

Thermal Degradation of Polymers. Part III. Vacuum Pyrolysis of Poly(*m*-aminostyrene); the Products Volatile at Pyrolysis Temperature Which Are Liquid or Gaseous at Room Temperature*

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Synopsis

The products obtained on degradation of poly(*m*-aminostyrene) in vacuo are described. The effect of molecular weight and pyrolysis temperature are discussed and the behavior of poly(*m*-aminostyrene) compared with that of polystyrene. Quantitative analytical methods using ultra-violet spectroscopy and gas liquid chromatography are described for *m*-aminostyrene and *m*-toluidine. The possible mechanisms of degradation to yield the products are discussed.

INTRODUCTION

In two previous papers^{1,2} we reported studies on poly(*m*-aminostyrene) homopolymers and copolymers with styrene and other related polymers by thermogravimetric and differential thermal analysis. We found poly(*m*-aminostyrene) to be more thermally stable in air than polystyrene and ascribed this to its inherent anti-oxidant character.

It was also shown that poly(*m*-aminostyrene), poly(*m*-hydroxystyrene), and poly(*p*-*N,N*-dimethylaminostyrene) homopolymers and copolymers with styrene show both a change in stability and thermogram shape with molecular weight.

In addition a qualitative assessment of the fractions from thermal degradation of poly(*m*-aminostyrene) in vacuo was made. We now report studies of the fractions from the pyrolysis of poly(*m*-aminostyrene), volatile at pyrolysis temperature, which are liquid or gaseous at room temperature in vacuo.

The complete thermal degradation of this molecule has been studied in order to assess the effect of the amino substituent upon the thermal degradation pattern. In addition to the α hydrogen atoms in the backbone capable of undergoing transfer there is the additional possibility of transfer from the amino grouping.

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EXPERIMENTAL

Materials

m-Aminostyrene and its homopolymer were prepared as previously described.² Two poly(*m*-aminostyrenes) I and II having intrinsic viscosities at 25° in aniline of 0.80 and 0.45 were used in this study. The polymers were ground to fine powders in an agate pestle and mortar and dried to constant weight at 63°/0.1 mm prior to pyrolysis.

APPARATUS AND PROCEDURE

Ultra-violet Spectroscopy (UV)

Spectra were recorded on a Unicam spectrophotometer model S.P. 800 using 1-cm silica cells. Optical density measurements were made using a Hilger-Watts Uvispek spectrophotometer with 0.5-cm silica cells. UV spectra of the polymers, *m*-aminostyrene, and *m*-toluidine were recorded in 0.1 N hydrochloric acid.

Mass Spectrometry (MS)

Spectra were recorded using AEI mass spectrometers, models MS 2, MS 9 and MS 10.

Gas Liquid Chromatography (GLC)

Chromatograms were recorded on a Pye Panchromatograph with a pyrex glass column (5' × 4 mm) packed with 10% polyethylene glycol (4000) on Chromosorb G. A flame ionization detector was used as the sensing element, and the column after programming the temperature at 3° per minute up to 200° with nitrogen passing was operated at 150°.

Infrared Spectroscopy (IR)

Spectra were recorded on a Perkin-Elmer spectrophotometer model 257. Liquid samples were run as films between sodium chloride plates. Polymer samples were run as 2% suspensions in potassium bromide.

Nuclear Magnetic Resonance (NMR)

Spectra were recorded on a Varian NMR spectrometer model A60A with sample spinning. Spectra from 2% solutions in deuteriochloroform were recorded.

Vacuum Pyrolysis Apparatus

The system used is shown diagrammatically in Fig. 1 and is basically similar to that used by Madorsky and co-workers³ for the pyrolysis of polymers at high temperatures.

