

Thermal Degradation of Polymers. VI. Vacuum Pyrolysis of Poly(*p*-N,N-dimethylaminostyrene). The Residue and the Fraction Volatile at Pyrolysis Temperature, Involatile at Room Temperature

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Synopsis

The effect of the extent of degradation of poly(*p*-N,N-dimethylaminostyrene) on the quantity and composition of the residue and the effect of pyrolysis temperature on the fraction volatile at pyrolysis temperature are discussed. The behavior of poly(*p*-N,N-dimethylaminostyrene) is compared to that of polystyrene. A significant difference has been found for the behavior of the residue from poly(*p*-N,N-dimethylaminostyrene), which is ascribed to a crosslinking reaction involving the dimethylamino substituent. Mechanisms to account for the observed products of degradation have been suggested and are discussed.

INTRODUCTION

In a previous paper¹ we reported the effect of temperature on the products of degradation from poly(*p*-N,N-dimethylaminostyrene) (PDAS) volatile at pyrolysis and at ambient temperature under high vacuum. Polystyrene (PS) degradation was similarly monitored under identical conditions for comparative purposes. Four major differences were observed for these fractions.

(a) The liquid fraction from PDAS contained 11 components which included secondary and primary amines.

(b) The monomer yield from PDAS was significantly lower than that from PS.

(c) The methyl-substituted components corresponding to toluene in PS degradation were present in increased quantity in the PDAS liquid fraction.

(d) The gaseous fraction was more complex and contained methane.

Mechanisms involving methyl group migration to chain radicals, thereby reducing the "zip length," were proposed to account for the reduced monomer yield, and the complexity of the products from PDAS was accounted

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for on the basis of methyl migration followed by hydrogen abstraction reactions. We now report studies on (a) the fraction volatile at pyrolysis temperature and involatile at ambient temperature and (b) the residue.

EXPERIMENTAL

Materials

The materials were as previously described.¹

Apparatus and Procedure

Mass spectrometry (MS), ultraviolet spectroscopy (UV), nuclear magnetic resonance (NMR), and gas-liquid chromatography (GLC) measurements were carried out as previously described in part V.¹ Infrared spectra were recorded as previously for soluble components. The residue from PDAS at temperatures above 275°C was however insoluble, and spectra were obtained in the following manner. Films of PDAS were cast on sodium chloride plates from toluene solution prior to pyrolysis. The films were then pyrolyzed on the sodium chloride support in a similar manner to the bulk polymer.

Vacuum Pyrolysis

Studies were carried out in the apparatus previously described.^{1,2} Pyrolysis was effected as before and the two fractions were obtained as described below.

Fraction III—The Residue. Samples of PDAS and PS were pyrolyzed for 30 min at temperatures between 200° and 325°C. The glasses obtained in the porcelain boat were used for intrinsic viscosity determination by the method described previously.¹

Fraction IV—The Oil Fraction. This was obtained from PDAS after pyrolysis at temperatures between 340° and 500°C as a viscous oil in the pyrolysis tube. A general pyrolysis time of 30 min was again used, and 24 hr was allowed for the system to come to equilibrium.¹ The oil was qualitatively analyzed by IR and MS using an AEI MS12 mass spectrometer fitted with a direct probe. Probe temperatures between ambient and 360°C were employed and the components of fraction IV were effectively fractionated.

The oil fractions from PS and PDAS (after equilibration) were subjected to GLC analysis for monomer. The oil from PS contained no residual monomer, and the oil fraction was extracted from the quartz tube with chloroform (3 × 25 ml) and the portions combined in a stainless-steel crucible preheated to constant weight. The crucible was then heated to constant weight in a vacuum oven at 60°C/10 mm of Hg. The percentage volatilized converted to oil was then calculated.

GLC analysis of the oil fraction from PDAS after 24 hr and seven days at 10⁻⁶ cm of Hg showed that it still contained entrained monomer.¹ However, from a knowledge of the amount of material volatilized and the quan-

tity of fraction I, the quantity of fraction IV was calculated making the assumption that fraction II, the gaseous fraction, was negligible when compared to fractions I and IV.

