Vacuum Pyrolysis of Polystyrene Oligomers

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SYNOPSIS

Oligomers of polystyrene (PS) obtained from initial degradation studies of an anionic polymerized styrene have been degraded *in vacuo* using the molecular still method at temperatures between 150 and 250°C. The volatile decomposition products were separated and characterized by gel permeation chromatography, gas liquid chromatography, infrared spectroscopy, mass spectroscopy, and nuclear magnetic resonance. The products of pyrolysis showed that at 150°C the major component formed was the dimer, whereas at 250°C, the trimer was the major component. © 1993 John Wiley & Sons, Inc.
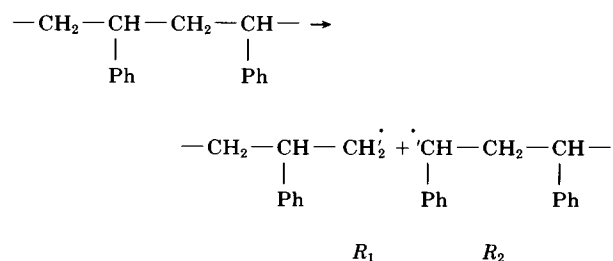
INTRODUCTION

The mechanisms and products of thermal degradation of polystyrene (PS) is well documented.[1-3] In addition to styrene, which is the most important product formed, there are many other products such as toluene, α-methylstyrene, and ethylbenzene. The method of pyrolysis is, however, known to confer variation in the nature and relative amounts of the products formed. Using a molecular still,[4] four main fractions can be isolated:

(i) A gaseous fraction that is volatile at all experimental temperatures.

(ii) A monomeric fraction, V_{25}, that is volatile at all experimental temperatures but involatile at the liquid nitrogen temperature of −196°C.

(iii) An oil fraction that is volatile at pyrolysis temperature but involatile at ambient temperature.

(vi) A residue that is involatile at all experimental temperatures.

The V_{25} fraction is known to contain the monomeric components such as styrene, toluene, ethylbenzene, and α-methylstyrene, whereas the oil fraction is known to contain oligomers of styrene from the dimer to possibly the heptamer. The mechanisms

of formation of these products are also well known. Principally, PS degrades into two types of primary radicals, R_1 and R_2:

$$-CH_2-CH-CH_2-CH- \rightarrow$$
$$\qquad\ \ | \qquad\qquad |$$
$$\qquad\ \ Ph \qquad\quad\ Ph$$

$$-CH_2-CH-CH_2^{\cdot} + {}^{\cdot}CH-CH_2-CH-$$
$$\qquad\ \ | \qquad\qquad | \qquad\qquad |$$
$$\qquad\ \ Ph \qquad\quad\ Ph \qquad\quad Ph$$

$$\qquad\qquad R_1 \qquad\qquad R_2$$

Thereafter, reactions from the intramolecular and intermolecular transfer of labile hydrogen atoms give the products enumerated above.

It is believed that similar reactions could take place in oligomeric PS during degradation, thereby giving similar monomeric products. This article reports on the finding of pyrolysis of PS oligomers.

EXPERIMENTAL

Materials

PS of M_n 220,000 (M_w/M_n 1.20) was initially pyrolyzed at 400°C to give the oligomeric fraction as described under Pyrolysis Procedure below. The fraction was collected, isolated, and purified as described under Pyrolysis Procedure. The fraction was found[5] by gel permeation chromatography to consists of dimers (12.1%), trimers (66.5%), and heptamers (11.8%).

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Infrared Spectroscopy (IR)

Spectra were recorded on a Nicolet Fourier transform infrared spectrophotometer in the mid-infrared range (4000–400 cm^{-1}) at a resolution of 4 cm^{-1}. Samples were run as films between sodium chloride plates.

Mass Spectrometry (MS)

Spectra were recorded on a Kratos MS45 double-focusing mass spectrometer.

Gel Permeation Chromatography (GPC)

A polymer solution of 0.2% (w/v) in tetrahydrofuran was passed through a series of three styragel columns at a flow rate of 1 mL min^{-1}. The concentration by weight of solute in the eluate was monitored by a Knauer differential refractometer. Calibration was effected using narrow distribution polystyrene standards. The chromatograms were analyzed by an on-line computerized program that provided molecular weight averages from peak maxima (M_p). The molecular weight average of the dimer and trimer were computed by applying a linear extrapolated calibration curve (from PS M_n 580 to dodecane M_n 170) to the chromatograms obtained from the fractions after pyrolysis. Furthermore, the use of GPC to separate a mixture of styrene oligomers into their respective n-mers reported by Fujishiege and Ohguri[6] enabled the assignment of component peaks to be made.

