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Laser Desorption Mass Spectrometry of Chemically and Electrochemically Prepared Poly(2-vinylthiophene)

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ABSTRACT: We have used laser desorption Fourier transform mass spectrometry to determine the molecular weight distributions of three forms of poly(2-vinylthiophene): polymer **A**, the classic, free radical-initiated form, polymer **B**, produced as a precipitate during the anodic oxidation of the monomer, and polymer **C**, formed as an insoluble film on the anode during the same oxidation. We have obtained molecular weight distributions for all three of these products in the form of Na^+-attached species. Analysis of the mass spectral data allows us to reach several conclusions. For polymer **A**, initiation takes place by benzoate radicals, and this reaction is faster than decomposition of benzoate radicals to phenyl radicals and carbon dioxide. Propagation takes place by the well-established radical mechanism, and termination occurs mainly by chain transfer to monomer with some disproportionation. For polymer **B**, two mechanisms are consistent with the mass spectral data. The first involves free radical chain propagation involving loss of a proton after the initiation step. Termination can occur by combination, disproportionation, or chain transfer. The second mechanism involves combination of two initially formed radical cations with subsequent cationic propagation. Termination involves the loss of two protons. The second mechanism alone does not adequately explain the data. For polymer **C**, infrared spectral data support a mechanism that involves initial ring–ring radical coupling followed by loss of two protons and further oxidation of the resulting dimer, leading to a polymer containing some cross-linking. The mass spectral data are consistent with this interpretation.

Introduction

Exact measurement of the distribution of molecular weights in synthetic polymers presents a considerable experimental challenge. The most commonly used methods for characterizing molecular weights of polymers provide either number-average molecular weights, M_n (osmometry, cryoscopy, ebulliometry, end-group titration), or weight-average molecular weights, M_w (light scattering). Solution viscosity measurements yield viscosity-average molecular weights, which lie between M_n and M_w. Information about the distribution of the molecular weights of a polymer can be obtained from this type of experimental data using the calculated value of the polydispersity index, M_w/M_n, but this only gives a rough picture. In some cases more precise information can be obtained using size exclusion chromatography (SEC). However, this technique requires the use of a standard polymer of similar form to that of the polymer under investigation. In situations where such a standard is not available the use of dissimilar standards may lead to erroneous results.

Recently there has been increasing interest in the use of ionization in combination with mass spectrometry for characterization of polymer molecular weight distributions. Various "soft" ionization techniques such as laser desorption,[1–7] fast atom bombardment,[8] and field desorption[9] have been used. All these techniques result in the formation of pseudomolecular ions such as $(MNa)^+$, $(MK)^+$, or $(MH)^+$ with (ideally) little or no fragmentation of the oligomers. This allows the accurate mass of each oligomer and its contribution to the overall molecular weight distribution to be measured. Laser desorption Fourier transform mass spectrometry (LD-FTMS) is a particularly powerful technique for measurements of this type as its combines the advantages of laser desorption, which has been shown to give accurate number- and weight-average molecular weights[1,2] with the high resolution capability of Fourier transform mass spectrometry.[7]

In this paper we report LD-FTMS data for three different forms of poly(2-vinylthiophene) (PVTh). These data show some fragmentation but also show molecular weight distributions characteristic of oligomeric distributions. One form of the polymer (polymer **A**) was prepared chemically using benzoyl peroxide as initiator. The other two forms were prepared electrochemically by anodic oxidation of 2-vinylthiophene in acetonitrile solution using tetrabutylammonium tetrafluoroborate as supporting electrolyte.[10,11] In this system initiation occurs at the anode and propagation occurs in the bulk medium from which one product polymer (polymer **B**) precipitates. Simultaneously another product (polymer **C**) forms on the anode. The electrochemical production of polymers has become an active area of research since the discovery that conducting polymers can be prepared this way.[12] Although many polymers have been prepared using this method, to date there has only been one report of a molecular weight distribution for an electrochemically prepared polymer: cathodically prepared poly(4-methyl-4′-vinyl-2,2′-bipyridine)-containing metal complexes.[13] The high resolution capability of the FTMS technique allows us to draw some conclusions regarding the reaction mechanisms involved in the formation of the three different polymer forms.