RESULTS AND DISCUSSION

Fraction III—The Residue

This fraction was colorless in case of PS, but varied from a pale yellow-green transparent glass to a green transparent glass containing black fibers as the percentage degradation was increased from 10% to 90% for PDAS. IR spectra recorded after 20%, 50%, and 75% weight loss were compared with those of the undegraded polymer. No significant differences could be detected, except for loss of resolution in the region 1500–1100 cm^{-1} in case of PDAS.

Comparative studies have been made on the effect of degradation temperature upon molecular weight for PS and PDAS. It has been suggested that with PS^{3,4} scission of "weak links" occurs prior to the point at which weight loss may be measured. Measurements on the effect of pyrolysis temperature on molecular weight were made by intrinsic viscosity determination. The results obtained are shown in Table I. It appears that PS and PDAS exhibit similar behavior until 275°C when weight loss and subsequent crosslinking of PDAS begins with resulting insolubility in toluene. This behavior closely parallels that observed previously for poly(*m*-aminostyrene) by Still and Jones.⁵ Prior to 275°C, a decrease in molecular weight appears to begin between 225 and 250°C without weight loss. This observation is similar to that of Jellinek³ and Grassie and Kerr⁴ who found that PS exhibited a decrease in molecular weight above 250°C. Jellinek,³ from a consideration of the work of Farmer and Sundralingham⁶ on hydroperoxide decomposition, has suggested that chain scission results from the existence of a limited number of hydroperoxide groups on the α -carbon atoms in the polystyryl main chain.

This would appear however to be unlikely for two reasons. (a) Cumene hydroperoxide, which may be regarded as a model compound for Jellinek's postulated structures in PS is known to decompose at 150°C with an

TABLE I
Effect of Pyrolysis Temperature on the Molecular Weight of PDAS and PS residues

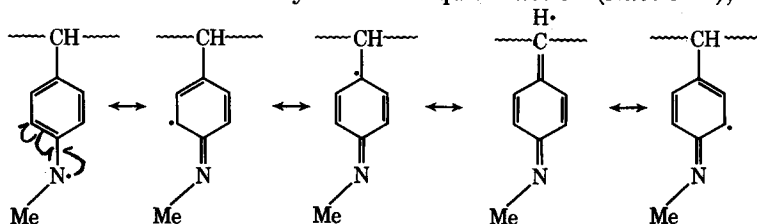
Pyrolysis temp., °C	[η] ₀		Percentage gel from PDAS residue, %
	PS	PDAS	
Ambient	1.63	0.98	0
225	1.63	0.98	0
250	1.05	0.69	0
275	0.85	0.58	4
300	0.60	— ^a	100
325	0.55	— ^a	100

^a Insoluble in toluene.

activation energy of 122 kJ/mole,⁷ which is significantly less than activation energies determined for thermally and radically initiated PS (189–273 kJ/mole).^{3,8–11} (b) The effect is also present in PDAS where residual hydroperoxide groups are unlikely in the midst of the vast excess of peroxide decomposing antioxidant units.

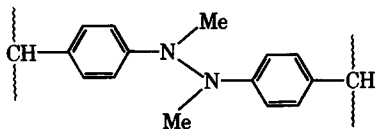
It would appear likely, therefore, that some weak link due to structural abnormalities such as that caused by an abnormal propagation or transfer step during polymerization is responsible for this molecular weight drop.

