

# Thermal Degradation of Polymers. XXIV. Vacuum Pyrolysis of Poly(*p*-N,N-diethylaminostyrene); the Residue and the Fraction Volatile at Pyrolysis Temperature, Involatile at Room Temperature

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

## Synopsis

Comparative studies were made of the residue and the fraction volatile at pyrolysis temperature, involatile at ambient temperature obtained from polystyrene and poly(*p*-N,N-diethylaminostyrene) degraded under identical conditions. Poly(*p*-N,N-diethylaminostyrene) yielded a crosslinked glassy residue after pyrolysis at temperatures greater than 250°C, and crosslinking is accompanied by N-alkyl group scission as shown by mass spectrometry. The components of the fraction volatile at pyrolysis temperature, involatile at ambient temperature were separated and identified by GPC and mass spectrometry. Mechanisms involving N-alkyl and N-aryl bond scission are proposed to account for the observed products. Quantitative studies on the effect of pyrolysis temperature and polymer molecular weight on the residue and the volatile fraction are described and discussed. No molecular weight dependence was observed for this system in the range studied.

## INTRODUCTION

In a previous paper<sup>1</sup> we reported the effect of temperature and polymer molecular weight on the products of degradation of poly(*p*-N,N-diethylaminostyrene) (PDEAS) volatile at pyrolysis and ambient temperature under high vacuum. Polystyrene (PS) was monitored under similar conditions for comparative purposes. Five major differences were observed for these fractions:

- a. The liquid fraction from PDEAS contained a greater number of components than that from PS. It was found to contain primary and secondary amines and aromatic hydrocarbons in addition to the N,N-diethylamino-substituted analogs of the compounds obtained from PS.
- b. The N,N-diethyl-substituted component corresponding to toluene was present in increased quantity but was not molecular weight dependent.
- c. The monomer yield from PDEAS was lower than from PS but was not molecular weight dependent.
- d. Compounds indicative that ethyl radicals combined with chain radicals were identified.
- e. The gaseous fraction was more complex, and ethane, butane, and methane were identified.

Mechanisms involving ethyl group migration to chain radicals, thereby reducing the "zip length," were proposed to account for the reduced monomer yield together with the increased frequency of hydrogen transfer leading to precursor radicals for oligomer formation. The complexity of the products from PDEAS

was accounted for on the basis of N-alkyl and N-aryl bond scission and the subsequent reactions of the radicals so generated which led to molecules containing units of changed structure which decomposed to yield the observed products.

We now report studies on (a) the fraction volatile at pyrolysis temperature involatile at room temperature and (b) the residue.

## EXPERIMENTAL

**Materials.** The materials were as previously described.<sup>1</sup>

**Apparatus and Procedures.** Nuclear magnetic resonance (NMR) and gas-liquid chromatography (GLC) were carried out as previously described in part XXI.<sup>2</sup> Infrared spectra were recorded as previously for soluble components. PDEAS, which yielded a partially soluble or insoluble residue on pyrolysis, was cast on rock salt plates from toluene or chloroform with subsequent pyrolysis of these thin films. Torsional braid analysis (TBA), gel permeation chromatography (GPC), gas-liquid chromatography/mass spectrometry (GLC/MS), and mass spectrometry (MS) were carried out as described previously in part XXII.<sup>3</sup>

**Vacuum Pyrolysis.** Studies were carried out in the apparatus previously described.<sup>2,4</sup> Pyrolysis was effected using a Pyrex glass tube sample container closed at one end, and samples of the two fractions were obtained and characterized in a similar manner to that described for *PmDAS*.<sup>3</sup>

## RESULTS AND DISCUSSION

Comparative studies were made on PS and PDEAS.

### Fraction III—The Residue

The appearance and solubility characteristics of the residue obtained after pyrolysis of PS and PDEAS samples of different molecular weights in the temperature range of 350–400°C are summarized in Table I. The data in the table indicate that PS and PDEAS behave in a different manner on pyrolysis, with PDEAS apparently crosslinking. This behavior is similar to that observed for poly(*p*-N,N-dimethylaminostyrene) (PDAS)<sup>4</sup> and *PmDAS*.<sup>3</sup> The behavior of *PmDAS*, which yields a glassy or fibrous residue on cooling dependent on the molecular weight of the original polymer, is however not duplicated by PDEAS in the molecular weight range studied. IR and elemental analysis on samples of PDEAS partially degraded at 400°C gave results which failed to show any significant changes from the original polymer.

