

**Thermal Degradation of Polymers. Part IV.
Vacuum Pyrolysis of Poly(*m*-aminostyrene).
The Residue and the Fraction Volatile at
Pyrolysis Temperature Involatile at
Room Temperature**

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Synopsis

The effect of the extent of degradation of poly(*m*-aminostyrene) on the quantity and composition of the residue and the effect of pyrolysis temperature on the fraction volatile at pyrolysis temperature are discussed. The behavior of poly(*m*-aminostyrene) is compared to that of polystyrene; a significant difference has been found for the behavior of the residue from poly(*m*-aminostyrene), which is ascribed to a crosslinking reaction involving the amino substituent. Mechanisms to account for the observed products of degradation have been suggested and are discussed. Relative thermal stability studies have also been made and compared with results from polystyrene.

INTRODUCTION

In previous paper¹ we reported the effect of molecular weight and pyrolysis temperature on the products of degradation of poly(*m*-aminostyrene) volatile at pyrolysis temperature and liquid or gaseous at room temperature. We found that the nature and composition of the pyrolysis products were independent of molecular weight. Pyrolysis temperature was found to affect the yield of monomer obtained, and this was similar in behavior to that reported for polystyrene.² A mechanism of degradation to account for monomer production was proposed, similar to that for polystyrene.³ The other major product in the monomer fraction, *m*-toluidine, was found to be constant independently of pyrolysis temperature and two possible mechanisms for its formation were discussed.

The composition and quantity of the gaseous fraction was essentially independent of the pyrolysis temperature. The products in this fraction were accounted for on the basis of cracking of the pyrolysis products in the hot zone of the furnace.

We now report studies on (a) the fraction volatile at pyrolysis temperature and involatile at room temperature, (b) the residue, and (c) relative thermal stability measurements.

EXPERIMENTAL

Materials

As previously described in Part III.

Apparatus and Procedure

Mass spectrometry, (MS), infrared and ultraviolet spectroscopy (IR, UV), nuclear magnetic resonance (NMR), and gas-liquid chromatography (GLC) measurements were carried out as previously described in Part III.

Electron Spin Resonance (ESR). Spectra were recorded on a Varian ESR spectrometer model E.3 and samples were compared with a standard containing 3×10^{15} spins.

Thermogravimetric Analysis (TGA). Studies on the residue were carried out in static air using a Stanton thermobalance model HT-M programmed for a heating rate of 3° per minute nominal. Samples were contained in preignited recrystallized alumina crucibles, Royal Worcester size WA2. All temperatures quoted are furnace wall temperatures and all curves were corrected for buoyancy effects. Sample sizes were 100 mg.

Vacuum Pyrolysis. Studies were carried out in the apparatus previously described.¹ Polymer pyrolysis was effected as before and the two fractions were obtained as described below.

Fraction IV—the residue—was obtained at low-percentage degradation as a yellow glass which darkened in color until at high conversion a slight black residue was obtained. UV and IR studies were carried out on this fraction, and the effect of percentage degradation on the intrinsic viscosity of the residue was investigated.

Intrinsic Viscosity Measurements on the Residue. The residue was not completely soluble in the solvents used for the characterization of linear poly(*m*-aminostyrene). Thus the insoluble “gel” was removed for its estimation by the following procedure.

The glasses obtained from the pyrolysis of poly(*m*-aminostyrene) at 315°C for periods of 10, 20, 45, 90, 180, and 360 minutes were broken into small pieces. Two separate samples were weighed into two 10 ml volumetric flasks which were made up to the mark with aniline. The flasks were flushed with nitrogen and placed in an air oven at 60°C for 12 hr. The solution after such treatment contained undissolved polymer which was removed by centrifugation at 3000 rpm for 20 min.

The centrifuge tubes were preheated to constant weight at 100°C/0.1 mm. The solution was decanted from the gel and the tube was again heated to constant weight and the weight of gel obtained by difference. This weight was used to correct the concentrations used in subsequent intrinsic viscosity studies.

The intrinsic viscosity of the soluble part of the residue was determined by the dilution procedure previously described.⁴

Fraction V—the oil fraction volatile at pyrolysis temperature—was obtained by pyrolysis of poly(*m*-aminostyrene) samples carried out as pre-

viously described.¹ The furnace was preheated to pyrolysis temperature in the region of 340–500°C. A general pyrolysis time of 30 min was used but the lower temperatures required longer heating times to yield measurable quantities of product.