The crosslinking reaction observed with PDAS but not with PS could have occurred during the degradation process or alternatively during the cooling of the residue to ambient temperature prior to examination. MacCallum¹² has suggested that crosslinking by breaking and formation of a chemical bond at temperature as high as 500°C is unlikely unless it is accompanied by aromatization leading ultimately to carbonization. Such behavior has been found by Youren¹³ in the pyrolysis of ethylene-propylene–diene terpolymers after 1:5 and 1:5:9 hydrogen transfer reactions. PDAS, however, produces only a small percentage of residue (<2%) after treatment at temperatures in excess of 450°C. The cross-linked residues produced by PDAS after 10% to 90% weight loss gave on reheating to 360°C a quantity of monomer identical to that from a similar weight of the untreated polymer. This observation suggests that crosslinking may arise as a result of combination of radicals during the cooling period. Radicals obtained from PDAS as a result of scission of the nitro–methyl group bond are stabilized by resonance. This scission is shown to occur from the analysis of the liquid fraction (fraction I),



and transfer of the associated methyl radical accounts for reduced monomer yields of PDAS cf. PS. These stabilized radicals would be expected to be colored. PS would not be expected to yield radicals of this type since their formation would involve homolytic cleavage of a strong aromatic C–H bond in the pendent benzene ring.

In the case of PDAS, ESR studies have shown the presence of trapped radicals in the cooled glasses; PS, however, showed no such evidence of radicals. Combination of these radicals, derived from PDAS, on cooling would lead to structures of the type



in which the N-N bond is thermolabile having a bond dissociation energy of 189 kJ/mole which may be compared with that for the C-C bonds in the polystyryl main chain as typified by the C-C bond one removed from phenyl ring, as in case of isopropyl benzene (252 kJ/mole).^{14,15} On reheating, therefore, the crosslinks would break preferentially and would not inhibit unzipping. An alternative possibility is that transfer of a tertiary hydrogen atom from the backbone to the stabilized radical occurs, yielding a radical which crosslinks by combination or crosscombination.

Fraction IV—The Oil

Madorsky^{16,17} found a similar fraction on the pyrolysis of PS which he showed to consist of dimer, trimer, and some tetramer. The composition

TABLE II
Compounds Expected in PDAS Oil Fraction by Analogy with those Found for PS

Compound	Molecular Weight
<i>Dimer fraction</i>	
$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \\ \text{N}(\text{Me})_2 \qquad \text{N}(\text{Me})_2 \end{array} \quad (\text{I})$	282
$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \\ \text{N}(\text{Me})_2 \qquad \text{N}(\text{Me})_2 \end{array} \quad (\text{II})$	294
<i>Trimer fraction</i>	
$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \qquad \qquad \\ \text{N}(\text{Me})_2 \qquad \text{N}(\text{Me})_2 \qquad \text{N}(\text{Me})_2 \end{array}$	429
$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \qquad \qquad \\ \text{N}(\text{Me})_2 \qquad \text{N}(\text{Me})_2 \qquad \text{N}(\text{Me})_2 \end{array}$	441

of the fraction remained constant, independent of pyrolysis temperature, and trimer constituted the major component of the fraction.

By analogy with PS, the oil fraction from PDAS would be expected to contain the compounds shown in Table II. This, however, makes the assumption that the degradation is as simple as that for PS and that this fraction is unaffected by the methyl migration reaction found on analysis of fraction I.

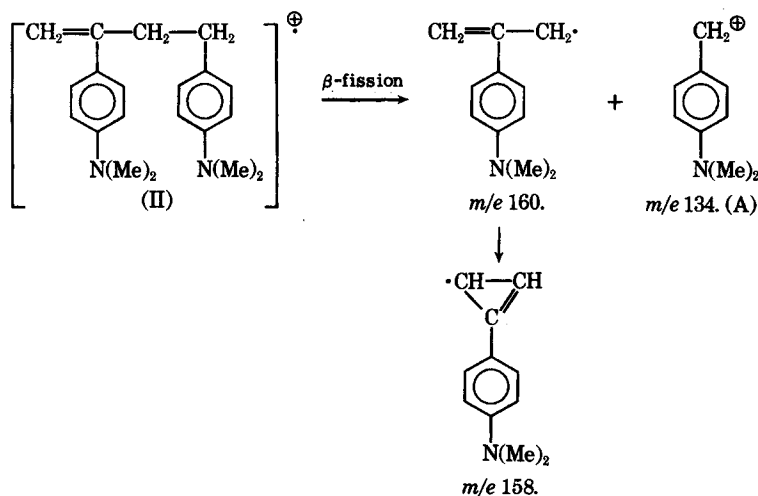
That this is not the case can be seen from the qualitative studies performed on PS and PDAS. The IR spectra of both oils revealed significant absorptions not present in the IR spectra of the respective monomers as shown in Table III.

