

Thermal Degradation of Polymers. XXI. Vacuum Pyrolysis of Poly(*m*-N,N-dimethylaminostyrene); the Products Volatile at Pyrolysis Temperature, Liquid at Room Temperature

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Synopsis

The products obtained on degradation of poly(*m*-N,N-dimethylaminostyrene) in vacuo are described. The effects of molecular weight and pyrolysis temperature are discussed and compared with those observed for polystyrene under similar conditions. The liquid products of pyrolysis were separated and identified by gas-liquid chromatography using Kovats' retention index and by mass spectrometry. Product analysis revealed significant differences between the products of degradation of the two polymers, and mechanisms involving N-alkyl and N-aryl bond scission are proposed and discussed to account for this behavior. The degradation behavior of poly(*m*-N,N-dimethylaminostyrene) shows a marked molecular weight dependence. This is discussed in terms of the differences in the physical forms of the polymer produced on heating, namely, formation of a "melt" or retention of the original "fibrous" identity. Quantitative studies on the liquid fraction are also described and the behavior compared with results obtained on polystyrene.

INTRODUCTION

This work is a continuation of investigations into the thermal degradation behavior of ring-substituted styrene polymers. Previous papers¹⁻⁵ have reported vacuum pyrolysis studies on polymers based on *m*-aminostyrene, *p*-N,N-dimethylaminostyrene, *p*-hydroxystyrene, and *p*-methoxystyrene. We now report the thermal degradation behavior in vacuo of systems derived from *m*-N,N-dimethylaminostyrene (*m*-DAS).

EXPERIMENTAL

Materials

m-DAS was synthesized from acetophenone by the known route.⁶ The monomer was dried over anhydrous potassium carbonate and distilled yielding a clear colorless liquid as main fraction in 69% yield bp 54–56°C/0.05 mm, $N_D^{25^\circ\text{C}}$ 1.5767, lit.⁷ bp 105/2 mm, $N_D^{22^\circ\text{C}}$ 1.5863. Proton NMR gave the following absorptions on the δ scale: a singlet at 2.65 (6); a quartet of doublets 5.00, 5.15 (1) and 5.45, 5.75 (1); a complex multiplet centred at 6.70 (5).

ANAL. Calcd. for $\text{C}_{10}\text{H}_{13}\text{N}$: C, 81.63%; H, 8.84%; N, 9.52%. Found: C, 81.4%; H, 9.2%; N, 9.6%.

The monomer was homopolymerized in bulk under nitrogen at 70°C using

α,α' -azoisobutyronitrile (AZBN) as initiator at concentrations between 0.07% and 2.7% on monomer weight. High initiator concentrations gave polymers as solid blocks after 2 hr, while the low initiator concentrations gave polymers as viscous liquids which were removed from the oven after 6 hr and on cooling yielded clear elastomers. All polymers were purified by the dropwise addition of filtered 5% (w/v) solutions in AnalaR toluene to excess of methanol with vigorous mechanical stirring. The polymers were recovered by filtration, washed with methanol, and dried to constant weight at 111°/1.0 mm. This yielded *m*-DAS homopolymers 1 through 5 of atactic stereochemical configuration and different molecular weights. Styrene was similarly polymerized using AZBN and the polymers purified by reprecipitation yielding PS 6 and PS 7.

Characterization of PmDAS and PS samples was effected by

a. Dilution Viscometry. Intrinsic viscosities were determined in toluene at 25°C using a Sofica-Viscomatic automatic dilution viscometer.

b. Gel Permeation Chromatography (GPC). GPC analyses were carried out on representative samples of the PmDAS and PS homopolymers on a set of four columns connected in series. These columns consisted of beads of cross-linked PS gel of pore sizes 7×10^5 – 5×10^6 , 5×10^4 – 1.5×10^5 , 5×10^3 – 1.5×10^4 , and 7×10^2 – 2×10^3 Å. Polymer solutions (0.1%) in tetrahydrofuran were passed through the column at 1 ml/min at ambient temperature. Standard PS samples supplied by The Pressure Chemical Co., Pittsburgh, Pennsylvania, were used for calibration in the molecular weight range of 2×10^3 – 2×10^6 . All polymers gave a single peak of acceptable polydispersity.

c. Determination of Glass Transition Temperature (T_g). Differential scanning calorimetry (DSC) was used to determine the T_g of all samples. DSC studies were made using a Du Pont 900 thermal analyzer fitted with a DSC cell. Samples (≈ 5 mg) contained in a crimped aluminium pan were heated at 20°C/min in a static-air atmosphere and an empty crimped pan was used as inert reference. From the DSC curves recorded, the T_g was taken as the temperature defined by the intersection of the projected baseline with the line drawn along the point of inflexion of the trace leading into the transition. An average from five such determinations was recorded as the T_g .

Two representative samples of PmDAS were subjected to elemental analysis.

ANAL. Calcd for $C_{10}H_{13}N$: C, 81.63%; H, 8.84%; N, 9.52%. Found for PmDAS 1: C, 81.1%; H, 8.7%; N, 9.7%. For PmDAS 4: C, 81.6%; H, 9.1%; N, 9.6%. PmDAS samples 2, 3, and 5 gave for nitrogen N 9.5, 9.5, and 9.8%, respectively.

Table I gives a summary of the information derived from the three characterization methods for PmDAS and PS.

Apparatus and Procedures

Infrared Spectroscopy (IR). Spectra were recorded on a Grubb-Parsons Spectromajor. Liquid samples were run as films between rock-salt plates. Polymer samples were run as 1%–2% suspensions in potassium bromide discs or cast as films on rock-salt plates.

