

Thermal Degradation of Polymers. XXIII. Vacuum Pyrolysis of Poly(*p*-N,N-diethylaminostyrene); the Products Volatile at Pyrolysis Temperature, Liquid or Gaseous at Room Temperature

T. S. ELLIS and R. H. STILL, *Department of Polymer and Fibre Science, UMIST, Manchester, England*

Synopsis

The products obtained on vacuum pyrolysis of poly(*p*-N,N-diethylaminostyrene) are described. The effect of sample molecular weight and pyrolysis temperature are compared with that observed for polystyrene degraded under identical conditions. The liquid products were separated using gas-liquid chromatography and identified using Kovat's retention index and mass spectrometry. Significant differences were found between the products arising from the two polymers which are discussed in terms of mechanisms involving N-alkyl and N-aryl bond scission and the subsequent reactions of the generated radicals. Comparative quantitative studies are described and discussed.

INTRODUCTION

In two previous papers^{1,2} we reported the effect of pyrolysis temperature and polymer molecular weight on the products of pyrolysis of poly(*m*-N,N-dimethylaminostyrene) (*Pm*DAS) which was compared with polystyrene (PS) degraded under identical conditions. The *m*-N,N-dimethyl substituent was shown to influence the degradation behavior, and N-alkyl and N-aryl bond scission with resultant transfer reactions influenced the product composition and their nature relative to those from PS. Transfer reactions also resulted in the formation of crosslinked residues. The behavior of this system was compared and contrasted with the isomeric poly(*p*-N,N-dimethylaminostyrene).^{3,4} We now report the thermal degradation behavior in vacuo of systems derived from *p*-N,N-diethylaminostyrene (*p*-DEAS).

EXPERIMENTAL

Materials

p-N,N-Diethylaminostyrene was synthesized from N,N-diethylaniline by the known route.⁵ The monomer was dried over anhydrous sodium sulfate and distilled, yielding a clear colorless liquid as main fraction in 40% yield bp 88–90°C/0.1 mm, $N_D^{25^\circ\text{C}}$ 1.5814, lit.⁵ 90–93/0.3 mm, $N_D^{22^\circ\text{C}}$ 1.5845. Proton NMR gave the following absorptions on the δ scale: a triplet at 1.00 (6), a quartet at 3.15 (4), a quartet of doublets 4.85, 5.05 (1) and 5.35, 5.65 (1), doublets at 6.50 and 7.20 overlapping a quartet centered at 6.70, total (5).

ANAL. Calcd. for C₁₂H₁₇N: C, 82.29%; H, 9.71%; N, 8.00%. Found: C, 81.6%; H, 9.7%; N, 7.6%.

The monomer was homopolymerized in bulk under nitrogen at 70°C using α,α' -azobisisobutyronitrile (AZBN) at concentrations between 0.02% and 3.28% on monomer weight. Low initiator concentrations, 0.02%–0.09%, gave polymers as viscous liquids after 24 hr; the remainder were obtained as solid glasses after 5 hr. Purification was effected by precipitation as previously described for PmDAS,¹ and the samples were dried to constant weight at 128°C/1 mm Hg. This yielded PDEAS samples 1–6.

ANAL. Calcd. for C₁₂H₁₇N: C, 82.29%; H, 9.71%; N, 8.00%. Found for PDEAS 2: C, 82.3%; H, 9.6%; N, 7.9%. PDEAS 3–6 gave N, 7.9, 8.0, 7.9, and 7.9%, respectively.

The polymers were characterized by dilution viscometry, gel permeation chromatography (GPC), and differential scanning calorimetry by the methods reported in part XXI.¹ Table I gives a summary of the information derived from these characterization methods.

The data presented in Table I show PDEAS samples to have sensibly different molecular weights and that the T_g values change with molecular weight in the range studied.

Apparatus and Procedures

Infrared spectroscopy (IR), nuclear magnetic resonance (NMR), mass spectrometry (MS), and gas-liquid chromatography (GLC) were performed as previously described in part XXI.¹ The vacuum pyrolysis apparatus and pyrolysis procedures are also as previously described,^{1,2} with some slight modifications.

On removal of the furnace the system was continually evacuated for 4 hr and the products allowed to equilibrate for a further 16 hr. GLC confirmed the absence of measurable (>1 mg) amounts of monomer in the oil, fraction IV. N-Ethyl-*p*-toluidine was chosen as the internal standard for the determination of monomer in fraction I.