The characteristic C—H* out-of-plane (o.o.p.) vibration present in monomers of the type $\text{CH}_2=\text{CHX}$ is absent in case of PS but is present in PDAS at 990 cm^{-1} , indicating monomer entrainment as previously shown by GLC. These assignments are in agreement with the accepted structures for dimer and trimer as postulated by previous workers. In addition, studies on the oil fraction by MS using a heated probe has resulted in separation of the components of the oil fractions facilitating their qualitative analysis. The mass spectra obtained at various probe temperatures for PDAS are shown in Figures 1a to 1e.

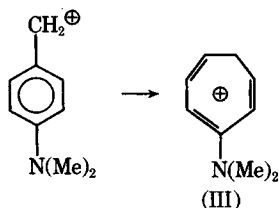
At ambient probe temperatures, only monomeric components are evident in particular residual monomer (m/e 146,147). Comparison of the spectrum with that of the monomer shows that peaks of mass 133 and 161 do not result from fragmentation of the monomer.

On the previous evidence for methyl migration the peak at m/e 133 suggests the presence of *p*-N-methylaminostyrene in the oil fraction, and by analogy with PS the peak at m/e 161 is due to α -methyl-*p*-N,N-dimethylaminostyrene which has been entrained in the oil. As the probe temperature is raised to 120°C , the dimeric species I and II as suggested in Table II become apparent (m/e 282 and 294).

The fragmentation pattern expected from such structures is

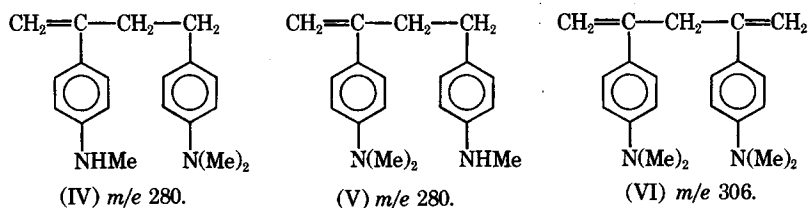


The ion A will also rearrange to yield the more stable tropylium ion III,

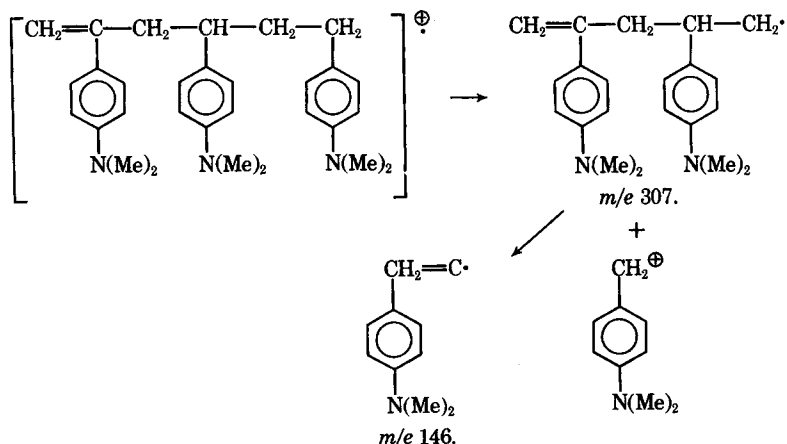


which is in agreement with the observed spectra. The other component of the dimer fraction m/e 282 will similarly give fragments of m/e 134 and 148, in general agreement with the observed spectra.

