Thermal Degradation of Polymers. V. Vacuum Pyrolysis of Poly(p-N,N-dimethylaminostyrene). The Products Volatile at Pyrolysis Temperature, Liquid or Gaseous at Room Temperature

R. H. STILL, *Department of Polymer and Fibre Science, U.M.I.S.T., Manchester, England* and M. B. EVANS and A. WHITEHEAD,* *Department of Chemical Sciences, The Hatfield Polytechnic, Hatfield, England*

Synopsis

The products obtained on degradation of poly (p-N,N-dimethylaminostyrene) in vacuo are described. The effects of molecular weight and pyrolysis temperature are discussed and the behavior compared with polystyrene under similar conditions. Product analysis has revealed significant differences between the products of degradation obtained from the two polymers, and mechanisms involving methyl-group migration have been proposed and discussed to account for the anomalous behavior of poly(p-N,N-dimethylaminostyrene). The liquid products of pyrolysis have been separated and identified by gas-liquid chromatography using the Kovats retention index, and quantitative analysis is also described. Analysis of the gaseous fraction by mass spectrometry is described.

INTRODUCTION

In two previous papers[1,2] we reported studies on the vacuum pyrolysis of m-aminostyrene polymers of different molecular weights and compared their behavior to that of polystyrene under similar conditions. Poly(m-aminostyrene) was found to behave similarly to polystyrene, yielding four fractions on pyrolysis.

The effect of pyrolysis temperature upon the nature and quantity of the degradation products was investigated and found to be very similar to that observed for polystyrene.

The major points of difference between the degradation of poly(m-aminostyrene) and polystyrene were (a) crosslinking within the residue at low extents of degradation, and (b) an increased monomer yield and an increased yield of the methyl-substituted degradation product, viz., m-toluidine if not of toluene. Such differences were ascribed to transfer reactions involving the hydrogen atoms of the amino grouping and to reactions involving electrophilic attack by radicals on the activated benzenoid rings of the polymer (due to the $+M$, $-I$ effect of the amino grouping). We

* Present Address: Revertex Ltd., Harlow, Essex, England.

now report studies on the fractions from the pyrolysis of poly(p-N,N-dimethylaminostyrene) (PDAS) volatile at pyrolysis temperature, which are liquid or gaseous at room temperature in vacuo. A comparison of the products of degradation in vacuo of polystyrene (PS) and PDAS has been made in order to assess the effect of the dimethylamino substituent on the degradation.

Transfer reactions involving hydrogen of the type observed during the degradation of poly(m-aminostyrene) cannot now occur. However, there is now the possibility of transfer reactions involving methyl radicals and/or dimethylamino radicals arising as a result of thermal cleavage of the nitrogen–alkyl, and/or the nitrogen–aryl bonds of the substituent in the phenyl ring.

EXPERIMENTAL

Melting points are corrected and all temperatures quoted are in degrees centigrade. Solvents were dried and distilled before use as described by Vogel.[3]

Materials

The monomer p-N,N-dimethylaminostyrene (DAS) was synthesized from p-N,N-dimethylaminobenzaldehyde by the known route.[4,5] The monomer after drying over anhydrous sodium sulfate was distilled yielding as main fraction 26 g 55% bp 80–82°/0.3 mm, $N_D^{25°}$ 1.6086; lit.[6] bp 81°/0.3 mm, $N_D^{25°}$ 1.6088. The monomer was homopolymerized in bulk under nitrogen at 70°C using α,α'-azobisisobutyronitrile (AZBN) as initiator at concentrations between 0.05% and 4.4% on monomer weight, yielding hard glasses after 22 hr. Copolymerization of DAS and styrene (S) in various molar ratios under similar conditions with an initiator concentration of 0.2% to 1.0% yield the copolymers as hard glasses after 16 hr.

All polymers were purified by the dropwise addition of a filtered 5% w/v solution (100 ml) of the polymer in Analar toluene to isopropanol (IL) with vigorous mechanical stirring. The fibrous precipitates were collected by filtration using a Buchner funnel without papers. The product was washed with isopropanol and dried at 70°C/0.1 mm to constant weight. The resultant product was redissolved in Analar toluene, reprecipitated, and dried to constant weight. This yielded PDAS homopolymers 1–7 of atactic stereochemical configuration and different molecular weights.

Characterization was effected by (a) determination of intrinsic viscosities in toluene at 25°C by the dilution procedure previously described for poly(m-aminostyrene)[7]; (b) determination of number-average molecular weights in toluene at 37°C. A Hewlett-Packard 502 high-speed membrane osmometer fitted with a standard cellophane membrane was employed. The data presented in Table I show the homopolymers to have sensibly different molecular weights.

