight yielded a 2.35:1 styrene-*m*-aminostyrene copolymer, sample 10A.

ANAL: Found C, (i) 88.32%; (ii) 83.30%; H, (i) 7.76%; (ii) 7.83%; N, (i) 3.90%; (ii) 3.70%. Calcd. for $C_8H_8/C_8H_9N = 2.35:1$ C, 88.45%; H, 7.70%; N, 3.85%. Intrinsic viscosity $[\eta]_0$ in aniline at 25° was 0.54.

A 1.15:1 styrene-*m*-aminostyrene copolymer, sample 11, was analyzed. Found: C, (i) 86.3%; (ii) 86.3%; H, (i) 7.72%; (ii) 7.79%; N, (i) 5.82%, (ii) 5.66%. Calcd. for $C_8H_8/C_8H_9N = 1.15:1$ C, 86.4%; H, 7.63%; N, 5.97%. Intrinsic viscosity $[\eta]_0$ in aniline at 25°C was 0.51.

A 0.5:1 styrene-*m*-aminostyrene copolymer, sample 12, was analyzed.

Found: C, (i) 83.67%; (ii) 83.61%; H, (i) 7.90%; (ii) 7.98%; N, (i) 7.93%; (ii) 7.94%. Calcd. for $C_8H_8/C_8H_9N = 0.5:1$ C, 84.21%; H, 7.60%; N, 8.19%. Intrinsic viscosity $[\eta]_0$ in aniline at 25°C was 0.50.

Poly(*m*-aminostyrene hydrochloride) was prepared by dissolving poly(*m*-aminostyrene), sample 4; $[\eta]_0$ was 0.45 (0.25 g) in the minimum quantity of 0.1*N* hydrochloric acid (21 ml), and an excess (2 ml) was added. Concentrated hydrochloric acid (30 ml) was added dropwise with vigorous

stirring, to precipitate the polymer. The precipitate was dissolved in water (10 ml) and added dropwise to concentrated hydrochloric acid (50 ml) with stirring; the white precipitate was obtained by filtration through a No. 3 sinter under suction. The product was dried *in vacuo* over calcium chloride and potassium hydroxide pellets. The product was ground to a fine powder and dried at 60°C and 0.1 mm.

m-Hydroxystyrene was prepared from *m*-aminostyrene by a modification of the procedure of Matsui.⁶ *m*-Aminostyrene (10.25 g) was dissolved in concentrated sulfuric acid (25 g) and distilled water (600 ml); a white solid precipitated, which was insoluble in excess distilled water (200 ml). The solution was cooled to 0–5°C with mechanical stirring, and an ice-cold aqueous solution of sodium nitrite (6.2 g) in water (20 ml) was added dropwise during 5 min; the solid dissolved, yielding a pale-yellow solution. A cold, aqueous, 1% urea solution (20 ml) was added, to destroy the excess of nitrous acid. The solution was decanted into a 3-liter flask equipped with a reflux condenser and heated on a boiling-water bath until nitrogen ceased to be evolved (30 min). The solution was steam-distilled, and the distillate (1 liter) was extracted with ether and dried over anhydrous sodium sulfate, and the ether was removed by distillation, yielding crude *m*-hydroxystyrene as a pale-yellow oil (4.85 g). It had a boiling point of 53°C at 0.1 mm, yielding as the main fraction 2.45 g (40%); $n_D^{25} = 1.5810$ (lit.⁶ $n_D^{31} = 1.5790$).

m-Hydroxystyrene was polymerized in bulk at 70°C under nitrogen with α, α' -azobisisobutyronitrile (0.4%). After 90 min a pale-yellow glass was obtained, which was dissolved in dioxane and added to water, yielding a white solid (1.4 g), 57%. It was soluble in sodium hydroxide solution and acetone, unlike that previously prepared by Matsui, which was insoluble in these solvents. The polymer was dried to constant weight at 63°C at 0.1 mm.

ANAL. Found: C, 80.04%; H, 6.45%; O, 13.38%. C_8H_8O requires C 79.99%; H 6.72%, O 13.29%.

The polymer was characterized by intrinsic viscosity determinations in 0.2*N* sodium hydroxide solution at 25°C, yielding $[\eta]_0 = 0.41$. Similarly, with an initiator concentration of 0.1% a polymer of $[\eta]_0 = 0.59$ was prepared.

Styrene was polymerized with α, α' -azobisisobutyronitrile at two different initiator concentrations, yielding polystyrenes (samples 13 and 14) of molecular weights 150,000 and 210,000, respectively, as derived from the Mark-Houwink equation $[\eta]_0 = KM^\alpha$, where $[\eta]_0$ was determined in toluene at 25°C, and the constants *K* and α are those reported by Green⁷ to be $K = 1.16 \times 10^{-4}$ and $\alpha = 0.72$.

