# Thermal Degradation of Polymers. XV. Vacuum Pyrolysis Studies on Poly(p-methoxystyrene) and Poly(p-hydroxystyrene)

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## Synopsis

The monomers p-hydroxystyrene (p-HS) and p-methoxystyrene (p-MS) have been synthesized and polymerized using azobisisobutyronitrile as free-radical initiator. The polymerization behavior of p-HS is anomalous, and a mechanism is suggested to account for this phenomenon. Poly(p-hydroxystyrene) (PHS) and poly(p-methoxystyrene) (PMS) homopolymers have been subjected to vacuum pyrolysis at temperatures in the range of 300–500°C. The products of degradation have been identified and qualitatively and quantitatively analyzed and the degradation behavior of the two systems compared with polystyrene. PHS shows anomalous behavior resulting from the high reactivity of the p-HS monomer and the facility for transfer afforded by the proton of the hydroxyl substituent. Mechanisms to account for the degradation behavior of each system are discussed.

## INTRODUCTION

This work is a continuation of investigations into the thermal degradation behavior of ring-substituted styrene polymers. Previous papers[1-11] have reported the degradation behavior of polymers based on m-aminostyrene, m-N,N-dimethylaminostyrene, p-N,N-dimethylaminostyrene, p-N,N-diethylaminostyrene, m-hydroxystyrene, and their copolymers with styrene.

We now report the synthesis, characterization, and thermal degradation behavior in vacuo of systems derived from p-hydroxystyrene (p-HS) and p-methoxystyrene (p-MS).

## EXPERIMENTAL

### Materials

p-Methoxystyrene was prepared by the following route:



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$p$-Methoxybenzaldehyde (28 g) was allowed to react with methylmagnesium iodide, from magnesium turnings (5 g) and methyl iodide (30 g), using the method previously reported for the preparation of $p$-N,N-dimethylamino-$\alpha$-methylbenzyl alcohol.[5]  On distillation a main fraction, 17 g, bp 101–101.5°C/1.0 mm Hg, was collected in 68% yield $N_D^{25}$ 1.5310, lit. $N_D^{25}$ 1.5312.[12]

$p$-Methoxy-$\alpha$-methylbenzyl alcohol (I) was distilled in portions (8 g) at $\simeq 7$ mm Hg from a 25-ml distillation flask, fitted with a fractionating head and nitrogen leak, into a receiver cooled in ice/salt.  The flask was heated by a micro-Bunsen, and considerable reflux from the flask neck was allowed.  The monomer was dried using anhydrous sodium sulfate, filtered, and redistilled.  A fraction (12 g) bp 44–45°C at 0.5 mm Hg $N_D^{25}$ 1.5551 was collected in 82% yield; lit.[12] bp 45–46°C, $N_D^{13}$ 1.5642.  GLC investigation revealed one component.

$p$-Methoxystyrene was polymerized in bulk at 70°C in soda-glass tubes in a nitrogen atmosphere for 8–12 hr using azobisisobutyronitrile (AZBN) at 0.3 and 1.3% by weight on monomer weight.  This yielded poly($p$-methoxystyrenes) (PMS) I and II in 92.5% and 94.0% yield after two reprecipitations from 5% solutions in Analar toluene into excess methanol.

ANAL.  Found for PMS C, 80.79; H, 7.99; O, 11.2 I:  2.  Found for PMS II:  C, 80.51; H, 7.64; O, 11.85.  Calculated for $C_9H_{10}O$:  C, 80.56; H, 7.51; O, 11.93%.

PMS I and II were characterized by osmometry in toluene solution at 37°C using a Hewlett–Packard 502 high-speed membrane osmometer fitted with a standard cellophane membrane.  PMS I had $\overline{M}_n$ of 218,600, and PMS II had $\overline{M}_n$ of 55,600.  PMS I was also characterized by intrinsic viscosity determination in toluene at 25°C using an Ostwald viscometer BS/U/M2, and had $[\eta]_o$ of 0.94.

$p$-Hydroxystyrene was prepared by the following route:



III　　　　　　　　　　　　　　　IV
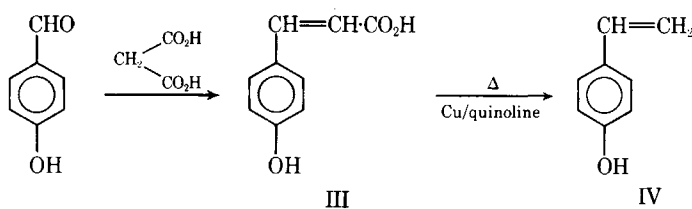
$p$-Hydroxycinnamic acid (III) was prepared in the following manner.  Malonic acid (104 g), $p$-hydroxybenzaldehyde (122 g), and aniline (5 ml) were dissolved in freshly distilled pyridine (150 ml) and allowed to react for three weeks as described by Overberger.[13]  Compound (III) so obtained was recrystallized from a water/methanol mixture (3:1 v/v) giving a crystalline product, 98 g, mp 213–214.5°C in 60% yield; lit.[14] mp 210.5–211°C.