TABLE I

Molecular Weights of Poly(p-N,N-dimethylaminostyrene) Homopolymers

Sample no.	[AZBN], % (on monomer weight)	$[\eta]_0$	$\bar{M}_n$
1	0.05	0.98	520,000[a]
2	0.2	0.42	102,000
3	0.4	0.33	71,990
4	0.6	0.28	45,700
5	1.0	0.24	34,300
6	1.6	0.18	24,200
7	4.4	0.13	12,200[a]

[a] Calculated using the Mark-Houwink equation $[\eta]_0 = KM^\alpha$, where $K = 6.2 \times 10^{-4}$ and $\alpha = 0.56$ as evaluated from the graph of $\log._{10} [\eta]_0$ vs. $\log_{10} [\bar{M}_n]$ for PDAS samples 2, 3, 4, 5, and 6.

Two representative samples of PDAS, 3 and 4, were subjected to elemental analysis for nitrogen.

ANAL. Calcd for $C_{10}H_{13}N$: N, 9.52%. PDAS 3 Found: N, (I) 9.41%, (II) 9.42%. PDAS 4 Found: N, (1) 9.50%, (II) 9.47%.

Copolymerization of DAS and S yielded copolymers 8–11 which were characterized in toluene by the procedure described above, and the data is presented in Table II.

All copolymer samples were analyzed by combustion analysis.

ANAL. Calcd for $C_{10}H_{13}N : C_8H_8 = 1:2$. C, 87.84%; H, 8.22%; N, 3.94%. DAS:S, 8, Found: C, 88.02%; H, 8.26%; N, 3.70%.

ANAL. Calcd for $C_{10}H_{13}N : C_8H_8 = 1:1$. C, 86.01%; H, 8.42%; N, 5.57%. DAS:S, 9, Found: C, 86.13%; H, 8.57%; N, 5.45%; DAS:S 11, Found: C, 86.34%; H, 8.55%; N, 5.95%.

ANAL. Calcd for $C_{10}H_{13}N : C_8H_8 = 2:1$. C, 84.37%; H, 8.60%; N, 7.03%. DAS:S, 10, Found: C, 84.30%; H, 8.56%; N, 7.11%.

Styrene was polymerized using AZBN at different initiator concentrations (0.1 → 1.0% yielding polystyrenes PS 12, $[\eta]_0 = 0.79$, $\bar{M}_n = 113,000$; PS 13, $[\eta]_0 = 0.23$, $\bar{M}_n = 46.080$; and PS 14, $[\eta]_0 = 1.63$, $\bar{M}_n = 308,000$.

TABLE II

DAS:S Copolymer Composition and Molecular Weights

Sample no.	Approx. molar ratio DAS:S	AZBN, %	$[\eta]_0$	$\bar{M}_n$
8	1:2	1.0	0.24	37.000[a]
9	1:1	1.0	0.23	36,300
10	2:1	1.0	0.23	36,300[a]
11	1:1	0.2	0.79	324,000[a]

[a] Calculated as previously, see Table I.

Apparatus and Procedures

Ultraviolet Spectroscopy (UV). Spectra were recorded on a Unicam spectrometer Model SP.800 using 1-cm silica cells.

Mass Spectrometry (MS). Spectra were recorded using AEI mass spectrometers Models MS.12 and MS.10 (modified to MS.102C specification).

Gas-Liquid Chromatography (GLC). Chromatograms were recorded on a Phillips PV.4000 gas chromatograph equipped with Pyrex columns (3 m × 4 mm) packed with 5% polyoxyethylene glycol 20M on Chromosorb G or 5% neopentyl glycol adipate on Chromosorb G. A flame ionization detector was used as the sensing element, and the column, after programming the temperature at 3°/min up to 200°C with nitrogen passing, was operated at various temperatures as shown in Tables III, IV, and V.

Infrared Spectroscopy (IR). Spectra were recorded on a Perkin-Elmer spectrophotometer Model 237. Liquid samples were run as films between sodium chloride plates. Polymer samples were cast from suitable solvents on sodium chloride plates.

Nuclear Magnetic Resonance (NMR). Spectra were recorded from 2% solutions in deuterochloroform using a Varian NMR spectrometer Model A60A with sample spinning.

Vacuum Pyrolysis Apparatus. The system used was described in detail in a previous paper.[1] A schematic diagram is shown in Figure 1.

Pyrolysis Procedure. A dried sample of polymer (100 mg) was subjected to pyrolysis under vacuum as described for poly(m-aminostyrene)[1] with
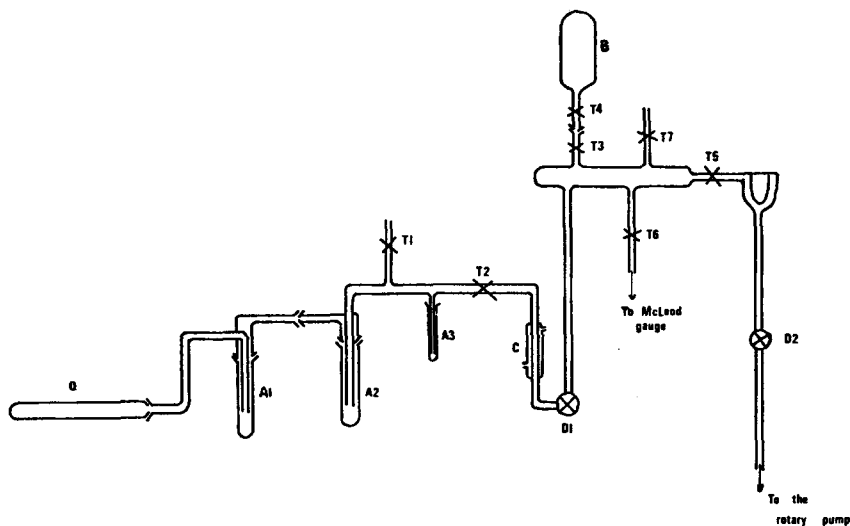