After the furnace was removed, the system was left pumping for 1 hr. Air was then admitted and the quartz tube was detached from the system. The oil was removed from the tube by extraction with three aliquots of redistilled chloroform (25, 10, 10 ml). The extracts were combined and placed in a stainless steel crucible preheated to constant weight. The chloroform was then removed by evaporation and the crucible heated to constant weight in an air oven at 60°C.

Number-Average Molecular Weight Determinations. Studies were carried out using a Gallenkamp ebulliometer. Chloroform was chosen as the solvent and the instrument was calibrated using benzil as standard prior to each determination.

Known weights of oil were admitted to the refluxing solvent in the ebulliometer by the following procedure. The oil was sealed in glass ampuls under nitrogen for storage purposes. The ampuls were broken open and weighed, chloroform (2 to 3 ml) was withdrawn from the ebulliometer vessel using a syringe with a long cannula, and the solvent was added to the ampul to dissolve the oil. The solution was then returned to the ebulliometer vessel. A further aliquot (2 to 3 ml) was removed from the vessel to rinse the ampul and this was returned to the vessel. After drying the ampul at 60°C to constant weight, the amount of oil added was found by difference.

Relative Thermal Stability Studies. The dried polymer sample (~50 mg) was weighed into a preignited porcelain boat and placed into the pyrolysis apparatus. The system was evacuated and the sample degassed for 2 hr, after which time the pressure was below 10^{-6} cm Hg. The furnace preheated to the required temperature at its "hot spot" was then located over the boat and the sample heated for exactly 30 min.

All volatile fractions were collected in the normal manner. After 30 min the furnace was removed and the system was allowed to cool to room temperature. Air was then admitted and the residue in the boat weighed.

In this manner polystyrene, poly(*m*-aminostyrene) I and II, and a 1.15:1 molar ratio copolymer of styrene and *m*-aminostyrene were studied.

RESULTS AND DISCUSSION

Fraction IV—The Residue

This fraction varied in color from a pale yellow to a black carbonaceous solid depending upon the extent of degradation of the sample. Infrared and ultraviolet spectra recorded at 5, 50, and 80% volatilization were identical with that of the undegraded polymer.

In the degradation of polystyrene, one of the most significant features is the molecular weight change of the residue accompanying degradation. The molecular weight of polystyrene has been shown to fall markedly in

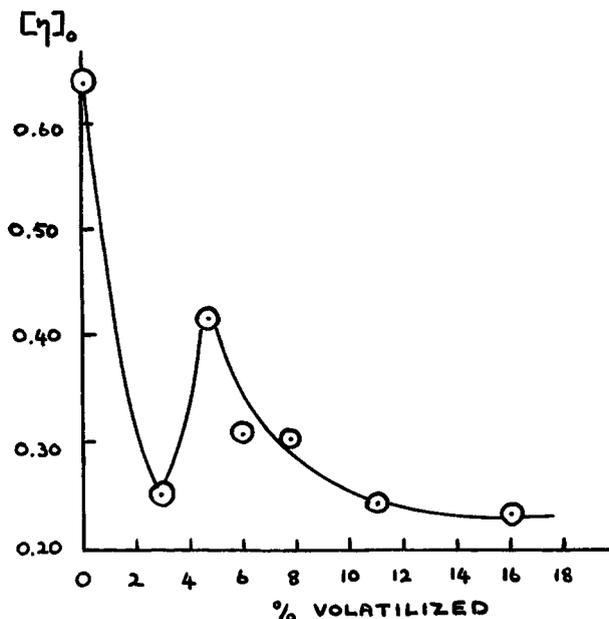


Fig. 1A. The effect of extent of degradation on the intrinsic viscosity of the soluble part of the residue.

the first few per cent weight loss and to stabilize at a value of 60–80,000 by a number of authors.^{5–8}

In order to establish if poly(*m*-aminostyrene) behaved similarly, intrinsic viscosity measurements were made on the residue. The poly(*m*-aminostyrene) residue after a few per cent weight loss shows an immediate difference in behavior to that observed for polystyrene. The residue becomes partially insoluble in aniline, the normal characterizing solvent for the linear polymer. The intrinsic viscosity of the soluble part of the residue was determined and the concentration terms were corrected for the insoluble material.

The effect of percentage degradation on intrinsic viscosity for a poly(*m*-aminostyrene) homopolymer $[\eta]_0 = 0.64$ prior to degradation is shown in Figure 1A. The graph indicates that intrinsic viscosity stabilizes to some extent at $[\eta]_0 = 0.25$.