Compound (III) was converted to $p$-hydroxystyrene (IV) by the following method.  (III) (98 g) was dissolved in redistilled quinoline (300 g) with warming.  This solution was added dropwise to copper powder (2 g) in a 50-ml distillation flask fitted with a lagged claisen head.  The flask was heated to approximately 250° under reduced pressure (<5 mm Hg) and the solution added at such a rate to give continuous distillation of a light-brown oil at approximately 110–120°C at 4–6 mm Hg.  The distillate was dissolved in peroxide-free ether (150 ml), mixed with crushed ice (200 g), and ice-cold 3$N$-sulfuric acid (1.2 liter) was added slowly with stirring.  The ether layer was removed and the aqueous portion extracted with further ether (3 × 20 ml).  The combined ethereal extract was

TABLE I
p-Hydroxystyrene Homopolymers

| Sample no. | % AZBN | $[\eta]_0$ | Yield, % |
|---|---|---|---|
| PHS I | 1.0 | 0.28 | 77 |
| PHS II | 0.6 | 0.30 | 82 |
| PHS III | 0.4 | 0.32 | 82 |
| PHS IV | 0.1 | 0.32 | 77 |
| PHS V | nil | 0.31 | 69 |
| PHS VI | nil[a] | 0.29 | 82 |

[a] 5% tert-butylcatechol added.

TABLE II
p-HS/S Copolymers

| Sample no. | p-HS:S approx. molar ratio | $[\eta]_0$ | Yield, % |
|---|---|---|---|
| p-HS/S VII | 1:2 | 0.33 | 76 |
| p-HS/S VIII | 1:1 | 0.28 | 79 |
| p-HS/S IX | 2:1 | 0.28 | 79 |

washed with ice-cold water, dried over Drierite, filtered, and the ether removed at 0°C under vacuum. A light-brown rubbery solid was obtained, from which p-hydroxystyrene monomer was extracted with 60–80°C petroleum ether (500 ml). Recrystallization at −30°C yielded white, crystalline plates, 15 g, mp 72.5°C in 21% yield; lit.[14] mp 73.5°C.

p-Hydroxystyrene (p-HS) was polymerized in the following manner. The monomer ($\simeq$4 g) was packed into a precooled (<−20°C) drawn soda-glass test tube, and AZBN (0.1–1.0% by weight on monomer weight) was added. The contents of the tube were quickly sealed under nitrogen and the tube was immediately placed in a thermostat bath maintained at 75°C. After a period of 15 min, a solid rod of polymer was formed. The tube was cooled in liquid nitrogen, and the polymer rod was obtained after removal of the glass.

Purification was effected by dissolving the polymer (4 g) in distilled methyl ethyl ketone (60 ml). The solution was filtered and then added dropwise to portions of mechanically stirred cyclohexane (3 × 500 ml). The product was initially dried at 70°C/0.1–0.3 mm Hg to constant weight. TG and DTA studies, however, revealed that the samples retained solvent which could only be removed by drying in the region of the glass transition temperature. As a result, all polymers were subsequently dried at 160°C/0.1 mm Hg to constant weight. Characterization was effected by determination of the intrinsic viscosity in 0.2N sodium hydroxide solution at 25 ± 0.01°C. A summary of the polymers prepared is given in Table I.

ANAL. Typical combustion analysis data are shown for PHS I: C, 79.72; H, 6.66; O, 13.67; and PHS II: C, 79.87; H, 6.71; O, 13.44. Calculated for $C_8H_8O$:: C, 79.97; H,6.71; O, 13.32%.

Copolymerization of styrene (S) and p-HS was achieved by dissolving AZBN (0.5% on total monomer weight) in a well-mixed solution of S and p-HS in a soda-glass tube. The tubes were sealed under nitrogen and placed in an oven at 70°C for 2 hr after which time a solid rod of polymer had formed.

Purification was effected by reprecipitation and characterization effected by combustion analysis and intrinsic viscosity determination in 0.2N sodium hydroxide.

TABLE III
Identification of Components in PMS Liquid Fraction by GLC[a]

| Component no. | Retention index of fraction 1 from PMS pyrolysis at 400°C | Retention index of a synthetic mixture | Compound |
|---|---|---|---|
| 1 | 1368.6 | 1368.6 | anisole |
| 2 | 1461.0 | 1461.1 | p-methylanisole |
| 3 | 1550.8 | 1551.2 | p-ethylanisole |
| 4 | 1688.4 | 1688.4 | p-methoxystyrene |
| 5 | 1962.4 | — | — |

[a] Column, PEG 20M on Chromosorb G, column temperature, 160°C; internal standard, o-bromoanisole.

A summary of the p-HS/S copolymers prepared is given in Table II.