TABLE I  
Appearance and Solubility Characteristics of PS and PDEAS Residues

Source of residue	Appearance	Solubility characteristics
PS 6 and 7 <sup>a</sup>	clear colorless glass	soluble in toluene and chloroform
PDEAS 1 and 5 <sup>b</sup>	clear yellow-brown glass	insoluble with gel formation

<sup>a</sup> See ref. 2.

<sup>b</sup> See ref. 1.

TABLE II  
 Weight Loss and Solubility Studies on PDEAS Residues<sup>a</sup>

Sample		200°C <sup>b</sup>	250°C	300°C	350°C
PDEAS 2	Solubility	S	S	Is	I
	Percent weight loss	0.1	0.1	2.6	69.6
PDEAS 4	Solubility	S	S	Is	I
	Percent weight loss	0.6	0.5	3.7	62.7

<sup>a</sup> I = Insoluble in toluene; Is = mainly soluble with slight amount of gel formation; S = soluble in toluene.

<sup>b</sup> Pyrolysis temperature.

Attempts were made to establish the temperature at which PDEAS became insoluble and if insolubility was related to volatile formation. A series of pyrolyses were carried out at temperatures below 350°C, and the results are summarized in Table II.

The results in Table II suggest that insolubilization is accompanied by volatile evolution, and this is confirmed by the increase in pressure observed on the pyrolysis rig at these temperatures. When the polymer was heated to 250°C after first degassing the system at a temperature 10°C above its  $T_g$  and the products obtained were monitored using MS for ions at  $m/e$  16 ( $\text{CH}_4^+$ ), 30 ( $\text{C}_2\text{H}_6^+$ ), and 58 ( $\text{C}_4\text{H}_{10}^+$ ), all were observed. No volatiles were detected at temperatures below 250°C. This behavior contrasts with that observed for *PmDAS*<sup>3</sup> but is similar to that of *PDAS*<sup>4</sup> where insolubility occurred at approximately 275°C. Studies were made by TBA on PDEAS samples in an attempt to establish if crosslinking occurred during the heating or cooling cycle. The results obtained for PDEAS are similar to those obtained by Stadniki and coworkers<sup>5</sup> for PS. This contrasts with the behavior reported for *PmDAS*<sup>3</sup> and confirms that PDEAS has a higher threshold temperature for crosslinking than *PmDAS*. No evidence was obtained for crosslinking during either the heating or cooling cycle in the temperature range ambient to 200°C, the limit of the apparatus used. This is however not surprising in view of the data presented in Table II, which suggest that crosslinking does not occur until temperatures greater than 250°C are attained.

Comparative studies were made on the effect of degradation temperature upon the molecular weight of PS and PDEAS and GPC studies (Fig. 1) showed that PS gave a molecular weight decrease at approximately 250°C as reported by previous workers.<sup>6,7</sup> PDEAS similarly showed no molecular weight decrease until 250–300°C and at temperatures in excess of this crosslinked residues were obtained. This behavior is similar to that observed for *PDAS*<sup>4</sup> but contrasts with that found for *PmDAS*<sup>3</sup> which crosslinks at significantly lower temperatures. The mechanism of crosslinking appears to be similar to that proposed for *PDAS*<sup>4</sup> and extended for *PmDAS*<sup>3</sup> to include both combination, abstraction, and disproportionation of alkaryl amino radicals generated on N-alkyl bond scission and the reactions of substituted phenyl radicals generated on N-aryl bond scission.