Fig. 1. Vacuum pyrolysis apparatus: A_1-A_3, product traps; B, gas-sampling bulb; C, condenser for diffusion pump; D_1, D_2, diffusion pumps; T_1-T_7, vacuum taps; Q, quartz pyrolysis tube.

minor modification of procedure.   The pyrolysis time used for all runs was
30 min, after which time the furnace was removed and the system allowed
to come to equilibrium for 24 hr.   Tap T_1 was then opened and nitrogen
admitted to the system, and the products of degradation condensed in
trap A_3 were allowed to warm up to ambient.   The contents of the trap
(fraction I) were extracted with Analar acetone (2×10 ml) and subjected
to qualitative and quantitative chemical analyses.

Monomer Determination.   Preliminary qualitative analysis of fraction
IV (the oil) from PDAS indicated that it contained appreciable quantities
of monomer, even after equilibration for seven days at 10^{-6} cm Hg.   As a
result, fractions IV and I from PDAS were extracted from the pyrolysis
tube and trap A_3, respectively, with acetone (2×10 ml) and combined for
analysis.   The oil fraction from PS did not contain free monomer, and
hence fraction I (the liquid) was extracted from trap A_3 with acetone
(2×10 ml) for subsequent analysis.

GLC analysis was effected in the following way: A known quantity
(± 0.0002 g) of internal standard was added to the solutions in acetone,
and the mixtures were injected onto the PEG 20M/Chromosorb G column.
Gas chromatograms of the fraction were obtained, and the peak areas of
the monomer component and internal standard were determined by cutting
out the peak and weighing it.   The average monomer:standard peak area
ratio was determined for six injections.   The detector response factor R
was similarly found by injecting onto the column a synthetic mixture of the
monomer and standard of known composition:

$$R = \frac{\text{peak area of monomer (g)}}{\text{peak area of standard (g)}}$$

From the monomer:standard peak area ratio, a knowledge of the response
factor, and the amounts of added standard in the liquid fraction, the mass
of monomer in the solutions of the liquid fractions of PS and PDAS was
calculated.

Minor Component Determination.   Acetone solutions of the liquid
fraction from PS and the combined oil and liquid fractions from PDAS
were injected onto the column.   The average peak areas of the component
of the fractions relative to the monomer peak area were determined from
six injections by weighing.   Comparison with the calculated amounts of
monomer in the fractions enabled the percentage volatilized converted to
the minor components to be calculated.

Pyrolysis Procedure for Gaseous Fraction.   The fraction volatile at
$-80°$C was obtained by pyrolysis with acetone/solid carbon dioxide in
Dewar vessels around traps A_1 and A_2, and tap T_2 was opened.   Tap T_6
was then closed and the diffusion pump D_1 operated.   In this way, gases
volatile at $-80°$ were pumped into the gas-handling part of the system.
Samples of the gas were obtained in the detachable bulb B and admitted
to the AEI MS.10 mass spectrometer.

RESULTS AND DISCUSSION

Vacuum pyrolysis of PDAS and PS has yielded the following fractions: fraction I, a liquid fraction volatile at pyrolysis and ambient temperatures but involatile at liquid nitrogen temperature; fraction II, a fraction gaseous at −80°C and at liquid nitrogen temperature; fraction III, a residue; fraction IV, an oil fraction volatile at pyrolysis temperature, involatile at ambient temperature.

This paper is concerned with the qualitative and quantitative analysis of fractions I and II and reports the effect of the molecular weight of the homopolymers and pyrolysis temperature upon the composition of these fractions. Studies on the effect of copolymer composition on monomer yield are also discussed.

Fraction I

Fraction I from PS was shown by UV, IR, NMR, GLC, and MS analysis to consist mainly of styrene with smaller quantities of toluene, ethyl benzene, and α-methylstyrene. The Kovats retention indices[8] of the compounds were determined by GLC using a synthetic mixture and are compared with fraction I obtained on pyrolysis of PS in Table III. In this way, the peaks in the chromatogram shown in Figure 2a were assigned using a secondary standard according to the method developed by Evans.[9]

TABLE III
Identification of Components in PS Liquid Fraction by GLC[a]

Retention index of fraction I from PS pyrolysis at 400°C	Retention index of synthetic mixture	Compound
716.2	714.0	benzene
902.9	902.5	toluene
1067.0	1067.7	ethylbenzene
1151.7	1151.7	styrene
1295.6	1294.7	α-methylstyrene

[a] Column, PEG 20M on Chromosorb G; column temperature, 120°C; internal standard, cumene.