TABLE I
Molecular Weights and Glass Transition Temperatures of *p*-N,N-Diethylaminostyrene Homopolymers

Sample no.	[AZBN] (on monomer), wt-%	$[\eta]_0$	T_g , °C	$\bar{M}_v \times 10^{-4}$ a	$\bar{M}_{\text{peak}} \times 10^{-4}$ b	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
PDEAS 1	0.02	0.85	107.0	40.327	30.000	—	—	—
PDEAS 2	0.06	0.76	105.0	33.022	25.000	27.910	15.320	1.82
PDEAS 3	0.09	0.63	104.0	23.622	20.000	23.630	12.140	1.95
PDEAS 4	0.44	0.35	103.5	8.269	8.200	—	—	—
PDEAS 5	1.58	0.27	101.5	5.203	3.400	—	—	—
PDEAS 6	3.28	0.22	100.5	3.609	2.300	5.322	1.996	2.67

^a \bar{M}_v calculated using $[\eta] = KM^\alpha$, where $K = 6.17 \times 10^{-4}$ and $\alpha = 0.56$.³

^b \bar{M}_{peak} refers to the "average molecular weight" determined from the calibration curve of $\log M$ versus elution volume, where \bar{M}_{peak} is the molecular weight at the maximum of the molecular weight distribution.

RESULTS AND DISCUSSION

Monomer and Polymer Preparation and Characterization

p-DEAS was prepared by the known route,⁵ and further confirmation of its structure was afforded by NMR spectroscopy. The quartet at δ 3.15 is due to the methylenic protons of the ethyl groupings attached to nitrogen and is well downfield of the triplet at 1.00 (methyl groups). The quartet of doublets at 4.85, 5.05, 5.35, and 5.69 may be assigned to the methylenic protons of the vinyl group and the quartet at 6.7 which was just discernible between a pair of doublets at 6.50 and 7.2 may be ascribed to the methyne proton of the vinyl group, while the doublets are due to aromatic protons in a *p*-disubstituted system where the substituents differ in their chemical and electronic nature. The polymerization of *p*-DEAS was effected using a nonoxidizing radical source to yield polymers of different molecular weights as indicated by intrinsic viscosity and GPC studies. The normal initiator concentration-molecular weight relationship was qualitatively obeyed. The T_g data are in accord with previous studies by Still and Oprea.⁵

Vacuum Pyrolysis Studies

Preliminary studies on PDEAS indicated that four fractions were produced on pyrolysis. These fractions were: fraction I, a liquid fraction, volatile at pyrolysis temperature but involatile at liquid nitrogen temperature; fraction II, a fraction gaseous at liquid nitrogen temperature and at -80°C ; fraction III, a residue; and fraction IV, an oil fraction, volatile at pyrolysis temperature but involatile at ambient temperature.

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

Fraction I—Qualitative Studies

On the basis of previous studies on poly(*p*-N,N-dimethylaminostyrene) (PDAS),^{3,4} poly(*m*-N,N-dimethylaminostyrene) (*Pm*DAS),^{1,2} and polystyrene (PS),³ fraction I would be expected to contain the N,N-diethylamino-substituted analogs of the pyrolysis components obtained from PS together with products arising from N-alkyl and N-aryl bond cleavage.

In order to identify the components present in fraction I, Kovat's retention indices were determined on two columns for compounds likely to be present, in a similar manner to that described for *Pm*DAS.¹ Possible degradation products which were available or synthesized are shown in Table II, together with their retention indices.

The Kovats indices recorded in Table II may be compared with those evaluated for components of the PDEAS liquid fraction (Fig. 1) shown in Tables III and IV together with the assignments made.

It can be seen that more components were separated on the Apiezon column than on Carbowax. Since it was impractical to synthesize and test all possible pyrolysis products, a number were left unidentified. Toluene, styrene, and N-ethyl-*p*-ethylaniline were also identified by retention studies using 15% ne-

TABLE II
GLC Retention Index Data for Available Theoretically Possible Components of the PDEAS
Liquid Fraction

