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Thermal Elimination of Poly(phenyl vinyl sulfoxide) and Its Polystyrene Block Copolymers

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ABSTRACT: Previously[1] it was shown that poly(phenyl vinyl sulfoxide) (PPVS) and its block copolymers are potentially interesting candidates for a precursor route to a synthesis of polyacetylene. In this paper we report studies on the thermal elimination of PPVS. Both thermal and spectroscopic techniques were employed. Thermogravimetric analysis and pyrolysis-mass spectrometry were the thermal methods used for the elucidation of the elimination of phenylsulfenic acid from the precursor polymer. Proton NMR and IR were the spectroscopic methods employed. The formation of *cis*- and *trans*-polyenes was observed in ^{1}H NMR. Preliminary studies on the conductivities show a relatively short conjugation length in the polyacetylene formed.

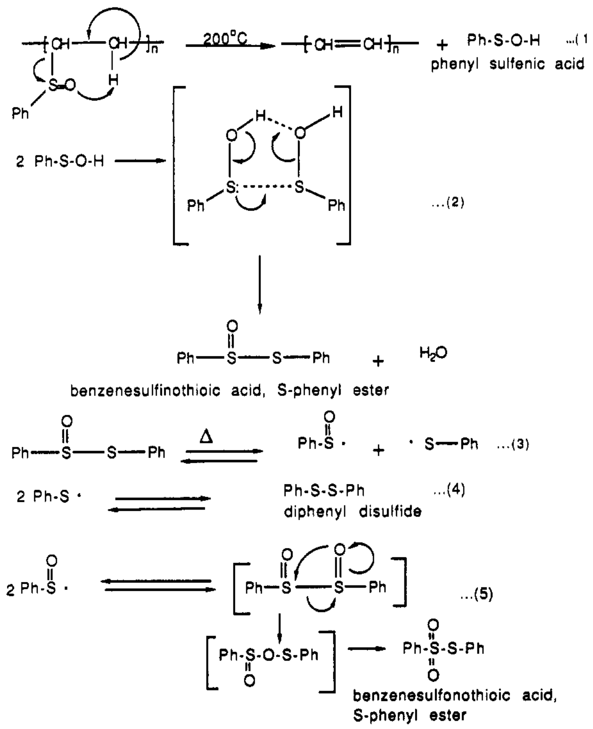
Introduction

We recently reported[1] studies on the anionic polymerization of phenyl vinyl sulfoxide and its block copolymers with styrene. The impetus for this study was the possibility of forming polyacetylene-like polymers upon thermal elimination of phenylsulfenic acid from poly(phenyl vinyl sulfoxide) (PPVS) (eq 1, Scheme I).[1] The conjugated polyene results from a six-electron sigmatropic thermal elimination. This type of elimination reaction is consistent with the use of vinyl sulfoxides as acetylene synthons first proposed by Kingsbury and Cram[2] and later utilized as acetylene equivalents in Michael addition-elimination[3-8] and Diels-Alder cycloaddition-elimination reactions.[9] Thus PPVS could be considered as a soluble precursor of polyacetylene similar to those synthesized by Feast[10,11] and Grubbs.[12]

Synthesis of PA from PPVS has potential advantages. Since polymerization of PVS proceeds through stable carbanions, the molecular weight distribution is expected to be narrow. Moreover, the control of molecular weight through the ratio of monomer to initiator is quite good, and thus formation of high molecular weight PPVS is possible. As a result a series of monodisperse PAs of known molecular weights is, in theory, possible. A second advantage of the sulfoxide precursor route to PA is the potential formation of A-B and A-B-A type copolymers with monomers such as styrene, butadiene, isoprene, etc., which are accessible through living anionic polymerizations. These may then be subjected to elimination to form block copolymers of styrene (or other monomers) and PA.

The synthesis of the homopolymers and styrene copolymers was described in a previous paper.[1] In the present paper we report our approach to the studies of the thermal elimination and possible formation of polyacetylene-like homopolymers and copolymers. Preliminary studies on the conductivities of the polyacetylene formed are also reported.