The position with PDEAS is more complex than for *PmDAS* since in addition to the reactions postulated for *PmDAS* there are abstractable hydrogen atoms in the methylene grouping of the N-ethyl grouping. If abstraction occurred, a

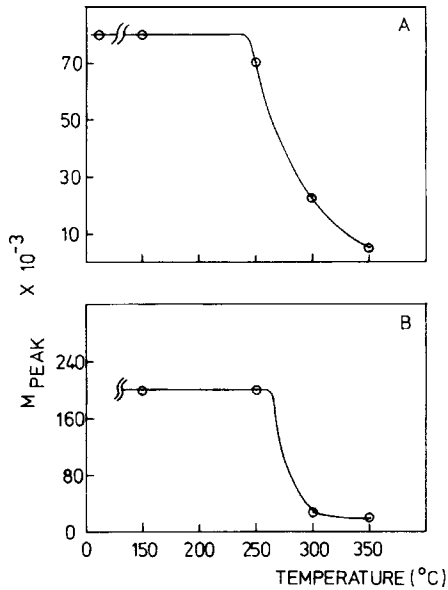
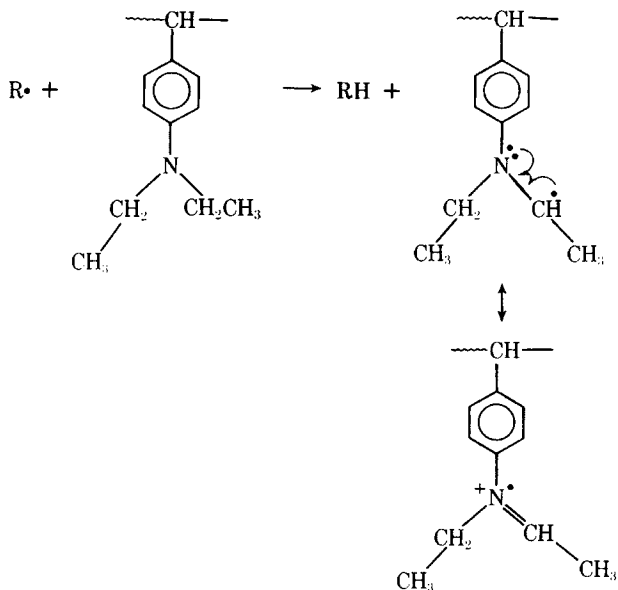


Fig. 1. Effect of degradation temperature on molecular weight: (A) PDEAS 4; (B) PDEAS 2.

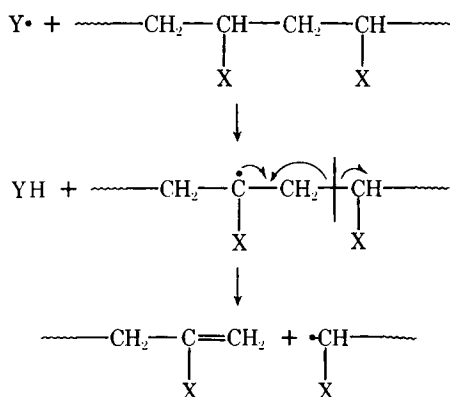
more complex system of crosslinks could result. Thus,

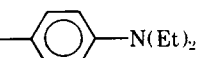


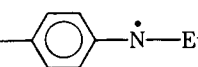
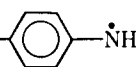
Such a radical would be capable of forming crosslinks by combination with other chain radicals. The relative frequency of hydrogen abstraction from an N,N-diethyl substituent will be small compared with abstraction from a tertiary carbon on the backbone. However, to produce insolubilization only a small number of such links is required.

Chain scission resulting in the observed molecular weight drop would also

appear to occur via the mechanism proposed for *PmDAS*<sup>3</sup>:



where X = 

Y = Et· :  or 

attached to the same or a separate chain.

The system is however extremely complex, and no direct evidence can be presented to validate the structures of the observed crosslinks. The thermal history of the sample also fails to alter the nature and quantity of the products of degradation. This suggests therefore that these crosslinks are either thermolabile or are present to such a low degree that they fail to inhibit the principal degradation reactions.

#### Fraction IV—The Oil

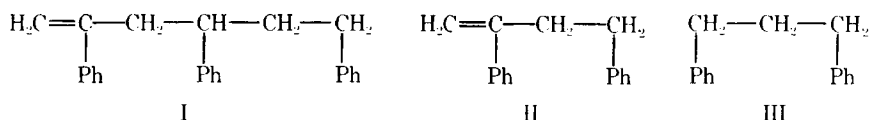
Previous studies on PS, PDAS, *PmDAS*, and other substituted styrene polymers<sup>3,4,8,9</sup> have shown that similar fractions were produced on pyrolysis. Analysis by IR, NMR, MS, and GPC has shown these fractions to consist mainly of substituted unsaturated dimeric and trimeric species similar to those observed for PS by Madorsky.<sup>10</sup> In addition, in the case of PDAS and *PmDAS*, dimers and trimers were identified in which the secondary amino function was present, giving further evidence of N-alkyl bond scission.

