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# Synthesis of Polyacetylene by Chemical Modification of Poly(phenyl vinyl sulfoxide)

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ABSTRACT: Poly(phenyl vinyl sulfoxide) (PPVS) can be used as an effective soluble precursor for the synthesis of polyacetylene (PA). Fairly long sequences of conjugated double bonds are obtained by a thermal elimination of benzenesulfenic acid from PPVS on condition that the conversion is conducted under dynamic vacuum and at moderate temperatures (50–80 °C). The IR study of PA(exPPVS) demonstrates that the conversion is high (>95%) and that the number of defects on the chain is low. The conversion of PPVS to PA follows a first-order kinetics, and this reaction has a large activation energy. These PA(exPPVS) can be oxidized or reduced as illustrated by the shift of their absorption spectra from the visible to the near-IR upon doping.

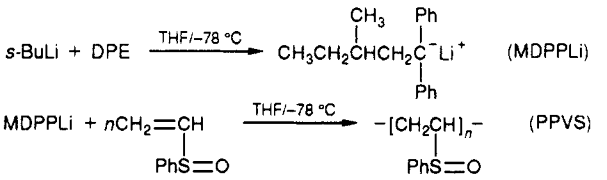
## Introduction

Previous work by Kanga et al.[1] has shown that poly(phenyl vinyl sulfoxide) (PPVS) is a potentially interesting candidate for a new precursor route to the synthesis of polyacetylene. A color change from white to yellow, red, and finally black is observed upon heating this polymer above room temperature. This indicates the formation of conjugated double bonds resulting from a thermal elimination of benzenesulfenic acid from the PPVS. This thermal elimination reaction has been extensively studied,[1] but little information about the polyenes formed can be found in the literature.[2] Before trying to take advantage of the interesting potentiality of this new precursor route to PA, it is necessary to know more about the type of conjugated system generated by this elimination reaction. The purpose of the work reported here is to characterize the PA(exPPVS) and to optimize the conditions for the thermal elimination in order to minimize the amount of defects and increase the conjugation length of the PA formed. The main interest of PPVS compared to other PA precursors, obtained by ring opening metathesis polymerization,[3-6] results from the possibility of preparing this polymer by anionic polymerization.[7] So the molecular weight of PPVS can be easily controlled by the ratio monomer to initiator, and narrow molecular weight distributions are expected. It is also possible to copolymerize PVS with a large variety of other monomers. Thus, the incorporation of monodispersed PA of a predetermined molecular weight, into the elaborate macromolecular structures (block copolymers, star- or comb-shaped macromolecules, networks etc.) accessible through anionic polymerization,[8] becomes possible.

## Experimental Section

**Purification of Monomer, Solvent, and Initiator.** Phenyl vinyl sulfoxide (PVS), purchased from Aldrich, was stirred over calcium hydride and distilled under high vacuum ($<10^{-4}$ mmHg). This procedure was repeated three times and the monomer coming from the final distillation was collected in ampules equipped with breakseals. THF was first distilled over sodium wire and then introduced, under vacuum, into a reaction flask connected to a vacuum line and containing pieces of sodium and benzophenone. Once the purple red color of the benzophenone dianon was obtained the THF was distilled, through the line, directly into the polymerization vessel. 1,1-Diphenylethylene (DPE) was distilled, under vacuum, over a sodium mirror; the purified DPE being collected directly in ampules equipped with breakseals. The *sec*-butyllithium (*s*-BuLi), purchased from Aldrich, was purified by sublimation under high vacuum in order to remove all traces of decomposition products and then redissolved in dry cyclohexane. The (3-methyl-1,1-diphenylpentyl)lithium (MDPPLi), used to initiate the polymerization of PVS, was prepared by reacting a slight excess of DPE with *s*-BuLi in THF at −78 °C.

**Polymerization Procedure.** The polymerization reactions were carried out at −78 °C under high vacuum, in sealed glass apparatus, using the conventional breakseal technique.[9] A solution of the monomer in THF was added to a stirred solution of MDPPLi and the polymerization was allowed to proceed for about 1 h.



$$s\text{-BuLi} + \text{DPE} \xrightarrow{\text{THF}/-78\ ^\circ\text{C}} \text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{HCH}_2\overset{\text{Ph}}{\underset{\text{Ph}}{\text{C}}}{}^{-}\text{Li}^{+} \quad (\text{MDPPLi})$$

$$\text{MDPPLi} + n\text{CH}_2{=}\underset{\text{PhS}{=}\text{O}}{\text{CH}} \xrightarrow{\text{THF}/-78\ ^\circ\text{C}} -[\text{CH}_2\underset{\text{PhS}{=}\text{O}}{\text{CH}}]_n- \quad (\text{PPVS})$$

After termination with methanol the poly(phenyl vinyl sulfoxide) (PPVS) was precipitated in diethyl ether and dried under vacuum at room temperature. Since the PPVS tends to degrade slowly at room temperature, the samples were stored in a freezer at −30 °C. PPVS of different molecular weights have been characterized by size exclusion chromatography (SEC) using polystyrene standards.