Scheme I



Experimental Section

Thermal elimination of the homo- and copolymers in the solid state was carried out by using a Thermolyne tube furnace with a suitably equipped pyrolysis tube. The polymer was coated as a thin uniform film from a solution in chloroform. The tube was then inserted into the Thermolyne furnace and connected to the vacuum line. A cold (-78 °C) trap was used between the line and the tube to trap any condensables. Elimination was carried out by gradually increasing the temperature to 180-200 °C and under high vacuum (10^{-6} Torr) for 1.5 h. The polymer after heating became dark black and shiny and was handled under argon (glovebag) at all times. The eliminated products obtained from the side of the tube outside the furnace were analyzed by MS, GC, and NMR.

The polymers after elimination were iodine doped under argon in the vapor phase at 20 °C for 12 h. The iodine content was

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Table I
TGA Data for PPVS Homopolymers, PPVO, and Polyacetylene

sample	first stage		second stage
	T_{onset},[d] °C	T_{max},[e] °C	T_{max},[f] °C
PPVS	120.2	205.2	480
	125.2	208.0	450
	134.2	210	460
(+)-PPVS	117.0	177	480
thermolyzed PPVS[a]			453
PPVO[b]	209	310	
polyacetylene[c]			476

[a] Thermal elimination of phenylsulfenic acid in vacuo at 200 °C for 2 h. [b] Obtained from oxidation of PPVS. [c] Genuine polyacetylene sample. [d] Temperature of onset of decomposition determined from the first derivative of the TGA curve (first stage). [e] Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (first stage). [f] Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (second stage).

determined by gravimetry. Conductivity measurements were performed either on thin films or on a pressed pellet in a temperature-controlled reactor. Electrical connections on the films were realized with a conductive glue (Electrodag). The measuring circuit consisted of a Keithley dc power supply and a Keithley electrometer. Polyacetylene used in our studies was synthesized by the Shirakawa method.[13]

High-temperature NMR was carried out on a Varian XL-300 NMR spectrometer. Acetic acid-d_4 was used as a solvent. A heavy-walled 5-mm tube was employed, and the polymer solution was sealed under a partial pressure of argon. The spectra were recorded at room temperature, and the temperature was increased in steps of 20 °C. A nitrogen atmosphere was used in the probe. Spectra were recorded at 60, 80, 100, 120, 140, and 150 °C. IR spectra were recorded on a Nicolet 60SX FT-IR spectrophotometer equipped with an Omega temperature controller. The polymer was mixed with diamond powder, mounted, and heated under a nitrogen atmosphere. The temperature was increased to 200 °C over a period of time at a heating rate of 5 °C/min, and the spectra were recorded continuously.

Pyrolysis-MS was carried out in an AEI MS-30 spectrometer. The polymer was inserted using a direct insertion probe. A gradient temperature from 100 to 500 °C was employed. Spectra were recorded continuously at various temperatures and processed by a Kratos data system. TGA was carried out on a Perkin-Elmer TGA7 thermogravimetric system. The polymers were usually scanned under a nitrogen sample purge (50 mL/min) from 50 to 900 °C at a heating rate of 10 °C/min.

Results and Discussion

TGA. Thermogravimetric analysis was employed as a useful technique to elucidate the elimination reaction in PPVS homopolymers (Table I) and copolymers (Table II). The structures of the homopolymers and copolymers listed in Tables I and II are shown in Figure 1 (also see ref 1).

PPVS homopolymers show two distinct stages of decomposition (Table I). Most thermograms also show loss of moisture/solvent etc., which may have been entrapped in the polymer matrix, at ca. 100 °C. The first stage of decomposition shows an onset at ca. 120 °C and reached a maximum rate (seen from its first derivative) at ca. 200 °C. There is usually an 80% loss in the first stage, which corresponds to the elimination of phenylsulfenic acid (Figure 2). The theoretical loss of phenylsulfenic acid would correspond to 83% loss, assuming complete elimination of phenylsulfenic acid. The temperature of elimination of phenylsulfenic acid from PPVS homo- and copolymers is lower than that of most vinyl polymers containing pendant electronegative groups X which can give polyacetylene-like polymers on elimination of HX. This was extensively studied by Montaudo et al.[14,15]