Apparatus and Procedure

Thermogravimetric Analysis. A Stanton thermobalance, model HT-M, was used, programmed for a linear heating rate of 3°/min (nominal) in

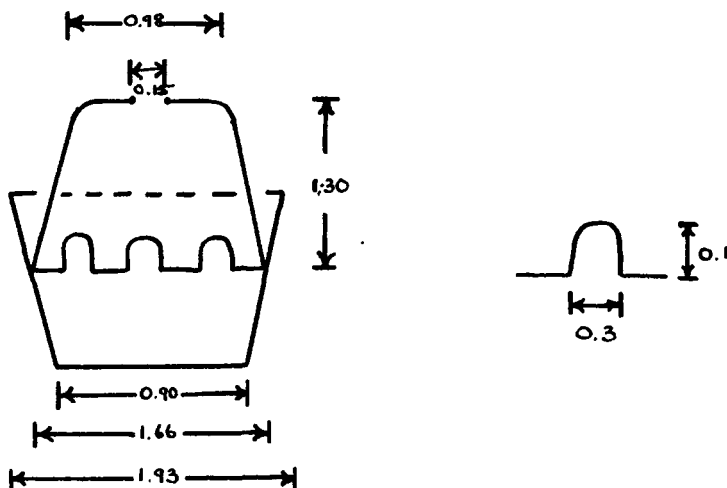


Fig. 1. Covered Crucible (all measurements in centimeters).

static air. Approximately 100 mg of material was employed in each experiment, and samples were contained in preignited, recrystallized alumina crucibles (Royal Worcester, size WA 2) in all experiments except those involving poly(*m*-aminostyrene hydrochloride). This polymer was found to lose volatiles so rapidly that particles of solid were ejected from the crucible. In these experiments a covered crucible of the type shown diagrammatically in Figure 1 was used. In this way solid was prevented from being ejected from the crucible, while volatiles were relatively free to leave the crucible. The lower crucible was a normal WA2, and the upper crucible had a hole drilled in the base and a series of indentations (six) around the circumference, through which volatiles were lost. The crucible was preignited prior to use, and a buoyancy correction was made in the experiments in which it was used. Its effect on the loss of volatiles is discussed in the next section.

In experiments carried out in a dynamic gas atmosphere pure (white spot) nitrogen was employed at a flow rate of 400 ml/min.

All temperatures quoted for TGA experiments are furnace wall temperatures.

Differential Thermal Analysis. The DTA was carried out with a laboratory-built DTA equipment based on designs of Hogson⁸ and Wilburn⁹ for the crucible holder and measuring system, respectively. Samples diluted with 50% recrystallized alumina were heated in static air at 10 °/min (nominal).

RESULTS AND DISCUSSION

TGA results in static air and dynamic nitrogen have shown that for all polystyrene, poly(*m*-aminostyrene), poly(*p*-*N,N*-dimethylaminostyrene), and poly(*m*-hydroxystyrene) polymers no stable intermediate compounds

were formed during pyrolysis. However, in the case of poly(*m*-aminostyrene hydrochloride) this compound shows a horizontal plateau at 300–340°C, and effluent analysis indicates that an acid gas is evolved in the region