**Thermal Transformation of PPVS.** DSC measurements were performed on PPVS powder contained in airtight steel capsules sealed under dry argon atmosphere using a Perkin-Elmer DSC-4 calorimeter. Thermal conversion of the precursor polymer to PA was achieved in the solid state by heating, under dynamic vacuum ($<5 \times 10^{-5}$ Torr), PPVS films cast on quartz or KBr plates from THF solutions. The transformation reaction was followed by UV–vis–near-IR and IR spectroscopy, the thickness of the films used being lower than 0.1 μm for the UV–vis–near-IR and about 1 μm for the IR studies. The decomposition compounds were trapped at −78 °C and analyzed by gas chromatography coupled with mass spectroscopy, $^1$H and $^{13}$C NMR, and IR spectroscopy.

**Doping of the PA(exPPVS).** The PA(exPPVS) films were oxidized (p-doping) using iodide in the vapor phase or in solution in pentane. The n-type doping (reduction) was realized with various organopotassium compounds in solution in THF. The dopants used—the potassium salts of fluorenone radical ion (FOK) and naphthalene radical ion (NK)—were prepared as previously described.[10] The doping reaction was studied by UV–vis–near-IR spectroscopy.

## Results and Discussion

The SEC data for the PPVS used in this study are given in Table I. The molecular weight was varied from 4000

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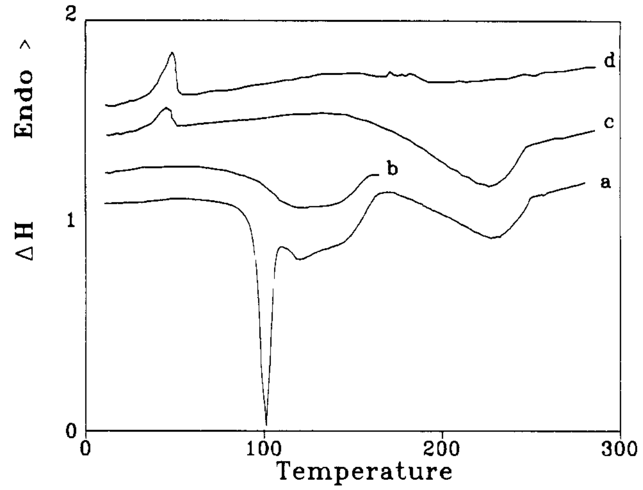


**Figure 1.** DSC thermograms: (a) PPVS powder; (b) same amount of PPVS but previously scanned up to 110 °C; (c) sample b cooled down to 0 °C and scanned again; (d) sample a scanned a second time.

**Table I**
**SEC Characterization of the Various PPVS**

| $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|
| 4 200 | 5 100 | 1.2 |
| 13 000 | 21 000 | 1.6 |
| 18 000 | 31 000 | 1.7 |

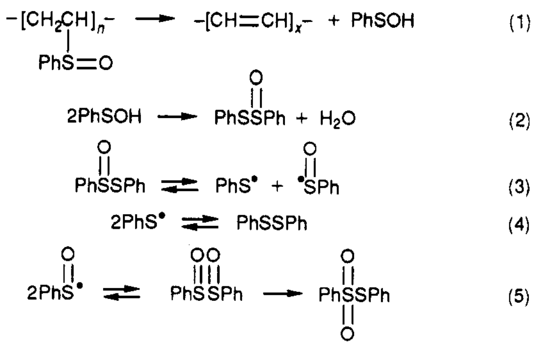
up to about 20 000, with polydispersity between 1.2 and 1.7. The increase of the polydispersity observed for the largest PPVS either suggests a problem of stability of the living PPVS–lithium or is related to the great difficulty encountered to purify the monomer.

1. **Study of the Thermal Elimination Reaction. (a) DSC Measurements.** The DSC analysis of our samples extended from 0 to 300 °C at a heating rate of 5 deg/min. Figure 1a shows a DSC thermogram of PPVS powder which reveals three exothermic peaks ranging from 86 to 110 °C, 110 to 165 °C, and 175 to 250 °C. This sample was then cooled down to 0 °C and scanned a second time (Figure 1d). It no longer exhibits the above mentioned exotherms but endothermic peaks appear: a strong peak centered at 45–48 °C and several weak peaks between 150 and 190 °C. Another sample containing the same amount of PPVS powder was first scanned up to 110 °C (end of the first exothermic peak), cooled down to 0 °C, and then scanned up to 165 °C (Figure 1b). No endothermic peak is seen and the exothermic peak is identical to the second one in scan a. This sample is then scanned from 0 up to 290 °C (Figure 1c). Only the first endothermic peak observed in scan d is found, and its intensity is somewhat lower; the third exothermic peak stays unchanged. That demonstrates that the compound responsible for the peak at around 45–50 °C is formed mainly during the second exothermic reaction, the products responsible for the other endothermic peaks resulting from the exothermic reactions occurring above 165 °C.