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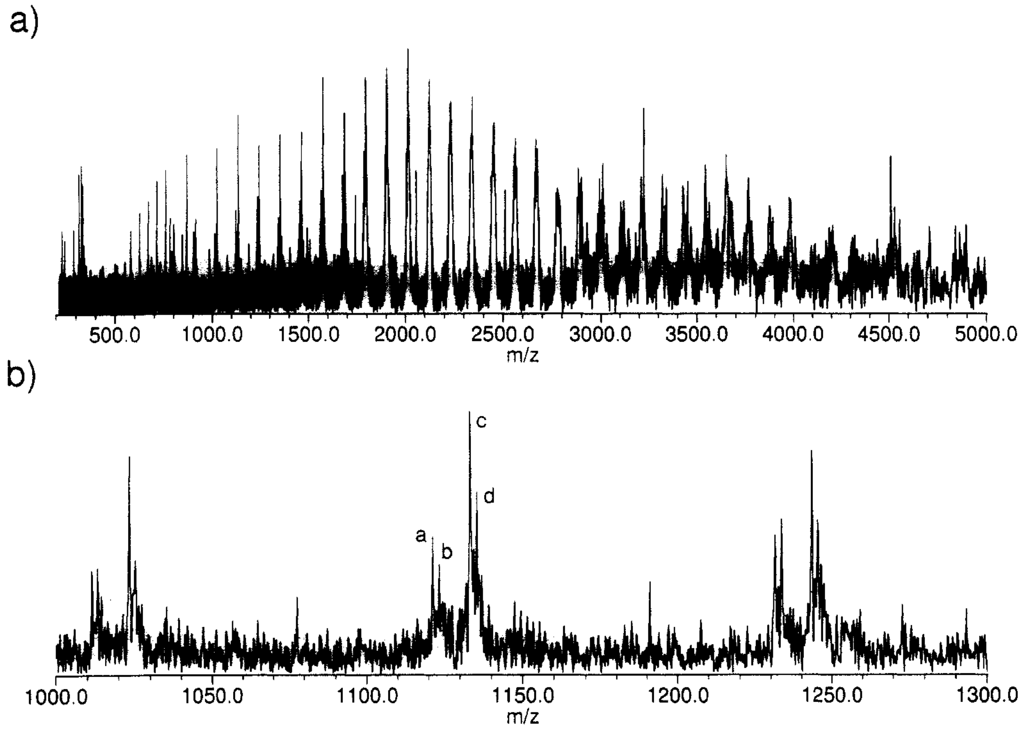


Figure 1. (a) FTMS laser desorption spectrum of polymer A. (b) Expanded portion of spectrum shown in (a).

Experimental Section

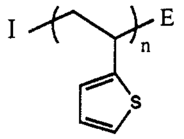
Chemical Polymerization. 2-Vinylthiophene was chemically polymerized in bulk using 5 mol % benzoyl peroxide (Baker) as initiator under an N_2 atmosphere for 24 h at 90 °C in a sealed polymerization ampule as described elsewhere.[10,11] For this work we employed a larger amount of initiator than previously to obtain polymer of molecular weight $\cong$ 2000. The product (polymer A) was then dissolved in chloroform, filtered, precipitated in methanol, filtered again, and dried in vacuo at 65 °C.