Q was a quartz tube (length 61 cm, external diameter 2.6 cm), which was attached by a quickfit joint to a detachable trap A₁. This trap was em-

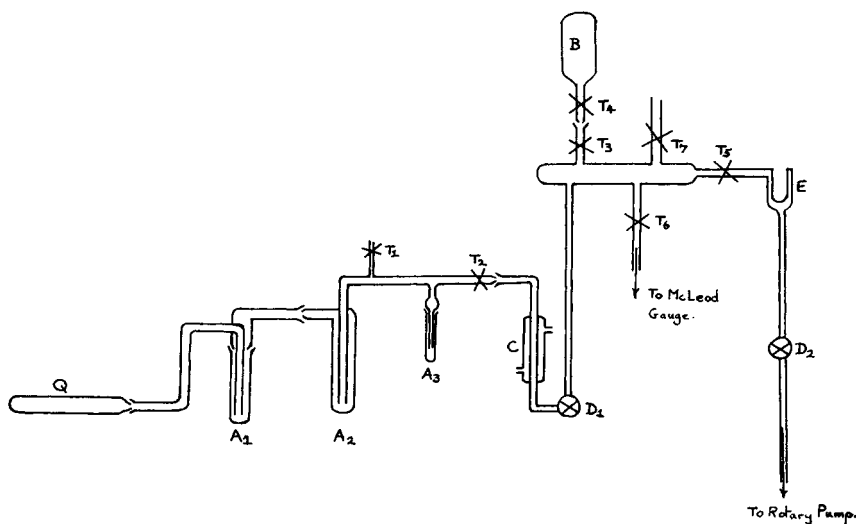


Fig. 1 Schematic representation of pyrolysis apparatus.

ployed to trap out the volatile products of degradation which condensed at liquid nitrogen temperature (-196°). Trap A_2 in conjunction with A_1 was capable of trapping out all the volatile components except for the gases most difficult to condense. Samples of the volatile liquids produced were generally obtained from the smaller detachable trap A_3 .

The gaseous products of degradation were handled in the system between taps T_2 and T_5 .

The system was evacuated by means of a rotary pump and a diffusion pump D_2 . Diffusion pump D_1 was used to pump gases into the calibrated sampling bulb B .

All taps and joints in the system were greased with Apiezon *L* grease.

The furnace was mounted on rails so that it could be moved over the tube Q in order to locate the polymer sample at the "hot spot." The furnace temperature was controlled using an Ether Instruments Thermistrol unit.

Pyrolysis Procedure

A dried, finely ground sample of poly(*m*-aminostyrene) (~ 50 mg) was weighed out into a preignited porcelain boat. The boat was placed at the end of the quartz tube which was then attached to the vacuum system. With all taps except T_1 open and the rotary and diffusion pump D_2 operating, the system was evacuated to 10^{-6} cm Hg over a period of 2 hr. A dewar vessel containing liquid nitrogen was then placed around trap A_1 and tap T_5 was closed.

The furnace preheated to the required temperature in the range 300 – 500° at its "hot spot" was placed over the polymer sample. (The "hot spot" was determined for a series of temperatures using a thermocouple

probe, and the polymer sample was located at this position by a stop on the rails.)

By manual control of the furnace temperature the sample temperature was raised to the furnace temperature without overshoot. The furnace was left in position for 30 min after which time it was wheeled back from the system. Tap T_5 was then opened and all gases volatile at liquid nitrogen temperature were pumped away. Tap T_5 was then closed and various procedures were then adopted as illustrated by the methods for monomer and *m*-toluidine determination below.

Monomer Determination

Pyrolysis was effected as under pyrolysis procedure as far as closure of tap T_5 . The liquid nitrogen dewar vessel surrounding trap A_1 was then removed and the trap was allowed to come to ambient temperature. Air was then admitted to the system and trap A_1 was detached. The contents of the trap was extracted with portions of 0.1 N hydrochloric acid (50, 25, 25 ml), which were combined and made up to 250 ml in a volumetric flask.

Aliquots (20 ml) of the above solution were diluted to 250 ml with 0.1 N hydrochloric acid, and the optical density of these solutions determined at 2480 Å.

Beer's Law was shown to be obeyed for *m*-aminostyrene in 0.1 N hydrochloric acid and a molar absorption coefficient of 14,100 was determined at 2480 Å and this value was used to calculate monomer yield. The only other component present in the monomer fraction to any significant extent was *m*-toluidine (~2%), which was found to have a negligible molar absorption coefficient at 2480 Å (170) when compared to *m*-aminostyrene.

m-Toluidine Determination

Pyrolysis was effected as under pyrolysis procedure, as far as closure of tap T_5 ; the liquid nitrogen dewar vessel around trap A_1 was then removed and placed around trap A_3 . Tap T_2 was then closed and the system maintained under vacuum for 2 hr during which time the liquid distilled into trap A_3 . Air was then admitted to the system and trap A_3 was detached.