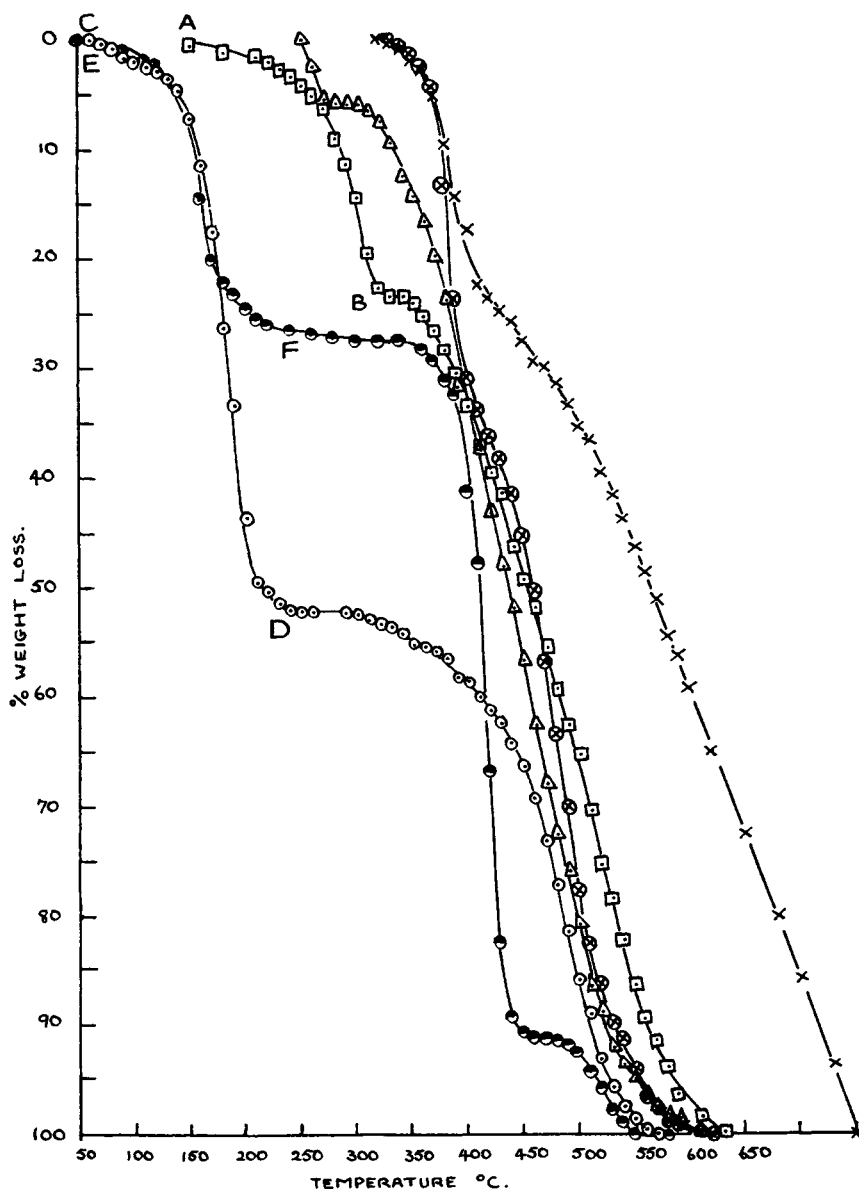


Fig. 2. TGA curves: (○) poly(*p*-vinyl trimethyl phenyl ammonium iodide); (●) *p*-vinyl trimethyl phenyl ammonium iodide-styrene copolymer (0.5:1 molar ratio); (◻) poly(*m*-aminostyrene hydrochloride), covered crucible; (Δ) poly(?-aminostyrene); (X) poly(*m*-aminostyrene), covered crucible, $[\eta]_0=0.45$; (⊗) poly(*m*-aminostyrene), normal crucible, $[\eta]_0 = 0.45$.

of 150–300°C. The weight loss that occurred was 23.3%; see A-B in Figure 2. This is in accord with the theoretical weight loss of 23.4% for the loss of hydrogen chloride. After the initial loss of hydrogen chloride, the polymer decomposes at the normal temperature for the decomposition of poly(*m*-aminostyrene), as is shown in Figure 2, where both polymers are compared under identical conditions in the covered crucible. The effect of the crucible was merely to slow down the later stages of the reaction; the procedural decomposition temperature was not affected.

Similarly poly(*l*-aminostyrene), sample 15, which is not a linear polymer, shows a horizontal plateau at 270–300°C after an initial weight loss at 250°C; see Figure 2. This polymer, because of its mode of preparation via nitration of a polystyrene sample,¹⁰ is certainly crosslinked, being insoluble in common solvents for linear poly(*m*-aminostyrene). It probably contains, in addition to some unreduced nitro groupings, more than one amino grouping per benzene nucleus. It is also certainly oxidized, being brown in color, in contrast to linear poly(*m*-aminostyrene), which is white. The complete characterization of the sample is impossible because of the insolubility, but it is thought that substitution is predominantly in the para position.

TGA traces similar to that for poly(*l*-aminostyrene) have been obtained by subjecting linear poly(*m*-aminostyrene) powder to ultraviolet irradiation ($\lambda = 2537 \text{ \AA}$) in air for 24 hr when surface oxidation is evident from its discoloration.

The intermediate formation of stable products on TGA in static air was also observed with the polymeric quaternary ammonium salts derived by reaction of methyl iodide with poly(*p-N,N*,*-dimethylaminostyrene*) homopolymers and copolymers with styrene. Here again effluent analysis and weight loss observations indicate the loss of methyl iodide (curves C-D and E-F), leaving the polymer to decompose at its normal temperature (Fig. 2).

The stability of the substituted polymers has been compared to that of polystyrene in terms of the procedural decomposition temperature (PDT),

TABLE II

Polymer	PDT, °C	
	Air	Nitrogen
Polystyrene	260	350
Poly(<i>m</i> -aminostyrene)	310–370*	360
Poly(<i>m</i> -hydroxystyrene)	290–340*	340
Styrene- <i>m</i> -aminostyrene copolymer, 2.35:1	280–300*	320
Poly(<i>p-N,N</i> -dimethylamino- styrene)	230	350
Styrene- <i>p-N,N</i> -dimethylamino- styrene copolymer, 2:1	340	330

* Dependent on molecular weight.

the temperature at which the first observable weight loss occurs. A summary of the PDT data obtained for the polymers studied in static air and dynamic nitrogen is shown in Table II.

The stabilities of the polymers studied in dynamic nitrogen were found to be of similar orders, and the molecular weight did not affect either the PDT or the shape of the thermogram obtained to any significant extent in any case.

The PDT data obtained in static air, however, shows that there are marked differences in the stabilities of the polymers studied, as compared with polystyrene.

The PDT in static air for all poly(*m*-aminostyrene) homopolymers and copolymers have been compared to polystyrene samples 13 and 14, as shown in Tables IIIA and B.