Nuclear Magnetic Resonance (NMR). Spectra were recorded from 2% solutions in carbon tetrachloride or deuteriochloroform using a Varian H.A. 100 (100 MHz), a Perkin-Elmer R32 (90 MHz), or a Perkin-Elmer "HITACHI" R20

TABLE I
Molecular Weights and Glass Transition Temperatures of *m*-N,N-Dimethylaminostyrene (*m*-DAS) and Styrene (S) Homopolymers

Sample no.	AZBN % (on monomer weight)	$[\eta]_0$	$T_g, ^\circ\text{C}$	$\bar{M}_v \times 10^{-4}$	\bar{M} peak $\times 10^{-4}$ c	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
PmDAS 1	2.64	0.15	82.5	1.821 ^a	1.700	—	—	—
PmDAS 2	1.67	0.19	82.5	2.778 ^a	2.800	—	—	—
PmDAS 3	0.75	0.27	83.5	5.203 ^a	3.800	7.517	2.683	2.80
PmDAS 4	0.07	0.94	85.0	48.267 ^a	35.000	—	—	—
PmDAS 5	0.13	1.02	85.0	55.846 ^a	37.000	49.000	16.910	2.90
PS 6	1.19	0.22	100.0	3.571 ^b	2.500	5.265	1.882	2.80
PS 7	0.02	1.82	106.0	67.180 ^b	58.000	—	—	—

^a Calculated using the Mark-Houwink equation with $K = 6.17 \times 10^{-4}$ and $\alpha = 0.56^3$

^b Calculated using $K = 1.16 \times 10^{-4}$ and $\alpha = 0.72$.⁸

^c \bar{M} peak refers to the "average molecular weight" determined from the calibration curve where \bar{M} peak is the molecular weight at the maximum of the distribution.

(60 MHz) instrument depending on the quantity of material available and the information required.

Mass Spectrometry (MS). Spectra were recorded using an A.E.I. mass spectrometer model MS902. When gas chromatography was used in conjunction with mass spectrometry a PYE 104 gas chromatograph was used with a column packed with 10% SE-30 on Celite 545, (80–100 mesh) operated at 200°C together with the MS 902.

Gas-Liquid Chromatography (GLC). Chromatograms were recorded on a Pye-Panchromatograph equipped with Pyrex columns (2 m × 4 mm) packed with 10% Carbowax 20M on Chromosorb W, AW-DMCS, (80–100 mesh) or 15% Apiezon N on Celite 545 (80–100 mesh) operated at various temperatures as shown in Tables II through V.

Vacuum Pyrolysis Apparatus. The system used was essentially that described in previous papers,^{1,3} with an Edwards Pirani 14 vacuum gauge replacing the Mcleod gauge.

Furnace and Ancillary Control Equipment. A Stanton-Redcroft low mass furnace (Model LM 8100) was used in conjunction with a Stanton-Redcroft LVP temperature programmer with its thermocouple located in the hot zone of the furnace.

Pyrolysis Procedure. A dried sample of polymer (100 mg) was subjected to pyrolysis in vacuo (3×10^{-4} cm Hg) as described in previous papers,^{1,3} with minor modification of procedure. After a pyrolysis time of 45 min the furnace was removed and the products allowed to equilibrate (PS, 3 hr; *PmDAS*, 4 hr). Preliminary studies on *PmDAS* showed that the gaseous products were more substantial than those from PS as indicated by the dramatic increase in pressure. For this reason it was considered necessary to continually evacuate the system during pyrolysis to effect efficient removal of volatiles.

Pyrolysis of PS was performed using a preignited open porcelain boat (length 6.5 cm, width 0.4 cm, depth 0.4 cm) and a Pyrex glass tube (length 6.0 cm, internal diameter 0.7 cm) closed at one end as sample container, whereas *PmDAS* was studied using only the glass tube sample container. After the equilibration period nitrogen was admitted to the system and fraction I allowed to warm to ambient.

Monomer Determinations. Estimation of the monomer in fraction I was effected in a similar manner to that described for PDAS.³ The contents of the trap (fraction I) were extracted with AR acetone (2 × 2.0 and 1 × 1.0 ml) and a known quantity (± 0.0002 g) of internal standard added (PS, isopropylbenzene; *PmDAS*, N-ethylaniline). From GLC analysis the average monomer:standard peak area was determined for six injections, and monomer was estimated using a calibration constructed from solutions of known composition. Analysis of fraction IV showed monomer to be absent.

Minor Component Determination. Quantitative determination of the "toluene" component was performed using an identical procedure to that described for the monomer. Identification of the minor components in fraction I (Kovats' indices) was effected by injection of the "neat" pyrolysate.

Oil Determination (Fraction IV). The oil fractions from PS and *PmDAS* were extracted from the quartz tube with chloroform (3 × 15 ml) and the solvent removed in a vacuum oven at ambient/1 mm Hg until constant weight was achieved (4–5 hr).

Analysis of the Gases (Fraction II). The vacuum system used in these studies allowed only simple qualitative assessment of the magnitude of the gaseous fraction by monitoring the pressure changes indicated by the Pirani gauge. Pyrolysis at the inlet of the MS 902 mass spectrometer, operating in a high-resolution mode, permitted identification of some of the gases produced.