ANAL. Found for p-HS/S VII. C, 87.71; H, 7.40; O, 4.89. Calculated for $C_8H_8O:C_8H_8 = 1:2$. C, 87.76; H, 7.36; O, 4.87. Found for p-HS/S VIII. C, 85.57; H, 7.23; O, 7.20. Calculated for $C_8H_8O:C_8H_8 = 1:1$. C, 85.68; H, 7.19; O, 7.13. Found for p-HS/S IX. C, 83.43; H, 7.07, O, 9.50. Calculated for $C_8H_8O:C_8H_8 = 2:1$. C, 83.69; H, 7.02; O, 9.29%.

## Apparatus and Procedures

**Mass Spectrometry (MS).** Spectra were recorded using an AEI mass spectrometer MS10 (modified to MS 10 2C specification).

**Gas–Liquid Chromatography (GLC).** Chromatograms were recorded on a Phillips PV. 4000 gas chromatograph equipped with Pyrex columns (3m × 4 mm) packed with 5% polyoxyethylene glycol 20M on Chromosorb G. A flame ionization detector was used as the sensing element, and the column, after programming the temperature at 3°/min up to 200°C with nitrogen passing, was operated at various temperatures as shown in Tables III and IV.

**Infrared Spectroscopy (IR).** Spectra were recorded on a Perkin–Elmer spectrophotometer Model 237. Liquid samples were run as films between sodium chloride plates. Polymer samples were cast from suitable solvents onto sodium chloride plates.

**Vacuum Pyrolysis Apparatus.** The system used was that described in detail in previous papers.[3,4,5,6] Pyrolysis procedure, methods for monomer, and minor component determination, and the pyrolysis procedure for the gaseous fraction are as previously described for poly(p-N,N-dimethylaminostyrene).[5]

Fraction III—The Residue. Samples of PMS 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. PHS was not amenable to this treatment since the residue produced was insoluble in solvents for the unheated polymer.

Fraction IV—The Oil Fraction. Pyrolysis was effected in the temperature range of 300–500°C using a general pyrolysis time of 30 min, followed by an equilibriation time of 24 hr.[5] The oil fraction from PMS was a viscous, colorless oil, while that from PHS was a red, viscous oil surrounded by a white solid.

The oils were qualitatively analyzed by IR and MS. The oil fractions were subjected to GLC analysis for monomer which was absent. Quantitative studies were made on the oil fraction from PMS which was extracted from the quartz

TABLE IV
Identification of Components in PHS Liquid Fraction by GLC[a]

| Component no. | Retention index of fraction I from PHS pyrolysis at 400°C | Retention index of a synthetic mixture | Compound |
|---|---|---|---|
| 1 | 1947.0 | 1947.0 | phenol |
| 2 | 2018.3 | 2018.7 | p-cresol |
| 3 | 2102.3 | 2101.1 | p-ethylphenol |
| 4 | 2305.8 | 2305.6 | p-hydroxystyrene |
| 5 | 2360.2 | — | — |

[a] Column, PEG 20M on Chromosorb G, column temperature, 200°C; internal standard, 2,3-dimethylphenol.

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 Hg.

## RESULTS AND DISCUSSION

### Polymer Preparation and Characterization

The preparation and polymerization of $p$-MS proceeded smoothly, and the normal initiator concentration/molecular weight relationship was qualitatively observed.

However, with $p$-HS, reference to Table I shows that changes in AZBN concentration produce little change in molecular weight (as reflected by the intrinsic viscosity) for the PHS homopolymers. Even when 5% tert-butylcatechol is present or when $p$-HS is heated alone, the rate of polymerization and the molecular weight of the polymer produced remain at constant values, suggesting that a nonradical mechanism operates. In addition, the rate of polymerization of $p$-HS is much greater than that of S or $p$-MS.

The preparation of $p$-HS via the decarboxylation of $p$-hydroxycinnamic acid is also anomalous in that very low yields are obtained by the methods of Schmid[15] and Auwers[16] which give yields >40% for the ortho isomer. Further to this, Sovish[14] has found that $p$-HS polymerizes at 0°C to give low molecular weight polymers. Sovish has, on the basis of his studies, suggested alternative modes of polymerization involving propagation via addition to the aromatic ring system. He further considers that the combined resonance and inductive effects of the hydroxyl group on the propagating radical may be responsible for the anomalous behavior.
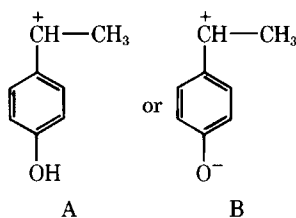
However, the Hammet $\sigma$-constants[17] for $p$-OMe, $p$-OH, and $p$-N(Me)$_2$ are, respectively, $-0.27$, $-0.37$, and $-0.83$. Thus, $p$-MS and $p$-HS would be expected to behave similarly, while $p$-N,N-dimethylaminostyrene would be expected to show a more exaggerated anomalous behavior which was not observed.[5]