In view of the studies reported in part XXIII<sup>1</sup> on the liquid fraction from PDEAS, it was expected that products showing evidence of N-alkyl bond scission would be obtained. In addition, products showing loss of both alkyl groups, and also N-aryl bond cleavage, resulting in systems containing unsubstituted phenyl rings, should be detectable. IR and NMR indicated that the secondary amino function was present, and chemical tests indicated that species were present that contained the primary aromatic amino grouping as in the liquid fraction. GPC<sup>2</sup> using the system described for *PmDAS* and the calibration line for *p*-DEAS, PS, S, and dimeric styrene species indicated the components listed in Table III were present in the oil fraction from PDEAS.

The situation reported in Table III is similar to that of *PmDAS*<sup>3</sup> in that pentamer is again absent. This behavior, which contrasts with that of PS, may be

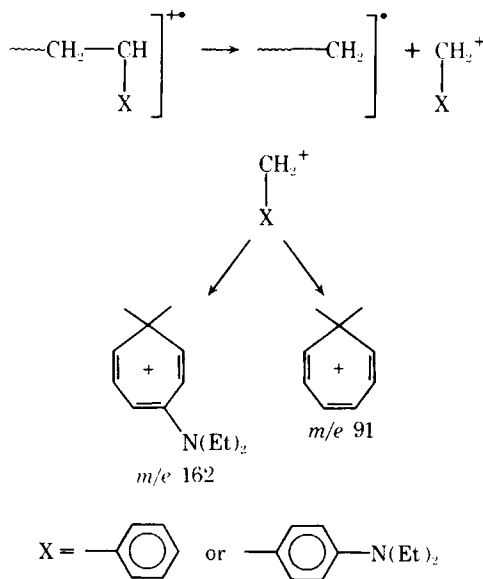
rationalized in terms of the relative volatility of pentamers derived from PS, *Pm*DAS, and PDEAS. This suggests that such species, if formed, would possibly fragment further in the hot zone of the furnace. In addition, with PDEAS an insoluble component of the oil fraction was obtained at the exit point of the quartz pyrolysis tube from the furnace. This suggests that the less volatile oligomeric materials such as pentamer may crosslink in the furnace in a similar manner to the residue.

A detailed qualitative analysis of the soluble portion of the oil fraction was performed using GLC/MS and heated probe studies on the MS902 mass spectrometer. GLC/MS was limited in its use because of the involatility of the components under analysis. PS gave two major components, compound I (*m/e* 312), compound II (*m/e* 208), and a minor component III (*m/e* 196):



in agreement with previous work.<sup>11</sup>

In the case of PDEAS only fragments of monomeric type were observed of which monomer *p*-DEAS (*m/e* 175) was most abundant and was present in amounts below the limits of quantitative estimation by GLC. The mass spectra of the PS and PDEAS oil fractions contained base peaks at *m/e* 91 and 162, which correspond to the respective tropylium ions formed by fragmentation of the oligomers present:



On the basis of these tropylium ions and the molecular ions observed at different temperatures, it was possible to assign structures to components present in both PS and PDEAS oil fractions (Table IV).

The presence of an ion at *m/e* 134 appears to confirm the presence of oligomers containing the secondary amino function. Such oligomers yielding the secondary

TABLE III  
GPC Analysis of PDEAS Oil Fraction

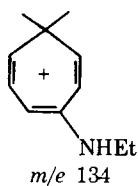
Component no.	Molecular weight at peak maximum	Assignment
1	177	monomeric fragments
2	233	
3	346	dimers
4	501	trimers
5	831	tetramer

TABLE IV  
Molecular Ions of Components of the Oligomer Fractions of PS and PDEAS<sup>a</sup>