Table II
TGA Data of Styrene–PVS A–B Diblock and A–B–A Triblock Copolymer

sample	first stage		second stage
	T_{onset},[a] °C	T_{max},[b] °C	T_{max},[c] °C
1. polystyrene			445
2a. AB85	127	216	437
2b. HAB85[d]			460
2c. OAB85[e]	200	310	
3a. ABAS1	136	207	441
3b. HABAS1[f]			425

[a] Temperature of onset of decomposition determined from the first derivative of the TGA curve (first stage). [b] Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (first stage). [c] Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (second stage). [d] Thermolyzed AB85. [e] Oxidized AB85. [f] Thermolyzed ABAS1.

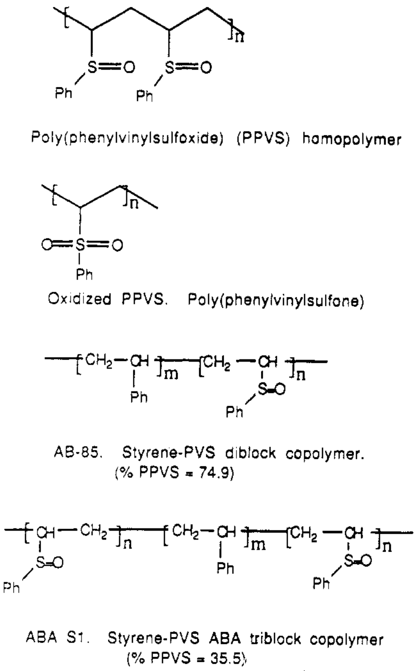

Figure 1. Structures of PPVS homopolymer and its styrene block copolymers.

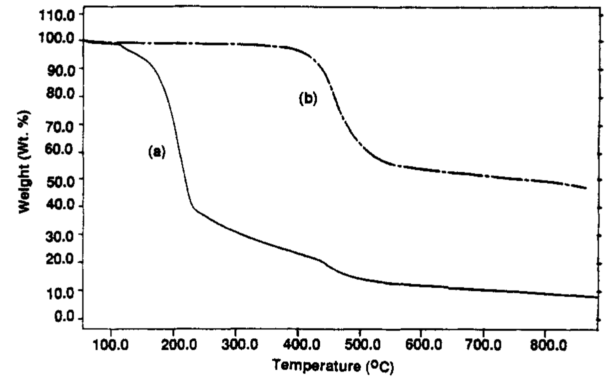

Figure 2. Weight percent vs temperature (TGA) curves for PPVS homopolymer: (a) before thermolysis; (b) after thermal elimination of phenylsulfenic acid in vacuo at 200 °C for 2 h.

The second stage of decomposition in the TGA of the homopolymer starts at 380 °C and shows a maximum rate of decomposition around 450 °C. This is typically the temperature at which the polyene sequences in polyacetylene start to degrade yielding various alkyl aromatics.[14-17] Table I also summarizes the data from the TGA curves of the thermolyzed PPVS. The thermogram (Figure 2b) is conspicuous by the total absence of the first step of

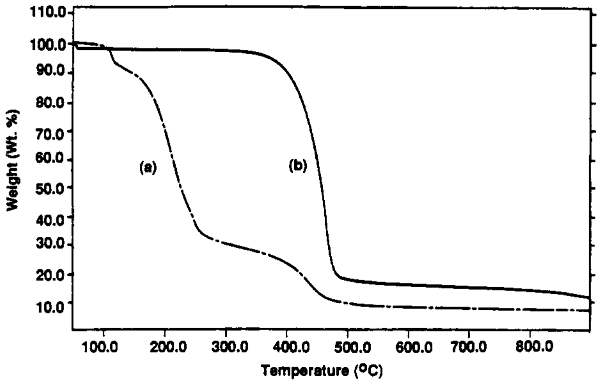

Figure 3. Weight percent vs temperature (TGA) curves for styrene–PVS copolymer (sample AB85, Figure 1): (a) before thermolysis; (b) after thermolysis in vacuo at 190 °C for 1.5 h.