Electropolymerization. Electrochemical polymerization of 2-vinylthiophene was carried out in acetonitrile solution using tetrabutylammonium tetrafluoroborate as supporting electrolyte, 0.5 in.^{2} platinum foil as working and counter electrodes, and a reference electrode consisting of a capillary tube which contained $Ag/AgBF_4$ (0.01 M). Full experimental details are reported elsewhere.[11] After 3 h we observed two different products in the cell. One was a precipitate in the bulk of the anolyte solution (polymer **B**), and the other was a dark coating on the platinum working electrode (polymer **C**). The contents of the cell were poured into methanol and filtered. The precipitate was dissolved in chloroform, filtered, and reprecipitated into methanol. This material (polymer **B**) was then dried in vacuo at 65 °C for 24 h. Polymer **C** as formed on the electrode has a conductivity of 10^{-4} S cm^{-1}.[10,11] The coated electrode was removed from the cell and placed in a fresh cell containing only acetonitrile and tetrabutylammonium tetrafluoroborate. The cell potential was reversed and set to a value of −1.5 V. This process dedoped the polymer to yield a nonconducting form of polymer C (10^{-12} S cm^{-1}). After dedoping, the polymer film was peeled from the electrode, rinsed in chloroform, and dried. Polymer C is not soluble in any known solvent.

Laser Desorption Fourier Transform Mass Spectrometry. Mass spectra were recorded using a Millipore-Extrel (Madison, WI) Fourier transform mass spectrometer interfaced with a Tachisto 215 pulsed CO_2 laser. The spectrometer is equipped with a 7-T superconducting magnet and solids autoprobe and employs differentially pumped source and analyzer cells separated by a 2 mm conductance limit. For these experiments, all ion detection was carried out in the source cell. The CO_2 laser is directed into the mass spectrometer through a quartz window in the source flange and is focused onto the tip of the solids probe to an approximately 1 mm^2 spot size by an off-axis paraboloid mirror mounted on the source cell assembly. The laser delivers approximately 10^6–10^8 W/cm^2 per 80 ± 40 ns pulse. Delay times of 5–10 s after desorption and prior to excitation allowed desorbed neutrals to pump away. For polymers A and B samples were dissolved in chloroform, deposited on a stainless steel probe tip, and evaporated to dryness before being introduced into the vacuum chamber. Polymer C was rubbed onto the rough surface of the stainless steel probe. Initial data for all three polymer samples indicated sodium ion attachment, so sodium was added in the form of NaCl for subsequent samples.

Results and Discussion

We expect poly(2-vinylthiophene) to have the general formula

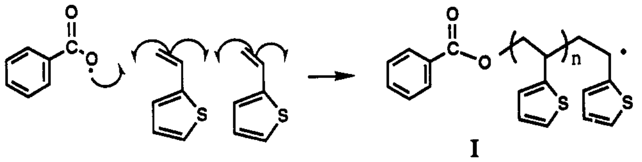


where I and E (initiator and terminator groups, respectively) depend on the method of preparation. The repeat unit, C_6H_6S, has a mass of 110 Da.

Polymer A. Figure 1 shows laser desorption spectra of polymer A. Figure 1a shows what appears to be a fragment ion region, with m/z values of less than 800, and a molecular weight region ranging from about m/z = 900 to m/z = 4000. The molecular weight region has the characteristics of an oligomeric distribution: peaks with separation equal to the molecular weight of the repeating unit and peak intensities that increase and then decrease as the mass increases. Addition of NaCl resulted in enhancement of peaks in the oligomeric region as seen in an expanded portion of the spectrum shown in Figure 1b. Both spectra clearly show a repeat unit of 110 Da. The expanded portion of the spectrum shows a main series of peaks with m/z = [121 + n(110) − 1 + 23] (c) with a slightly less intense series of peaks with m/z = [121 + n(110) + 1 + 23] (d).

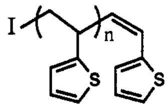
Two other less intense series of peaks are observed with $m/z = [n(110) + 23]$ (b) and $m/z = [n(110) - 2 + 23]$ (a). The 121 mass unit increments correspond to the $C_6H_5CO_2$ group from the benzoyl peroxide initiator, and the 23 mass unit increments result from addition of Na^+ added as dopant. There are no peaks due to phenyl-attached oligomers or oligomers containing two benzoate groups.