RESULTS AND DISCUSSION

Monomer and Polymer Preparation and Characterization

The preparation of *m*-DAS was effected by the known route,⁶ and further confirmation of its structure was obtained from NMR spectroscopy. The singlet at $\delta = 2.65$ may be assigned to the methyl groups attached to nitrogen whereas the quartet of doublets at $\delta = 5.00, 5.15, 5.45,$ and 5.75 are due to the methylenic protons, vicinal to the aromatic nucleus. The methyne proton geminal to the aromatic nucleus is deshielded to such an extent that it is obscured by the aromatic protons. A chemical shift of $\delta = 6.7$ is expected for such a proton,⁹ and integration of the complex multiplet observed supports this interpretation. The polymerization of this monomer was effected using a nonoxidizing free-radical source to yield polymers of different molecular weights as indicated by intrinsic viscosity and GPC analysis. The T_g data are in accord with previous studies by Still and Oprea.⁶

Vacuum Pyrolysis Studies

Preliminary studies on *PmDAS* indicated that four fractions were observed on pyrolysis similar to those obtained previously for PS and other substituted styrene polymers.¹⁻⁵ *PmDAS* gave 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; and fraction IV, an oil fraction volatile at pyrolysis temperature, involatile at ambient temperature.

This paper is concerned with the qualitative and quantitative analysis of fraction I and reports the effect of molecular weight of the homopolymers and pyrolysis temperature upon the quantity and composition of this fraction.

Preliminary studies on PS using open preignited porcelain boats indicated that a further fraction could be discerned on the quartz pyrolysis tube above the boat. A thin but substantial film was deposited at this point which was shown by GPC to consist of polymer splashed from the degrading mass. A reduced sample mass and an increased boat size had little effect on the magnitude of this splashing. The problem was overcome using a Pyrex glass tube sealed at one end as the sample container. Preliminary studies were made on PS in an open porcelain boat and the partly closed tube. This was done to allow direct comparison of the two sample containers and to effect a calibration of the system by comparison with results of previous workers^{1,3} who used open boats in their studies.

In Figures 1 and 2 are presented the results obtained on PS samples of different molecular weights for percentage volatilization, percentage volatilization as monomer, and percentage volatilization as fraction IV, versus pyrolysis temperature, for the two sample containers used.

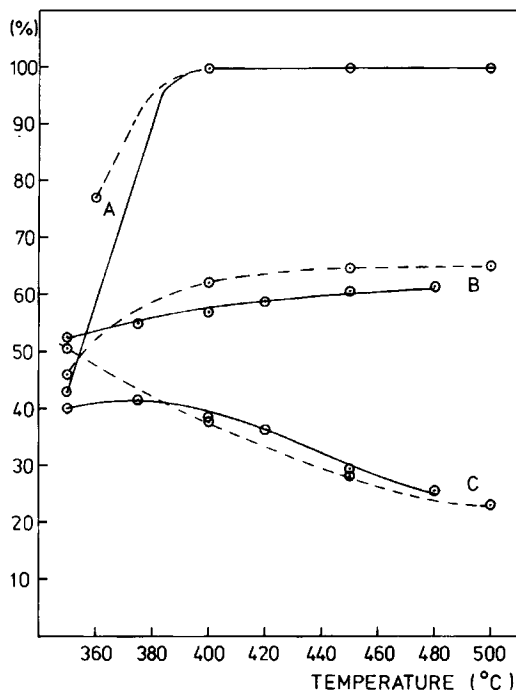


Fig. 1. Vacuum pyrolysis studies on PS using different sample containers: (—) glass tube; (---) porcelain boat; (A) percentage volatilized; (B) percentage volatilized as monomer; (C) percentage volatilized as fraction IV; (○) average from three runs.

Significant differences were observed for the two sample containers when volatilization was incomplete. PS in a porcelain boat gave a monomer yield of 46% at 350°C comparable with that found by Still and Jones¹ of 43% at 340°C and that found by Madorsky¹⁰ of 42% at 336°C. The ratio of nonmonomer: monomer of 1.1 at 350°C, although not in rigid agreement with previous work [1.4 (ref. 11) and 1.47 (ref. 3) at 345°C], was within the experimental error expected for differently prepared polymers subjected to pyrolysis in different apparatus. The ratio of nonmonomer:monomer at 350°C when a glass tube was used was 0.76. This is to be expected however, since the results obtained when the porcelain boat was used contained a contribution to fraction IV due to polymer splashing which resulted in an overestimation of the amount of the nonmonomer fraction.

At temperatures in excess of 400°C where complete volatilization occurs, the differences observed between the monomer and fraction IV yields for different sample containers were minimal and unaffected by the molecular weight of the PS sample used.

Pyrolysis employing a glass tube as sample container gave a decreasing nonmonomer:monomer ratio from 0.75 to 0.43 as the temperature increased from 350 to 480°C while a boat gave a ratio decreasing from 1.1 to 0.4. These results are of course numerically at variance with previous work by Still and Whitehead⁴ on PS pyrolyzed in an open boat (1.47 to 0.79 at temperatures 345 to 500°C) but are consistent in their overall trend. This effect has been attributed to the balance between unzipping to monomer and transfer reactions, where the un-