The three exothermic peaks can be attributed to different steps in the decomposition reaction of PPVS to PA, and the endothermic peaks reveal the formation of side products. It is well-known that PA is stable under argon until above 300 °C so that none of the observed exotherms are due to polymer thermal decomposition.[11]

These observations support the reaction scheme (Scheme I) proposed by Kanga et al.[1]

**Scheme I**



$$-[CH_2CH(S(=O)Ph)]_n- \longrightarrow -[CH{=}CH]_x- + PhSOH \quad (1)$$

$$2PhSOH \longrightarrow PhS(O)SPh + H_2O \quad (2)$$

$$PhS(O)SPh \rightleftharpoons PhS^{\bullet} + {}^{\bullet}S(O)Ph \quad (3)$$

$$2PhS^{\bullet} \rightleftharpoons PhSSPh \quad (4)$$

$$2PhS(O)^{\bullet} \rightleftharpoons PhS(O)S(O)Ph \longrightarrow PhS(O)_2SPh \quad (5)$$

The first DSC exotherm ranging from 85 to 110 °C can be attributed to the cyclic, sigmatropic thermal elimination of benzenesulfenic acid from PPVS leading to the formation of PA (eq 1, Scheme I). Benzenesulfenic acid being unstable,[12] it dimerizes to form the phenyl benzenethiosulfinate (PhS(O)SPh) (eq 2, Scheme I). This last compound itself is thermally unstable[13] and disproportionates (eq 3, Scheme I), leading to the formation of diphenyl disulfide (eq 4, Scheme I) and phenyl benzenethiosulfonate (eq 5, Scheme I). It seems reasonable to consider that it is this decomposition of PhS(O)SPh which gives rise to the second exothermic peak. This assumption is confirmed by the presence of the endothermic peak at around 45–48 °C which can be attributed to melting of diphenyl disulfide. The peaks corresponding to vaporization of the byproducts are absent, as can be anticipated from their high boiling points. The last exothermic peak may be assigned to further thermal decomposition of $PhS(O)_2SPh$ producing PhSSPh, as indicated by the increase of the endotherm at 45–48 °C, and other compounds responsible for the small endotherms between 150 and 190 °C.

The DSC curve (Figure 1a) has been subjected to more detailed analysis. If the assignment of DSC peaks is correct, then the activation energy for the formation of double bonds can be deduced from the first exothermic peak according to the method put forward by Rogers et al.[14,15] A plot of log $d$ versus $1/T$ gives a straight line whose slope corresponds to $EA/2.303R$. Here $d$ is the distance of the peak from its base at the temperature $T$ and it is proportional to the heat involved and the rate constant for the thermal decomposition at this temperature. The activation energy EA calculated for this process, according to this method, is 418 ± 40 kJ/mol (100 ± 10 kcal/mol). This very high value shows that the thermal elimination of benzenesulfenic acid occurs in a narrow temperature domain. Another interesting fact, revealed by this DSC study, is that the formation of double bonds occurs at relatively low temperatures (<100 °C).

**(b) Characterization of the Side Products.** During thermal transformation of PPVS under dynamic vacuum ($<5 \times 10^{-5}$ Torr) a crystalline deposit is formed on the unheated glass walls of the apparatus. These side products were collected and analyzed by gas chromatography–mass spectroscopy, nuclear magnetic resonance, and IR spectroscopy. The gas chromatography–mass spectroscopy study has shown that in fact a pure compound was collected: a single peak is found in the GC trace and the mass spectrum obtained for this peak (Table II) corresponds to diphenyl disulfide. The 200-MHz $^1H$ NMR spectrum of the crude product, trapped under these conditions and dissolved in acetone-$d$ (Figure 2a), confirms that PhSSPh is recovered. Only two peaks centered at 7.5 ppm (integration: 1.0) and 7.3 ppm (integration: 1.5) are observed; these peaks can be assigned respectively to the four ortho and the six other aromatic protons. A melting point of 58–59 °C has been determined for the

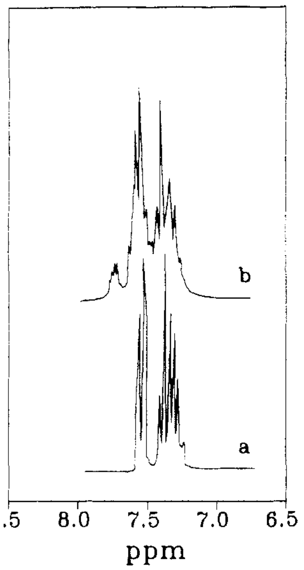


**Figure 2.** $^1$H NMR (200 MHz) of the decomposition products: (a) deposited on the glass walls; (b) trapped at −78 °C.