Weighed samples of the liquid from trap A_3 were obtained and Analar *p*-toluidine (5% on the liquid weight) was added together with methylene chloride (0.2 ml) to dissolve the mixture. Samples (0.5 μL) were admitted to the GLC column. Good separation of the isomeric toluidines was achieved with symmetrical peaks. Three injections were made for each liquid sample and peak areas were obtained by triangulation. The *m*-toluidine content was calculated by reference to the ratio of the peak areas of *p*-toluidine: *m*-toluidine; the response factor for isomeric compounds being identical.

Pyrolysis Procedure for Gaseous Fractions

The fraction volatile at liquid nitrogen temperature was obtained by pyrolysis with liquid nitrogen dewar vessels around traps A_1 and A_2 and tap T_2 open.

Tap T_5 was closed and the diffusion pump D_1 operated. In this way gases volatile at liquid nitrogen temperature were pumped into the gas handling part of the system. Samples of gas were obtained in the sample bulb B and admitted to the M.S. 10 spectrometer.

The fraction volatile at ambient temperature was obtained by removing the liquid nitrogen dewar vessels from traps A_1 and A_2 and allowing the contents to rise to ambient. The gases were then pumped into the gas handling part of the system, sampled and analysed by mass spectrometry.

RESULTS AND DISCUSSION

Vacuum pyrolysis of poly(*m*-aminostyrene) has yielded the following fractions:

- I a fraction which is liquid at room temperature
- II a fraction which is gaseous at room temperature but not at liquid nitrogen temperature
- III a fraction which is gaseous at liquid nitrogen temperature
- IV a residue
- V a fraction volatile at pyrolysis temperature, involatile at room temperature which appeared as an oily condensate around the walls of the quartz tube

This paper deals with the qualitative and quantitative analysis of fractions I \rightarrow III and reports the effect of molecular weight of the polymer, and pyrolysis temperature upon the composition of these fractions.

Fraction I was shown by UV, IR, NMR, GLC, and MS analyses to consist mainly of *m*-aminostyrene with smaller quantities of *m*-toluidine and traces of aniline, *m*-ethylaniline, and α or β methyl-*m*-aminostyrene.

By reference to the retention indices⁴ of these amines determined by GLC for a synthetic mixture as shown in Table I, the peaks in the chromatogram shown in Figure 2 were assigned.

TABLE I

Compound	Synthetic mixture	Fraction I (pyrolysis at 385°)	Fraction II (pyrolysis at 476°)
Aniline	1787.7	1784.9	—
<i>m</i> -Toluidine	1870.5	1870.5	1873
<i>m</i> -Ethylaniline	1953.8	1953.8	1951
<i>m</i> -Aminostyrene	2115.2	2115.2	2114

One peak in the chromatogram marked ? was not assigned but from mass spectral evidence (peaks at mass numbers 131 and 132) the presence of α or β methyl-*m*-aminostyrene was indicated. By analogy with the products of degradation of polystyrene the GLC peak with a larger retention index than that for *m*-aminostyrene has been ascribed to α -methyl-*m*-