These observations confirm that polymerization takes place via the well-established radical mechanism, with the reaction initiated by the benzoate radical:

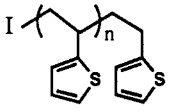


I

Because no chains containing two benzoate groups are observed, we conclude that chain termination does not take place by combination of radicals but probably by disproportionation and chain transfer to monomer. Termination of **I** by disproportionation is expected to give rise to peaks in two series: $m/z = [121 + n(110) - 1 + 23]$ (**II**) and $m/z = [121 + n(110) + 1 + 23]$ (**III**):

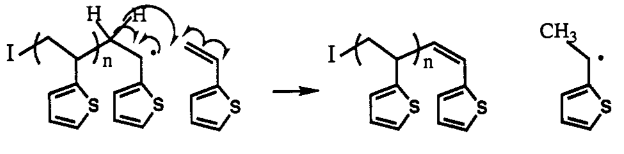


II



III

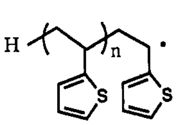
Termination of **I** by chain transfer to monomer yields **II** and a monomer radical:



II

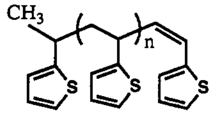
The reaction provides another source for peaks in the $m/z = [121 + n(110) - 1 + 23]$ series. This mechanism, involving free radical propagation with termination by both disproportionation and chain transfer, is consistent with the observation of a main series of peaks with $m/z = [121 + n(110) - 1 + 23]$ and a less intense series of peaks with $m/z = [121 + n(110) + 1 + 23]$.

After chain transfer to monomer, the monomer radical initiates propagation to produce **IV**:

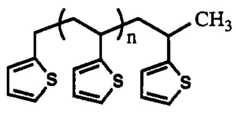


IV

Termination of **IV** by disproportionation would lead to peaks in two series: $m/z = [n(110) + 23]$ (**V**) and $m/z = [n(110) + 2 + 23]$ (**VI**):



V



VI

Termination of **IV** by chain transfer would lead to peaks in the series $m/z = [n(110) + 23]$ i.e., **V**.

Because we observe a series of peaks corresponding to $m/z = [n(110) + 23]$ in the spectrum and because peaks in the series $m/z = [n(110) + 2 + 23]$ are of very low relative abundance, we can conclude that termination occurs mainly by chain transfer.

Fragmentation of structures **II** and **III**, involving loss of the terminal benzoate group plus a hydrogen atom (benzoic acid being the eliminated neutral molecule) would lead to ions in the series $m/z = [n(110) - 2 + 23]$ and $m/z = [n(110) + 23]$, respectively. This process could provide a contribution to both the $m/z = [n(110) + 23]$ series and the $m/z = [n(110) - 2 + 23]$ series.

Because we observe no peaks due to phenyl-attached polymers, we conclude that decomposition of benzoate radicals to phenyl radicals and carbon dioxide proceeds more slowly than the reaction of benzoate radical with 2-vinylthiophene in the initiation step of the polymerization reaction. The DP of polymer **A** runs from $n = 8$ ($m/z = 1023$) to $n = 35$ ($m/z = 3993$). Using peak intensities for the corresponding ions, polymer **A** was calculated to have $M_n = 2284$, $M_w = 2556$, and a polydispersity index $(M_w/M_n) = 1.12$.