**Table II**
**Mass Spectrometry Data for the Decomposition Product Deposited on the Unheated Glass Walls of the Reactor**

| *m/z* | intensity | positive-ion fragments |
|---|---|---|
| 218 | 1000 | PhSSPh |
| 185 | 170 | PhSPh |
| 154 | 156 | PhPh |
| 109 | 761 | PhS |
| 65 | 274 | SS |

crude product, the reported value for the melting point of diphenyl disulfide sold by Aldrich being 58–60 °C.

The $^1$H NMR spectrum of the crude product collected in a cold trap (−78 °C) during the thermal transformation of PPVS under dynamic vacuum ($<5 \times 10^{-5}$ Torr) is given in Figure 2b. Again, only aromatic protons are seen; however in addition to the two peaks at 7.5 and 7.3 ppm, a new peak at 7.7 ppm appears. This latter peak may be assigned to the strongly upfield-shifted protons on the ortho position of a phenyl attached to an SO or $SO_2$ group. The peak at 7.7 ppm strongly decreases with time (about 50% over the first 24 h), indicating that the compounds bearing SO or $SO_2$ groups undergo further decomposition. The IR spectrum of the compounds collected in the cold trap shows bands at 1144 and 1327 cm$^{-1}$, which may be assigned to the O=S=O stretch and S—S stretch of $PhS(O)_2SPh$, and at 1436, 1471, and 1573 cm$^{-1}$, coming from the diphenyl disulfide. A trapping at low temperature is also necessary to prevent other side products than PhSSPh, such as $PhS(O)_2SPh$ (Scheme I), from being removed from the reaction vessel under dynamic vacuum.

All these observations demonstrate that the thermal decomposition of PPVS follows the general scheme proposed by Kanga et al. It appears however that the abstraction of benzenesulfenic acid from PPVS occurs already at temperatures lower than those reported before.

**2. Characterization of the PA(exPPVS) Formed.** IR and UV–vis spectroscopy were used to gain information on the type of conjugated system it is possible to achieve by the thermal decomposition of PPVS as well as on the kinetics of this conversion.

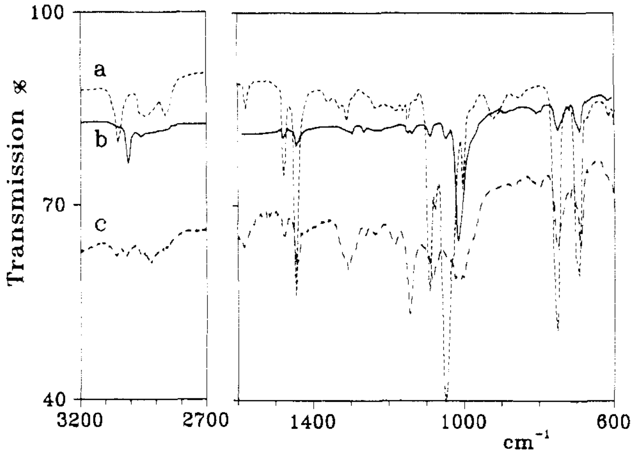


**Figure 3.** IR spectra of PPVS (- - -) after 15 h of heating at 80 °C under dynamic vacuum (—); after 15 h of heating at 80 °C under argon followed by vacuum pumping at 120 °C for 10 h (– – –).

**(a) Influence of the Experimental Parameters on the Conjugation Length of the PA(exPPVS). IR Study.** Figure 3 gives the IR spectra of a pure PPVS film (a), the same film heated at 80 °C under dynamic vacuum (about $10^{-5}$ Torr) for 15 h (b) and a similar film heated at 80 °C for 15 h under a normal pressure of argon (c).

The transformation of PPVS to PA upon heating under vacuum is demonstrated by the spectral changes between Figure 3a and b. The absorption at 1048 cm$^{-1}$ due to the S=O stretch of the sulfoxide group vanishes and a single band at 1010 cm$^{-1}$ characteristic of long sequences of conjugated trans double bonds is formed. Only *trans*-polyenes are obtained even if the thermal conversion is conducted at temperatures as low as 50 °C. These results are coherent with a stereospecific elimination of benzenesulfenic acid via a five-membered six-electron transition state, as proposed by Cram.[16] The strong attenuation of the absorptions assigned to the phenyl groups (691, 749, 1442, and 1475 cm$^{-1}$) shows that, under these experimental conditions, the benzenesulfenic acid as well as its decomposition products are removed from the film. A quantitative analysis of the residual absorptions at these wavelengths allows an estimation of the conversion level; it is found to be higher than 95%. The spectral changes in the absorption range of the C—H stretch are also noteworthy: the band at 3050 cm$^{-1}$ originating from the phenyl ring as well as the two bands at higher wavelength corresponding to CH and $CH_2$ (Figure 3a) are replaced by a single band at 3010 cm$^{-1}$ assigned to =C—H (Figure 3b). This observation confirms that very few sp$^3$ carbons (conjugation defects) are left behind on the PA(exPPVS) chain. The IR spectrum of PA(exPPVS) is identical to those of other polyacetylenes reported in the literature.[11,17,18]