These results are consistent with the findings of previous workers.[10] Fraction I from PDAS was similarly qualitatively analyzed by UV, IR, NMR, and chemical tests and shown to consist of monomer together with compounds containing substituted and unsubstituted amino groupings. Inspection of the chromatogram obtained from the liquid fraction from PDAS pyrolysis reveals the complexity of this system (Fig. 2b). The presence of 11 components posed two problems with respect to the choice of an internal standard for qualitative and quantitative analysis by GLC. These were (a) an internal standard with a retention time intermediate between that of components 1 and 11 which did not interfere with the minor components could not be found; (b) choice of an internal standard
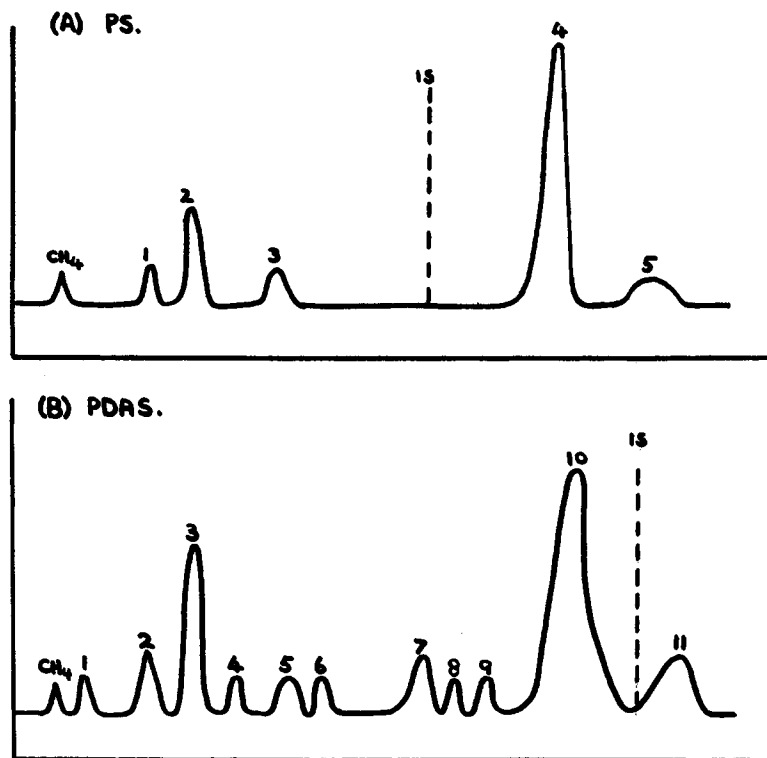
Fig. 2. Gas–liquid chromatogram for polystyrene and poly(p-N,N-dimethylaminostyrene) liquid fractions. IS = Internal standard.

with a retention time greater than component 11 would have led to error in determination of the relative retentions of the lower-boiling components. In order to eliminate these errors, the two major components, 3 and 10, were identified by analogy with the major products from PS and poly(m-aminostyrene) pyrolyses using as internal standard p-anisidine, as shown in Table IV.

TABLE IV

Identification of the Two Major Components in PDAS Liquid Fraction by GLC[a]

Component no. in Fig. 2B	Rxs observed for product from pyrolysis of PDAS at 500°	Rxs observed for synthetic mixture	Compound
3	0.3422	0.3421	N,N-dimethyl-p-toluidine
10	0.8554	0.8535	p-N,N-dimethyl-aminostyrene

[a] Column, PEG 20M on Chromosorb G; column temperature, 210°C; internal standard, p-anisidine.

TABLE V

GLC Retention Index Data[a] for Theoretically Possible Components of PDAS Liquid Fraction

Possible pyrolysis product	Retention index	Possible pyrolysis product	Retention index	PDAS pyrolysis component no. in Fig. 2B	Retention index
Aniline	1766.7	N-Methyl-3,4-xylidine	1853.2	1	1426.5
p-Toluidine	1833.9	N-Methyl-2,4-xylidine	1951.2	2	1603.4
p-Ethylaniline	1919.9	N,N-Dimethylaniline	1604.8	3	1673.9
2,4-Xylidine	1976.0	N,N-Dimethyl-p-toluidine	1673.9	4	1717.9
3,4-Xylidine	1888.9	N,N-Dimethyl-p-ethyl-aniline	1758.9	5	1759.9
Methylamine	—[b]	N,N-Dimethyl-2,4-xylidine	1798.1	6	1791.8
Dimethylamine	—[b]	N,N-Dimethyl-3,4-xylidine	1690.2	7	1816.3
Trimethylamine	—[b]	p-N,N-Dimethylaminostyrene	1957.5	8	1836.1
N-Methylaniline	1719.8	Benzene	—[b]	9	1892.6
N-Methyl-o-toluidine	1816.2	Toluene	—[b]	10	1957.1
N-Methyl-p-toluidine	1790.2	Ethylbenzene	—[b]	11	2018.2
N-Methyl-m-toluidine	1728.3	Styrene	1207.7		
N-Methyl-p-ethylaniline	1892.8				

[a] Column, PEG 20M on Chromosorb G; column temperature, 210°C; internal standard, N,N-dimethyl-p-toluidine.