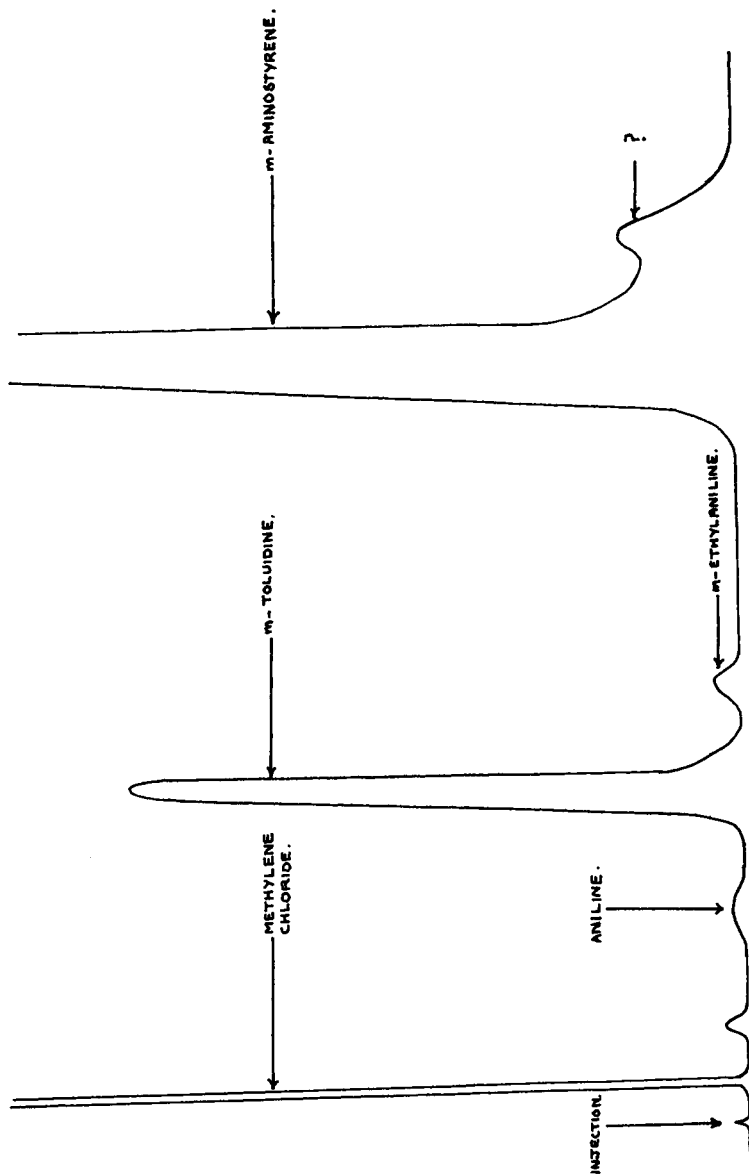


Fig. 2. G.L.C. trace from liquid fraction.

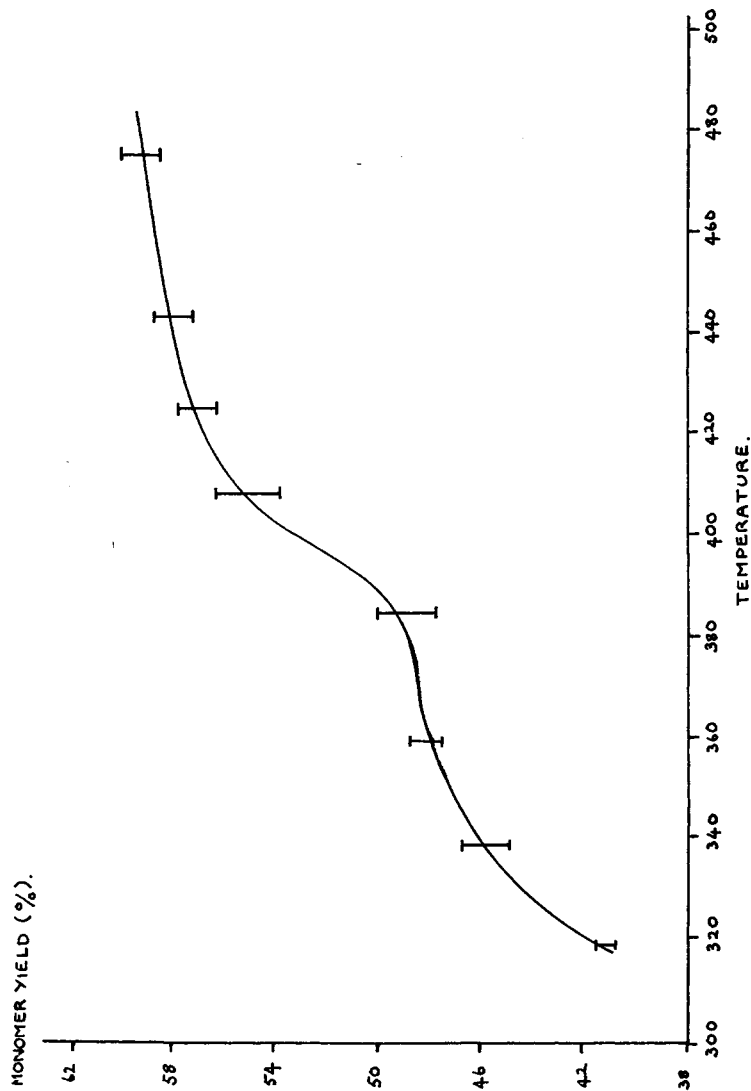


Fig. 3. The effect of pyrolysis temperature on monomer yield.