TABLE IIIA

Sample No.	$[\eta]_0$	PDT, °C
Poly(<i>m</i> -aminostyrene)		
1	0.64	330
2	0.54	330
3	0.49	350
4	0.45	340
5	0.37	350
6	0.31	370
7	0.80	310
8	1.22	330
9	0.45	350

TABLE IIIB

Styrene- <i>m</i> -aminostyrene, copolymers molar ratio	Sample No.	$[\eta]_0$	PDT, °C
2.35:1	10A	0.54	300
2.35:1	10B	1.15	280
1.15:1	11	0.51	300
0.5:1	12	0.50	300
Polystyrene	13	—	260
	14	—	260
Poly(<i>p</i> -aminostyrene)	15	—	250

The effect of molecular weight on the PDT of poly(*m*-aminostyrene) is small, those polymers of lower molecular weight in general being slightly more stable. The results bear out previous observations of the PDT of poly(*m*-aminostyrene), sample 15 being anomalous in the series, as previously indicated.

In the case of the copolymers the introduction of *m*-aminostyrene units into the polystyrene chain manifests itself in an increased thermal stability, as compared with polystyrene, at all compositions studied.

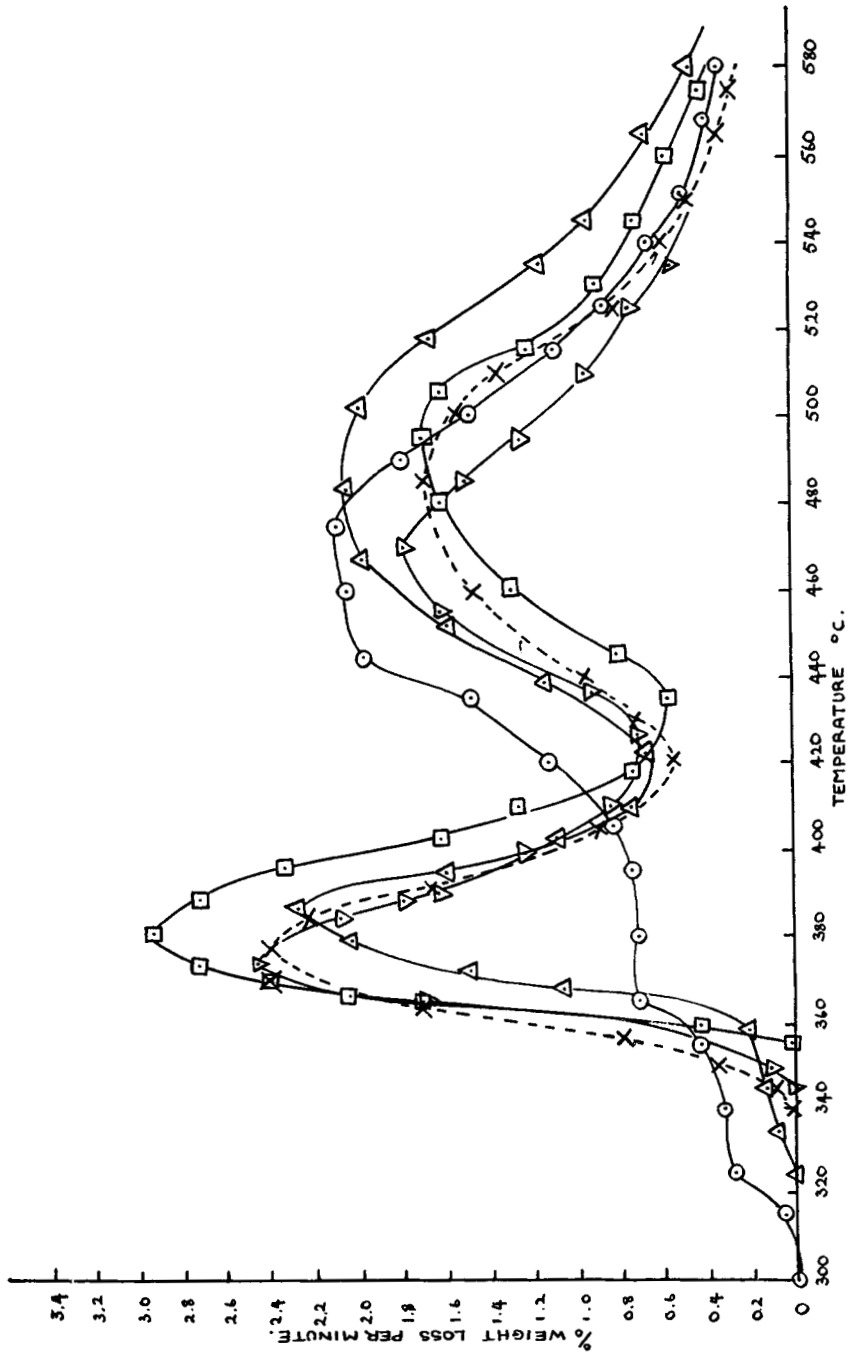


Fig. 3. Poly(*m*-aminostyrene) homopolymers, TGA curves. Intrinsic viscosity $[\eta]$: (□) 0.31; (▽) 0.37; (X) 0.45; (△) 0.64; (○) 0.80.