Reference compound	I_{obs}^a	I_{obs}^b	Reference compound	I_{obs}^a	I_{obs}^b
Diethylamine	802.2	c	N,N-Diethyl- <i>p</i> -toluidine	1708.7	1342.7
Triethylamine	812.4	c	N-Ethylaniline	1740.9	1184.5
Ethylamine	840.7	c	Aniline	1764.5	1635.0
Benzene	985.7	—	N,N-Diethyl- <i>p</i> -Ethylaniline ^d	1791.4	1424.8
Toluene	1090.9	—	N-Ethyl- <i>p</i> -toluidine	1806.6	1276.4
Styrene	1293.5	—	<i>p</i> -Toluidine	1828.9	1133.7
α -Methylstyrene	1363.0	—	N-Ethyl- <i>p</i> -ethylaniline ^d	1893.7	1361.7
<i>p</i> -Ethylstyrene	1481.4	1157.2	<i>p</i> -Ethylaniline	1917.6	1218.0
N,N-Diethylaniline	1648.6	1261.8	<i>p</i> -N,N-Diethylaminostyrene	2005.2	1523.8

^a 10% Carbowax 20M on Chromosorb W,AW-DMCS (80-100 mesh), temperature 165°C. Compounds listed in order of retention index.

^b 15% Apiezon N on Celite 545 (80-100 mesh), temperature 190°C. Components now appear in a different relative order because of changed column polarity.

^c Retention times too short for accurate determination of retention index.

^d The tertiary amines synthesized in this study were made from triethyl phosphate and the requisite primary amine using the method of Thomas and co-workers.⁶ The secondary amines were prepared from the primary amine using ethyl iodide.⁷ Structures were confirmed by combustion analysis, NMR, and other spectroscopic methods.⁸

TABLE III
GLC Analysis^a of PDEAS Liquid Fraction

Component no. in Fig. 1	PDEAS liquid fraction I_{obs}	Retention index of reference compound I_{ref}	Identity
1	791.6	—	?
2	1110.0	—	?
3	1295.0	1293.5	styrene
4	1398.7	—	?
5	1482.7	1481.4	<i>p</i> -ethylstyrene
6	1627.8	—	?
7	1659.6	—	?
8	1709.3	1708.7	N,N-diethyl- <i>p</i> -toluidine
9	1792.2	1791.4	N,N-diethyl- <i>p</i> -ethylaniline
10	1840.4	—	?
11	1876.1	—	?
12	1965.3	—	?
13	2005.8	2005.2	<i>p</i> -N,N-diethylaminostyrene
14	2074.2	—	?
15	2108.3	—	?
16	2146.6	—	?

^a Carbowax column at 165°C.

openly glycol adipate on Chromosorb W,AW-DMCS operated at 165°C. GLC/MS studies were employed in order to complement retention index studies and to provide a means of identification of components where the reference material was not available.

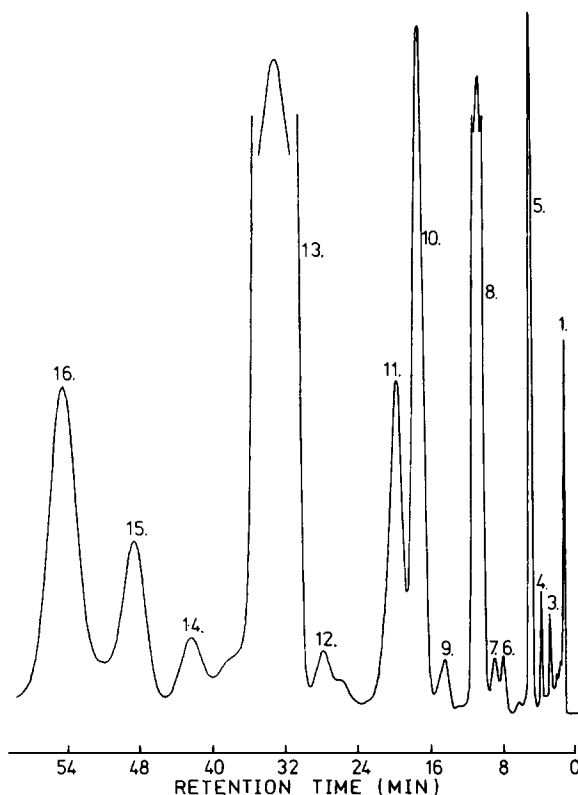


Fig. 1. GLC analysis of liquid fraction from PDEAS. Column 10% Carbowax 20M on Chromosorb W,AW-DMCS (80-100 mesh) operated at 165°C.