As the probe temperature is increased further to 180°C, the unsaturated dimer II is still evident but the saturated dimer I is no longer present. In addition, peaks at m/e 280 and 306 suggest the presence of secondary amines IV and V and the doubly unsaturated dimer VI:



Dimers such as IV and V would yield substituted tropylium ions of m/e 134 and 120, respectively, which are evident in Figure 1c. At higher temperatures (Fig. 1d, 250°C, and Fig. 1e, 340°C), unsaturated and saturated trimer and tetramer are evident from peaks at m/e 441, 429 trimers as in Table II and tetramer at m/e 576 and 588. In each case the substituted tropylium ion III (m/e 134) is present in the fragmentation pattern, suggesting fragmentation of the trimer and tetramer of the type shown below for the unsaturated trimer:



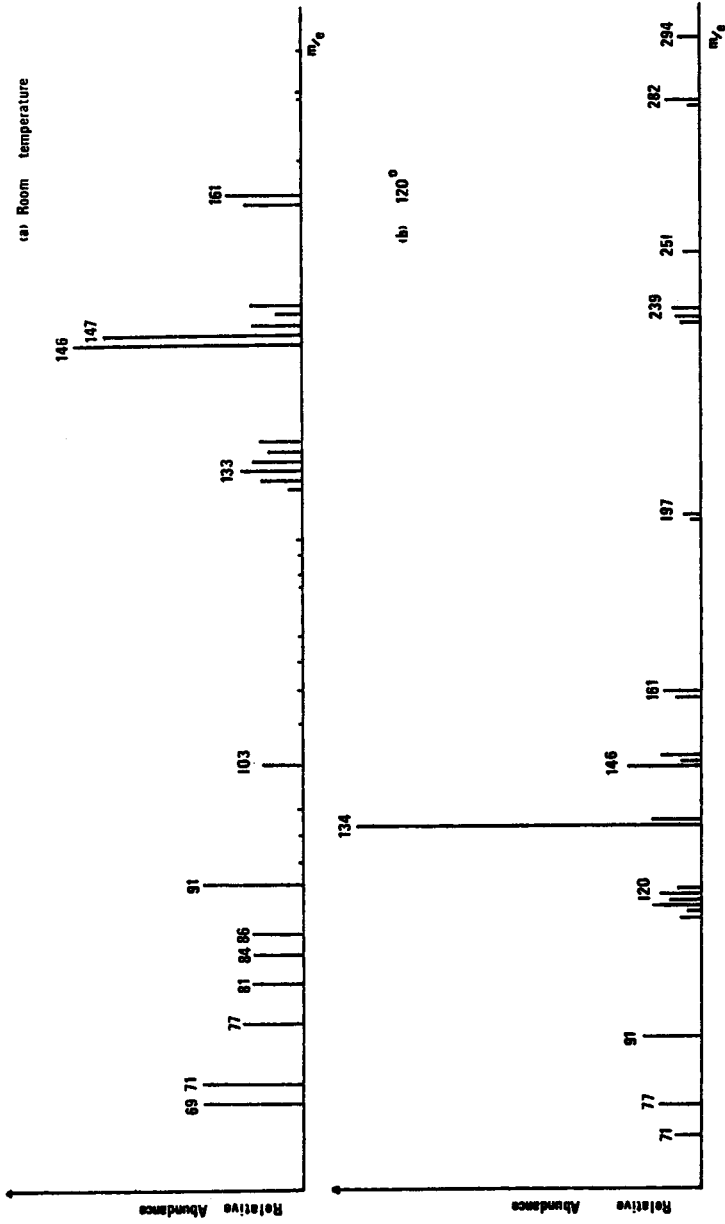


Fig. 1 (continued)