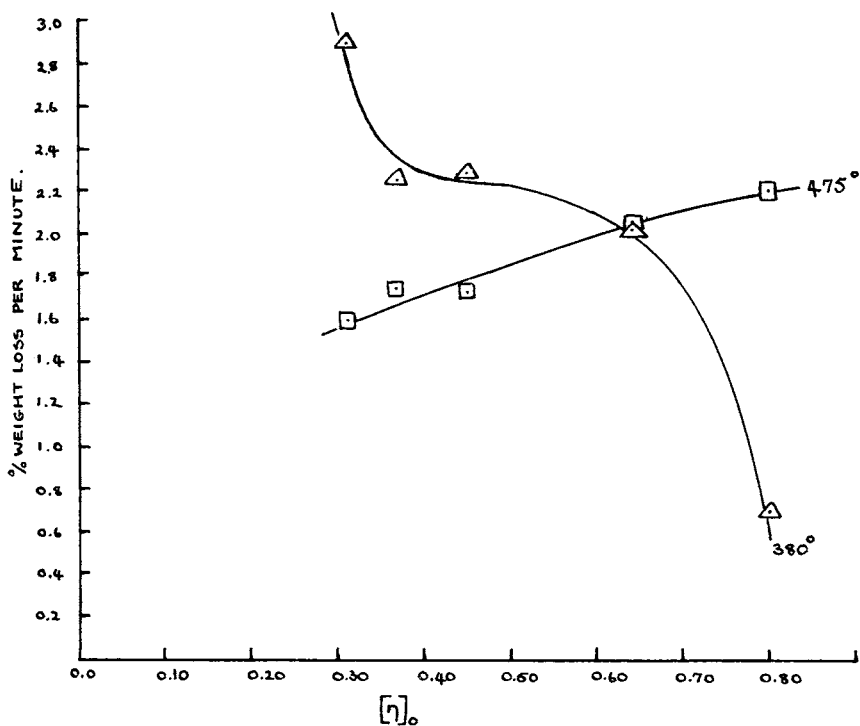


Fig. 4. Poly(*m*-aminostyrene) homopolymers: per cent weight loss versus intrinsic viscosity.

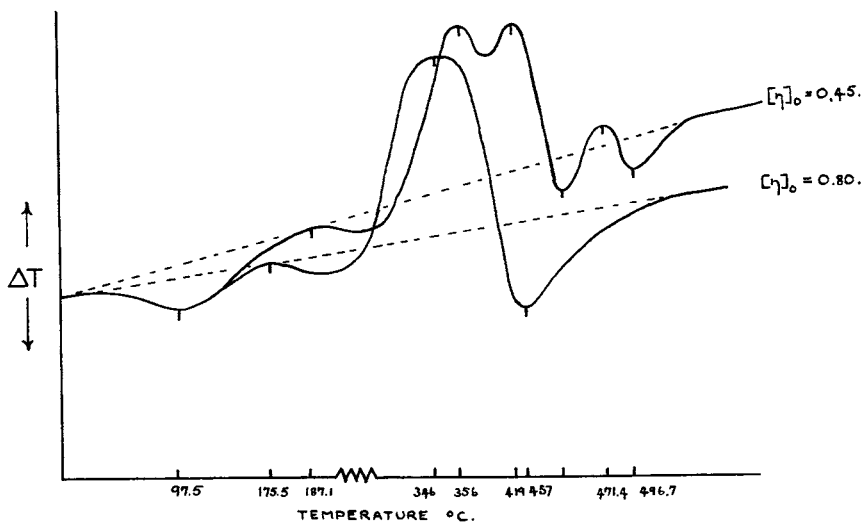


Fig. 5. DTA curves: in air for poly(*m*-aminostyrene) homopolymers; dotted line is baseline.