[b] Retention times too small to make accurate measurement of relative retention ratio (Rxs = $\frac{Rx}{Rs}$ where Rs = retention time of internal standard) and retention index I (I <1200). The secondary amines studied were prepared by the monoalkylation (Rx) of the corresponding primary amine by the method of Frankland.[11]

Subsequently, the identified component 3, N,N-dimethyl-p-toluidine, was used as internal standard for the qualitative identification and the quantitative determination of the 11 components. In order to facilitate the identification of components 1 to 11, a list of possible pyrolysis products was drawn up, making due allowance for methyl or dimethylamino group-transfer reactions as a result of N-alkyl group or N-aryl group bond break-age together with subsequent hydrogen abstraction, radical substitution, and/or combination reactions. The possible products are listed in Table V, together with their retention indices which are compared with those of components 1 to 11.

TABLE VI
GLC Analysis[a] of PDAS Liquid Fraction

Component no. in Fig. 2B	Retention index (obs) of fraction I from PDAS pyrolysis at 500°	Retention index (ref.) of synthetic mixture	Compound
1	1426.5[b]	—	—
2	1603.4	1604.8	N,N-Dimethylaniline
3	1673.9	1673.9	N,N-Dimethyl-p toluidine
4	1717.9	1719.8	N-Methylaniline
5	1759.9	1758.9	N,N-Dimethyl-p-ethyl-aniline
6	1791.8	1790.2	N-Methyl-p-toluidine
7	1816.3	1816.2	N-Methyl-o-toluidine
8	1836.1	1833.9	p-Toluidine
9	1892.6	1892.8	N-Methyl-p-ethylaniline
10	1957.1	1957.5	p-N,N-Dimethylamino-styrene
11	2018.2[c]	—	—

[a] Column, PEG 20M on Chromosorb G; column temperature, 210°C; internal standard, N,N-dimethyl-p-toluidine.

[b] No reference compound found having this retention index.

[c] α-Methyl-p-N,N-dimethylaminostyrene not available.

In this way, the four p-N,N-dimethylamino components (2, 3, 5, and 10) were readily identified by retention coincidence, and the identity of the α-methylstyrene component (11) was inferred by analogy with the products of degradation of PS and from a peak of m/e 161 in the mass spectrum. No compound having a retention index comparable with component 1 was observed, but the identity of the other components was indicated.

In order to eliminate assignments due to pure coincidence, a synthetic mixture of the "identified components" was made and their retention indices compared with that of the pyrolysis product on two columns under different temperature conditions. In this manner, the identity of all components except component 8 was confirmed, as shown in Tables VI and VII.

TABLE VII
GLC Analysis[a] of PDAS Liquid Fraction

Component no.	Retention index obs.	Retention index ref.	Compound
1	1206.9	—	—[b]
2	1470.8	1468.0	'N,N-dimethylaniline
3	1542.3	1542.4	N,N-dimethyl-p-toluidine
4	1568.4	1566.5	N-methylaniline
5	1629.5	1629.1	N,N-dimethyl-p-ethylaniline
6	1644.6	1642.0	N-methyl-p-toluidine
7	1654.1	1652.9	N-methyl-o-toluidine
8	—	—	— ?[c]
9	1731.0	1729.9	N-methyl-p-ethylaniline
10	1789.0	1787.6	p-N,N-dimethyl-aminostyrene
11	1856.9	—	?[d]

[a] Column, neopentyl glycol adipate on Chromosorb G; column temperature, 180°C; internal standard, N,N-dimethyl-p-toluidine.

[b] No reference compound available having this retention (see also Table VI).

[c] Very bad tailing observed making retention measurement in both cases difficult and positive identification of p-toluidine suspect.

[d] Compound α-methyl-p-N,N-dimethylaminostyrene not available.

Quantitative analysis were also made, and the conversion of polymer to the respective components is shown in Tables VIII and IX for pyrolysis effected at 500°C for PDAS and PS.