The same thermal treatment on PPVS, but under a normal pressure of dry argon, leads to a much more complicated IR spectrum (Figure 3c), similar to the one reported in ref 1. The absorption at 1048 cm$^{-1}$ is replaced by two strong absorptions at 1144 and 1325 cm$^{-1}$, probably due to the O=S=O and S—S stretch, and the absorptions assigned to the phenyl group at 691, 749, 1442, and 1475 cm$^{-1}$ remain much stronger, as in Figure 3b. The absorption around 1000 cm$^{-1}$ is broad and somehow shifted to lower wavenumbers, pointing to shorter and ill-defined sequences of conjugated double bonds. The spectrum around 3000 cm$^{-1}$ shows only a small peak at 3010 cm$^{-1}$ assigned to the =C—H stretch, whereas the bands attributed to the C—H stretch in the phenyl ring (3050 cm$^{-1}$) and on the –CH and –$CH_2$ remain relatively important. This confirms that the carbons on the chain are only partially converted to sp$^2$. It appears that, under these experimental conditions, the polymers obtained

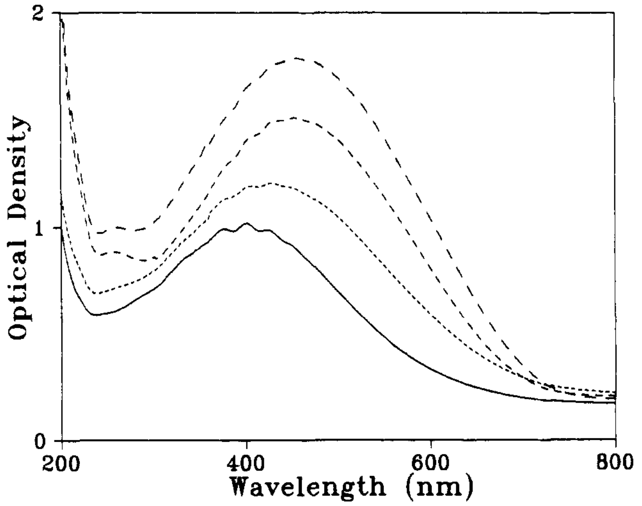


**Figure 4.** UV-visible spectra of PA(exPPVS) obtained after thermal treatment of PPVS at 180 °C (—), 120 °C (- - -), 80 °C (– – –), and 60 °C (— —).

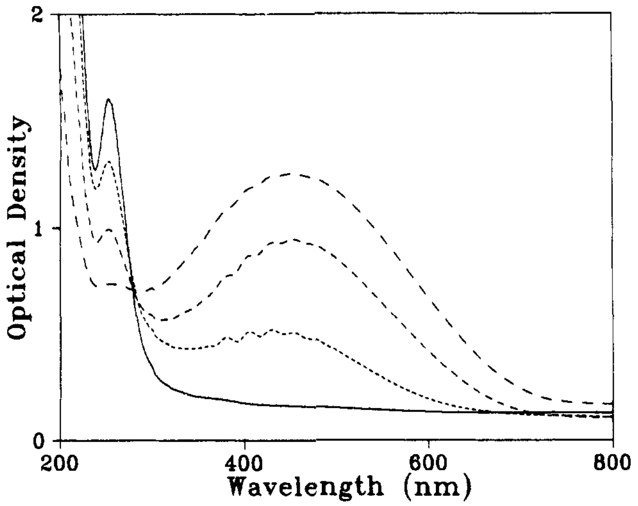


**Figure 5.** Evolution of the absorption spectrum upon heating of PPVS at 80 °C. Reaction time: $t = 0$ (—), 30 min (- - -), 60 min (– – –), and 240 min (— —)

contain large amounts of defects. Moreover the spectrum is not modified after an additional heating at 80 °C under dynamic vacuum for 2 h and even further heating at 120 °C under vacuum for an additional 10 h induces no changes. As these additional heat treatments do not produce any changes, it is possible to conclude that the defects are not unreacted PVS units (as could be anticipated from the disappearance of the absorptions at 1048 and 1091 cm$^{-1}$) but that they result from the addition of side products on the double bonds, probably via radicals coming from the cleavage of the S—S bonds.

This IR study has demonstrated that it is possible to find conditions under which PPVS can be converted to PA by a simple heat treatment. The formation of defects on the PA chain can be minimized if the benzenesulfenic acid and its decomposition products are removed from the polymer film by vacuum pumping as soon as they are formed. All the further results reported in this paper refer to thermal conversion of PPVS to PA under dynamic vacuum.