Table III
Data from the Pyrolysis-MS of Homo-PPVS

positive-ion fragments	m/z
A. At T = 190 °C	
PhSSPh	218[a]
$PhSO_2SPh$	250
PhSPh	185
PhPh	154
$PhSO_2$	141
PhSO	125
PhSH	110
PhH	78
H_2O	18
B. At T = 450 °C	
PhSH	110[a]
propylanthracene	220
ethylanthracene	206
methylanthracene	192
anthracene	178
propylnaphthalene	170
ethylnaphthalene	156
methylnaphthalene	142
naphthalene	128
propylbenzene	120
xylene	106
toluene	91
benzene	78
H_2O	18

[a] Base peak.

decomposition seen in the precursor PPVS at ca. 200 °C. The TGA curve of the thermolyzed PPVS is comparable to the thermogram of polyacetylene. The thermogram of thermolyzed PPVS is also comparable to the second step of degradation in the vinyl polymers studied by Montaudo[14] and TGA of polyacetylene from the literature.[16,17]

The elimination of phenylsulfenic acid would be expected to be a cyclic, sigmatropic, six-electron elimination as shown before. A "zipper" mechanism is most likely; the formation of one double bond would create a "seed" for the formation of the next and so on down the chain. It has been well documented in sulfoxide eliminations[18,19] that the ease of hydrogen abstraction decreases in the order allylic > benzylic > secondary > tertiary. Thus, formation of one double bond would create an allylic site for the next and elimination would proceed more easily.

Sulfenic acids are notorious for their instability[2,19] and under ambient conditions dehydrate immediately to form the anhydride. In our case phenylsulfenic acid is expected to dehydrate to give the anhydride benzenesulfinothioic acid *S*-phenyl ester (PhS(O)SPh) (phenyl benzenethiolsulfinate). This dehydration reaction is shown in eq 2, Scheme I. The sulfenic acids associated by hydrogen bonding may be functioning as both S nucleophiles and S electrophiles.[20] The sulfenic acid dehydration reaction is essentially irreversible. Kice and Cleveland[21] suggest that the dehydration reaction in phenylsulfenic acid is favored over its hydration (hydrolysis of the phenyl benzenethiolsulfinate) by a factor of at least 10^6. The thiolsulfinate itself is not thermally stable[22] and disproportionates rather readily.

The thermal elimination of phenylsulfenic acid is seen only in sulfoxides. On oxidation of PPVS to poly(phenyl vinyl sulfone) (PPVO)[1] the polymer becomes thermally stable. This is corroborated by the TGA curve of PPVO (entry c, Table I). Only one degradation step is seen at a high temperature (300 °C). Thus we see a distinct difference in the thermal behavior of sulfoxides and sulfones.

Table II summarizes the TGA data of the copolymers of styrene and PVS, and Figure 3 shows a typical thermogram of styrene–PVS copolymer. Once again two distinct stages of decomposition are seen in the TGA thermogram of the copolymer (both A–B and A–B–A). The first stage of decomposition shows an onset that varies from 120 to 140 °C. However, the maximum rate of elimination is around 210 °C for most polymers. This corresponds to the first stage in the decomposition of homo-PPVS wherein phenylsulfenic acid would be expected to eliminate through a sigmatropic elimination step to form what would be styrene–acetylene block copolymers. It is significant to note that polystyrene degrades at a much higher temperature (entry 1, Table II). Thus at the lower temperatures used for the elimination of phenylsulfenic acid the polystyrene block would be mostly unaffected. This is also shown by pyrolysis–MS, which will be discussed later.

The second stage of decomposition in the block copolymers occurs around 440–450 °C, which is the temperature at which styrene depolymerizes by an unzipping mechanism (entry 1, Table II)[23,24] and at which the polyene sequences of the polyacetylene block rearrange and decompose to yield various aromatic hydrocarbons.[16,17]

The sample AB85 containing 74.9% of sulfoxide in the A–B copolymer was oxidized with 30% H_2O_2.[1] The oxidized copolymer shows only one high-temperature degradation stage (entry 2c, Table II), although one would expect to see two stages corresponding to the sulfone decomposition at 300 °C and polystyrene depolymerization at 450 °C.