Polymer B. Figure 2 shows laser desorption spectra of polymer **B**. Figure 2a shows a fragment ion region (below $m/z = 1000$) and a well-separated molecular weight region which runs from about $m/z = 1500$ to $m/z = 3700$. In this case, even more so than in the case of polymer **A**, the molecular weight region looks similar to what would be expected for an oligomeric distribution. Expansion of the molecular weight region (Figure 2b) shows a repeat unit of 110 Da. However, in this case there appears to be no identifiable end group or groups which are different from the repeat unit. The oligomers are detected as a series of peaks that correspond to $[n(110) + 23]$ plus or minus a small number of hydrogen atoms. Accurate identification of the peaks in a spectrum such as this is complicated by the presence of isotopes. Sulfur exists as ^{32}S (95.0%), ^{33}S (0.76%), ^{34}S (4.22%), and ^{35}S (0.02%); carbon is present as ^{12}C (98.89%) and ^{13}C (1.11%); and hydrogen exists as ^{1}H (99.985%) and ^{2}H (0.015%).[14] Consequently, signals which appear as single peaks in Figure 2b are actually clusters of peaks. Figure 3a shows the high resolution experimental data for the pentadecamer ($n = 15$). Figure 3b shows the expected isotopic distribution for $[(C_6H_6S)_{15} + Na]^+$ calculated using the probabilities for the different isotopes of all the atoms in the ion. Comparison of the expected isotopic distribution with the experimentally obtained distribution does not show good agreement. This can be seen by looking at the relative peak intensities. Although in both cases the most abundant ion is that with $m/z = 1675$, in the experimental data the next most abundant ion is that with $m/z = 1673$, while in the calculated distribution, the second most abundant ion has $m/z = 1674$. A "best" fit to the experimental data is obtained from a mixture of equal amounts of $[(C_6H_6S)_{15} + 2H + Na]^+$, $[(C_6H_6S)_{15} + Na]^+$, and $[(C_6H_6S)_{15} - 2H + Na]^+$. The calculated expected isotopic distribution for this mixture is shown in Figure 3c and was obtained by calculating the expected isotopic distributions for the three ions, adding them together, and normalizing to the most intense peak. This calculated distribution shows good agreement with the experimental distribution. The relative abundances of the five most intense peaks ($m/z = 1673$ to $m/z = 1677$) now agree well, and the calculated-isotopic distribution fits the experimental distribution if it is assumed that the less intense peaks on either side of