**UV–Vis Study.** More quantitative results concerning the conjugated sequences formed during the thermal conversion of PPVS to PA can be derived from the UV–vis spectra. It is well-known that the absorption maximum in the visible region of a polyene is displaced to higher wavelength when the number of conjugated double bonds increases.[19,20]

Figure 4 shows that the conjugation length is notably influenced by the transformation temperature: a decrease from 180 to 50 °C leads to a red shift of about 100 nm. The best conjugated PA(exPPVS) were obtained at 50 °C and had an absorption maximum at around 500 nm corresponding to polyene sequences of about 20–30 conjugated double bonds. But it is important to note that much longer conjugated sequences are present in these compounds, as demonstrated by the extension of the absorption band to higher wavelength; the optical density at 600 nm being still about half the one at the maximum. Nevertheless the main conjugation length remains shorter than the main degree of polymerization, implying that a nonnegligible amount of defects is present on the chain.

**(b) Kinetics of the Thermal Conversion of PPVS to PA.** The kinetics of the thermal conversion of PPVS to PA upon heating at 80 °C under vacuum is illustrated in Figure 5. The absorption in the visible region characteristic of polyenes develops at the expense of the absorption at 260 nm coming from the phenyl sulfoxide group. The presence of an isobestic point indicates that the reaction we are looking at is a simple transformation of one species to an other (eq 1, Scheme I).

It is also important to note that the shape of the absorption spectrum at low conversion levels is very similar to the one of the fully converted product. This indicates that the main number of conjugated double bonds between two defects is almost independent from the conversion level. This is in agreement with a "zipper" mechanism for the elimination of benzenesulfenic acid: the formation of a first double bond is random, and the allylic hydrogen so created, easier to remove,[21,22] constitutes the "starting point" of the "zip". Simple statistical considerations show that, on such a regular polymer, each time an uneven number of carbon atoms is present between two neighboring "first created double bonds", a defect ($-CH_2-$ or $-CH(PhSO)-$) is left behind on the chain. If such a mechanism is correct, a decrease of the number of starting points on a chain should lead to an increse of the amount of conjugated double bonds in each segment. This could explain the influence of the transformation temperature on the conjugation length of the PA(exPPVS) (Figure 4): a decrease of the temperature reduces the formation of starting points more than the propagation rate of the "zip". The amount of conjugation defects on the PA(exPPVS) chains can be strongly reduced if the transformation of PPVS is realized at lower temperature, but the simultaneous decrease of reaction rate sets a kinetic limitation.

The thermal conversion of PPVS to PA follows a first-order kinetics (Figure 6) in agreement with eq 1 in Scheme I. From the variation of the reaction constant with temperature (Table III), we could derive an activation energy of 113 kJ/mol (27 kcal/mol). This value is much smaller that the one given by the DSC measurements, and this large difference cannot just be attributed to experimental incertitude. It should be mentioned however that the kinetic study was made under dynamic vacuum and it is well-known that under these conditions the decomposition of compounds like phenyl benzenethiosulfinate is largely favored;[23] thus the transformation reaction may be greatly affected and may begin at a notably lower temperature under vacuum.

**(c) Air Stability.** PA(exPPVS) as other PA are air sensitive. It is well-known that oxygen acts first as a dopant for PA, leading to a partially reversible increase of the electrical conductivity; longer exposure to air induces an irreversible destruction of the conjugated chains.[24] This