The values of K and α in the Mark-Houwink equation have not been determined for the system, but if $K = 1.0 \times 10^{-4}$ and $\alpha = 0.7$ are taken as reasonable approximations,⁶ $[\eta]_0$ is found to have values of 0.22 to 0.27 in the molecular weight range 60–80,000.

Thus it appears that stabilization occurs at a similar value to that for polystyrene and further studies on a variety of poly(*m*-aminostyrenes) of different molecular weights have indicated this to be the case.

In addition we have utilized the observation made in an earlier paper⁴ that poly(*m*-aminostyrene) on TGA in static air shows a molecular weight

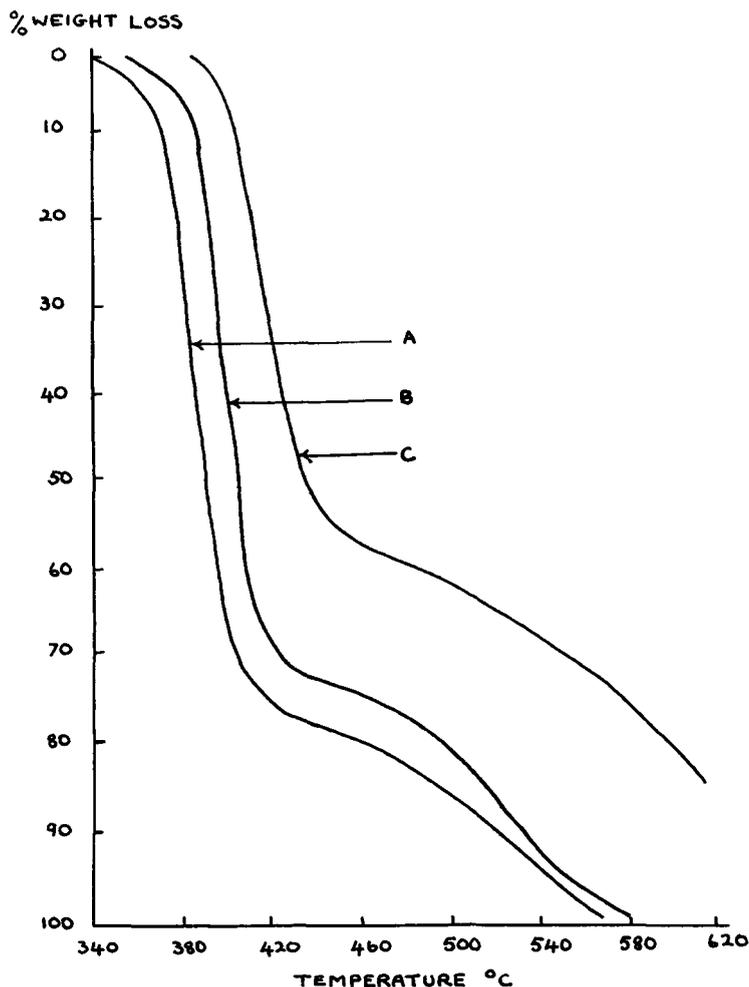


Fig. 1B. TGA curves of the residues from the degradation of poly(*m*-aminostyrene) I: *A*, residue after 48.3% weight loss (displaced 20° toward the ordinate); *B*, residue after 12.6% weight loss; *C*, residue after 5.2% weight loss (displaced 20° away from the ordinate).

effect upon thermogram shape. Thus the thermograms of the residue after a few per cent weight loss should become identical if stabilization occurs. Thermograms for residues after different extents of degradation are shown in Figure 1B whence it can be seen that the traces do become essentially identical.

Similar studies on polystyrene would not, however, provide information concerning the molecular weight of the residue since no such molecular weight effect is observed on thermogram shape.

Figure 2 shows the effect of extent of degradation upon the percentage of insoluble material present in the residue. As pyrolysis proceeds, the