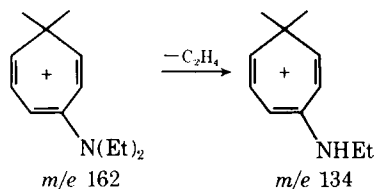
PS <i>m/e</i>	PDEAS <i>m/e</i>	Assignment
196	338	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \\ \text{X} \quad \quad \text{X} \end{array}$
208	350	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \\ \text{X} \quad \quad \text{X} \end{array}$
220	362	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{CH}_2 \\   \quad \quad   \\ \text{X} \quad \quad \text{X} \end{array}$
312	525	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \quad \quad   \\ \text{X} \quad \quad \text{X} \quad \quad \text{X} \end{array}$
416	—	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \quad \quad   \quad \quad   \\ \text{X} \quad \quad \text{X} \quad \quad \text{X} \quad \quad \text{X} \end{array}$
194	336	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}=\text{CH} \\   \quad \quad   \\ \text{X} \quad \quad \text{X} \end{array}$
298	511	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}-\text{CH}=\text{CH} \\   \quad \quad   \quad \quad   \\ \text{X} \quad \quad \text{X} \quad \quad \text{X} \end{array}$
402	—	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}=\text{CH} \\   \quad \quad   \quad \quad   \quad \quad   \\ \text{X} \quad \quad \text{X} \quad \quad \text{X} \quad \quad \text{X} \end{array}$

<sup>a</sup> In PS, X = ; in PDEAS, X = .

amino-substituted tropylium ion on fragmentation:



The situation with PDEAS is however more complex than that reported previously for *PmDAS*<sup>3</sup> since this ion may also be generated from an *N,N*-diethyl-substituted tropylium ion by loss of ethylene:

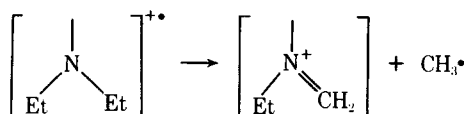


This was seen in the case of *N*-ethyl-*p*-toluidine which gave the following principal ions:

Intensity	69	23	31	100	23	13	52	25
<i>m/e</i>	135	134	121	120	118	106	91	77

If the ion at *m/e* 134 is the substituted tropylium ion, then the ion at *m/e* 106 may arise by loss of ethylene from this ion.

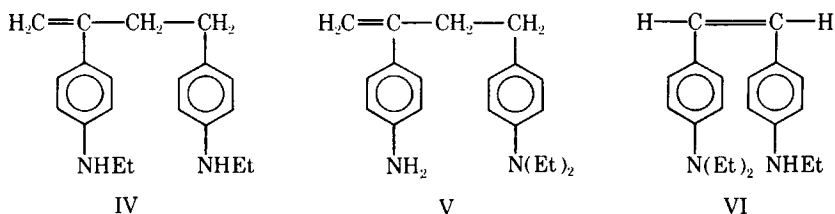
The interpretation of the spectra from PDEAS was further complicated by the observation that in monomeric compounds cleavage of the alkyl group  $\beta$  to nitrogen was the preferred fragmentation process:



Thus, in the spectrum of *N*-ethyl-*p*-toluidine the base peak occurs at M-15. On the basis of IR and NMR studies on the oil and previous studies on the liquid fraction, it was however possible to make the structural assignments shown in Table V for the oligomers containing the secondary amino grouping.

In all cases throughout this study (Tables IV–VI) where a molecular ion has been cited as evidence for a given structure, the corresponding fragment ion at M-15 has also been identified.

Consideration of the compounds listed in Table V indicates that isomerism further complicates the interpretation of the complex spectra obtained. Thus a molecular ion of *m/e* 294 could result from any of the structures shown below:





All such species would yield an ion at M-15, i.e., *m/e* 279 found in the spectra. In addition, V would be expected to give a primary amino-substituted tropylium



TABLE V  
Oligomers Containing Secondary Amino Groupings in the PDEAS Oil Fraction<sup>a</sup>