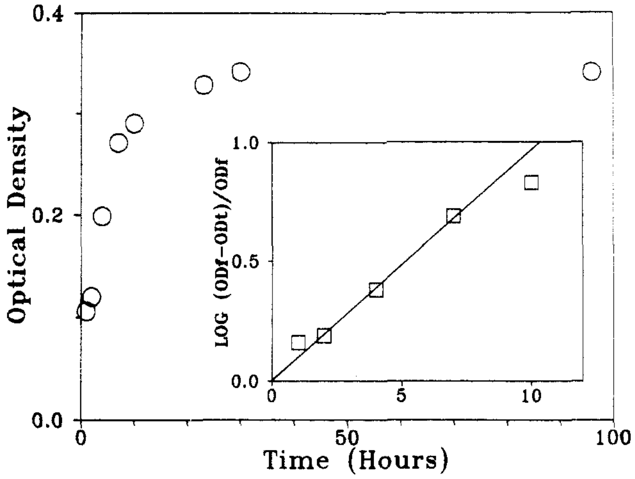


**Figure 6.** Kinetics of thermal conversion of PPVS at 60 °C.

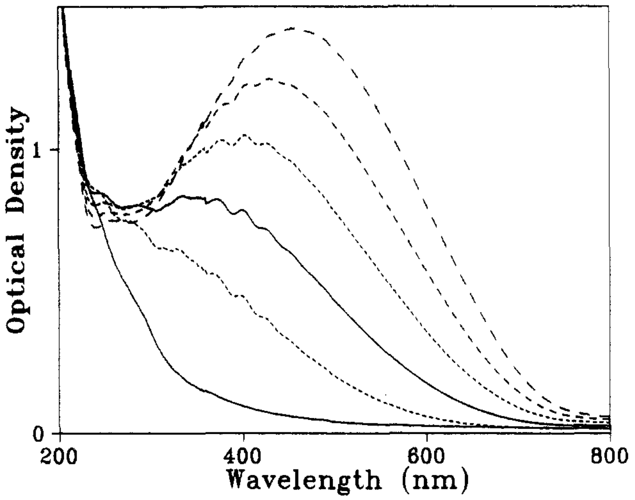


**Figure 7.** Changes in the absorption spectrum of PA(exPPVS) as a function of exposure time $t$ to air: from top to bottom $t$ = 0, 6, 12, 24, 64, and 113 h.

**Table III**
**Variation of the Rate Constant of the Thermal Transformation of PPVS to PA as a Function of Temperature**

| temp, °C | rate constant, min$^{-1}$ |
|---|---|
| 50 | $5.8 \times 10^{-4}$ |
| 60 | $3.8 \times 10^{-3}$ |
| 80 | $2.2 \times 10^{-2}$ |

destruction can be easily followed by UV–vis spectroscopy (Figure 7). Addition of oxygen on the double bonds decreases the length of the conjugated sequences, as shown by the blue shift of the absorption spectrum as a function of exposure time to air. In order to get more quantitative information on the kinetics of this oxidation, we have followed the variation of the total amount of conjugated material given by the area of the peak in the visible range (area) (Figure 8). A straight line is obtained if log ($area_{t=0}$/$area_t$) is plotted as a function of time. This result can be observed for two very different situations: (i) the oxidation is diffusion controlled, or (ii) it is a first-order reaction.

(i) Such a linear relationship is established in diffusion kinetics, where the uptake of a permeant ($O_2$) can be written in an equivalent expression:

$$\ln\frac{M_{\max}}{M_{\max}-M_t} = \ln\frac{\text{area}_{t=0}}{\text{area}_t} = \frac{\pi^2 D}{l^2} + Cte$$

$M_{\max}$ is the total amount of PA, $M_t$ the part oxidated at time $t$, $D$ the diffusion coefficient of oxygen into the PA film, and $l$ the thickness of the film in centimeters. This last parameter can be estimated from the optical density at the absorption maximum. Using an extinction coefficient of $3 \times 10^5$ cm$^{-1}$,[25] a value of $6 \times 10^{-6}$ cm is found. A diffusion coefficient of about $4 \times 10^{-17}$ cm$^2$·s$^{-1}$ can be derived from the slope of the straight line in Figure 8. This value, several orders of magnitude lower than the diffusion coefficients of dopants into "Durham" PA (i.e. $3 \times 10^{-12}$ cm$^2$·s$^{-1}$ for K$^+$ [26]) seems rather unreasonable. Furthermore, complete doping of a PA(exPPVS) film of about 1000 Å with an organoalkaline compound takes only a few minutes. Thus it is very unlikely that it is the diffusion of oxygen into the PA(exPPVS) film which constitutes a rate-limiting step. Also the observation that the conjugation lengths decrease after short times of exposure to air seems to confirm that all the PA chains are in contact with oxygen from the beginning.

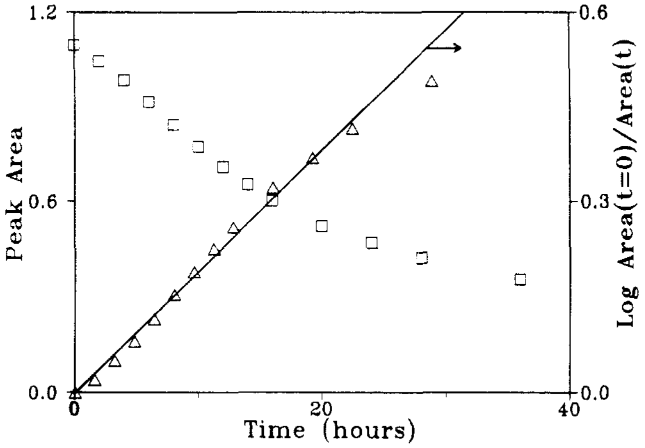


**Figure 8.** First-order kinetics of the oxidation reaction of PA(exPPVS).

(ii) An alternative explanation for our results is that the oxidation of PA(exPPVS) in air is a first-order reaction. That must in fact be the case, as the concentration of oxygen stays constant. An apparent rate constant can be derived from the slope of the straight line in Figure 8. The value found, $2.5 \times 10^{-4}$ min$^{-1}$, is more than 2 orders of magnitude lower than the rate constants reported for "Shirakawa" type PA exposed to pure oxygen.[27] So, even if we take into account the fact that our samples were studied in air, they seem notably more stable against oxygen.