It is of significance that replacement of the hydroxyl proton by a methyl group eliminates the anomalous behavior. In addition, $m$-HS does not behave anomalously.[3,18] Thus, any postulated mechanism must involve the hydroxyl proton and the position of substitution of the hydroxyl grouping. The canonical
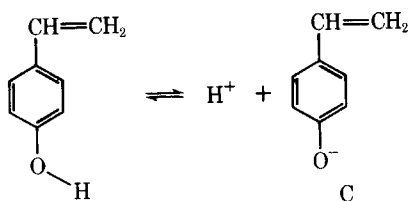
forms which may be written for $p$-HS as a result of the electronic effects of the hydroxyl grouping include the two extreme states shown below:
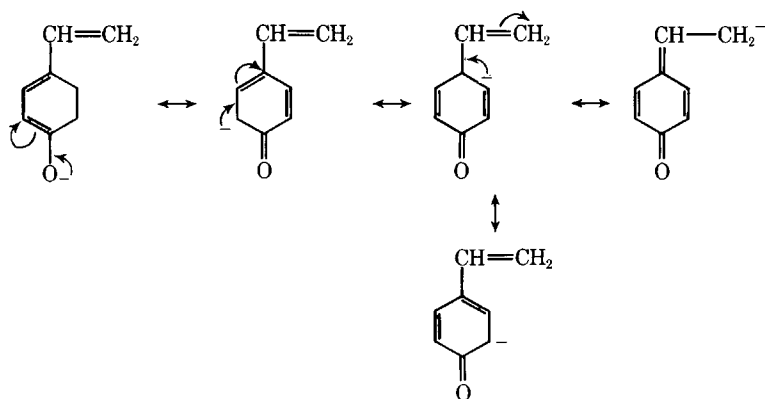
$$\begin{array}{ccc}
\text{CH}=\text{CH}_2 & & \text{CH}-\text{CH}_2^- \\
\text{(ring)} & \longleftrightarrow & \text{(ring)} \\
\ddot{\text{O}}-\text{H} & & {}^+\text{O}-\text{H}
\end{array}$$
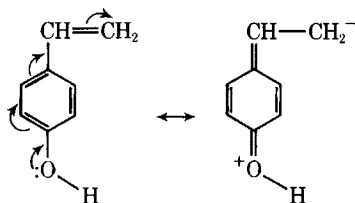
Intra- or intermolecular proton transfer from the hydroxyl grouping to the $\beta$-carbon atom could result in the production of species A and B capable of initiating cationic polymerization:

$$\begin{array}{ccc}
\overset{+}{\text{CH}}-\text{CH}_3 & & \overset{+}{\text{CH}}-\text{CH}_3 \\
\text{(ring)} & \text{or} & \text{(ring)} \\
\text{OH} & & \text{O}^- \\
\text{A} & & \text{B}
\end{array}$$

Alternatively, in the melt phase, the material may be regarded as dissociating to give the stabilized phenoxide ion and a proton capable of initiating polymerization:

$$\begin{array}{ccc}
\text{CH}=\text{CH}_2 & & \text{CH}=\text{CH}_2 \\
\text{(ring)} & \rightleftharpoons \text{H}^+ + & \text{(ring)} \\
\text{O}-\text{H} & & \text{O}^- \\
 & & \text{C}
\end{array}$$

The phenoxide ion (C) is resonance stabilized, with the following contributing canonical forms:

$$\text{CH}=\text{CH}_2 \text{ (ring, O}^-\text{)} \longleftrightarrow \text{CH}=\text{CH}_2 \text{ (ring, O)} \longleftrightarrow \text{CH}=\text{CH}_2 \text{ (ring, O)} \longleftrightarrow \text{CH}-\text{CH}_2^- \text{ (ring, O)}$$

$$\updownarrow$$

$$\text{CH}=\text{CH}_2 \text{ (ring, O)}$$

That $m$-HS does not behave in an anomalous manner can be explained on the basis of its extreme canonical forms which do not involve activation of the $\beta$-carbon atom:
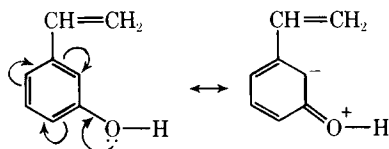


Further to this, the stabilization afforded to the $m$-phenoxide ion obtained on dissociation, i.e.,
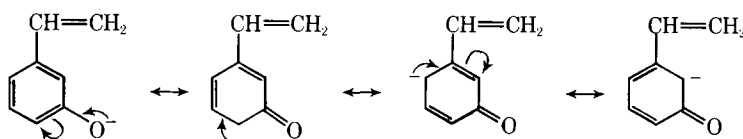


is significantly less, making this process energetically less favorable. On this basis, $p$-DAS and $p$-MS behave normally since, although the $\beta$-carbon atoms are activated, there is not a proton for transfer and dissociation cannot occur.

Since the mechanism postulated for $p$-HS is essentially a self-initiated process, it will lead to a large number of active centers resulting in a short kinetic chain length and hence to low molecular weight products.