aminostyrene. Attempts to synthesize this monomer to clarify⁵ the position have so far failed.^a

The quantity of polymer converted to aniline, *m*-ethylaniline and α -methyl-*m*-aminostyrene was less than 0.1% of the polymer volatilized. Accordingly, attention was directed to the quantitative determination of the monomer and *m*-toluidine content of the fraction. The effect of molecular weight and sample pyrolysis temperature was investigated.

The molecular weight of the original polymer sample was found not to affect the quantity or composition of this fraction.

The effect of pyrolysis temperature on monomer yield is shown in Figure 3, where it can be seen that monomer yield increases with temperature in the range studied. A similar effect has been reported recently for polystyrene by Kamebe and Shibaski.⁶ We have also studied polystyrene and

TABLE II

Pyrolysis Temperature	Percentage volatilized converted to monomer ^a	Percentage volatilized converted to <i>m</i> -toluidine ^a
320	41.3	3.2
340	45.7	2.2
360	48.3	2.4
385	48.9	2.5
409	55.4	2.3
427	57.3	2.4
444	58.2	2.5
476	59.2	2.2
500	60.7	2.7

^a Average value from four runs.

have made monomer determinations by a UV method after separating the products into fractions. We confirm the results of the previous workers in that the monomer yield from polystyrene was found to rise from 43% at 340° to 56% at 500°.

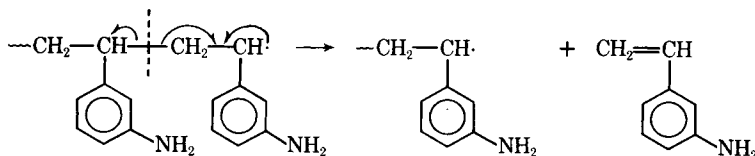
The production of *m*-toluidine is not affected by increasing the pyrolysis temperature as is shown in Table II below where the effect of pyrolysis temperature on monomer and *m*-toluidine production is compared.

The following mechanisms are suggested to account for monomer and *m*-toluidine production.

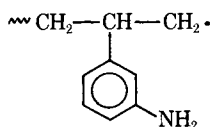
^a Further work since the original submission of this paper has resulted in the successful synthesis and characterization of α -methyl-*n*-aminostyrene. Its G.L.C. retention index was found to be identical with that of the unknown product of degradation. R. H. Still, and R. V. Forth, unpublished work.

Monomer Production

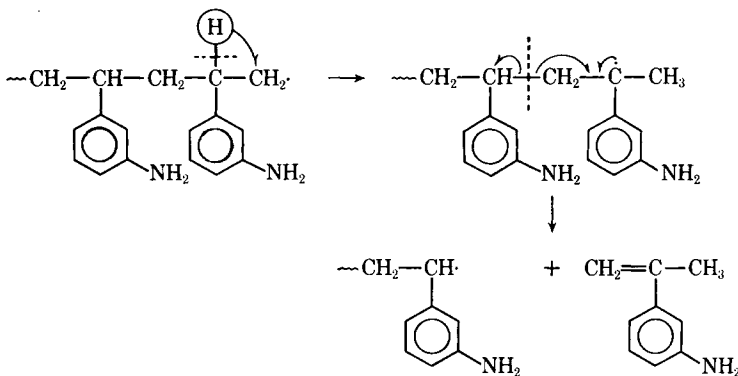
Arises as a result of "unzipping" from macroradicals of the type shown below.