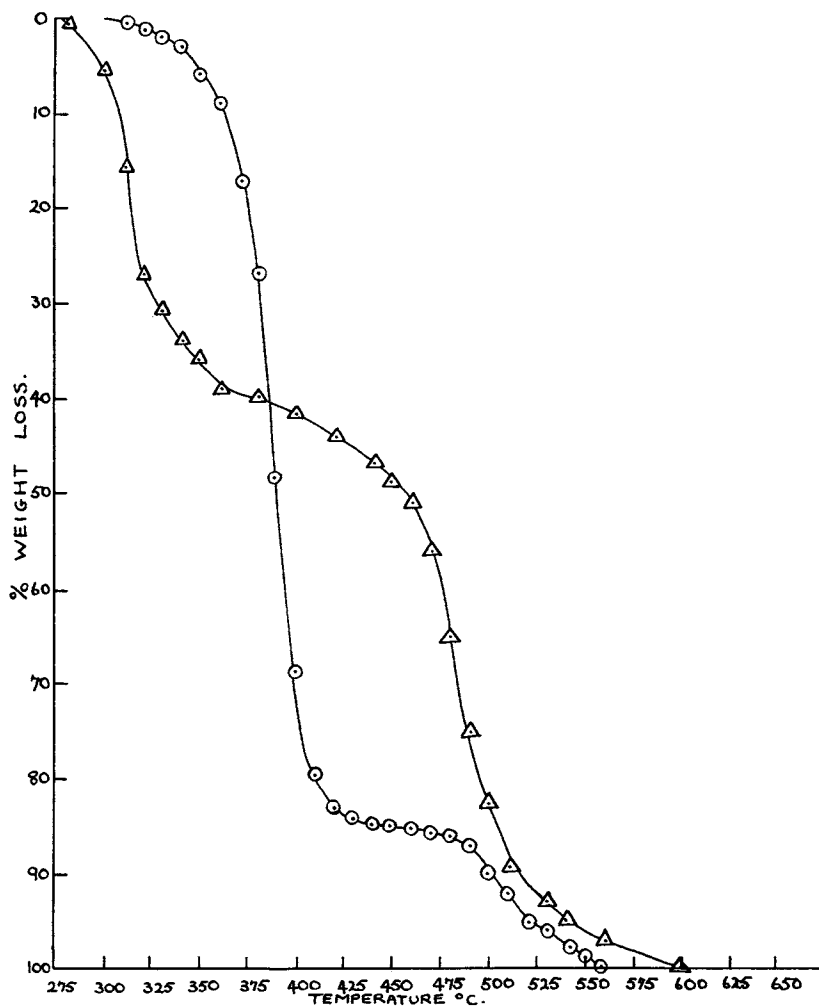


Fig. 6. TGA curves for 2.35:1 molar ratio styrene-*m*-aminostyrene copolymers. Intrinsic viscosity $[\eta]_0$: (○) 0.50 (sample 10A); (Δ) 1.15 (sample 10B).

The effect of molecular weight and copolymer composition upon the thermal degradation of these polymers is not evident merely from a study of the PDT data given in Table III.

TABLE IV

Poly(<i>m</i> -amino- styrene), sample No.	$[\eta]_0$	Avg. mol. wt. ratio	PDT, °C
7	0.80	3.27	310
1	0.64	2.45	330
4	0.45	1.59	340
5	0.37	1.22	350
6	0.31	1.00	370

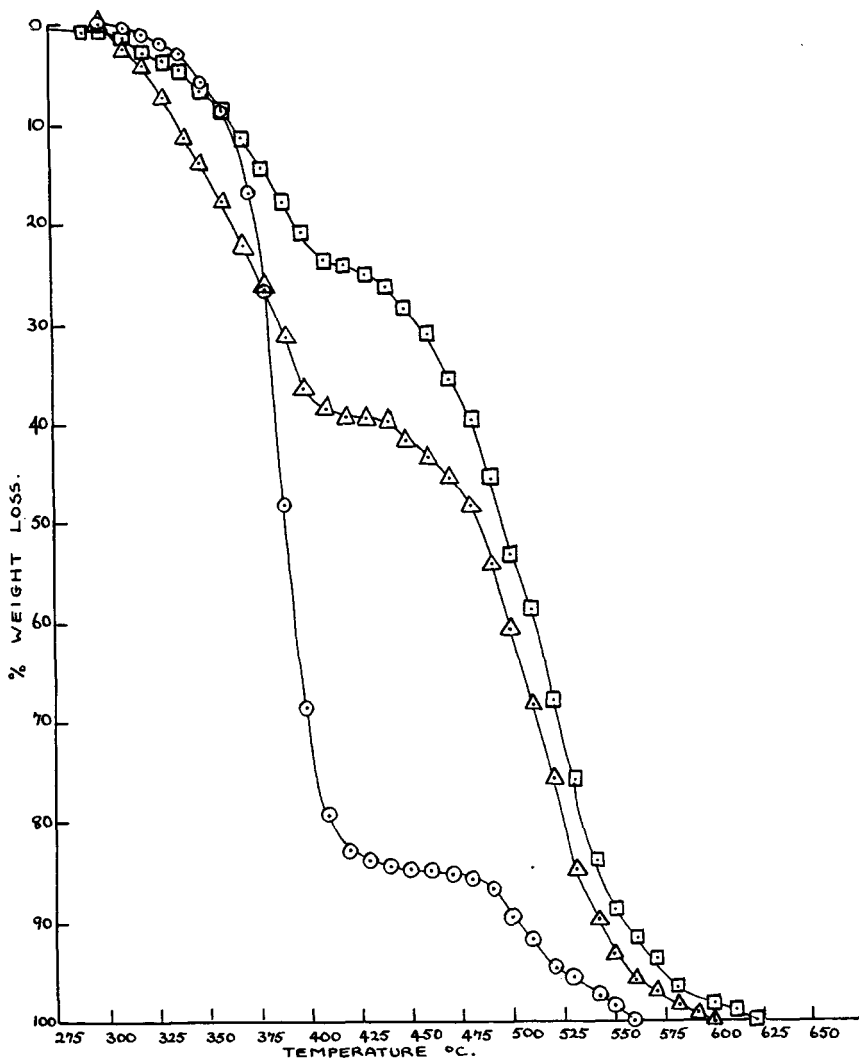


Fig. 7. TGA curves for styrene-*m*-aminostyrene copolymers. Molar ratios: (○) 2.35:1 (sample 10A); (△) 1.15:1 (sample 11); (◻) 0.50:1 (sample 12).