**3. Doping of the PA(exPPVS).** The UV–vis–near-IR spectra of three fully $I_2$ doped PA films obtained by thermal treatment of PPVS respectively at 180, 120, and 80 °C are presented in Figure 9. Upon oxidation (p-doping), a broad absorption appears in the near-IR range, as expected for doped polyenes. The displacement to higher wavelength of the peak around 1000 nm, originating from the midgap absorption,[28] reflects just the red shift of the absorption maximum of the corresponding undoped PA (Figure 4).

The n-doping of PA(exPPVS) is illustrated in Figure 10. Two organopotassium compounds, fluorenone radical ion K (FOK) and naphthalene radical ion K (NK), having redox potentials of −1.29 and −2.5 V vs SCE, were used. These salts are able to reduce the "Shirakawa" PA, in which the conjugated sequences are very long, up to a doping level (expressed in K$^+$ per CH) of 0.3% and 15%, respectively.[10] The spectrum in Figure 10b shows that the weak reductor FOK can transfer electrons only to the part of PA(exPPVS) having the longest polyene sequences, probably those consisting of more than about 100 conjugated double bonds. The strong dopant, NK, reduces

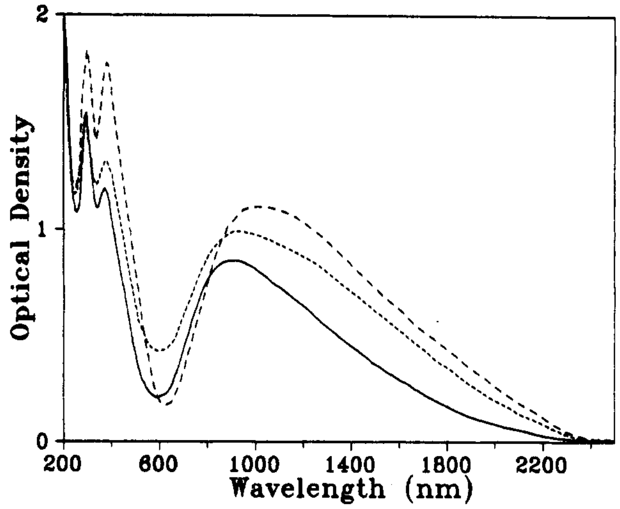


**Figure 9.** UV–vis–near IR spectra of three fully $I_2$ doped PA(exPPVS). The PA were obtained by thermal decomposition of PPVS at 180 °C (—), 120 °C (- - -), and 80 °C (– – –).

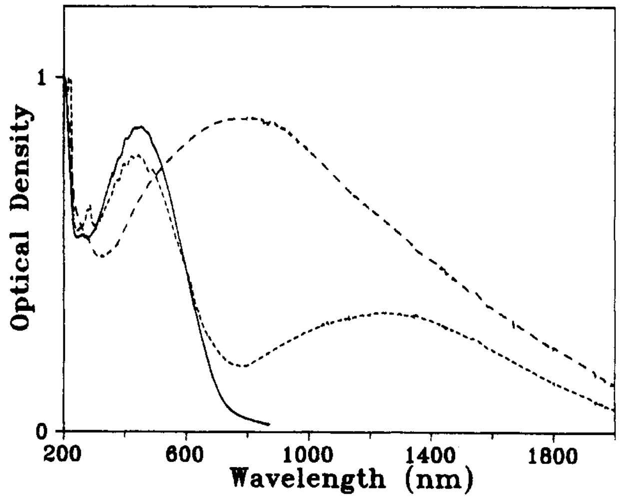


**Figure 10.** UV–vis–near IR spectra of PA(exPPVS) (—), after n doping with fluorenone radical ion K (- - -) and highly $K^+$ doped with naphthalene radical ion K (– – –).

all the PA(exPPVS), as shown by the total disappearance of the peak around 500 nm (Figure 10c); this is not unexpected, as NK is even able to transfer electrons to dienes.[9]

## Conclusions

This paper shows that polyacetylene with fairly long sequences of conjugated double bonds can be obtained by a thermal elimination of benzenesulfenic acid from poly(phenyl vinyl sulfoxide). In order to reduce the amount of $sp^3$ defects of the chains, it is necessary to remove the side products as soon as they are formed; that is best achieved by a thermal treatment under dynamic vacuum. The length of the polyene sequences so obtained increases if the thermal conversion is conducted at relatively low temperatures (<80 °C). But the decrease in elimination rate of benzenesulfenic acid sets a limit to attempts to make use of this observation to increase the conjugation length any further. Another way to try to improve this conjugation length could be to create, on the end of the PPVS chain, a starting point for the "zipper". Attempts in this direction are underway in our laboratory. The stability in air of these PA(exPPVS) has been studied. These compounds can be highly n or p doped.

Here we demonstrated that PPVS is an effective soluble precursor for PA. We have taken advantage of this new route to PA to synthesize, via anionic polymerization, soluble polystyrene–PA block copolymers.[29]

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