The spectra obtained indicated that the minor components were present in greater yield than from PmDAS, confirming the visual results obtained on GLC analysis. GLC/MS confirmed the presence of styrene (m/e 104), *p*-toluidine (m/e 107), *p*-ethylstyrene (m/e 132), N,N-diethyl-*p*-toluidine (m/e 163), N,N-diethyl-*p*-ethylaniline (m/e 177), and *p*-N,N-diethylaminostyrene (m/e 175). In addition, evidence was obtained for α -methyl-*p*-N,N-diethylaminostyrene (m/e 189) (14? in Fig. 1), *p*-aminostyrene (m/e 119) (16? in Fig. 1), N-ethyl-*p*-aminostyrene (m/e 147) (15? in Fig. 1), α -propyl-*p*-N,N-diethylaminostyrene, 2-(*p*-N,N-diethylaminophenyl)pent-1-ene (m/e 217) (? in Fig. 1), and 2-(*p*-N,N-diethylaminophenyl)butane (m/e 205) (10? in Fig. 1).

As a result of GLC and GLC/MS studies the compounds listed in Table V were identified in the PDEAS liquid fraction.

The N,N-diethylanilines with the exception of α -propyl-*p*-N,N-diethylaminostyrene, 2-(*p*-N,N-diethylaminophenyl)pent-1-ene, and 2-(*p*-N,N-diethylaminophenyl)butane, are the N,N-diethylamino-substituted analogs of the products found for PS and are similar to the N,N-dimethylamino compounds found for PDAS and PmDAS.^{1,3} The presence of the monoalkyl anilines confirms that N-alkyl bond scission occurs as with PDAS and PmDAS.^{1,3} The presence of aromatic hydrocarbons also indicates that N-aryl bond cleavage occurs as also found for PmDAS. These compounds arise as a result of the re-

TABLE IV
 GLC Analysis^a of PDEAS Liquid Fraction

Retention index of PDEAS liquid fraction I_{obs}	Retention index of reference compound I_{ref}	Identity
575.7	—	?
863.2	—	?
930.6	—	?
951.0	—	?
1017.4	—	?
1067.2	—	?
1134.9	1133.7	<i>p</i> -toluidine
1157.7	1157.2	<i>p</i> -ethylstyrene
1206.7	—	?
1239.6	—	?
1267.5	—	?
1277.3	1276.4	N-ethyl- <i>p</i> -toluidine
1343.2	1342.7	N,N-diethyl- <i>p</i> -toluidine
1376.0	—	?
1410.1	—	?
1422.3	—	?
1423.0	1424.8	N,N-diethyl- <i>p</i> -ethylaniline
1445.0	—	?
1524.3	1523.8	<i>p</i> -N,N-diethylaminostyrene
1600.5	—	?
1639.6	—	?

^a Apiezon column at 190°C.

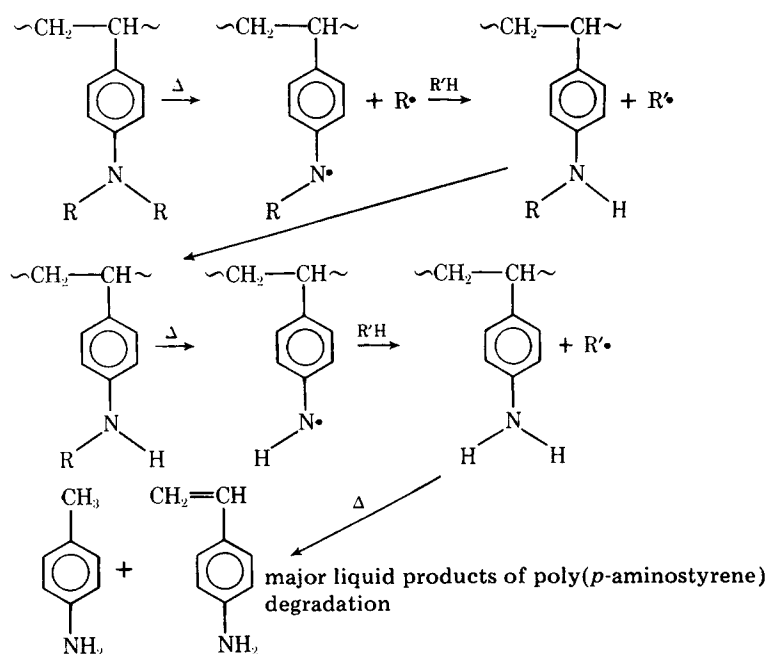
 TABLE V
 Components Identified in the PDEAS Liquid Fraction