Data on the rate of weight loss versus temperature for five of the homopolymers studied are plotted in Figure 3. Their absolute molecular weights are unknown, since the constants in the Mark-Houwink equation have not been evaluated for the system. However, if 0.8 is taken as a realistic value for α ,¹¹ the average molecular weight ratio may be calculated relative to sample 6, as is shown in Table IV.

The data presented in the table show the polymers to have significantly different molecular weights, and it is evident that molecular weight has a profound effect on the thermal degradation patterns of these samples.

Polystyrene samples 13 and 14, by contrast, show identical behaviors although their average molecular ratio is 1:1.40. That molecular weight has a profound effect on the thermal degradation can be further shown by plotting percent weight loss per minute against $[\eta]_0$ at a constant temperature, taken as the temperature at which maximum weight loss occurs for the two processes occurring in the degradation, respectively 380 and 475°C; see Figure 4.

In accord with the rates of weight loss presented in Figure 3 the thermograms obtained for the two most extreme polymers, with $[\eta]_0$ of 0.31 and 0.80, show a two-process weight loss curve and a smooth curve, respectively, with intermediate behavior for the other polymers; that is, the first process gradually decreases as $[\eta]_0$ increases.

This molecular weight effect is further borne out from a study of the DTA traces obtained for the two extreme polymers (Fig. 5), which show the mechanisms of degradation to differ.

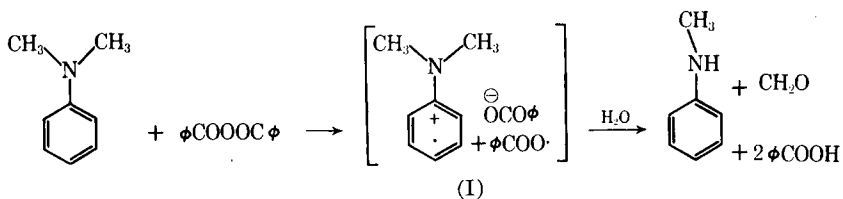
With the copolymers a molecular weight effect has been shown to be operative in the case of the copolymer of 2.35:1 molar ratio, where two samples of differing molecular weight were available (samples 10A and 10B), and the thermograms for these polymers are shown in Figure 6.

It can be seen again that, as the molecular weight increases, the first process of degradation is reduced, as in the case of poly(*m*-aminostyrene), and again the higher molecular weight polymer has the lower PDT: 280 as compared with 300°C. The effect of altering the composition of the copolymers shows itself in the nature of the thermograms obtained. The polymers have similar $[\eta]_0$ values, and each shows a plateau indicating a region of low weight loss; this plateau appears at lower percentage weight loss as the concentration of styrene in the polymer increases; see Figure 7.

The observation that the homopolymers in static air had thermal stability that was higher than polystyrene, whereas the copolymers had stabilities intermediate between that of polystyrene and poly(*m*-aminostyrene), suggests that the stability may be a direct result of the concentration of amino groupings.

Homopolymers of *m*-hydroxystyrene, *p*-*N,N*-dimethylaminostyrene, and the 2:1 copolymer of *p*-*N,N*-dimethylaminostyrene and styrene have also been studied; the thermograms are shown in Figure 8. A similar molecular weight effect can be seen to be operative in the case of the two homopolymers. The PDT data for these polymers are recorded in Table II, from which it can be seen that the greater thermal stability of the styrene copolymers of *p*-*N,N*-dimethylaminostyrene and *m*-aminostyrene than that of polystyrene are indicative of inhibition of the oxidative initiation of degradation. Similarly, the greater PDT's of poly(*m*-hydroxystyrene) and poly(*m*-aminostyrene) in air may also be ascribed to the well-known anti-oxidant behavior of amines and phenols, which are often used as stabilizers for polyolefins.¹² Such compounds react by decomposing the peroxides and hydroperoxides produced by reaction of oxygen with the polymer chain and thereby prevent the loss of volatiles at lower temperatures. The

behavior of poly(*p-N,N*-dimethylaminostyrene) in air, showing a low thermal stability, is probably due to reaction with oxygen, leading to formaldehyde, which is volatile at the temperature of pyrolysis. The loss of alkyl groups from nitrogen is well known in the oxidation of aromatic amines.¹² Horner,¹³ for example, explains the dealkylation of dimethylaniline by benzoyl peroxide with the following equation involving the Würster radical ion intermediate (I):



The molecular weight effects shown in Figures 3, 4, and 6 for *m*-aminostyrene polymers are also shown by other polymers that have antioxidant properties: poly(*m*-hydroxystyrene) and poly(*p-N,N*-dimethylaminostyrene), Figure 8. This effect possibly may be ascribed to the gradual release of short chains containing unreacted antioxidant groupings from within the coiled macromolecule, leading to the inhibition of the oxidative initiation of degradation. For the low molecular weight polymers there are a greater number of short chains initially available, leading to a longer retardation period and, hence, a higher PDT. This eventually leads to a greater rate of weight loss when the number of available antioxidant groupings is reduced. In the case of the higher molecular weight polymers there are, on the average, fewer short-chain molecules available, leading to a lower PDT, but the rate of weight loss does not increase so rapidly. This lowering in the rate of weight loss is probably due to the slower release of antioxidant groupings, which continue to retard partially the process of oxidative initiation of degradation.