The method of preparation of $p$-HS involves the use of dilute sulfuric acid, and residual acid could possibly be responsible for the phenomenon. However, Overberger[13] has prepared $p$-HS in good yield by vacuum sublimation of $p$-hydroxycinnamic acid, and this worker found that the monomer polymerized at room temperature to yield low molecular weight polymer.

A sample of $p$-HS was prepared by this route free from possible acid impurities, and its behavior on DSC was compared with that prepared by the route reported in the experimental section. Figures 1 and 2 show the thermograms obtained using DSC in nitrogen. Sovish $p$-HS polymerizes immediately on melting ($\simeq$
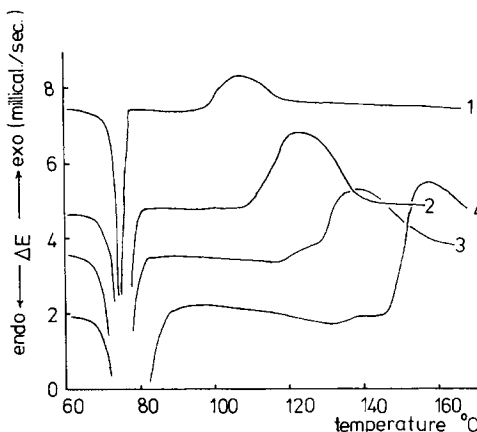


Fig. 1. DSC thermograms for Overberger p-HS in nitrogen: (1) heating rate 2°C/min; (2) heating rate 5°C/min; (3) heating rate 10°C/min; (4) heating rate 24°C/min.
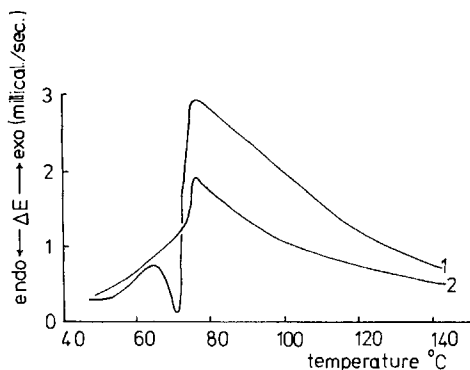
Fig. 2. DSC thermograms for Sovish p-HS in nitrogen: (1) heating rate 10°C/min; (2) heating rate 5°C/min.

75°C), as shown by the onset of an exotherm. Overberger $p$-HS, although polymerizing rapidly, does so at temperatures in excess of the melting point which are dependent on the heating rate (98°C at 2°C/min, 136°C at 20°C/min). It is, therefore, probable that both processes play significant roles in the polymerization of Sovish $p$-HS resulting in the observed behavior.

## Vacuum Pyrolysis Studies

Vacuum pyrolysis of PMS and PHS has yielded the following fractions: fraction I, a liquid volatile at pyrolysis temperature and ambient temperatures but involatile at liquid nitrogen temperature; fraction II, a fraction gaseous at liquid nitrogen temperature; fraction III, a residue; fraction IV, an oil fraction volatile at pyrolysis temperature, involatile at ambient temperature.

This paper is concerned with the qualitative and quantitative analysis of these four fractions and reports the effect of polymer structure and pyrolysis temperature on the composition and quantity of these fractions.

### Fraction I

Fraction I from PMS was shown by UV, IR, NMR, GLC, and MS analysis to consist mainly of $p$-methoxystyrene, with smaller quantities of anisole, $p$-methylanisole, $p$-ethylanisole, and an unknown compound 5 (Table III).

The Kovats retention indices[19] of the compounds were determined by GLC using a synthetic mixture and are compared with the fraction obtained on pyrolysis of PMS in Table III.

The composition of fraction I from PHS was similarly analyzed, and the components are shown in Table IV. In this way, the peaks in the chromatogram shown in Figure. 3A and B were assigned using a secondary standard according to the method developed by Evans.[20]

These results are similar to those found by Still and Whitehead for polystyrene[5,6] (PS) and are consistent with findings for PS by previous workers.[21]

The highest boiling component (5), Tables III and IV, by analogy with PS is probably the para-substituted $\alpha$-methylstyrene. This assignment is supported
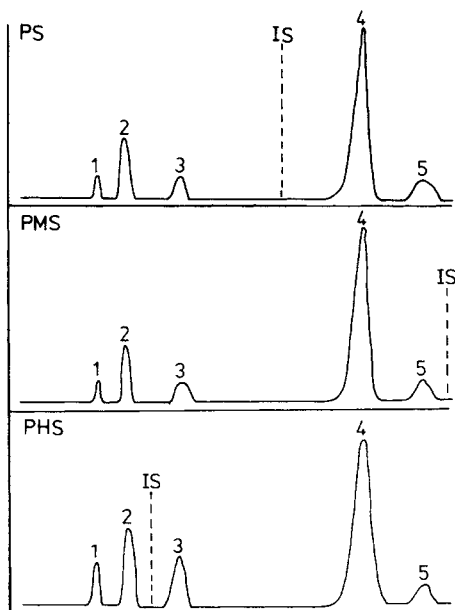
Fig. 3. Gas chromatograms for PS, PHS, and PMS liquid fractions.  PS Component; (1) benzene; (2) toluene; (3) ethylbenzene; (4) sytrene; (5) $\alpha$-methylstyrene; (IS) cumene.

by a peak of mass number 148 in the mass spectrum of the PMS liquid fraction.