Several copolymers were subjected to thermolysis in vacuo at 190 °C. The products are brittle cellophane-like transparent yellow films. The TGA of the heated copolymers is also summarized in Table II (entries 2b and 3b). Once again, only one high-temperature degradation step was noted around 450 °C. This also confirms the almost quantitative elimination of phenylsulfenic acid from the copolymer.

Pyrolysis–Mass Spectrometry. Montaudo[14,15] carried out studies of thermal degradative mechanisms in vinyl polymers with a pendant electronegative group that on elimination would lead to the formation of polyene structures. Ours being a similar system, it was decided to carry out pyrolysis–MS on PPVS homo- and copolymers.

Distinct differences were found in the MS of PPVS at low and high pyrolysis temperatures. The MS at low pyrolysis temperature (<190 °C) was consistent with the elimination of phenylsulfenic acid and its further reactions (Scheme I, eqs 2–5). The positive-ion fragments (m/z) in the pyrolysis–MS of homo-PPVS at 190 °C along with the assignments of the peaks are summarized in Table IIIA. The m/z 218 (PhSSPh) peak was observed as the base

Table IV
Data from the Pyrolysis–MS of Styrene–PVS Copolymer

positive-ion fragments	m/z
A. At T = 150 °C	
PhS	109[a]
$PhSO_2SPh$	250
PhSSPh	218
PhSPh	185
PhPh	154
$PhSO_2$	141
PhSO	125
PhSH	110
PhH	78
Ph	77
H_2O	18
B. At T = 435 °C	
$PhCH{=}CH_2$	104[a]
propylanthracene	220
ethylanthracene	206
methylanthracene	192
anthracene	178
naphthalene	128
propylbenzene	120
toluene	91
benzene	78

[a] Base peak.

peak. The MS was compared with the actual MS reported in the EPA/NIH Mass Spectral Data Base. From the comparison we conclude that the MS observed at low temperatures is mainly due to PhSOSPh, $PhSO_2SPh$, and PhSSPh, which were also previously identified.

There was no indication of the presence of phenylsulfenic acid, which corroborates our conclusion that it dehydrates to the sulfinothioic ester immediately upon formation (Scheme I, eq 2). Although PhSOSPh is detectable, it is mainly its disproportionation products ($PhSO_2SPh$ and PhSSPh) that constitute the MS at low temperatures. At high pyrolysis temperatures (>400 °C) a totally different picture emerges (Table IIIB). The base peak is m/z 110 (PhSH), which indicates the presence of the decomposition products in the polymer matrix (mainly PhSSPh and $PhSO_2SPh$). However, the most intense peaks are due to alkyl aromatic hydrocarbons, seen as periodic clumps of high-mass peaks.[14,15] Polyacetylene exhibits a similar pyrolysis–MS at 490 °C[14] showing toluene as the base peak and other substituted aromatics of higher masses.

According to Chien et al.,[17] in the pyrolysis of polyacetylene the initiation process of degradation is probably the thermal excitation of bonding π electrons to the antibonding state resulting in bond dissociation to form vinyl radicals followed by intramolecular electron migration and ring closure leading directly to benzene. Other alkyl aromatics can be accounted for by a series of proton–electron migrations which may be quantum-mechanical tunneling in nature. The formation of alkyl aromatics probably involves cleavage of cross-linked polyacetylene chains at high temperatures (>450 °C).[14]

Like the homopolymer, the copolymer also shows distinct differences in the decomposition at low and high pyrolysis temperatures. At low temperatures (<190 °C) (Table IVA) once again we see the MS due to the elimination of phenylsulfenic acid and its further reactions. From the total ion current it is seen that the polystyrene block is mostly unaffected even at 225 °C. Formation of styrene, which is indicative of depolymerization of the polystyrene block, is only beginning around 225 °C. This result was significant for our purpose since we can safely carry out the elimination of the copolymers at lower temperatures without significantly degrading the polystyrene block in the copolymer.

Formation of styrene is greatly accelerated at temperatures above 250 °C, and, in fact, above 300 °C styrene becomes the base peak in the mass spectrum (Table IVB). Once again, at higher temperatures we see (although to a lesser extent because of polystyrene degradation) alkyl aromatics typical of polyacetylene decomposition.