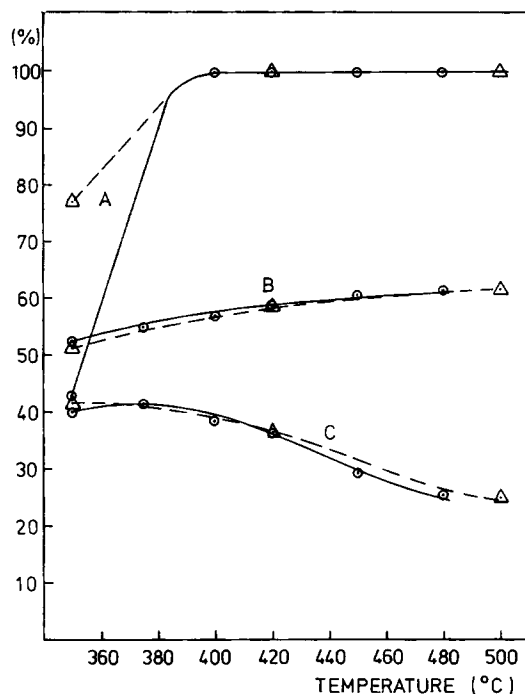


Fig. 2. Effect of molecular weight on vacuum pyrolysis of PS: (--- Δ ---) PS 6; (— \circ —) PS 7; (A) percentage volatilized; (B) percentage volatilized as monomer; (C) percentage volatilized as fraction IV.

zipping process gradually increases in rate more than the transfer processes as the temperature increases.

At temperatures prior to complete volatilization, the percentage weight loss was found to be dependent on polymer molecular weight, for example, PS 6, 76% and PS 7, 43% at 350°C, the lower molecular weight polymer suffering a greater percentage weight loss at a specific temperature, an observation previously reported by Madorsky and co-workers.¹²

While weight losses differ, the composition of the products changes little as shown by nonmonomer to monomer ratios of 0.77 for both polymers. This suggests that this phenomena is not associated with the more ready volatilization of oligomer fractions formed by random scission of the low molecular weight sample.

In view of the difficulties associated with the use of an open boat, a pyrex tube closed at one end was employed for studies on PmDAS.

Vacuum Pyrolysis of PmDAS: Fraction I—Qualitative Studies

Fraction I from PS was shown by IR, NMR, GLC, GLC/MS, and MS analysis to consist mainly of styrene with smaller quantities of benzene, toluene, ethylbenzene, isopropylbenzene, *n*-propylbenzene, α -methylstyrene, and *trans*- β -methylstyrene as shown in Table II. Fraction I from PmDAS would be expected to contain the *m*-*N,N*-dialkylamino-substitued analogs of the components found for PS, together with species indicative of *N*-alkyl bond cleavage and transfer as found for PDAS.³

TABLE II
Retention Indices for PS Liquid Fraction

Component no. in Fig. 3(a)	Retention index of components in PS fraction I	Retention index of reference compounds I_{ref}^a	Retention index of components in PS fraction I	Retention index of reference compounds I_{ref}^b	Compound
	I_{obs}^a		I_{obs}^b		
	472.4	—	392.8	—	—
	793.8	—	592.5	—	—
	853.3	—	635.4	—	—
	911.3	—	719.6	—	—
1	972.6	973.4	688.5	686.2	benzene
2	1073.4	1072.9	795.8	795.1	toluene
3	1159.4	1158.4	884.5	883.6	ethylbenzene
4	1203.6	1202.1	—	938.3	isopropylbenzene
5	1239.5	1238.5	—	970.6	<i>n</i> -propylbenzene
6	1281.9	1282.6	924.8	924.2	styrene
	—	1291.1	—	961.4	allylbenzene
	—	1337.6	—	1069.2	<i>n</i> -butylbenzene
7	1351.4	1352.2	1006.9	1006.1	α -methylstyrene
8	1423.6	1423.6	1057.4	1056.9	<i>trans</i> - β -methylstyrene

^a Column 15% Carbowax 20M on Chromosorb G (60–80 mesh), temperature 115°C.

^b Column 15% Apiezon N on Celite 545 (80–100 mesh), temperature 100°C.

In order to identify components of the PS liquid fraction, Kovats' retention indices¹³ of compounds likely to be present were determined by GLC on two different columns using mixtures of reference compounds. The Kovats index (I_{ref}) was evaluated using *n*-alkanes (C₅-C₂₂) and a computer program¹⁴ which allowed the calculation of the index for a series of unknowns using ten *n*-alkanes of any carbon number as calibration. In this way the peaks in the chromatogram, Figure 3(a), were assigned as shown in Table II. These results are consistent with the findings of previous workers.^{3,15,16} The components prior to benzene are products arising from cracking reactions.

Fraction I from PmDAS was shown to consist of monomer and compounds containing disubstituted and monosubstituted amino groupings by IR, NMR, and chemical tests. The number of products obtained was also found to be independent of pyrolysis temperature and polymer molecular weight.

Inspection of the chromatogram, Figure 3(b), obtained from the liquid fraction reveals the complexity of this system. The large number of peaks (17) made their assignment by the use of Kovats' retention indices alone very difficult. In order to facilitate identification, 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 or N-aryl group bond breakage together with subsequent hydrogen abstraction, radical substitution, and/or combination reactions. Possible adducts which were available or synthesized are listed in Table III, together with their retention indices determined on two columns.

The Kovats indices recorded in Table III may be compared with those evaluated for components of the PmDAS liquid fraction separated on the same columns under identical conditions shown in Tables IV and V, together with the assignments made.

It can be seen that more components were separated on the Apiezon column, and since it was impractical to synthesize and test all possible pyrolysis products a number were left unidentified using this method of analysis. For this reason GLC/MS was employed, not only to compliment retention index studies but where standard compounds were not available as the sole means of identification.