The major product in each case can be seen to be monomer. Accordingly, attention was directed to the quantitative determination of the effect of molecular weight and pyrolysis temperature on monomer yields from the two polymers. Molecular weight was shown not to affect monomer yields from PS or PDAS in the range studied (46,000–308,000 for PS; 12,000–520,000 for PDAS). The effect of pyrolysis temperature on

TABLE VIII
PDAS Minor Component Yields

Component no.	Identity	Polymer volatilized converted to component, %
1	?	0.1
2	N,N-Dimethylaniline	0.2
3	N,N-Dimethyl-p-toluidine	2.8
4	N-Methylaniline	0.4
5	N,N-Dimethyl p-ethylaniline	0.4
6	N-Methyl-p-toluidine	0.4
7	N-Methyl-o-toluidine	0.4
8	p-Toluidine	0.4
9	N-Methyl-p-ethylaniline	0.4
10	p-N,N-Dimethylaminostyrene	36.3
11	α-Methyl-p-N,N-dimethylaminostyrene	0.7

TABLE IX
PS Minor Component Yields

Component no.	Identity	Polymer volatilized converted to component, %
1	Benzene	0.2
2	Toluene	1.1
3	Ethylbenzene	1.0
4	Styrene	56.0
5	α-Methylstyrene	0.9

TABLE X
Effect of Pyrolysis Temperature on Monomer Yields from PS and PDAS

Pyrolysis temp. °C	PDAS volatilized converted to monomer,[a] %	PS volatilized converted to monomer,[a] %
345	18.3	35.8
395	33.5	49.1
445	39.2	53.3
500	34.4	54.8

[a] Average value from four runs.

monomer yield is shown for both polymers in Table X. The results for PS are in accord with those of Kamebe and Shibaski[12] and confirm previous work by Still and Jones.[2] The monomer yield from PDAS is significantly lower at all temperatures than that from PS, as can be seen from the data presented in Table X.

That the mechanism of degradation of PDAS is significantly different from that of PS has been shown by product analysis. Three major differences are apparent: (a) methyl migration or transfer occurs; (b) there is a decreased monomer yield relative to PS; (c) an increased proportion of the liquid fraction is converted to the methyl-substituted di- and mono-methylanilines and the methyl-substituted primary amine p-toluidine.

The presence of the mono N-methyl components clearly indicates that methyl groups are lost from the dimethylamino groupings during degradation. The absence of the alkylamines methylamine and dimethylamine from the degradation products indicates that N-aryl bond cleavage does not occur. This is consistent with the expected bond strengths of the N-aryl and N-alkyl bonds.[13,14] The presence of p-toluidine suggests that in some cases both methyl groups may be lost. However, the exact fate of the migrating methyl group cannot be assessed from product analysis of the liquid fraction alone, and additional information afforded by analysis of the gaseous fraction II has proved important to the solution of the problem. Qualitative analysis of the gaseous fraction from PDAS and PS again reveals a complexity foreign to PS. The PDAS mass spectrum shows peaks at m/e 16, 28, 42 of methane, ethylene, and propylene, whereas that from PS showed only ethylene in significant amounts. It is reasonable to conclude that the methane produced in the case of PDAS pyrolysis arises from the migrating methyl group and that the ethylene in both cases

arises by cracking of the backbone and is probably related in case of PS to the production of benzene. Propylene production in case of PDAS may possibly arise by the interaction of ethylene with the migrating methyl radical or by cracking of the backbone of the polymer containing a migrated methyl group, i.e., an α-methyl structure.

Thus, the recipient of the migrated methyl group would appear to be methane and the N-methyl-o-toluidine component. Methane would be formed by abstraction of a tertiary hydrogen atom from the polymer backbone by the methyl radical:

stabilized by resonance
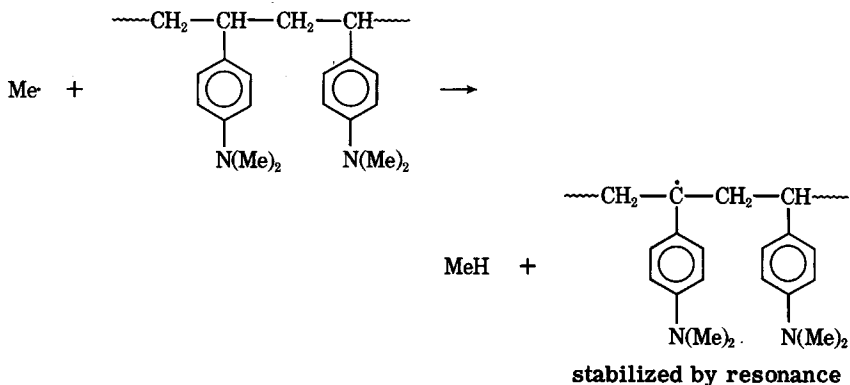
The presence of N-methyl-o-toluidine suggests that some degree of inter-repeat unit transfer followed by hydrogen abstraction occurs:

(A)
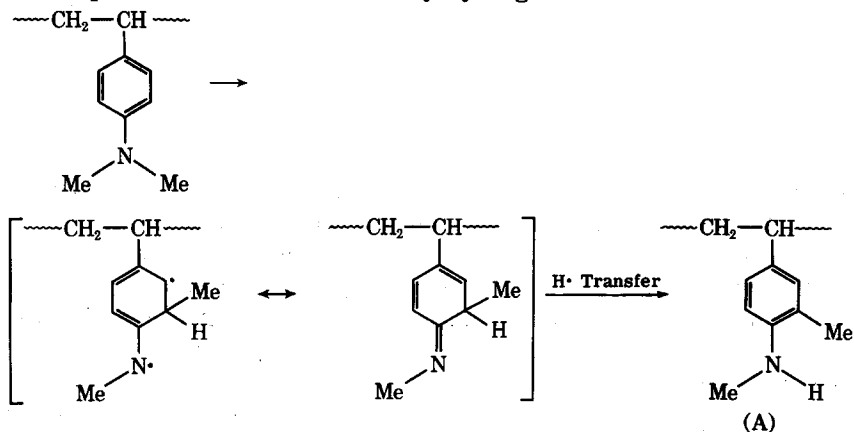
Polymer chains containing units such as A would then break down in the manner which has been suggested for PS to yield N-methyl-o-toluidine, N-methyl-2,4-dimethylaniline, and N-methyl-2-methyl-4-ethylaniline, analogous to benzene, toluene, and ethylbenzene derived from PS. It would be expected that N-methyl-2,4-dimethylaniline would be the major component, followed by N-methyl-2-methyl-4-ethylaniline, with much smaller quantities of N-methyl-o-toluidine if the behavior follows that of PS and other substituted polystyrenes, including PDAS where N,N-dimethyl-amino-p-toluidine is the major component after monomer (see Table VIII). The production of N-methyl-o-toluidine, however, appears to be

anomalous since neither N-methyl-2,4-dimethylaniline nor N-methyl-2-methyl-4-ethylaniline were found among the products of degradation.

The reduced monomer yield for PDAS compared with that for PS and other substituted polymers may be explained in terms of methyl-radical reactions involving transfer and hydrogen abstraction, which result in a decrease in "unzip length" for PDAS. Such reactions may occur in the following ways:
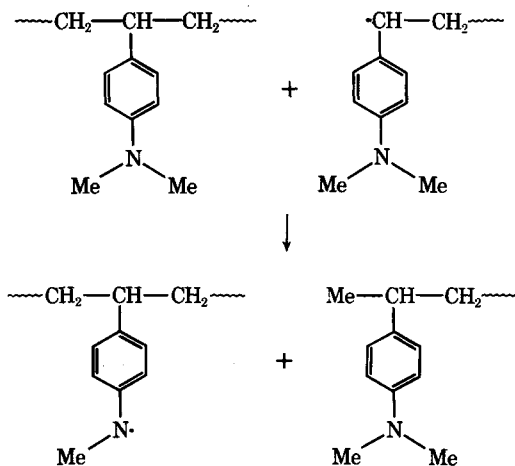
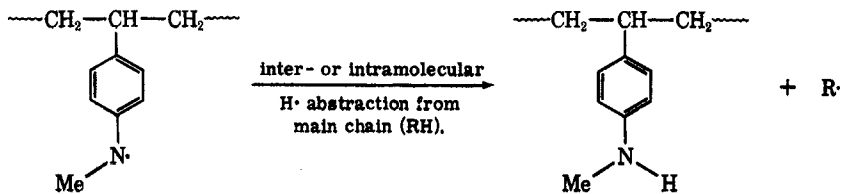(a) Intra-repeat unit transfer to active chain radical:

Resonance stabilized
radical.
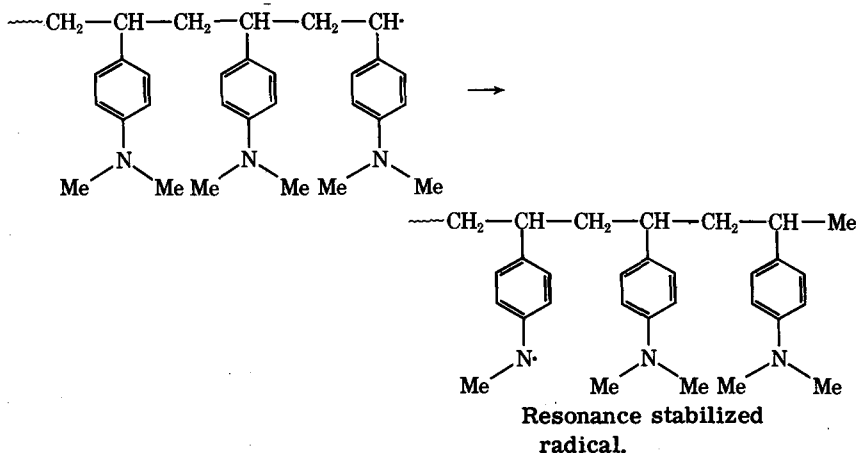
(b) Intra-repeat unit transfer to active chain radical:
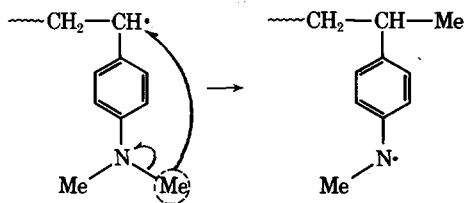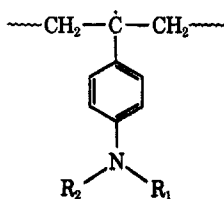

(c) Intermolecular transfer to active chain radical:

These reactions (a → c) may be followed by hydrogen abstraction from the polymer backbone leading to units containing the secondary amino grouping. Thus,

where R· is

and $R_1 = R_2 = Me$, $R_1 = H$
$R_2 = Me$; or $R_1 = R_2 = H$

and such radicals may be either on same chain or different chains depending on the mode of H abstraction. These radicals can also be produced by hydrogen abstraction by methyl radicals resulting in the formation of methane (see above). This reaction is specific to PDAS, and as a result
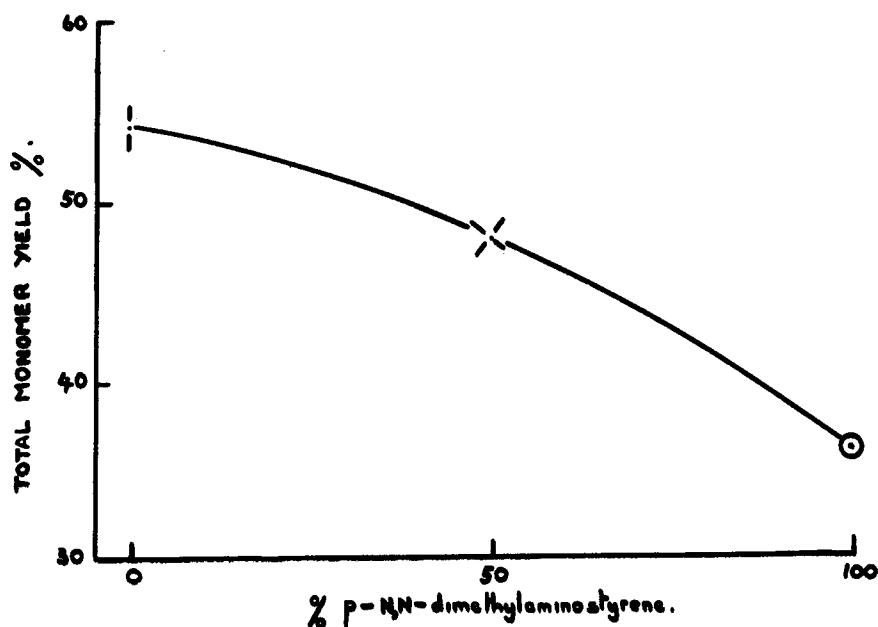

Fig. 3. Effect of —N(Me)₂ concentration on monomer yield: (¦) PS; (✕) S:DAS 1:1 copolymer; (⊙) PDAS. Complete volatilization of polymer sample of 425°C.

this type of radical will be present in greater concentration in the degrading PDAS melt than the corresponding radical derived from PS. The subsequent reactions of these radicals, viz., combination, rearrangement, and disproportionation, leads to reduction in the "unzip length" and hence monomer yield and to an increase in the quantity and complexity of the minor products.

The effect of methyl migration on monomer yield is further shown by studies on the effect of the N,N-dimethylamino group concentration in the polymer on monomer yield on pyrolysis. The results obtained for monomer yield on pyrolysis of PDAS, DAS:S 1:1 copolymer, and PS at 425°C are shown in Figure 3. It can be seen that as the concentration of DAS in the polymer is reduced, the total monomer yield increases.

The degradation of polymer chains containing dimethylamino substituents and rearranged substituents (—NH$_2$ and —NHMe as a result of methyl migration) by mechanisms similar to those accepted for PS can effectively explain the observed products of pyrolysis.

Qualitative and Quantitative studies on fractions III and IV will form the subject of part VI of this series and will present further evidence for methyl-group migration during the pyrolysis of PDAS.

References

1. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13**, 1555 (1969).
2. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13**, 2033 (1969).
3. A. I. Vogel, *Textbook of Practical Organic Chemistry*, 3rd ed., Longmans, London, 1956.
4. C. S. Marvel and D. W. Hein, *J. Amer. Chem. Soc.*, **70**, 1895 (1948).
5. C. L. Arcus and W. A. Hall, *J. Chem. Soc.*, **794**, 4199 (1963).
6. D. T. Mowry, M. Renoll, and W. F. Huber, *J. Amer. Chem. Soc.*, **68**, 1105 (1946).
7. R. H. Still, A. L. Mansell, and P. B. Jones, *J. Appl. Polym. Sci.*, **13**, 401 (1969).
8. E. Kovats, *Helv. Chim. Acta*, **41**, 1915 (1958).
9. M. B. Evans, *J. Chromatogr.*, **12**, 2 (1963).
10. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.
11. P. F. Frankland, F. Challenger, and N. Nicholls, *J. Chem. Soc.*, **115**, 198 (1919).
12. H. Kamebe and Y. Shibaski, *Kobunshi Kagaku*, **21** (225), 65 (1964).
13. T. L. Cottrell, *The Strengths of Chemical Bonds*, 2nd ed, Butterworths, London, 1958.
14. V. I. Vedeneyev, L. V., Gurvich, V. N., Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, *Bond Energies Ionization Potentials and Electron Affinities*, Edward Arnold, London, 1966.