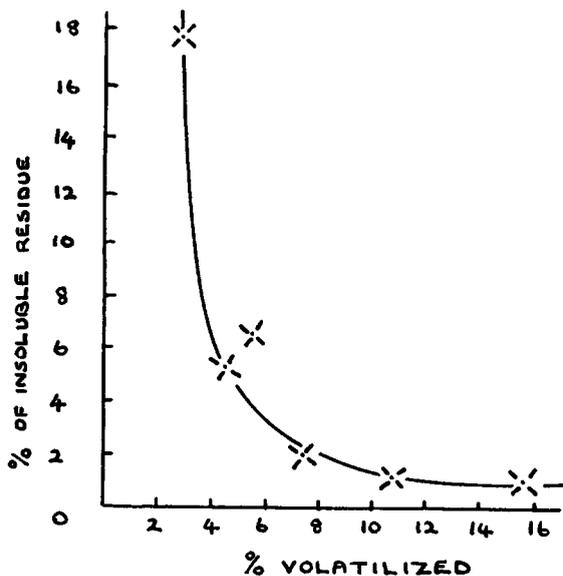
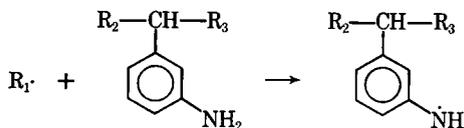
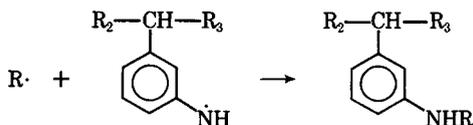


Fig. 2. Effect of extent of degradation on the amount of insoluble "gel."

amount of insoluble material falls, which suggests that a process such as



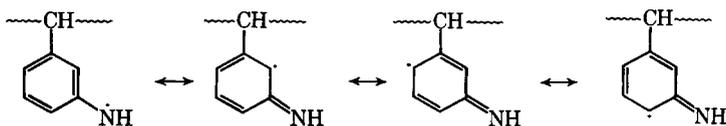
occurs during the thermal degradation of poly(*m*-aminostyrene), where $R_1 \cdot$ represents a polymer chain radical. The radical produced by hydrogen abstraction from the primary amino grouping cannot depropagate, and on cooling the molten polymer termination may occur to some extent by combination, viz.,



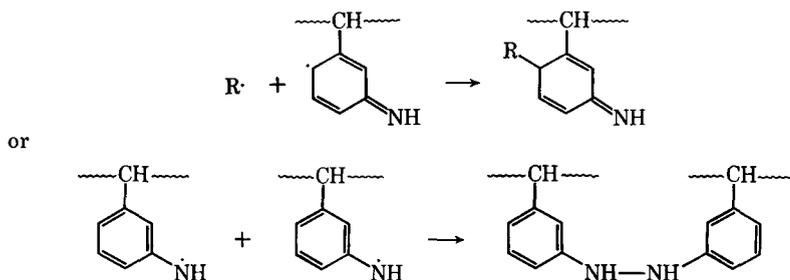
where $R \cdot$ is any macroradical. The resulting molecule will be large and nonlinear, and hence insoluble.

As degradation proceeds, R , R_2 , and R_3 will become shorter and hence the amount of insoluble material will become less.

In addition the coloration of the residue could be ascribed to a resonance-stabilized radical of the type

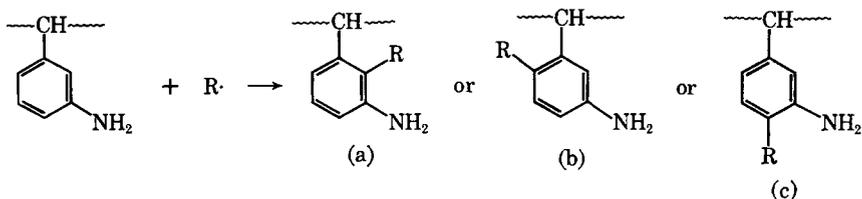


On cooling such radicals could terminate



to yield colored products, or could be trapped in the glass. ESR measurements show that a significant number of radicals are trapped in the glass. However, since no hyperfine structure could be resolved, it was not possible to identify the radicals.

An alternative explanation for the "crosslinking" might be the radical substitution in the ortho and para positions to the amino grouping in the benzene rings which would be activated toward an electron-deficient species:



Compounds of the type (a) and (b) would be unlikely on the basis of steric hindrance by the polystyryl main chain preventing attack. Compounds of the type (c) could possibly form to give initially nonlinear insoluble molecules which become soluble as degradation proceeds. Radical abstraction from nitrogen would appear, however, to be a more realistic process.

Fraction IV—The Oil

In the degradation of polystyrene, Madorsky^{10,11} found a similar fraction which he showed to consist of dimer, trimer, and some tetramer. The composition of the fraction remained constant, independent of pyrolysis temperature, and the trimer constituted the major component of the fraction.

By analogy with polystyrene, the oil fraction from poly(*m*-aminostyrene) would be expected to contain the compounds shown in Table I.