A relative amount of each component of the oligomeric fractions were determined using the relative areas of the components in the chromatogram by assuming that the total area under the chromatogram was proportional to the amount of material injected onto the columns.

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H- and ^{13}C-NMR spectra were recorded using solutions in deuterochloroform with tetramethylsilane as the internal reference. The ^{1}H-NMR spectra were obtained at 220 MHz using a Perkin-Elmer R32 instrument, whereas the ^{13}C-NMR spectra were obtained at 20.1 MHz using a Bruker WP80 computer program-assisted instrument.

Gas–Liquid Chromatography (GLC)

GLC was performed on a Hewlett-Packard 5830A gas chromatograph equipped with a flame ionization detector and with a Pyrex glass column (2 m $\times$ 2 mm) packed with carbowax 20M on chromosorb G-AW-DMCS (80–100 mesh). The analysis was carried out at a programmed heating rate of 3°C min^{-1} from ambient to 200°C with nitrogen as the carrier gas. Components were identified by retention coincidence with authentic materials.

Pyrolysis Procedure

Pyrolysis studies using a molecular still were performed *in vacuo* using a pyrolysis rig and in procedures similar to that employed previously for vacuum pyrolysis of polymers.[5,7,8] The other conditions of pyrolysis were the following: quantity of pyrolyzed sample, 100 mg; pressure, 2.5×10^{-3} mmHg; duration, 45 min; and temperatures, 150 and 250°C. The degradation products were a liquid fraction, volatile at pyrolysis and ambient temperatures but involatile at liquid nitrogen temperature, and an oil fraction, volatile at pyrolysis temperature but involatile at ambient temperature and a residue.

Isolation

The residue was collected as obtained and was subjected to GPC studies. The oil fraction was dissolved with AnalaR chloroform (15 mL) into a preweighed specimen bottle. The solvent was removed in a vacuum oven (30°C/0.04 mmHg) to constant weight. IR, NMR, MS, and GPC were performed as described above. The liquid monomeric fraction was dissolved with AnalaR acetone (1.0 mL) using a microsyringe. Analysis of the fraction was performed by GLC, IR, and MS.

RESULTS AND DISCUSSION

The glassy yellowish mass collected as residue from the pyrolysis of the PS oligomer was found by the mass of the pyrolyzed sample to represent 15 and 5% at 150 and 250°C, respectively. The quantity of residue formed at 250°C was too small for analysis. The GPC chromatogram of the residue obtained at 150°C revealed a broad distribution with two peak maxima at M_p 360 and 500, respectively (Fig. 1), found to lie in between the M_p values corresponding to the trimer and heptamer (Table I) observed for the pyrolyzed oligomer. No monomeric fraction was observed at the pyrolysis temperature of 250°C. At 150°C, the sweet-smelling colorless liquid was shown by GLC to contain only one component whose retention time was found to be higher than previously determined retention times for known standards of
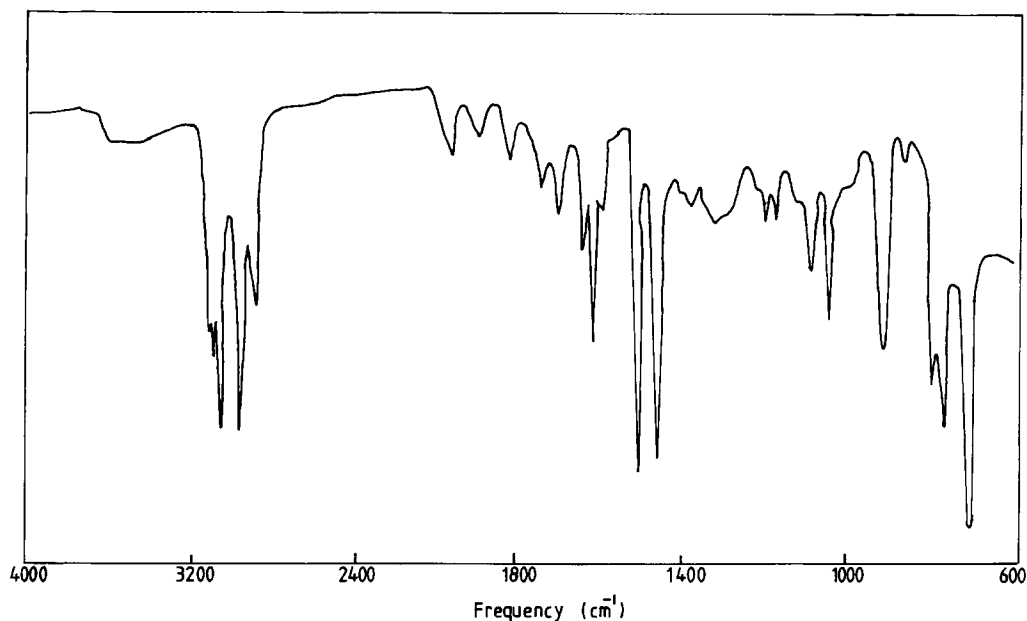
Figure 1   GPC chromatograms of fractions; dashed line represents chromatogram for degraded oligomeric fraction: (A) oligomeric fraction obtained at 150°C; (B) oligomeric fraction obtained at 250°C; (C) residue fraction obtained at 150°C.