GLC/MS confirmed the presence of *m*-methylstyrene (m/e 118), N,N-dimethyl-*m*-toluidine (m/e 135), *m*-N,N-dimethylaminostyrene (m/e 147), *m*-xylene (m/e 106), styrene (m/e 104), and N,N-dimethyl-*m*-ethylaniline (m/e 149). In addition, evidence was obtained for α -methyl-*m*-N,N-dimethylaminostyrene (m/e 161), 16? in Figure 3(b); N-methylaminostyrene (m/e 133), 14? in Figure 3(b); *trans*- β -methyl-N,N-dimethylaminostyrene (m/e 161), 15? in Figure 3(b); and α -ethyl-*m*-N,N-dimethylaminostyrene (m/e 175), 17? in Figure 3(b).

As a result of GLC and GLC/MS the compounds listed in Table VI were identified in the PmDAS liquid fraction.

The N,N-dialkylanilines, with the exception of α -ethyl-*m*-N,N-dimethylaminostyrene, are the N,N-dimethylamino-substituted analogs of the compounds found for PS and are similar to those found for PDAS.³ The presence of mono-N-alkylanilines confirms that N-alkyl bond scission occurs as in the case of PDAS.³ In addition, the presence of small amounts of aromatic hydrocarbons indicates that N-aryl bond cleavage also occurs. This could occur by loss of the N,N-dimethylamino or the N-methylamino radical resulting in the formation

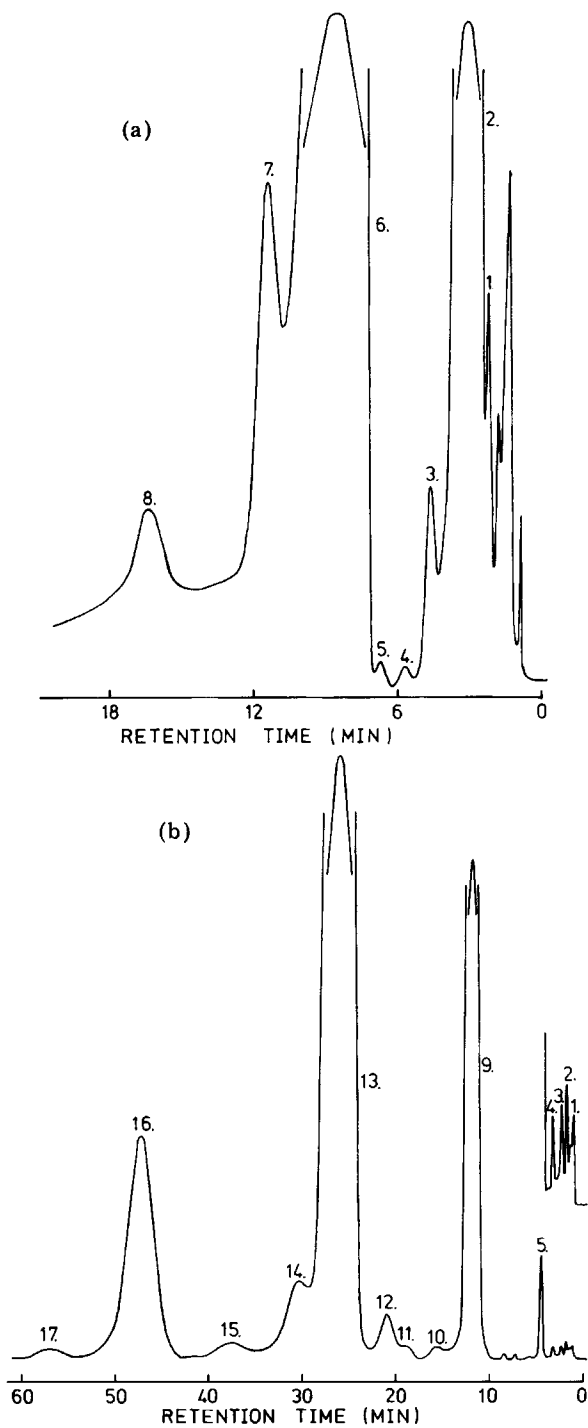


Fig. 3. GLC analysis of PS and PmDAS liquid fractions: (a) PS, 15% Carbowax 20M on Chromosorb G (60–80 mesh) operated at 115°C; (b) PmDAS, 10% Carbowax 20M on Chromosorb W, AW-DMCS (80–100 mesh) operated at 150°C.

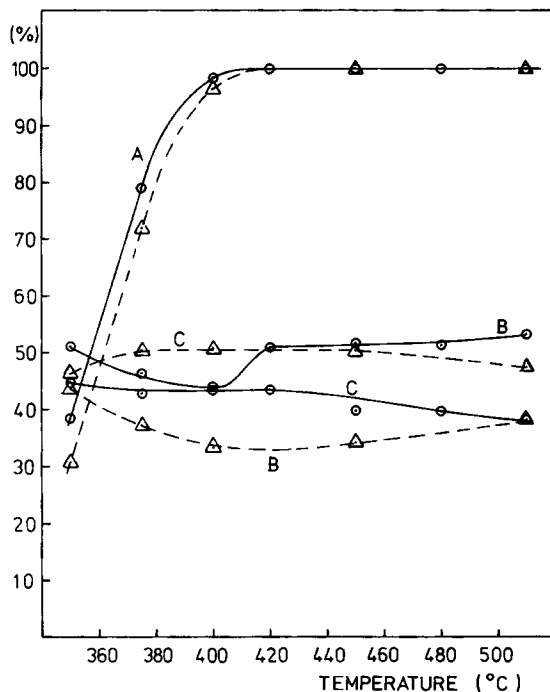


Fig. 4. Vacuum pyrolysis studies on PmDAS—effect of molecular weight: (---Δ---) PmDAS 2; (—○—) PmDAS 5; (A) percentage volatilized; (B) percentage volatilized as monomer; (C) percentage volatilized as fraction IV.