Nuclear Magnetic Resonance (NMR). The thermal elimination of phenylsulfenic acid from PPVS was monitored by ^{1}H NMR from 30 to 150 °C. The polymer was dissolved in glacial acetic acid-d_4 and sealed under a partial pressure of argon, necessary to improve resolution at high temperatures. Figure 4 shows the effect of temperature on the ^{1}H NMR of PPVS. It is seen that up to ca. 100 °C there was little change in the ^{1}H NMR. At 100 °C, however, we see several changes. The main-chain CH and CH_2 absorptions at δ 3.2 and 1.8, respectively, show a decrease in intensity. Simultaneously we see two peaks showing up in the vinyl region at δ 5.7 and 6.3. The aromatic absorptions become sharper. At 120 °C the CH and CH_2 absorptions have decreased further whereas the vinylic absorptions have intensified. At 150 °C all of the peaks disappear except for the aromatic absorptions, probably as a result of polymer precipitation.

We give the following interpretation of the above events. As the temperature is increased from room temperature to 100 °C, we see the formation of polyene linkages due to the sigmatropic 6π elimination of phenylsulfenic acid from PPVS as illustrated in Scheme I, eq 1. A decrease in the CH_2 and CH absorptions of the polymer backbone was noticed concurrent with the development of broad absorptions in the vinyl region. Table V summarizes the normalized area of the vinyl protons as compared to the normalized area of the sulfoxide methine from which the percentage of the polyene groups (both cis and trans) could be calculated. We see a dramatic increase in the percentage of polyene from 80 to 100 °C (10% to 40%). Obviously the polyenes form at the expense of the methylene and methine protons of PPVS. At this stage the polymer is still soluble because of the presence of a substantial percentage of the sulfoxide groups (Table V). Thus random and/or block copolymers of poly(acetylene-*b*-PVS) may be formed. The two peaks in the vinyl region indicate two different types of olefins; cis/trans or internal/terminal. The fact that we do not see a change in the chemical shift of the polyene peaks with temperature indicates that they are most likely due to geometric isomers. Also the chemical shifts observed (δ 5.8 and 6.3) are close to those observed in low-MW conjugated *cis*- and *trans*-polyenes from the literature[25–27] [*cis*-1,3,5-hexatriene, δ 5.1 (4 H), 5.9 (2 H), 6.7 (2 H); *trans*-1,3,5-hexatriene, δ 5.1 (4 H), 6.2 (4 H); (*E*,*E*)-octa-1,3,5,7-tetraene, δ 4.9–5.5 (4 H), 6.3 (6 H); (*E*,*E*,*E*)-nona-1,3,5,7-tetraene, δ 1.8 (3 H), 4.9–6.0 (2 H), 6.0–6.5 (7 H); (*E*,*E*,*E*)-deca-1,3,5,7,9-pentaene, δ 5.0–5.3 (4 H), 6.3 (8 H)]. Thus absorptions at δ 5.8 and 6.3 are reasonably attributable to *cis*- and *trans*-polyenes, respectively. Sharpening of peaks in the aromatic region is seen because of the formation of low molecular weight elimination products (Scheme I). At 150 °C all the peaks (except the aromatic absorptions of the eliminated products) disappear. At this stage (55% polyene, Table V) the polyene groups render the polymer insoluble and it precipitates out.

Infrared (IR). IR was used both for routine identification of homo- and copolymers and for the interpretation of the thermolysis process in PPVS. Unfortunately, we could not derive much information of