Classification	Compounds
Aromatic hydrocarbons	toluene, styrene <i>p</i> -ethylstyrene
N,N-Dialkylanilines	N,N-diethyl- <i>p</i> -toluidine N,N-diethyl- <i>p</i> -ethylaniline <i>p</i> -N,N-diethylaminostyrene α -Methyl-N,N-diethylaminostyrene 2-(<i>p</i> -N,N-Diethylaminophenyl)butane α -propyl- <i>p</i> -N,N-diethylaminostyrene
Mono-N-alkylanilines	N-ethyl- <i>p</i> -toluidine N-ethyl- <i>p</i> -ethylaniline N-ethyl- <i>p</i> -aminostyrene
Primary aromatic amines	<i>p</i> -toluidine <i>p</i> -aminostyrene

action previously discussed for *Pm*DAS degradation.¹ As with *Pm*DAS, no evidence was found for alkylamine formation. This may be because such compounds are lost from the trapping system on allowing them to reach ambient temperature or because retention studies at retention times less than 60 sec led to irreproducible values of the retention index.

In this system, as with *PmDAS*, no evidence was obtained for products arising from alkyl radical substitution into the substituted phenyl rings of the polymer and their subsequent degradation. This is in accord with observations that alkyl radicals favor abstraction of benzylic hydrogen atoms in alkyl benzenes rather than radical substitution reactions.⁹

In contrast to *PmDAS*, chemical tests (carbylamine and azo coupling), GLC, and GLC/MS studies have shown the primary amines *p*-toluidine and *p*-aminostyrene to be present in the *PDEAS* liquid fraction. This suggests that in some cases both alkyl groupings are lost from the same amino grouping, resulting in a copolymer containing some *p*-aminostyrene repeating units:

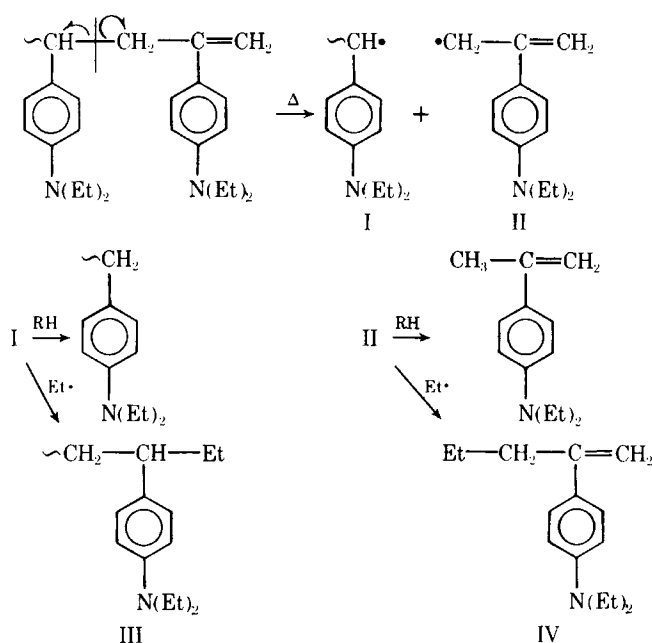


where $R = \text{Et}$ and $R'H$ is a polymer chain containing labile hydrogen atoms.

p-Toluidine was also identified among the *PDAS* degradation products,³ which suggests that *N,N*-dialkylamino groups in the para position are more prone to alkyl cleavage reactions. In addition, they appear to be more accessible to labile hydrogen atoms attached to the backbone of the same or adjacent chains than a grouping in the meta position which is partially buried within the macromolecule.

In the case of *PmDAS*, evidence was presented indicating that combination reactions occurred between chain radicals and methyl radicals produced by *N*-Me bond scission. If a similar mechanism is operative for *PDEAS*, the

products shown in the reaction scheme below should be obtained:



Subsequent degradation of units of the type III could yield 2-(*p*-N,N-diethylaminophenyl)butane, which together with IV, 2-(*p*-N,N-diethylaminophenyl)pent-1-ene, was shown to be present.

No evidence was found for N,N-diethylaniline formation, which suggests that the multicenter reaction as suggested for benzene production in PS¹⁰ does not operate.

Quantitative Studies

In a similar manner to *Pm*DAS, the liquid fraction from PDEAS contained two components in significant quantity. These components, 8 and 13 in Fig. 1, are N,N-diethyl-*p*-toluidine (DET) and *p*-DEAS. The overall degradation behavior of PDEAS was similar to that of PS (Fig. 2) in that molecular weight had relatively little effect on the percentage of monomer or DET produced at a specific temperature, as shown in Table VI and Fig. 2.