It is also of interest that 2:1 mixtures, by weight, of polystyrene powder and poly(*m*-aminostyrene) or of poly(*p-N,N*-dimethylaminostyrene) powders show increased PDT: 290 and 300°C, respectively. The results show that for these mixtures, of which only partial mixing was obtained by shaking the powders together, there is an increased stability conferred on the major component, polystyrene, indicative of antioxidant characteristics. The characteristics of these polymers may be of use where antioxidants having relatively high thermal stabilities are required.

The pyrolysis of poly(*m*-aminostyrene) in vacuo is in the course of study, and results so far obtained indicate that molecular weight has no significant effect on the degradation, as would be expected. The products of pyrolysis may be divided into four distinct fractions: (1) a gaseous fraction consisting of carbon dioxide, propane, propylene, methane, and ethane, (2) a liquid fraction containing mainly *m*-aminostyrene and *m*-toluidine together with traces of *m*-ethylaniline, aniline, and α -methyl-*m*-aminostyrene,

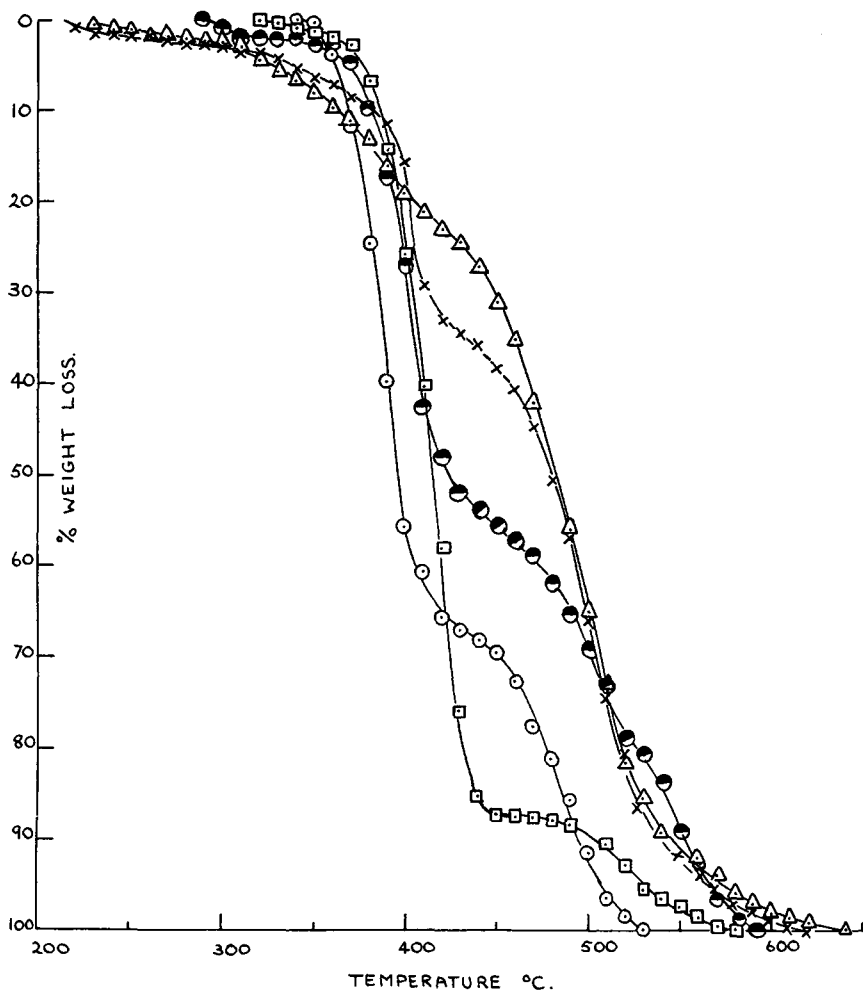


Fig. 8. TGA curves: (x) poly(*p*-*N,N*-dimethylaminostyrene), lesser mol. wt.; (Δ) poly(*p*-*N,N*-dimethylaminostyrene), greater mol. wt.; (\square) *p*-*N,N*-dimethylamino-styrene-styrene copolymer (0.50:1 molar ratio); (\circ) poly(*m*-hydroxystyrene), $[\eta]_0 = 0.41$; (\bullet) poly(*m*-hydroxystyrene), $[\eta]_0 = 0.59$.

(3) a gum, volatile at pyrolysis temperature but involatile at room temperature, consisting of dimer and trimer, and (4) a crosslinked residue.

Quantitative results and further investigations of the nature of the stability of amino-substituted styrene polymers will be the subject of a future communication.

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