monomeric products of the degradation of PS. The IR of the material (Fig. 2) was found to be very similar to the spectrum of 2,4-diphenyl-1-butene as reported by Sekiguchi et al.[9]:

$$CH_2-CH_2-C=CH_2$$

The bulk of the pyrolysis products was obtained as the oil fraction. They were shown from GPC to have single M_p values of 290 and 210 at 250 and 150°C, respectively. Indeed, no molecular ion greater than m/e 312 was observed from the two spectra, indicating that the trimer was the highest molecular weight species in the fractions. Both parent ions were present in both spectra, but at 250°C, the m/e 312 was predominant, whereas at 150°C, m/e

208 was predominant. The relative amount of the two components at the two temperatures, which could not be estimated from the MS spectra due to similarity in the fragmentation pattern of the trimer and dimer, was provided from nuclear magnetic resonance measurements.

On the basis of literature data,[9,10] the signals from the ^{13}C-NMR spectrum (Fig. 3) of the oil obtained at 250°C have been assigned as presented in Table II. It is believed that the main component is 2,4,6-triphenyl-1-hexene, **II**:

$$C^1=C^2-C^3-C^4-C^5-C^6-H$$

II

Table I   Analysis of the Oligomeric Fraction

Polymer	Peak No.	Retention Time GPC	Molar Mass Peak-Maxima	Assignment	Relative Amount of Component (%)
PS	1	1661	200	Dimer	12.1
	2	1615	310	Trimer	66.5
	3	1561	700	Heptamer	11.8

Figure 2   IR spectrum of dimer.

The signal δ112.55 is suggested to arise from another component containing a terminal olefinic carbon. The ratio of this signal to that at δ114.29 was 1 : 7. Similarly, the ratio of the unassigned signals at δ29.78 and 34.81 to the assigned C-6 and C-5 signals at δ33.71 and 37.39, respectively, was 1 : 7. This suggests that the signals are due to another com-

ponent, probably the dimer, that amounts to about 12.5% of the mixture. The ^{1}H spectra obtained for these two fractions were essentially similar to that of a pyrolyzed oligomeric fraction from high molar mass PS except for the signals at δ4.9–5.3 ascribed to the vinylic protons (Fig. 4). Two signals were observed in the spectrum of the fraction obtained
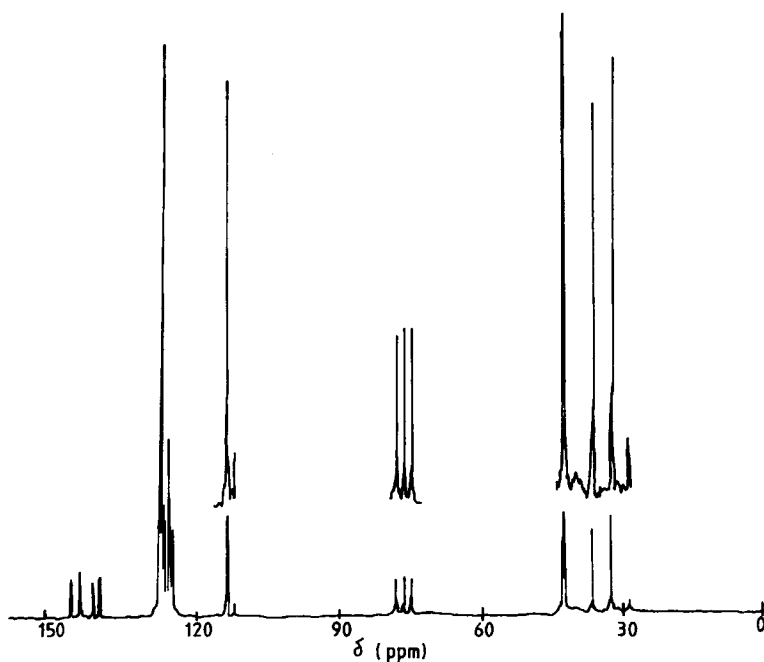
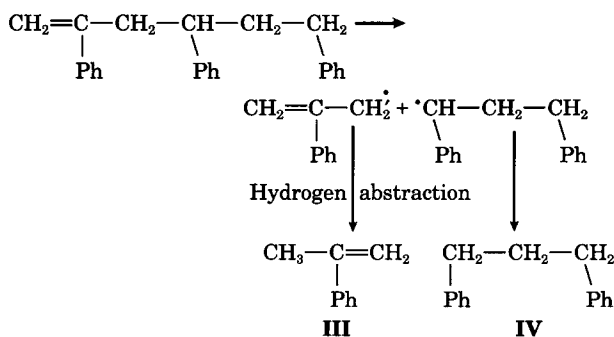**Figure 3**   ^{13}C-NMR spectrum for fraction obtained at 250°C.