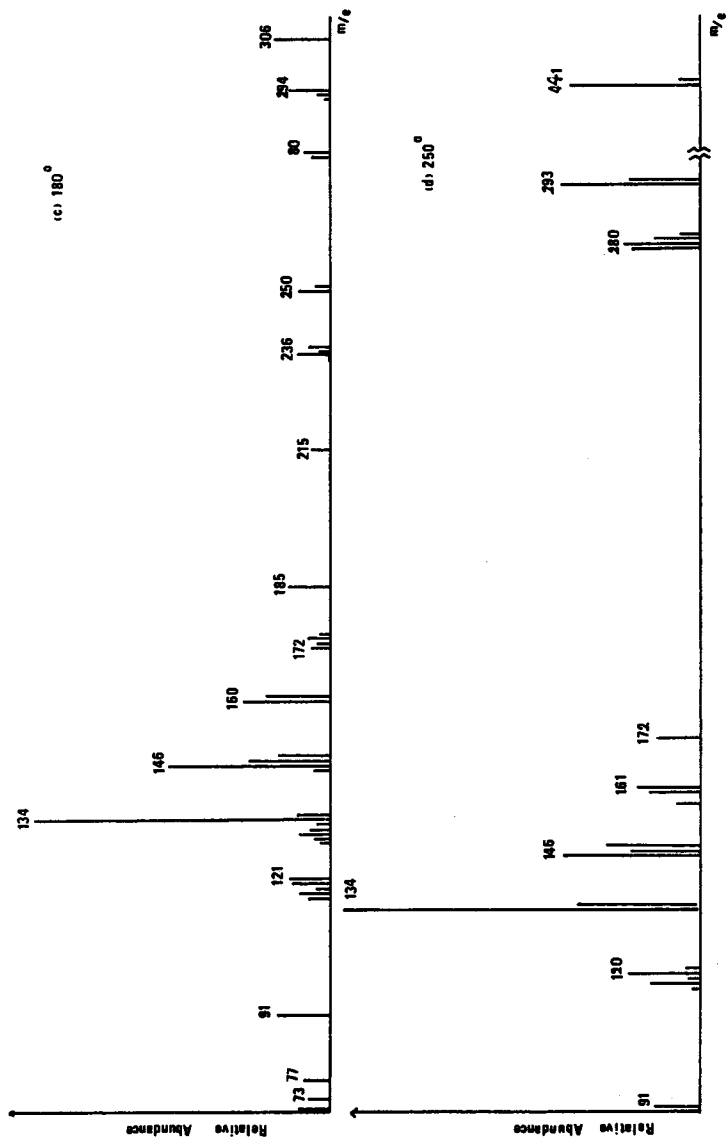


Fig. 1 (continued)