of a substituted phenyl radical which undergoes further abstraction and combination reactions as shown below:

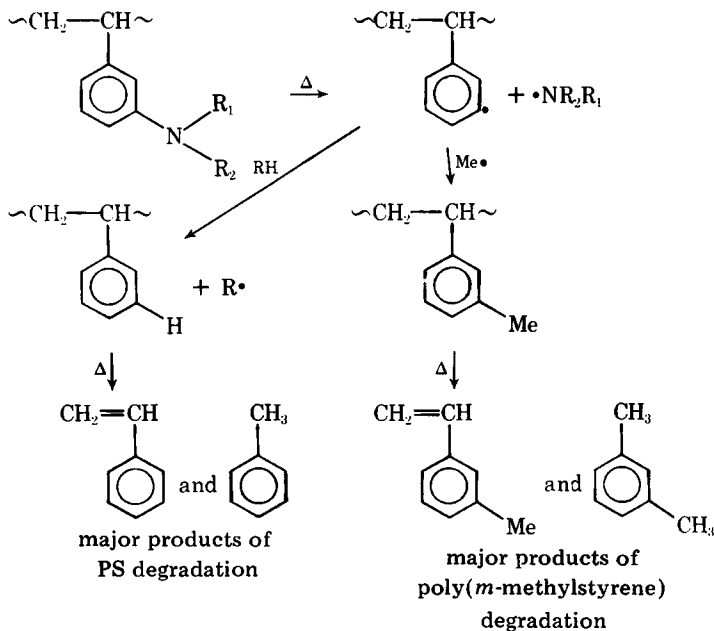


TABLE III
GLC Retention Index Data for Available Theoretically Possible Components of PmDAS Liquid Fraction

Reference compound	Retention index ^a	Retention index ^b
Dimethylamine	796.7	c
Methylamine	897.1	c
Benzene	967.0	d
Toluene	1069.7	812.1
Ethylbenzene	1160.9	d
<i>p</i> -Xylene	1169.2	918.5
<i>m</i> -Xylene	1175.8	917.8
<i>o</i> -Xylene	d	944.6
Styrene	1283.8	944.0
α -Methylstyrene	1353.3	1024.7
<i>m</i> -Methylstyrene	1388.1	1048.7
N,N-Dimethyl- <i>o</i> -toluidine ^e	1428.5	1100.6
<i>trans</i> - β -Methylstyrene	1430.1	d
2,5-N,N-Tetramethylaniline ^e	1511.5	1184.8
N,N-Dimethylaniline	1569.9	1138.3
N,N-Dimethyl- <i>p</i> -toluidine ^e	1642.5	1227.2
N,N-Dimethyl- <i>m</i> -toluidine	1653.2	1226.8
N,N-Dimethyl- <i>m</i> -ethylaniline ^e	1720.3	1298.1
N-Methylaniline	1726.6	1111.7
Aniline	1752.0	1017.1
N-Methyl- <i>m</i> -toluidine	1811.4	1207.9
<i>m</i> -Toluidine	1840.0	1116.9
<i>m</i> -N,N-Dimethylaminostyrene	1859.5	1353.1
N-Methyl- <i>m</i> -ethylaniline ^e	1886.6	1284.9
<i>m</i> -Ethylaniline	1924.3	1201.4
N-Methyl- <i>o</i> -toluidine	2056.2	1179.8
<i>m</i> -Aminostyrene	2100.8	1261.4

^a Column 10% Carbowax 20M on Chromosorb W, AW-DMCS (80–100 mesh), temperature 150°C. Components listed in order of retention index.

^b Column 15% Apiezon N on Celite 545 (80–100 mesh), temperature 150°C. Components now appear in different relative positions because of changed column polarity.

^c Not measured because retention times on this column less than 60 sec.

^d These compounds not detected by GLC/MS studies.

^e The tertiary amines synthesized in this study were made by interaction of trimethyl phosphate with the primary amine using the method of Thomas and co-workers.¹⁷ The secondary amines were prepared from the primary amine using methyl iodide.¹⁸ Structures were confirmed by combustion analysis and spectroscopic methods.¹⁹

where RH is a polymer chain containing a labile hydrogen atom and $R_1 = R_2 = \text{Me}$, or $R_1 = \text{H}$ and $R_2 = \text{Me}$.

The absence of *o*- and *p*-xylene and *o*- and *p*-methylstyrene suggests that *m*-xylene and *m*-methylstyrene were formed by the radical combination reaction shown above. The subsequent pyrolysis of the copolymer containing *m*-methylstyrene repeating units in addition to the normal units and those derived from other degradative routes rather than methyl radical attack on styrene and toluene giving the observed products. This is in line with observations on alkyl radical reactions on benzylic C–H bonds in alkyl benzenes rather than the ring.²⁰

The dimethylamino or monomethylamino radicals produced on degradation will undergo further reactions.²¹ The products from such reactions—methyl-

TABLE IV
 GLC Analysis^a of PmDAS Liquid Fraction

Component no. in Fig. 3(b)	PmDAS liquid fraction from pyrolysis I_{obs}	Retention Index of reference compound I_{ref}	Identity
1	812.9	—	?
2	1069.7	1069.7	toluene
3	1175.8	1175.8	<i>m</i> -xylene
4	1283.8	1284.8	styrene
5	1388.1	1387.4	<i>m</i> -methylstyrene
6	1458.8	—	?
7	1533.7	—	?
8	1575.4	—	?
9	1653.2	1653.6	N,N-dimethyl- <i>m</i> -toluidine
10	1720.3	1719.9	N,N-dimethyl- <i>m</i> -ethylaniline
11	1791.5	—	?
12	1811.4	1810.7	N-methyl- <i>m</i> -toluidine
13	1859.5	1858.6	<i>m</i> -N,N-dimethylaminostyrene
14	1957.5	—	?
15	2009.8	—	?
16	2043.8	—	?
17	2092.8	—	?