Table II ^{13}C Spectrum Analysis of Fraction Obtained at 250°C

Signals (ppm)	Relative Intensity	Assignment
29.78	0.56	
33.71	3.46	C-6
34.81	0.46	
37.39	3.12	C-5
43.42	3.31	C-3
43.70	3.66	C-4
112.55	0.47	
114.29	3.28	C-1
125.46	3.18	Main chain aliphatic carbon atoms
126.00	4.36	
126.26	6.45	
127.17	3.80	
127.62	8.29	
128.14	20.00	
141.00	1.44	Aromatic C-7″
142.23	1.29	C-7′
144.82	1.69	C-7
146.63	1.49	C-2

at 150°C, whereas four signals were observed in the spectra of both the pyrolyzed oligomeric sample and the fraction obtained at 250°C.

The similarity in the spectrum of the original oligomeric fraction and the pyrolytic product obtained at 250° indicates that the trimer that was the major component in the original fraction was also the predominant component in the fraction obtained at 250°C. The spectrum of the oil fraction showed two main signals at δ4.9 and δ5.2 and two small signals alternating in between the two main ones at δ5.0 and δ5.3. The ratio of intensity between the major and minor signals was 1 : 7, a ratio value similar to the one observed from the ^{13}C spectrum of the same fraction. The ^{1}H spectrum of the fraction from 150°C, therefore, suggests a predominance of the dimer, 2,4-diphenyl-1-butene. Indeed, expansion of the signals at δ7.0–7.4 from the ^{1}H spectrum of the product obtained at 150°C exhibited 10 major aromatic protons corresponding to two aromatic rings of the dimeric structure.

It is apparent, therefore, that the pyrolytic behavior of the oligomers appears to be temperature-dependent. Generally, however, the pyrolytic behavior did not result in the formation of the monomeric components, viz., styrene, toluene, benzene, and α-methylstyrene, as expected from the suggested structure of the oligomeric components. For example, 2,4,6-triphenyl-1-hexene is expected to give methylstyrene (**III**) and 1,3-diphenyl propane (DPP) (**IV**) as a result of allylic carbon cleavage:

$$CH_2=\underset{\underset{Ph}{|}}{C}-CH_2-\underset{\underset{Ph}{\backslash}}{CH}-CH_2-\underset{\underset{Ph}{\backslash}}{CH_2} \longrightarrow$$

$$CH_2=\underset{\underset{Ph}{|}}{C}-\overset{.}{C}H_2^{.} + \overset{.}{C}H-CH_2-\underset{\underset{Ph}{\backslash}}{CH_2}$$

Hydrogen abstraction

$$CH_3-\underset{\underset{Ph}{|}}{C}=CH_2 \qquad CH_2-CH_2-\underset{\underset{Ph}{\backslash}}{CH_2}$$

III   **IV**

Similarly, the formation of toluene (**V**) and α-methylstyrene (**VI**) was expected to arise from the terminal breakage of phenyl-substituted methylene group in, e.g., 2,4-diphenylbut-1-ene, **I**:

$$CH_2=\underset{\underset{Ph}{|}}{C}-CH_2-\underset{\underset{Ph}{|}}{CH_2} \longrightarrow CH_2=\underset{\underset{Ph}{|}}{C}-CH_2^{.} + \overset{.}{C}H_2$$

Hydrogen abstraction

$$CH_2=\underset{\underset{Ph}{|}}{C}-CH_3 \qquad \underset{\underset{Ph}{|}}{CH_3}$$