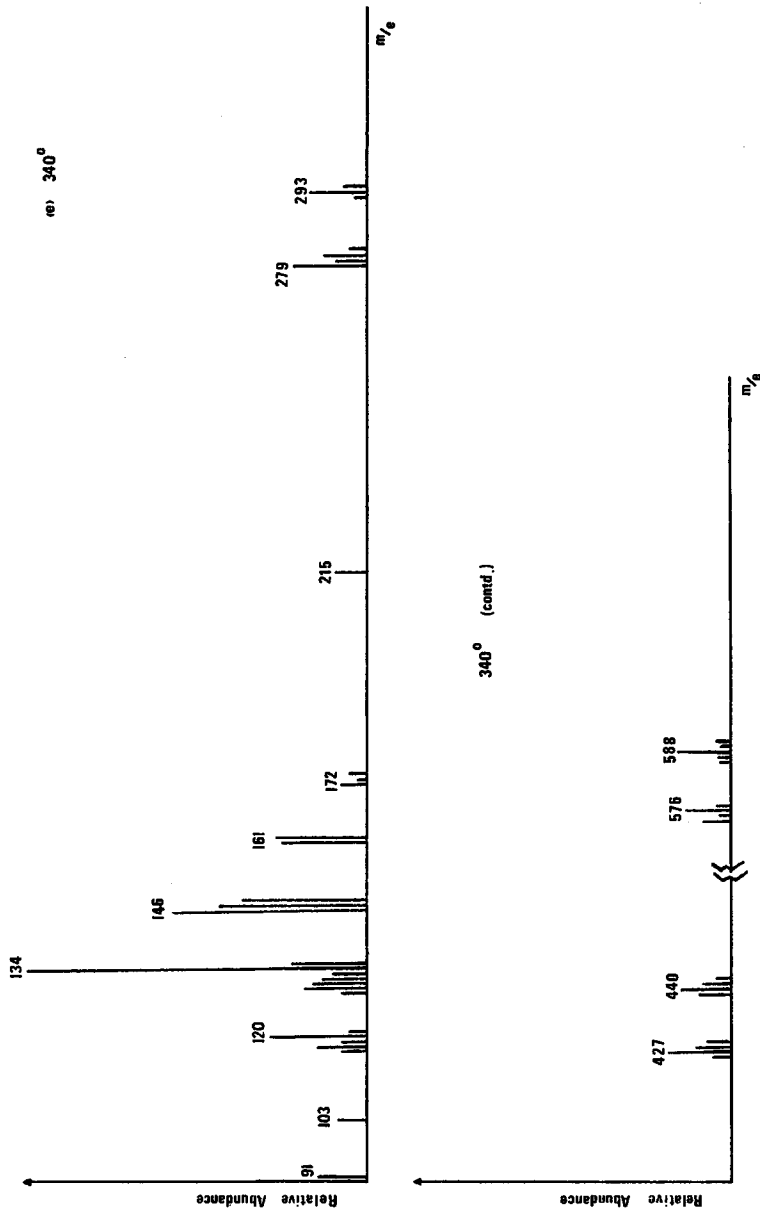


Fig. 1. Mass spectra of the oil at different probe temperatures.

TABLE III
Major Absorptions in the IR Spectra of PS and PDAS Oil Fractions

Absorption, cm^{-1}	Assignment in $\text{CH}_2=\text{CR}_2$
3080	C—H stretch
2940	— CH_2 —
2860	
895	CH_2 —o.o.p. def.
1630	C=C stretch

* Slight variation between PS and PDAS.

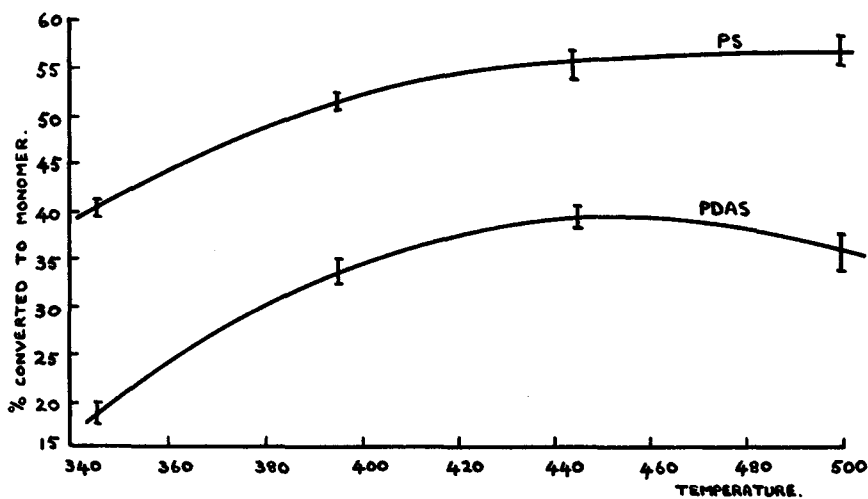


Fig. 2. Monomer production from polystyrene and poly(*p*-*N,N*-dimethylaminostyrene): I indicates span of points.