^a Carbowax column at 150°C.

amine, dimethylamine, and trimethylamine—were not detected by GLC or GLC/MS. This may be because they are lost from the liquid fraction on warming to ambient or because of their production in low yield or because of the difficulties in making accurate retention measurements on components with retention times less than 60 sec, i.e., component 1 in Table IV may be dimethylamine, for example.

The absence of products such as 2- or 4-methyl-*m*-N,N-dimethylaminostyrene suggests that methyl radical substitution in the substituted phenyl rings of the polymer does not occur. The production of α -ethyl-*m*-N,N-dimethylaminostyrene suggests that combination of chain radicals with alkyl radicals occurs:

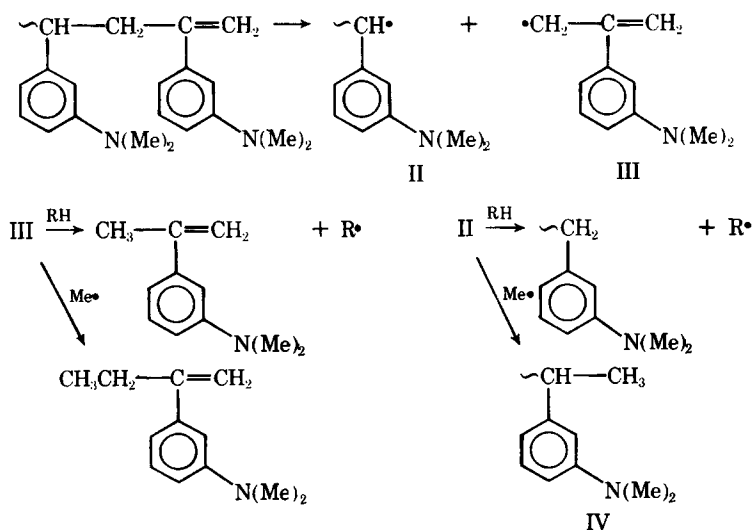


TABLE V
 GLC Analysis^a of PmDAS Liquid Fraction

Retention index of component of PmDAS liquid fraction I_{obs}	Retention index of reference compound I_{ref}	Identity
398.1	—	?
501.5	—	?
595.6	—	?
642.7	—	?
702.3	—	?
758.0	—	?
812.1	812.1	toluene
917.8	917.8	<i>m</i> -xylene
943.5	944.0	styrene
1002.2	—	?
1026.2	—	?
1048.9	1048.7	<i>m</i> -methylstyrene
1127.8	—	?
1171.3	—	?
1207.7	1207.9	N-methyl- <i>m</i> -toluidine
1226.5	1226.8	N,N-dimethyl- <i>m</i> -toluidine
1285.2	1284.9	N-methyl- <i>m</i> -ethylaniline
1298.7	1298.1	N,N-dimethyl- <i>m</i> -ethylaniline
1324.9	—	?
1352.9	1353.1	<i>m</i> -N,N-dimethylaminostyrene
1411.9	—	?
1446.2	—	?
1466.2	—	?
1486.5	—	?

^a Apiezon column at 150°C.

 TABLE VI
 Components Identified in PmDAS Liquid Fraction

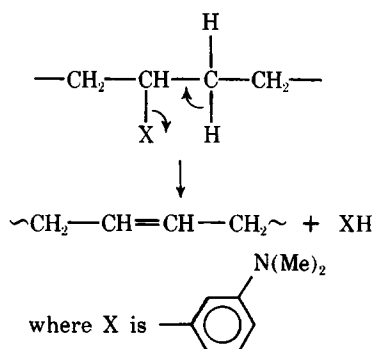
Classification	Compounds
Aromatic hydrocarbons	toluene, styrene, <i>m</i> -xylene, <i>m</i> -methylstyrene
Dialkylanilines	N,N-dimethyl- <i>m</i> -toluidine N,N-dimethyl- <i>m</i> -ethylaniline <i>m</i> -N,N-dimethylaminostyrene α -methyl- <i>m</i> -N,N-dimethylaminostyrene <i>trans</i> - β -methyl- <i>m</i> -N,N-dimethylaminostyrene α -ethyl- <i>m</i> -N,N-dimethylaminostyrene
Monoalkylanilines	N-methyl- <i>m</i> -toluidine N-methyl- <i>m</i> -ethylaniline N-methyl- <i>m</i> -aminostyrene

Subsequent degradation of units of type IV should yield N,N-dimethyl-*m*-isopropylaniline, which was not available for retention index measurements and was not detected by GLC-MS. By analogy with PS degradation, component 11 (Table IV) could possibly be this compound.

In the case of PDAS³ *p*-toluidine was observed among the products. No ev-

idence was found for *m*-toluidine production in this study, indicating that loss of two methyl groupings from the *m*-substituent did not occur.

The absence of *N,N*-dimethylaniline, the product analogous to benzene in *PmDAS* degradation, suggests that this product is not formed by the multicenter reaction proposed by Madorsky¹⁰ for benzene production in PS degradation:



It suggests that in the *PmDAS* system a dialkylamino-substituted phenyl radical may be generated which, because of the greater possibility of radical combination reactions than in PS, results in an enhanced formation of *N,N*-dimethyl-*m*-toluidine.