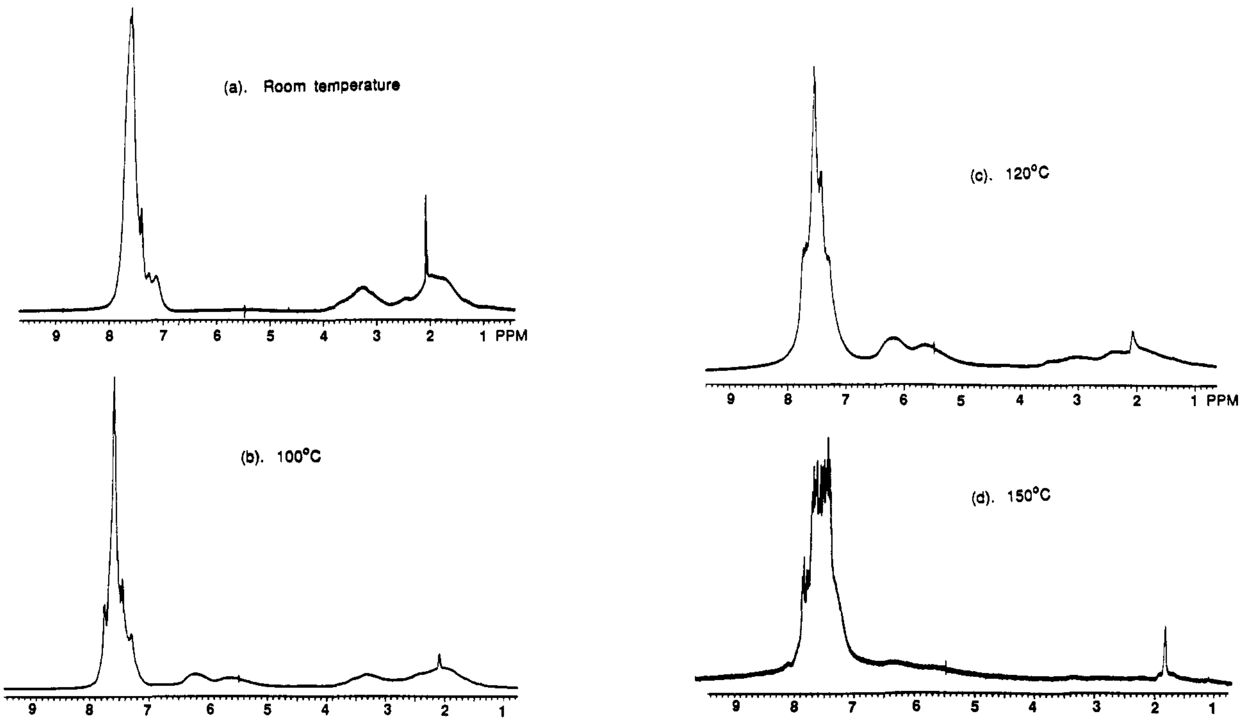

Figure 4. Change in the 300-MHz ^{1}H NMR spectra (in CD_3COOD) of PPVS homopolymer with temperature: (a) room temperature; (b) 100 °C; (c) 120 °C; (d) 150 °C.

Table V
Data from the High-Temperature 300-MHz ^{1}H NMR of PPVS in CD_3COOD

T, °C	area of polyenes[a]	area of PPVS methine[b]	% polyenes
80	0.1745	0.8255	9.56
100	0.5561	0.4439	38.5
120	0.7021	0.2979	54.1
140	0.7311	0.2689	57.6

[a] Normalized area of integration of the polyene absorptions at δ 5.7 and 6.3. [b] Normalized area of integration of the PPVS methine absorption at δ 3.2.

the polyacetylene absorptions from IR because of the high IR absorptivity of the residual sulfoxide groups which overlaps with the =CH bend absorption of polyacetylene.

A case in point is seen in Figure 5, which shows the change in IR of PPVS with temperature. The polymer was mixed with diamond powder and heated in situ under a flow of nitrogen. The spectra were scanned at various temperature intervals. At 30 °C we see the characteristic IR of PPVS showing a strong absorption at 1041 cm^{-1} due to the S=O stretch of the sulfoxide group. Upon heating the polymer to 240 °C, we see the disappearance of the 1041-cm^{-1} absorption concurrent with the appearance of a strong absorption at 1143 cm^{-1}, medium absorptions at 1323, 1436, and 1474 cm^{-1}, and a weak absorption at 1575 cm^{-1}. The IR of PPVS at 240 °C was identical with that of PhSSPh and $PhSO_2SPh$ (Sadtler). Thus the strong absorptions at 1143 and 1323 cm^{-1} are probably due to the O=S=O stretch and S–S stretch, respectively, of $PhSO_2SPh$, whereas the ones at 1436, 1474, and 1575 cm^{-1} are due to PhSSPh. Thus the eliminated products cloud the IR window and/or are left behind on the eliminated polymer, giving no useful information on the cis or trans =CH absorptions.