The infrared spectrum of the oil was almost identical with that of undegraded poly(*m*-aminostyrene) except for small additional peaks which indicated the presence of an olefinic bond. The ultraviolet spectrum in hydrochloric acid is shown in Figure 3 compared to that of poly(*m*-aminostyrene). The maximum at 2480 Å has been assigned to an olefinic double

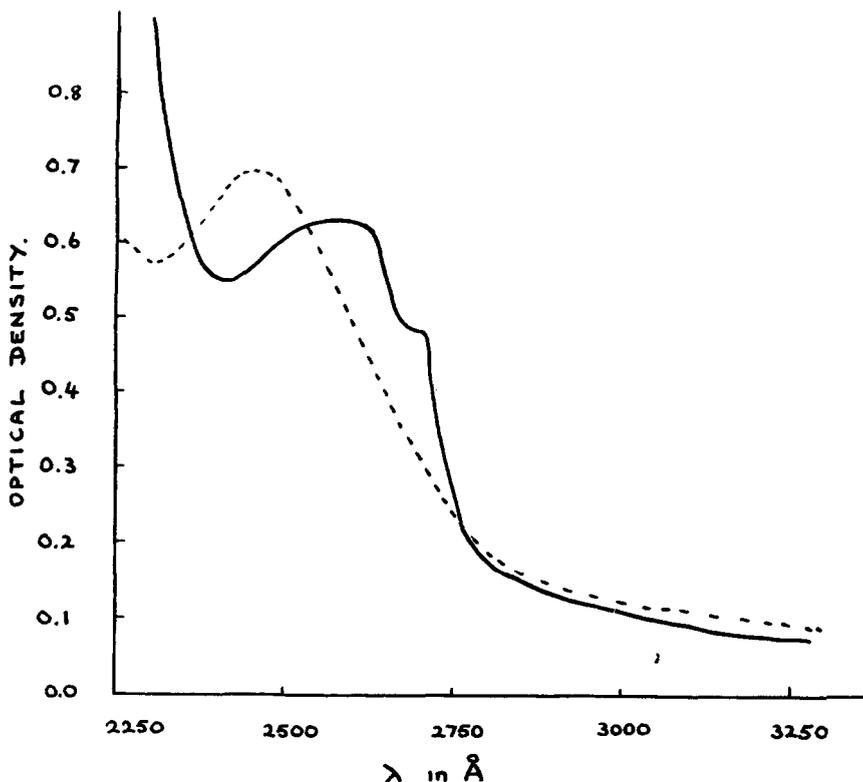


Fig. 3. Ultraviolet spectra: ---- oil fraction from the degradation of poly(*m*-aminostyrene) I at 400° in 0.1*N* hydrochloric acid at a concentration of 0.026 g/liter; — poly(*m*-aminostyrene) I in 0.1*N* hydrochloric acid at a concentration of 0.13 g/liter.

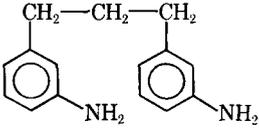
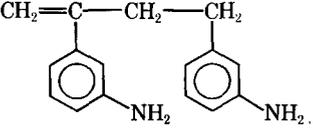
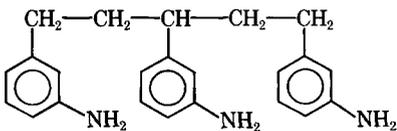
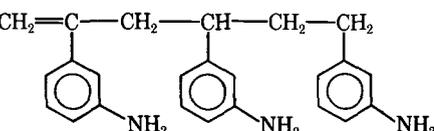
bond, and from a consideration of the molar extinction coefficients of the oil and monomer at 2480 Å, 2800, and 14,100 respectively, it would appear that one in four or five units in the oil fraction is associated with a double bond.

The mass spectrum of the oil obtained on the M.S.9 spectrometer is shown in Figure 4. It shows that the compounds illustrated in Table I are present in the oil. In addition to the peaks shown, peaks at mass numbers in the region of 460 indicated the presence of tetramer.

The NMR spectra are also in accord with the structures proposed in Table I. The following absorptions on the τ scale were found and have been given the following assignments: 2.8–3.7 multiplet (12 protons), substituted aromatic rings; 4.9–5.2 multiplet (1 proton), tertiary hydrogen atom; 6.5–6.8 singlet (6 protons), the amino grouping; 7.0–9.0 very broad ill-defined multiplet (9 protons), the methylene groups in the backbone.