The amount of DET produced was essentially independent of the molecular weight of the sample undergoing pyrolysis. This feature contrasts with the behavior of *Pm*DAS and may be ascribed to the fact that PDEAS samples behaved in a similar manner to PS on heating and formed a "melt." The monomer yield was similarly essentially independent of molecular weight and was less than for PS, indicating a greater tendency toward transfer reactions in this polymer as indicated previously in the nature of the degradation products obtained. This is further borne out by the fact that the yield of DET is higher than that for toluene from PS, which is consistent with the degradation of "aminostyrene" polymers.^{3,11} The amount of DET produced (2.7% at 500°C) is similar to the quantity of N,N-dimethyl-*p*-toluidine produced from PDAS (2.8% at 500°C).³

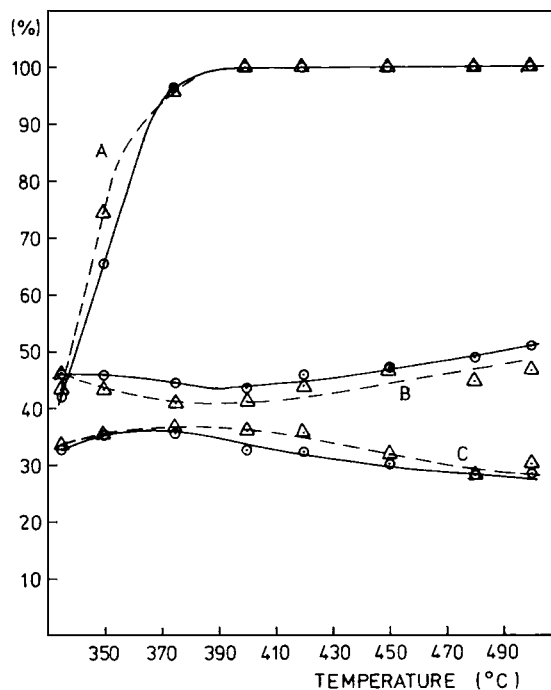


Fig. 2. Vacuum pyrolysis of PDEAS: (- - Δ - -) PDEAS 5; [— \circ —] PDEAS 1; (A) percentage volatized; (B) percentage volatized as monomer; (C) percentage volatized converted to fraction IV.

TABLE VI
Monomer and N,N-Diethyl-*p*-toluidine (DET) Production

	Pyrolysis temperature, °C	% Volatized	% Volatized as fraction IV	% Volatized as monomer	% Volatized as DET	DET as % of monomer	Non-monomer: monomer ratio
PDEAS 1	335	42.1	32.8	46.3	4.0	8.2	0.79
	350	65.6	35.3	46.0	3.6	7.2	0.84
	375	96.5	35.6	44.5	3.0	6.4	0.86
	400	99.8	32.6	43.6	2.7	5.9	0.81
	420	99.8	32.3	45.8	2.6	5.8	0.76
	450	99.8	30.1	47.0	2.6	5.4	0.69
	480	99.8	28.0	48.8	2.6	5.2	0.63
	500	99.8	28.3	50.9	2.7	5.1	0.61
PDEAS 5	335	43.2	33.6	46.4	4.4	8.6	0.82
	350	74.3	35.5	43.4	3.5	7.5	0.90
	375	95.8	36.5	40.9	3.1	6.9	0.97
	400	99.6	36.0	41.1	2.8	6.2	0.94
	420	99.9	35.7	43.8	2.8	6.1	0.88
	450	99.9	31.8	46.7	2.8	5.7	0.74
	480	100.0	28.2	44.6	2.6	5.6	0.69
	500	99.9	30.0	46.5	2.7	5.5	0.71

Fraction II—Gaseous Fraction

Significant pressure changes occurred during the pyrolysis of PDEAS, indicating that a gaseous fraction was formed. Direct pyrolysis on the inlet side of the MS-902 mass spectrometer followed by monitoring for ethane and butane indicated their presence in this fraction. Such products arise as a result of N-alkyl bond scission and the subsequent abstraction and dimerization reactions of the ethyl radical so generated. No attempt was made to monitor the system for ethylene production.

Qualitative and quantitative studies on fractions III and IV will form the subject of part XXIV of this series and will present further evidence for N-ethyl group cleavage during pyrolysis of PDEAS.

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