Quantitative analyses were also made for PMS, and the conversion of polymer to the respective minor components is shown in Table V for pyrolysis effected at 420°C.  The major product of the liquid fraction was monomer.  Accordingly, attention was directed toward the quantitative determination of the effect of molecular weight and pyrolysis temperature on monomer yield from PMS.  Molecular weight was shown not to affect monomer yield from PMS in the range studied, $219$–$56 \times 10^3$.  The effect of pyrolysis temperature on monomer yield is shown for PMS in Table VI.

The results for PMS are similar to those obtained by Still and co-workers[2,5] for PS and by Kamebe and Shibaski[22] for PS.  Qualitative and quantitative analysis has shown that the identity and quantity of the degradation products in the liquid fraction from PMS and PS are very similar.  As the pyrolysis temperature is increased, the quantity of monomer increases rapidly at first and then

TABLE V
PMS Minor Component Yields

| Component no. | Identity | Polymer volatilized converted to component, % | Component as % of monomer |
|---|---|---|---|
| 1 | anisole | 0.1 | 0.3 |
| 2 | $p$-methylanisole | 0.8 | 2.2 |
| 3 | $p$-ethylanisole | 0.7 | 2.0 |
| 5 | $\alpha$-methyl-$p$-methoxy-styrene | 0.7 | 2.1 |

TABLE VI

Effect of Pyrolysis Temperature on Monomer Yield from PMS

| Pyrolysis temperature, °C | PMS volatilized converted to monomer,[a] % |
|---|---|
| 345 | 35.8 |
| 395 | 49.1 |
| 445 | 53.3 |
| 500 | 54.8 |

[a] Average value from four runs.

at a reduced rate. It is probable that as the temperature of pyrolysis increases, the unzipping process increases in rate more than the transfer processes. As a result, the "zip length" increases, and a higher proportion of monomer is found. This phenomenon is also seen from the effect of pyrolysis temperature on the ratio of nonmonomer to monomer (Table VII). The value of 1.47 for PS is in good agreement with that found by Madorsky,[23,24] namely, 1.40. The liquid fraction from PHS could only be qualitatively analyzed since on extraction from the trap with 40–60°C petroleum ether, a white solid remained. This material was soluble in methyl ethyl ketone, and IR analysis showed it to be PHS. This indicated that the pyrolysis behavior of PHS was anomalous in that extensive repolymerization of the monomer occurred, indicative of the high reactivity of the $p$-HS system discussed in the preparative section. This behavior prevented quantitative analysis of the liquid fraction and evaluation of the effect of pyrolysis temperature on monomer yield.

## Fraction II

The gaseous fractions from PMS and PS were identical, mainly consisting of ethylene. No studies were made on the gaseous fraction from PHS.

## Fraction III—The Residue

This fraction was a very pale-green, transparent glass in the case of PMS which was soluble in toluene with slight gel formation in the later stages of degradation (>90% weight loss). PHS at low extents of degradation yielded a red, transparent glass insoluble in normal solvents for undegraded PHS. At high extents of degradation (>80% weight loss), a black, carbonaceous tar was obtained. The IR spectra after 20%, 50%, and 75% weight loss were compared with those of the

TABLE VII

Nonmonomer-to-Monomer Ratios PS and PMS

| Pyrolysis temperature, °C | PMS nonmonomer/ monomer | PS nonmonomer/ monomer |
|---|---|---|
| 345 | 1.8 | 1.47 |
| 395 | 1.6 | 0.96 |
| 420 | 1.1 | 0.87 |
| 445 | 0.9 | 0.86 |
| 500 | 0.83 | 0.79 |

TABLE VIII
Effect of Pyrolysis Temperature on the Molecular Weight of the PMS Residue

| Pyrolysis temperature, °C | $[\eta]_0$ |
|---|---|
| Ambient | 0.94 |
| 225 | 0.94 |
| 250 | 0.70 |
| 275 | 0.61 |
| 300 | 0.56 |
| 325 | 0.54 |

undegraded polymers. No significant differences could be detected, except for loss of resolution in the region 1500–1100 cm$^{-1}$ in the case of PHS.

Comparative studies have been made on the effect of degradation temperature upon molecular weight for PMS. No such studies could be made on PHS because of the insolubility of residue at weight losses in excess of 10%.