VI   **V**
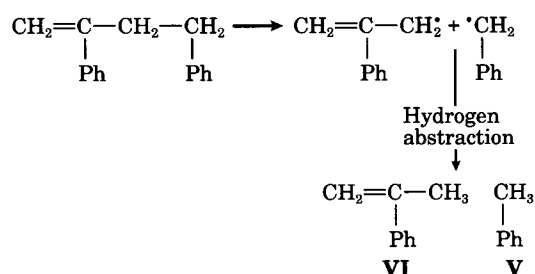
The absence of these products suggests that the necessary bond-breaking reactions did not occur either because the bond strengths for cleavage were not achieved or that the precursor species (dimer and timer) volatilize under conditions of the experiment as soon as formed. It is noted that if bond cleavages do occur, then the primary radicals must be able to abstract hydrogen atoms to give these expected products. However, if the concentration of
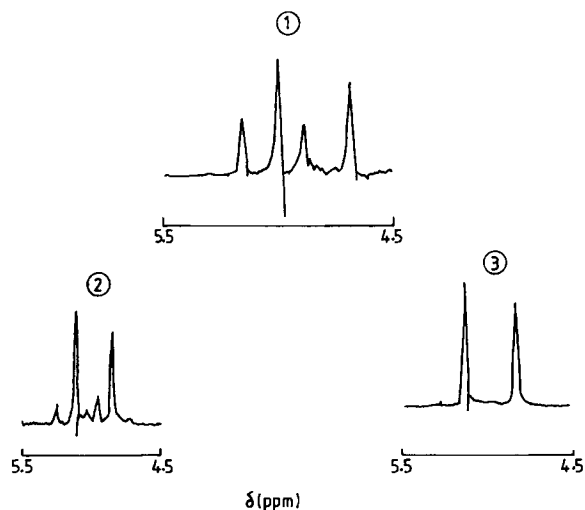

Figure 4 ^{1}H-NMR spectra for fractions (σ5.5–4.5): (1) obtained from degraded sample; (2) from fraction obtained at 250°C; (3) from fraction obtained at 150°C.

abstractable hydrogen atoms in the oligomeric fraction is significantly reduced relative to the situation in the original PS homopolymer melt, the radicals, if ever formed, would only recombine to effect stabilization, as no other termination method may be possible. This recombination of radicals may be used to explain the high molar mass of the residue obtained at 150°C.
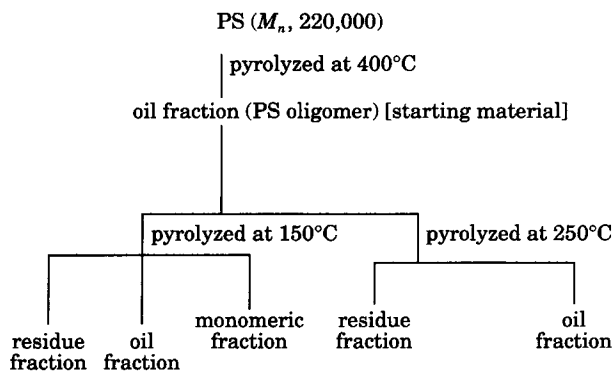
Evidence from GPC, NMR, and MS also indicated that the products formed at the two pyrolysis temperatures are olefinic and belonged essentially to one family of n-mers:

$$CH_2\!=\!C\!-\!(CH_2\!-\!CH)_n\!-\!H$$
$$||$$
$$PhPh$$
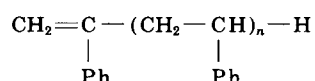
Although the reasons for this behavior remain unclear, this observation is supported by the result of the mass spectra of the fractions that did not reveal the presence of the saturated 1,3-diphenylpropane (DPP) with a mass unit of 196. DPP has been observed by other workers on PS degradation and its absence from the resulting mixture was very significant.

CONCLUSION

The various fractions isolated at the two pyrolysis temperatures can be schematically presented as

PS (M_n, 220,000)

| pyrolyzed at 400°C

oil fraction (PS oligomer) [starting material]

pyrolyzed at 150°C   pyrolyzed at 250°C

residue   oil   monomeric   residue   oil
fraction fraction fraction   fraction   fraction

Though a fraction presumably monomeric was isolated during pyrolysis at 150°C, GLC and IR, in fact, indicated a dimer.

The general degradative behavior of the oligomers seemed to have involved only the breakdown of the heavier oligomers, i.e., $n > 3$, into the trimer and dimer exclusively. The monomeric components were not formed probably because there were not enough abstractable hydrogen atoms in the oligomeric melt to affect termination reactions.

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