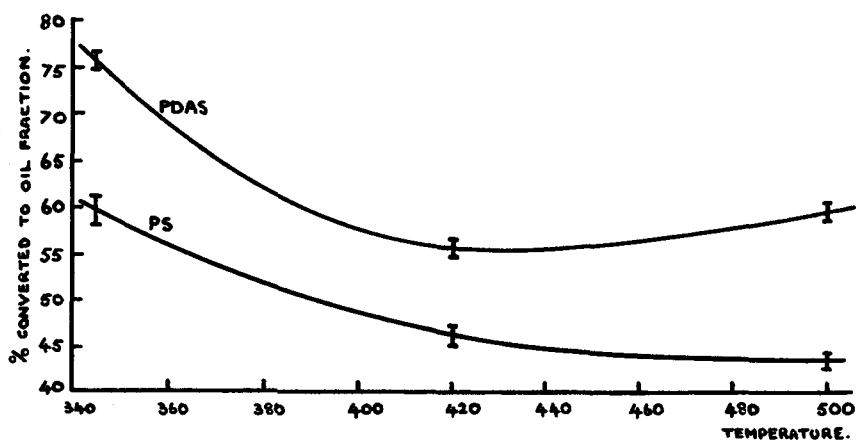
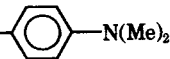
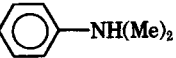


Fig. 3. Oil production from polystyrene and poly(*p*-*N,N*-dimethylaminostyrene): I indicates span of points.

TABLE IV
Components of PDAS 0.1 Fraction

m/e	•Assignment
280	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \\ \text{R} \qquad \qquad \text{R}' \end{array}$
280	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \\ \text{R}' \qquad \qquad \text{R}' \end{array}$
282	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \end{array}$
294	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \end{array}$
306	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{C}=\text{CH}_2 \\ \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \end{array}$
429	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \qquad \qquad \text{R} \end{array}$
441	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \qquad \qquad \text{R} \end{array}$
576	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \qquad \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \qquad \qquad \text{R} \qquad \qquad \text{R} \end{array}$
588	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\ \qquad \qquad \qquad \qquad \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \qquad \qquad \text{R} \qquad \qquad \text{R} \end{array}$
<p>where R = </p> <p>and R' = </p>	

It would appear that the components of the oil fractions from PDAS and PS are very similar, except for products arising as a result of methyl migration and subsequent hydrogen transfer. Thus, the mechanism of oil formation is similar to that proposed previously for poly(*m*-aminostyrene)⁵ with methyl group migration and hydrogen transfer reactions superimposed. Components identified in the PDAS oil fraction are summarized in Table IV.

In addition to the qualitative product analysis of the oil fraction, the effect of pyrolysis temperature on the quantity of the oil was investigated for both PS and PDAS. The results are shown in Figures 2 and 3 where the effect of pyrolysis temperature on monomer and oil production is shown respectively for each polymer. It can be seen that the polymers behave differently. The monomer yield from PS is higher than from PDAS at all temperatures, whereas for the oil fraction the converse is true. In both cases, however, as pyrolysis temperature increases, monomer yield increases and the oil yield falls. In general, the factor which affects the yield of monomer in vinyl polymer degradation is thought to be the balance between the depropagation reaction to yield monomer and intra- and intermolecular transfer reactions to yield nonmonomer.

TABLE V
Effect of Pyrolysis Temperature on Nonmonomer: Monomer Ratio

Pyrolysis temp., °C	Nonmonomer: monomer ratio	
	PDAS	PS
345	4.27	1.47
395	1.94	0.96
445	1.50	0.86
500	1.74	0.79

Thus, the effect of temperature upon the nonmonomer:monomer ratio yields information on the effects of temperature on these reactions and is shown for PDAS and PS in Table V. It can be seen that at all temperatures, the ratio for PDAS is much bigger than that for PS supporting methyl-group transfer reactions. As the temperature increases in both cases, the ratio rapidly decreases indicating that the rate of depropagation reaction increases at a very much faster rate than that of the transfer reactions. In the case of PDAS, the zip length (the amount of monomer produced per chain cleavage) is much smaller than that for PS and appears to increase in the same way as PS, until at 500°C it appears again to decrease. This behavior is reflected in terms of the quantity of monomer produced from PDAS which appears to pass through a maximum value at 445°C. This is possibly due to the influence of a small amount of carbonization on the unzipping process as described previously.

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