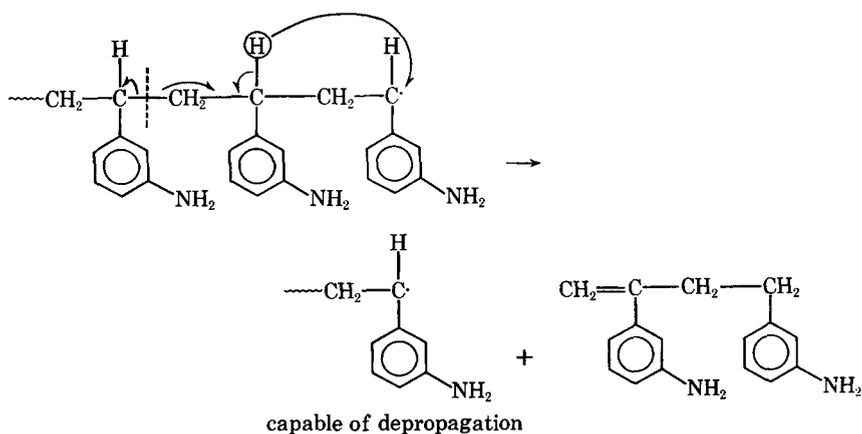
Complementary to the spectral studies, number average molecular weights have been determined and indicate a value of 316 ± 25 for the oil. This indicates that there is a larger proportion of trimer than dimer in the

TABLE I

Compound	Molecular weight
Dimer fraction 	262
	238
Trimer fraction 	345
	357

oil. In addition to the limits of accuracy of the method used, no change in number-average molecular weight was observed with increasing pyrolysis temperature, indicating that the composition of the oil does not change. Thus the oil fraction from poly(*m*-aminostyrene) closely parallels the behavior observed for the oil fraction from polystyrene.

The formation of the oil fraction may be accounted for on the basis of a series of intramolecular transfer reactions, one of which is illustrated for dimer formation below.



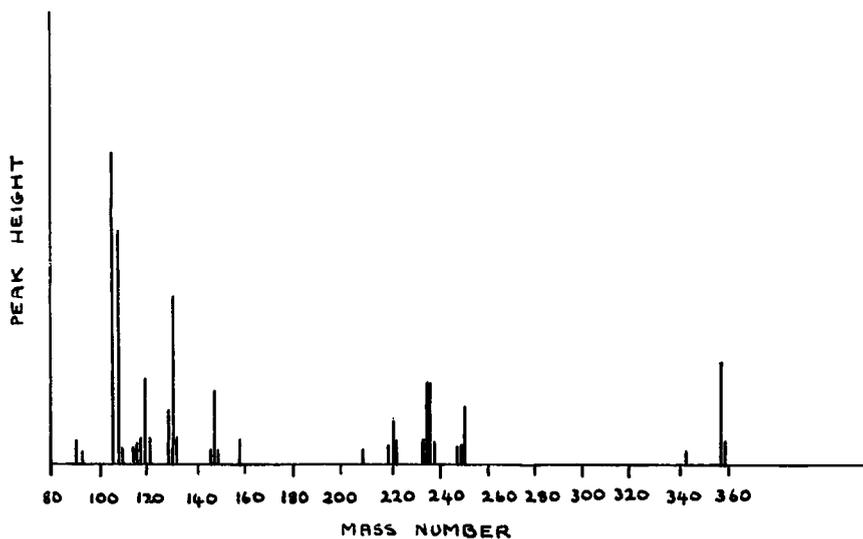


Fig. 4. Mass spectrum of the oil fraction. Sample obtained on a glass rod placed in the pyrolysis tube. Inlet temperature 200°C.