Preliminary conductivity measurements show $\sigma = 3\ \Omega^{-1}$ cm^{-1} for the thermolyzed PPVS ($CHI_{0.07}$) and $\sigma = 100\ \Omega^{-1}$ cm^{-1} for "Shirakawa" polyacetylene ($CHI_{0.1}$). The considerably lower value in the case of thermolyzed PPVS suggests formation of defects during thermal elimination leading to a decreased conjugation length. The elimination of phenylsulfenic acid has been shown by Cram[2] to be a stereospecific elimination involving a five-membered six-electron transition state (four electrons from the C–S and C–H bonds and two electrons as a lone pair on oxygen) and termed as a $_\sigma 2_s + _\sigma 2_s + _\omega 2_s$ sigmatropic elimination. However, at high temperatures and in the solid state a homolytic cleavage of the C–S bond is possible leading to sulfinyl and benzyl radical pairs.[2] Formation of defects at these homolytic bond cleavage sites is entirely possible and may account for the lower conductivity observed. The lower conductivity may also be due to the presence of residual elimination products. A more thorough investigation into this problem is required.

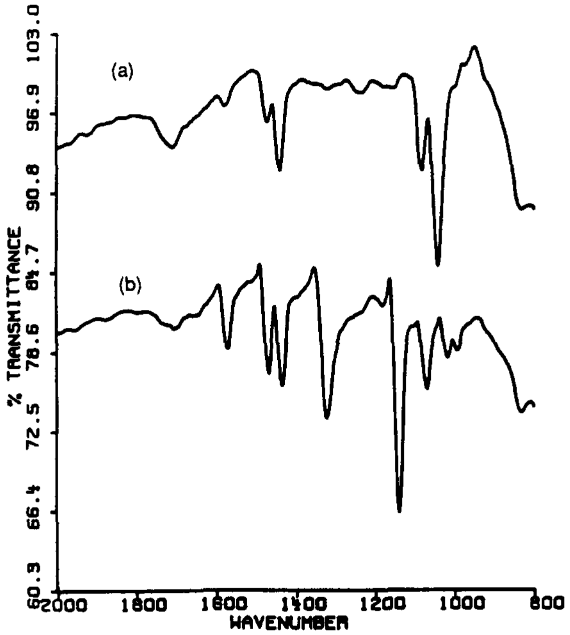

Figure 5. Change in the IR spectra of PPVS homopolymer with temperature: (a) 30 °C; (b) 240 °C (under nitrogen).

Conclusions

The thermal elimination of phenylsulfenic acid from PPVS homo- and copolymers was studied by TGA and pyrolysis–MS. The TGA of homopolymers typically show two degradation stages: one at lower temperature corresponding to elimination of phenylsulfenic acid and one at higher temperatures corresponding to polyacetylene degradation. Pyrolysis–MS was used for elucidating the fate of phenylsulfenic acid formed upon elimination. It was seen that the phenylsulfenic acid, once formed, irreversibly dehydrates to form the anhydride benzenesulfinothioic acid *S*-phenyl ester. This compound itself is not thermally stable and disproportionates rather readily to give diphenyl disulfide and benzenesulfonothioic acid *S*-phenyl ester. There was a decided difference in the pyrolysis–MS at low and high temperatures. At low temperatures MS corresponding to the elimination of phenylsulfenic acid and its further reaction was seen. At higher temperatures, however, formation of various aromatic hydrocarbons was seen typical of PA decomposition. Proton NMR was also used to characterize the elimination process and shows formation of *cis*- and *trans*-polyenes at high temperatures (>100 °C). A change in IR spectra with temperature was observed but gave no useful information about the polyenes formed.

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Registry No. PPVS (homopolymer), 87500-51-4; (PVS)-(styrene) (copolymer), 128731-83-9; phenylsulfenic acid, 27610-20-4.