Measurements on the effect of pyrolysis temperature on molecular weight of PMS for a constant pyrolysis time of 30 min were made by intrinsic viscosity determination. The results obtained are shown in Table VIII. This behavior is similar to that reported previously for PS. It can be seen that a decrease in molecular weight appears to begin between 225° and 250°C without weight loss, suggesting the scission of some weak link occurs due to structural abnormalities such as that caused by an abnormal propagation or transfer step during polymerization.

The crosslinking reaction observed for PHS could have occurred during the degradation process or, alternatively, during the cooling of the residue to ambient temperature prior to examination.

The crosslinked residue obtained from PHS after 10–80% weight loss gave on reheating to 360°C a monomer yield which was qualitatively identical with that produced from untreated PHS. At weight losses in excess of 80%, carbonization occurs giving a product which does not yield monomer on subsequent reheating. The behavior at weight losses less than 80% is similar to that observed by Still and Whitehead[6] for poly(p-N,N-dimethylaminostyrene) (PDAS) under similar conditions.

This observation suggests that crosslinking may arise as a result of combination of radicals during the cooling period. Radicals similar to those suggested for PDAS obtained by scission of the nitrogen–methyl group bond could be obtained from PHS by scission of the oxygen–hydrogen bond of the phenolic hydroxy grouping in the pendent phenyl ring:
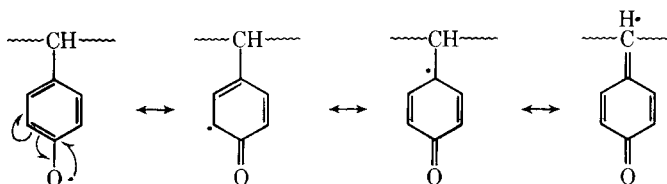


Such stabilized radicals would be expected to be colored. PS would not be expected to yield radicals of this type since their formation would involve homolytic cleavage of a strong aromatic C–H bond in the pendent benzene ring. Similarly, in the case of PMS the formation of such a radical species would result

from the scission of a C–O bond of comparable bond dissociation energy to that of the C–C bonds in the polystyrene main chain.

In the case of PHS, ESR studies have shown the presence of trapped radicals in the cooled glass. Combination of radicals derived from PHS on cooling could lead to structures of the type
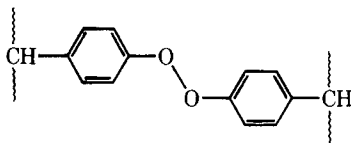


in which the O–O bond is thermolabile, having a bond dissociation energy of 155 kJ/mole which may be compared with that for the C–C bonds in the main chain as typified by the C–C bond one removed from the phenyl ring, as in the case of isopropylbenzene (252 kJ/mole).[25] On reheating, therefore, the crosslinks would break preferentially and would not inhibit unzipping. An alternative possibility is that crosslinking occurs by radical substitution in the substituted phenyl rings which are activated by the hydroxyl substituents.

### Fraction IV—The Oil

Madorsky found a similar fraction on pyrolysis of PS which he showed to consist of dimer, trimer, and some tetramer. The composition of the fraction remained constant, independent of pyrolysis temperature, and trimer constituted the major component of the fraction.

By analogy with PS, the oil fractions from PMS and PHS would be expected to contain the compounds shown in Table IX. Fraction IV from PMS was a

TABLE IX
Compounds Expected in PHS and PMS Oil Fraction
by Analogy with Those Found for PS[a]

|  | Molecular weight | |
|---|---|---|
|  | PHS | PMS |
| Dimer fraction |  |  |
| $CH_2$—$CH_2$—$CH_2$ <br> $\mid$        $\mid$ <br> R        R | 228 | 256 |
| $CH_2$=C—$CH_2$—$CH_2$ <br>    $\mid$       $\mid$ <br>    R      R | 240 | 268 |
| Trimer fraction |  |  |
| $CH_2$—$CH_2$—CH—$CH_2$—$CH_2$ <br> $\mid$       $\mid$       $\mid$ <br> R      R      R | 348 | 390 |
| $CH_2$=C—$CH_2$—CH—$CH_2$—$CH_2$ <br>    $\mid$      $\mid$      $\mid$ <br>    R     R     R | 360 | 402 |

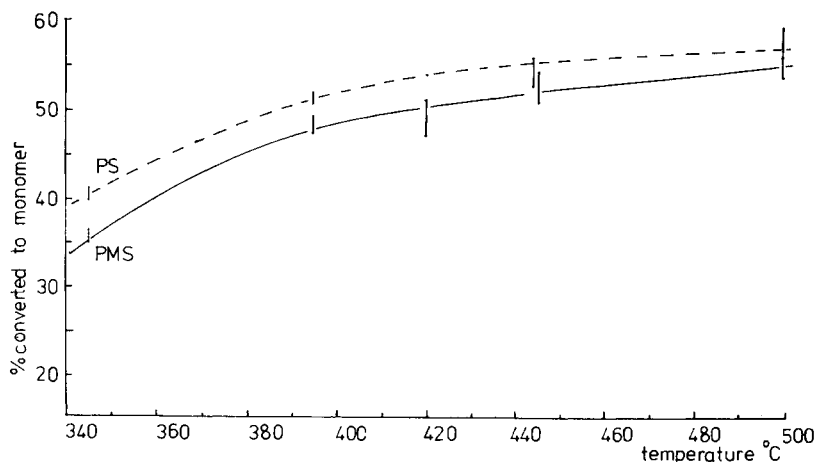[a] R = —⟨O⟩—OH for PHS, —⟨O⟩—OCH₃ for PMS.