<i>m/e</i>	Assignment
310	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\   \qquad \qquad   \\ \text{X} \qquad \qquad \text{Y} \end{array}$
282 <sup>b</sup>	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2 \\   \qquad \qquad   \\ \text{Y} \qquad \qquad \text{Y} \end{array}$
322	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}_2 \\   \qquad \qquad   \\ \text{X} \qquad \qquad \text{Y} \end{array}$
497	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\   \qquad \qquad   \qquad \qquad   \\ \text{X} \qquad \qquad \text{Y} \qquad \qquad \text{X} \end{array}$
308	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}=\text{CH} \\   \qquad \qquad   \\ \text{X} \qquad \qquad \text{Y} \end{array}$
483	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}-\text{CH}=\text{CH} \\   \qquad \qquad   \qquad \qquad   \\ \text{X} \qquad \qquad \text{Y} \qquad \qquad \text{X} \end{array}$
280 <sup>b</sup>	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}=\text{CH} \\   \qquad \qquad   \\ \text{Y} \qquad \qquad \text{Y} \end{array}$

<sup>a</sup> X =  and Y = .

<sup>b</sup> Oligomers which may contain two secondary amino or one primary and one tertiary amino function.

ion at *m/e* 106 also found in the spectra. This ion could also result from a mono N-ethyl-substituted tropylium ion by loss of ethylene. Thus, the formation of oligomers containing primary amino functions is difficult to confirm by MS, but such species are known to be present from chemical tests.

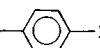
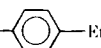

Reference to Tables IV and V indicates that components analogous to those from PS are formed together with components arising from N-alkyl bond scission.

In the PDEAS liquid fraction, evidence was obtained for N-aryl bond cleavage and radical abstraction and combination reactions, which resulted in the formation of products such as toluene, styrene, and *p*-ethylstyrene. Such reactions should, if they occur prior to oligomer formation, result in oligomers containing mono-alkylated and unsubstituted phenyl groupings. An ion at *m/e* 119 in PDEAS suggests that an ethyl-substituted tropylium ion is present. This evidence is however not conclusive since such ions are also present in the mass spectra of N,N-dialkylanilines.<sup>12</sup>

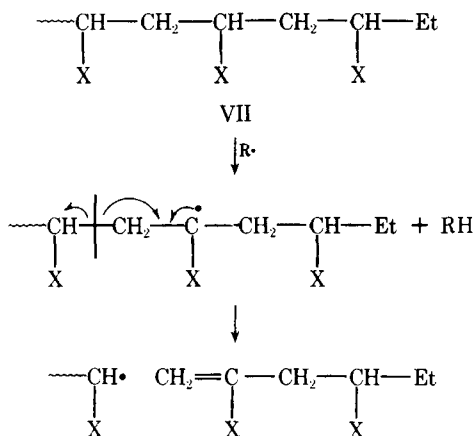
In the previous studies on the liquid fraction<sup>1</sup> evidence was also presented for products resulting from the combination of ethyl radicals with chain radicals. A similar situation arises prior to oligomer formation and gives products exemplified by compounds with *m/e* 364 and 378 (Table VI). Such oligomers would result from transfer of an ethyl radical to a chain radical to give VII, which sub-

TABLE VI  
Molecular Ions Showing Evidence for Oligomers Resulting After N-Aryl Cleavage and Transfer  
of Ethyl Radicals to Chain Radicals<sup>a</sup>

<i>m/e</i>	Assignment
293	$\begin{array}{c} \text{HC}=\text{CH}-\text{CH}_2 \\   \quad \quad   \\ \text{Z} \quad \quad \text{X} \end{array}$
295	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \\ \text{Z} \quad \quad \text{X} \end{array}$
307	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \\ \text{X} \quad \quad \text{Z} \end{array}$
482	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \quad \quad   \\ \text{X} \quad \quad \text{Z} \quad \quad \text{X} \end{array}$
279	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}_2 \\   \quad \quad   \\ \text{X} \quad \quad \text{Z}' \end{array}$
364	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}-\text{R} \\   \quad \quad   \\ \text{X} \quad \quad \text{X} \end{array}$
378	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}_2-\text{CH}-\text{R} \\   \quad \quad   \\ \text{X} \quad \quad \text{X} \end{array}$

<sup>a</sup> X = ; Z = ; Z' = ; R = Et.