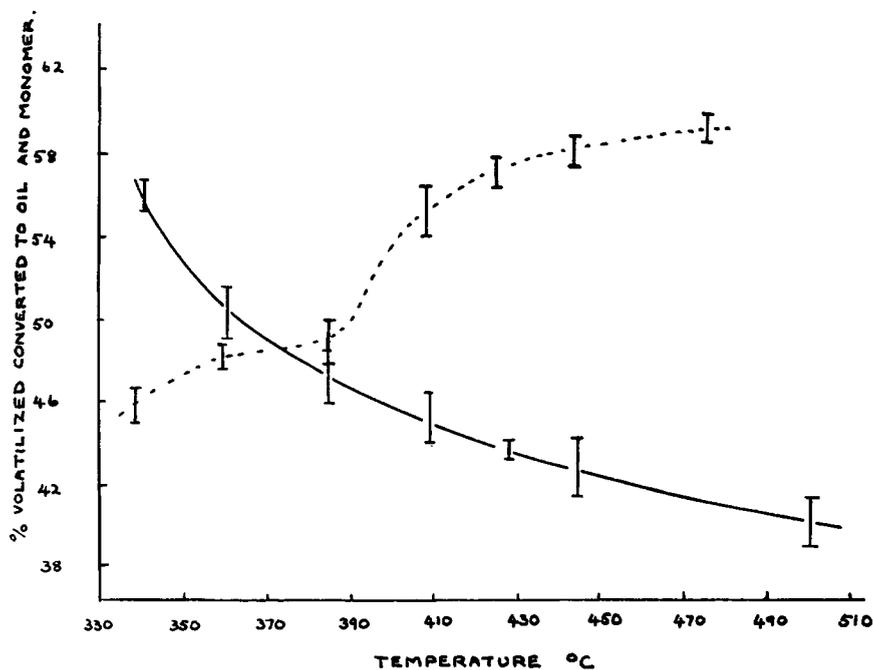


Fig. 5. Effect of pyrolysis temperature upon oil and monomer formation. Vertical bars represent span of points: - - - - monomer; ——— oil.

In addition to the quantitative product analysis of the oil fraction, the effect of pyrolysis temperature on the quantity of oil produced was investigated. The results are shown in Figure 5 where the effects of temperature on monomer and oil production are compared.

It can be seen that as the oil fraction decreases with increasing temperature, the monomer fraction increases. In general the factor which affects the yield of monomer in vinyl polymer degradation is thought to be the balance between the depropagation reaction to yield monomer and intramolecular transfer reactions to yield non-monomer. Thus the effect of temperature upon the non-monomer:monomer ratio yields information on the effects of temperature on these reactions and this is shown in Table II.

TABLE II

Pyrolysis temperature (°C)	Non-monomer:monomer ratio
320	1.42
340	1.19
360	1.07
385	1.05
409	0.81
427	0.74
444	0.72
476	0.69
500	0.65

It can be seen that the ratio decreases rapidly with increasing pyrolysis temperature, indicating that the rate of the depropagation reaction increases at a very much faster rate than that of the transfer reactions.

In the degradation of poly(*m*-aminostyrene) the zip length (the amount of monomer produced per chain cleavage) increases as the pyrolysis temperature increases and hence a higher proportion of monomer is found among the products.

Polystyrene has been similarly studied by Madorsky and Straus¹¹ who found that in the temperature range 330–380°C the monomer yield remained constant and the non-monomer:monomer ratio remained constant and equal to 1.40.

Recent work, however, by Kamebe and Shibaski² verified by us has shown that Madorsky's values for monomer yield are in error and that a similar reduction in the ratio should occur. Thus polystyrene and poly(*m*-aminostyrene) behave analogously in this respect and in terms of the products obtained in the oil fraction.

Relative Thermal Stability Studies

Measurements were made on a series of polymers using Madorsky's Th concept¹² which may be defined as the temperature at which a polymer sample loses half its weight under standard time conditions. In this study polymers were heated at constant temperature in the range 300–500°C for

30 min and the percentage weight loss determined and T_h evaluated. The data obtained is presented for a series of polymers in Figure 6 and Table III. Madorsky obtained a T_h value for polystyrene of 364° using different con-