Quantitative Studies

Reference to Figure 3(b) indicates that two components, 9 and 13, comprising *m*-DAS and *N,N*-dimethyl-*m*-toluidine, are produced in significant amounts, and quantitative studies were restricted to these two components.

The overall degradation behavior of *PmDAS* revealed a complexity foreign to PS not only in the nature of the components of the liquid fraction but also in the effect of molecular weight of the *PmDAS* sample on the overall composition of the products as shown in Table VII. The high molecular weight sample gave a monomer yield of 51% at 350°C comparable to that from PS. The monomer yield was then observed to decrease gradually as the pyrolysis temperature was increased to 400°C, and then it began to gradually increase again. The monomer yield obtained from this polymer was always below that from PS, whose monomer yield showed a marked independence of polymer molecular weight in the range studied (Fig. 2). *PmDAS* 2, in contrast to *PmDAS* 5, gave much lower monomer yields, an observation reflected in nonmonomer:monomer ratios at 450°C of 1.67 for *PmDAS* 2 and 0.85 for *PmDAS* 5. At high molecular weights the monomer yield from *PmDAS* was generally greater than those obtained from the isomerically related poly(*p*-*N,N*-dimethylaminostyrene) (PDAS), which gave monomer yields independent of molecular weight in the range studied³ and a nonmonomer:monomer ratio of 1.50 at 445°C for studies using an open boat. Thus, in some respects *PmDAS* 2 exhibits behavior more akin to PDAS.

The amount of toluene produced from PS at 450°C was 1.8% of the total polymer volatilized and was in reasonable agreement with previous work³ and unaffected by PS molecular weight. *PmDAS* gave greatly increased amounts of the "toluene" derivative, i.e., *N,N*-dimethyl-*m*-toluidine (DMT) relative to

TABLE VII
Monomer and N,N-Dimethyl-*m*-toluidine (DMT) Production from *Pm*DAS Samples on Pyrolysis

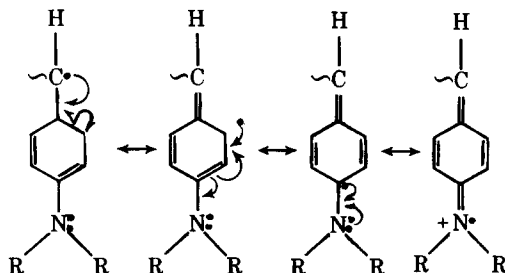
Pyrolysis temperature, °C	% Volatilized ^a	% Volatilized ^a as fraction IV	% Volatilized ^a as monomer	% Volatilized ^a as DMT	DMT ^a as % of monomer	Nonmonomer: monomer ratio ^{a,b}	
<i>Pm</i> DAS 5	350	38.4	44.7	51.1	5.3	9.4	0.98
	375	79.1	42.7	46.4	4.1	8.2	1.01
	400	98.3	43.5	44.0	3.9	8.2	1.07
	420	99.8	43.4	50.9	4.5	8.0	0.94
	450	99.8	39.7	51.6	4.2	7.6	0.85
	480	99.9	39.8	51.2	4.2	7.6	0.86
<i>Pm</i> DAS 2	510	99.9	38.2	53.2	4.2	7.2	0.80
	350	30.7	46.4	43.7	10.0	18.7	1.30
	375	72.0	50.5	37.2	9.4	20.2	1.61
	400	96.3	50.7	33.2	6.6	16.5	1.72
	450	99.8	50.3	34.2	6.8	16.5	1.67
	510	99.8	47.4	38.1	6.3	14.2	1.41

^a An average of three runs.

^b Nonmonomer includes the DMT component.

monomer, a feature consistent with the degradation behavior of other aminostyrene polymers.^{2,3} The production of DMT from *PmDAS* (Table VII), like the monomer, showed a strong dependence on polymer molecular weight. With the low molecular weight sample, the production of DMT constitutes a major degradation route.

In *p*-*N,N*-dialkylamino-substituted styrene polymers the chain radical formed on pyrolysis has a greater stability than that from PS due to the electronic effects of the substituent:



The chain radical derived from the *m*-dialkylamino polymer will have a similar stability to that from PS since the substituent is unable to contribute to the delocalization of the odd electron. This suggests that the monomer yields from *PmDAS* should be similar to those from PS. This is not the case and is due to the effects of N-alkyl and N-aryl bond cleavage which results in structures incapable of producing monomer and also yields radicals capable of terminating depropagation by combination, resulting in a decrease in "unzip" length and monomer yield. In addition, the large number of radicals produced in this system may abstract hydrogen from polymer chains, giving ideal precursor radicals for oligomer formation. These factors partly explain the reduced monomer yield relative to PS but do not explain the dependence of monomer yield and DMT yield on molecular weight. This may result from the physical differences observed for the two systems on pyrolysis; namely, *PmDAS* 1 forms a melt while *PmDAS* 4 remains as a fibrous material. This may result in less transfer reactions in *PmDAS* 4 because of reduced mobility, and the oligomer fraction may be unable to diffuse out of this system, resulting in the production of more monomer and DMT by secondary reactions.

Qualitative and quantitative studies on fractions III and IV will form the subject of part XXII of this series and will present further evidence for methyl group migration during the pyrolysis of *PmDAS* and discuss the nature of physical differences in form of *PmDAS* 1 and *PmDAS* 4 during pyrolysis.

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