Monomer is produced together with a radical capable of further depropagation. In addition within the polymer system there will be macroradicals of the type:



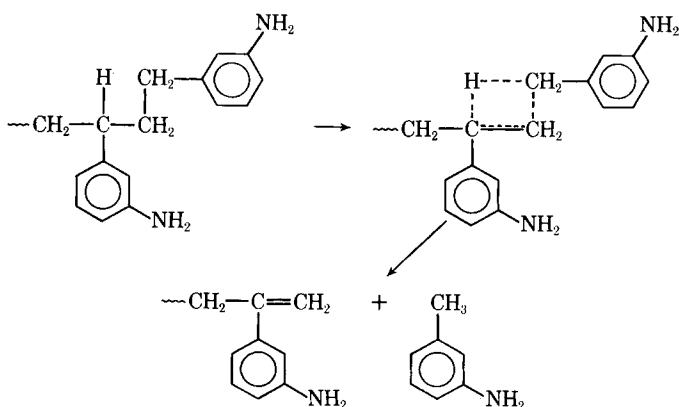
which cannot depropagate. However such macroradicals may either by intramolecular transfer of hydrogen give rise to a macroradical capable of depropagation and α -methyl-*m*-aminostyrene



or alternatively it may be deactivated by intermolecular or intramolecular hydrogen transfer to yield a terminal-methyl group.

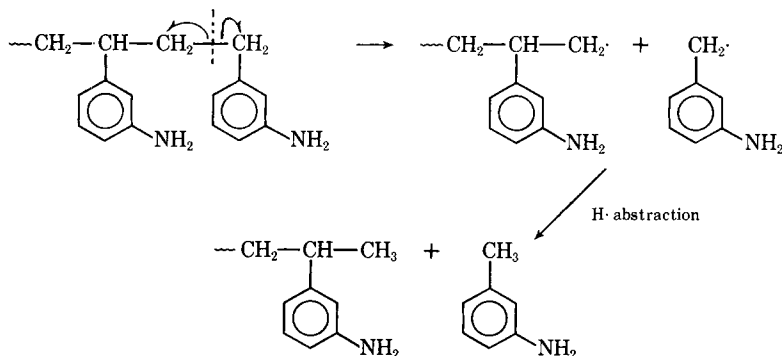
m-Toluidine Production

Two possible mechanisms are suggested which could be operative. The first mechanism involves an intramolecular nonradical hydrogen transfer process to a saturated (methylene) chain end with resultant terminal bond scission



This type of mechanism is very similar to that proposed by Madorsky⁷ to account for the absence of monomer in polyethylene pyrolysis.

The alternative mechanism involves terminal bond breakage to form radicals



Alternatively, the macroradical produced could yield α -methyl-*m*-aminostyrene and depropagate.

This type of mechanism could possibly be one of the end initiation processes known to occur for polystyrene,⁸ in which case toluene (a known degradation product) would be formed. The presence of a terminal methyl group on the chain may also account for traces of the other products observed viz. *m*-ethyl-aniline and α -methyl-*m*-aminostyrene.

The fact that the quantity of *m*-toluidine does not vary significantly with pyrolysis temperature may be interpreted as indicating that the average number of saturated chain ends present at high and low temperatures are similar.

Fractions II and III

Qualitative analyses have been made on these fractions using the MS 10 mass spectrometer without a pressure measuring device on the inlet.

The mass spectrum of Fraction II shows no peak above mass 44 and peaks at 44, 28, and 22 suggesting the presence of traces of carbon dioxide. A small peak at 43 suggests propylene, but no propane was found as shown by the absence of peaks at 45 and 46.

Further a peak at mass 30 and mass 26 indicated the presence of ethane and ethylene.

The mass spectrum of Fraction III showed it to contain hydrogen and methane only.

These products except for carbon dioxide arise as a result of thermal cracking of the degradation products. However, this fraction accounts for significantly less than 1% of the total polymer pyrolysed.

The carbon dioxide found in this fraction arises from the carbon dioxide absorbed by the basic macromolecule during its preparation, characterization, and storage.

The effect of pyrolysis temperature on the mass spectra obtained from Fractions II and III has been investigated and no change in spectra was observed. This indicated that this fraction does not change its composition with pyrolysis temperature. Similarly the quantity of gas produced with increasing temperature was found only to show a slight increase.

In order to obtain a fuller understanding of the mechanism of degradation, work is currently proceeding on the analysis of the remaining two fractions and the results will form the subject of a future communication.

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