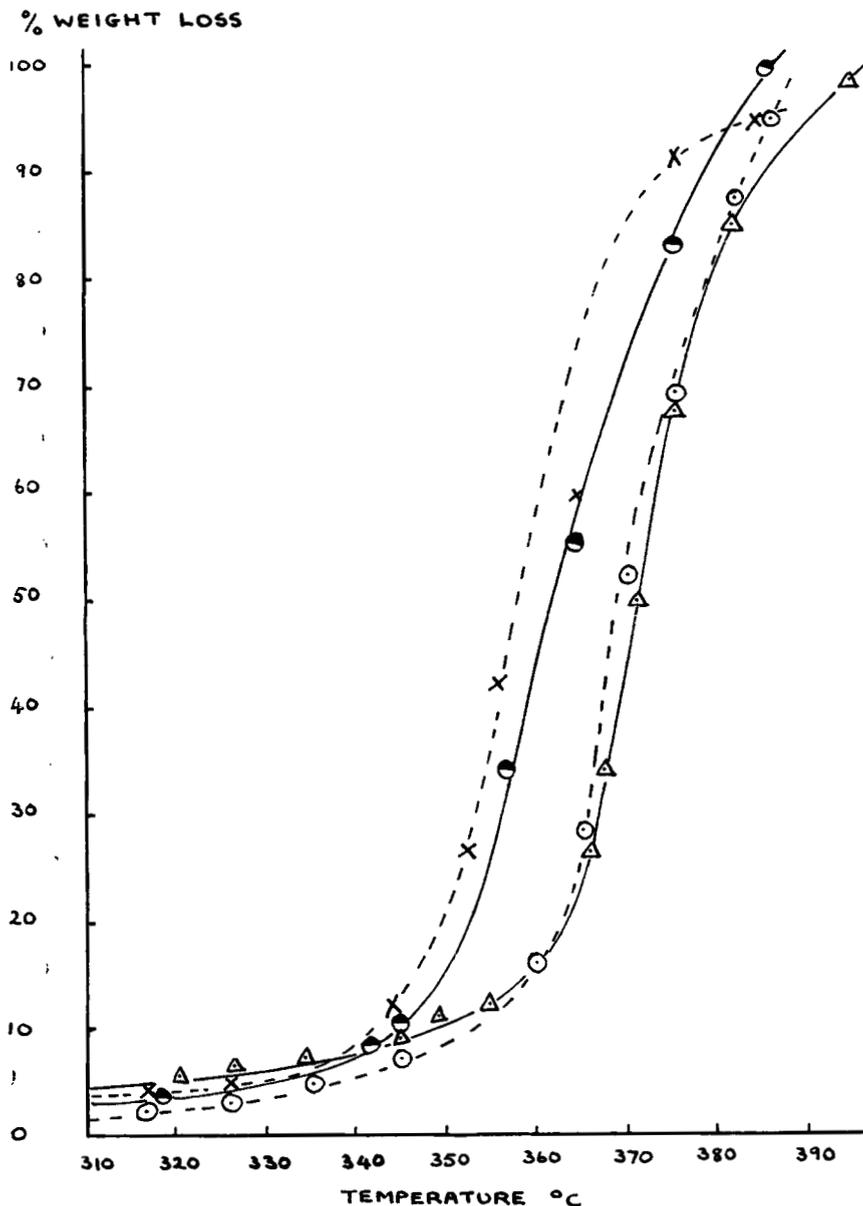


Fig. 6. Weight loss studies in vacuo: —x— polystyrene; —Δ— poly(*m*-aminostyrene) I; (○) poly(*m*-aminostyrene) II; (●) 1.15:1 molar ratio copolymer of styrene:*m*-aminostyrene.

TABLE III

Polymer	Th(°C)
Polystyrene	358
Poly(<i>m</i> -aminostyrene) I	369
Poly(<i>m</i> -aminostyrene) II	370
1.15:1 Molar ratio styrene: <i>m</i> -aminostyrene copolymer	362

ditions. Poly(*m*-aminostyrene) thus has a higher thermal stability in vacuo than polystyrene, and the copolymer shows intermediate behavior.

In the range studied, molecular weight has no effect upon Th or the weight loss/temperature curves obtained. This observation is in accord with previous observations on poly(*m*-aminostyrene)⁴ in nitrogen on thermogravimetric analysis.

The slight increase in stability over polystyrene may arise as the result of (a) a different mechanism of degradation operative in the early stages of degradation due to the radical scavenging properties of the amino grouping and (b) hydrogen bonding resulting in a decreased volatility of degradation products.

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References

1. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13**, 401 (1969).
2. H. Kamebe and Y. Shibasaki, *Kobunshi Kagaku*, **21** (225), 65 (1964).
3. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.
4. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13**, 401 (1969).
5. H. H. G. Jellinek, *Degradation of Vinyl Polymers*, Academic Press, New York, 1955.
6. N. Grassie and W. W. Kerr, *Trans. Faraday Soc.*, **53**, 234 (1957); *ibid.*, **55**, 1050 (1959).
7. S. L. Madorsky, *J. Polym. Sci.*, **9**, 133 (1952).
8. S. L. Madorsky, D. McIntyre, J. H. O'Hara, and S. Straus, *J. Res. Natl. Bur. Stds.*, **66A**, 307 (1962).
9. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 312.
10. S. L. Madorsky, *J. Res. Natl. Bur. Stds.*, **42**, 499 (1949).
11. S. L. Madorsky and S. Straus, *J. Res. Natl. Bur. Stds.*, **40**, 417 (1948).
12. S. L. Madorsky and S. Straus, *J. Res. Natl. Bur. Stds.*, **55**, 223 (1955).

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