Fig. 4. Effect of pyrolysis temperature on monomer yield for PS and PMS. ⌡ span of points.

colorless oil, that from PHS was a red oil surrounded by a white solid, the coloration suggesting either the presence of trapped radicals or extensive conjugation. The IR spectra of both oils revealed significant absorptions not present in the IR spectra of the respective monomers similar to those reported previously for PS and PDAS[6] and in accord with the structures suggested in Table IX.

The IR spectrum of the white solid surrounding the red oil from PHS was found to be identical to that of PHS, suggesting that monomer which had condensed in the quartz tube repolymerized. This is in accord with the high reactivity of $p$-HS noted during its polymerization and similar to the observations made on the liquid fraction.

The mass spectra obtained from PMS and PHS using the modified MS10 instrument were restricted by a mass limit of 200. However, base peaks at 121 and 107 correspond to the substituted tropylium ions formed by fragmentation of the dimers and possibly trimers and tetramers as described previously for PDAS,[6] namely,
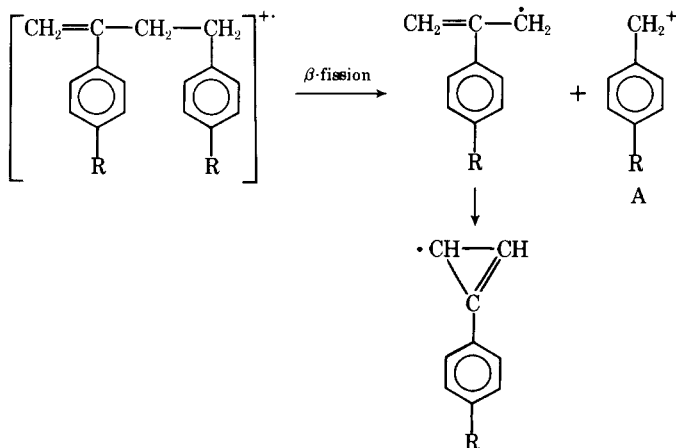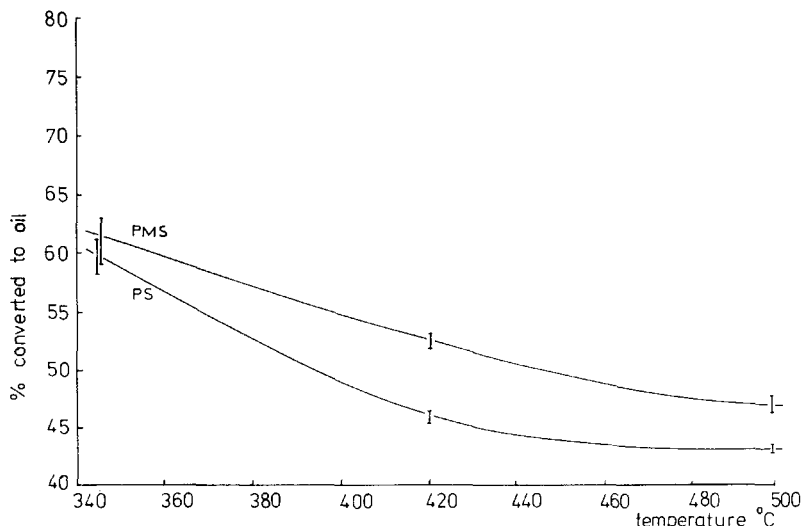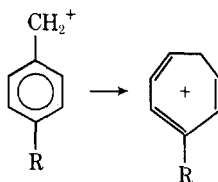
Fig. 5. Effect of pyrolysis temperature on oil yield for PS and PMS. ⎸ span of points.

where R = OCH$_3$ or OH.   The ion A will rearrange to yield the more stable tropylium ion:



Mass number when R = OH is 107; when R = OMe, it is 121.   Similar routes may be postulated for fragmentation of the trimer and tetramer to yield the base peaks.[6]

It would appear that the components of the oil fraction from PMS and PHS (apart from repolymerized monomer) are the substituted analogues of those observed for PS.

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 PMS. No quantitative studies were made on PHS because of the anomalous behavior of this system.   The results for PMS are shown in Figures 4 and 5 where the effect of pyrolysis temperature on monomer and oil production is compared for PS and PMS.   The monomer yield from PS is slightly higher than from PMS, 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.

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