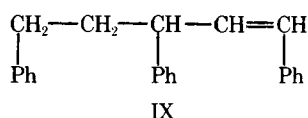
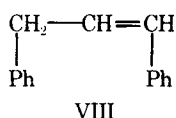
sequently yields oligomer by a variety of routes, one of which is shown:



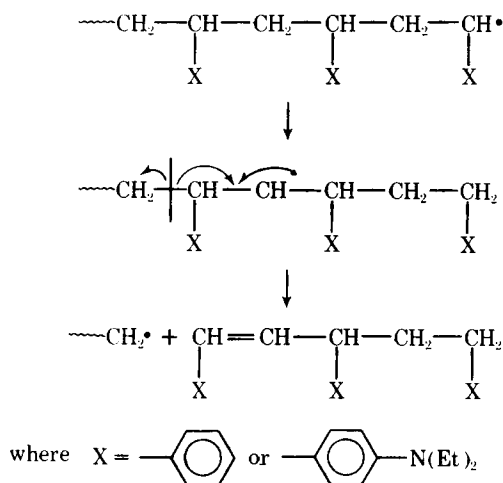
where R· is any radical in the degrading system.

In the case of PS, we, in common with other workers,<sup>13</sup> have reported the presence of 1,3-diphenylprop-1-ene (VIII), and in addition we have identified

triphenylprop-1-ene (IX) in the oligomer fraction:



It may be argued that such species may arise as a result of fragmentation of the unsaturated trimer and tetramer, respectively. However, probe studies showed the ion corresponding to VIII prior to the appearance of the ions associated with trimer and tetramer. In the case of PDEAS, further evidence may be cited for such structures in that the corresponding M-15 ion was also observed. A possible mechanism of formation of such species necessitates the transfer of a  $\beta$  hydrogen:



When PS is degraded, although hydrogen transfer is favored at the tertiary carbon atom, some  $\beta$  transfer may occur. It may be argued that the almost quantitative monomer yield from poly( $\alpha$ -methylstyrene) precludes  $\beta$  transfer. This observation however may be explained as being due to the methyl group sterically hindering  $\beta$  transfer or rendering the styryl radical less active as discussed by Simha and co-workers.<sup>14</sup>

From the products obtained from PDEAS it is apparent that its degradation behavior is similar to that observed for PDAS.<sup>4</sup> Its behavior is also similar to that observed for PS with N-alkyl and N-aryl scission and the subsequent reactions of the generated radicals superimposed.

One of the authors (T.S.E.) thanks the Science Research Council for a Research Studentship. The authors also thank Dr. W. T. Flowers of the Department of Chemistry, UMIST, for assistance in assigning the mass spectra and for useful discussion.

### References

1. T. S. Ellis and R. H. Still, *J. Appl. Polym. Sci.*, **23**, 2871 (1979).
2. T. S. Ellis and R. H. Still, *J. Appl. Polym. Sci.*, **23**, 2837 (1979).
3. T. S. Ellis and R. H. Still, *J. Appl. Polym. Sci.*, **23**, 2855 (1979).
4. R. H. Still and A. Whitehead, *J. Appl. Polym. Sci.*, **16**, 3207 (1972).
5. S. J. Stadniki, J. K. Gillham, and R. F. Boyer, *J. Appl. Polym. Sci.*, **20**, 1246 (1976).

6. H. H. G. Jellinek, *J. Polym. Sci.*, **3**, 850 (1948).
7. N. Grassie and W. W. Kerr, *Trans. Faraday Soc.*, **55**, 1050 (1959).
8. R. H. Still and P. B. Jones, *J. Appl. Polym. Sci.*, **13**, 1555 (1969).
9. R. H. Still and A. Whitehead, *J. Appl. Polym. Sci.*, **21**, 1199 (1977).
10. S. L. Madorsky, *J. Res. Natl. Bur. Stand.*, **42**, 499 (1949).
11. H. Staudinger and A. Steinhof, *Ann.*, **517**, 35 (1935).
12. T. S. Ellis, Ph.D. Thesis, Victoria University of Manchester, England, 1977.
13. H. D. R. Schuddemage and D. O. Hummel, *Adv. Mass. Spectr.*, **4**, 857 (1968).
14. R. Simha, L. A. Wall, and P. J. Blatz, *J. Polym. Sci.*, **5**, 615 (1950).

Received March 30, 1978