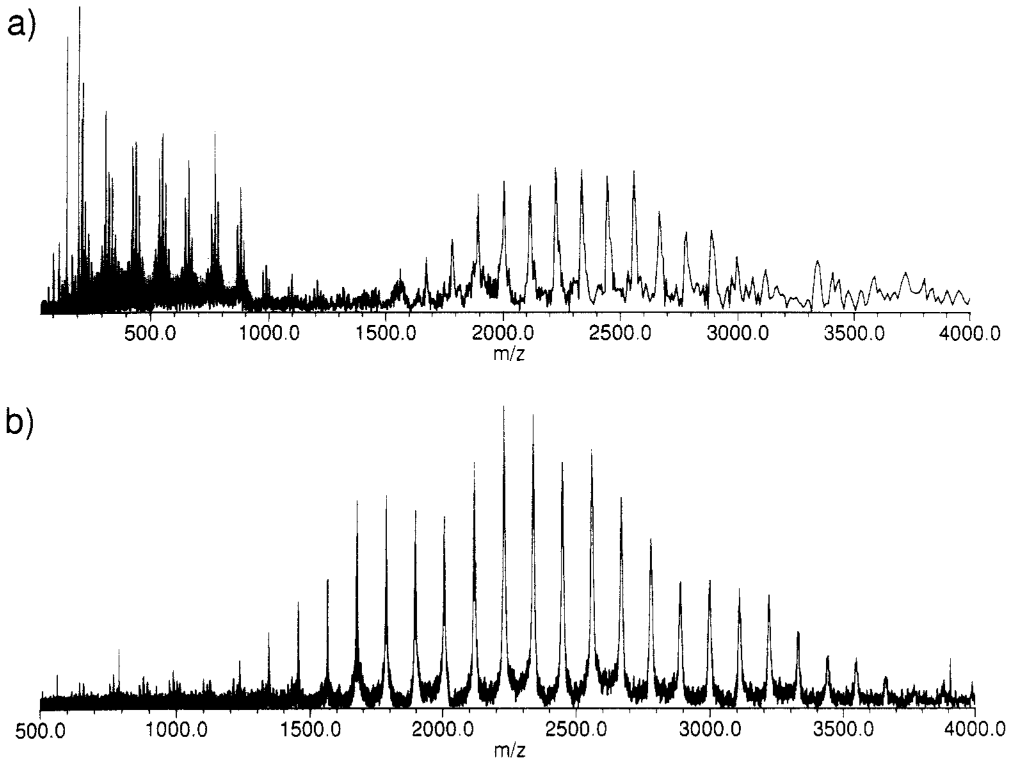


Figure 2. (a) FTMS laser desorption spectrum of polymer **B**. (b) Expanded portion of spectrum shown in (a).

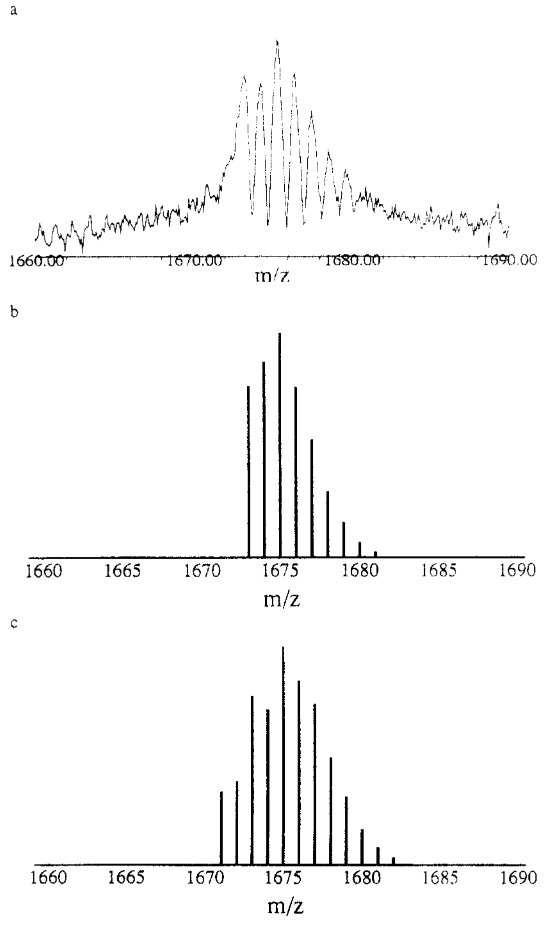
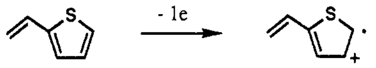


Figure 3. (a) High resolution spectrum showing the isotopic distribution for the pentadecamer ($n = 15$) of polymer **B**. (b) Calculated isotopic distribution for $[(C_6H_6S)_{15} + Na]^+$. (c) Calculated isotopic distribution for equal amounts of $[(C_6H_6S)_{15} + 2H + Na]^+$, $[(C_6H_6S)_{15} + Na]^+$, and $[(C_6H_6S)_{15} - 2H + Na]^+$.

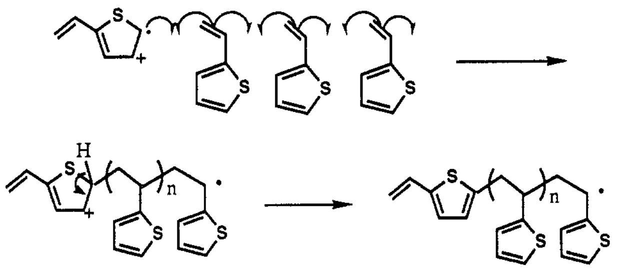
the calculated distribution lie in the unresolved shoulders of the experimental data.

Computer modeling and cyclic voltammetry show the highest electron density and most readily oxidizable site to be the ring structure.[11] We propose that the monomer is initially oxidized to the radical cation:



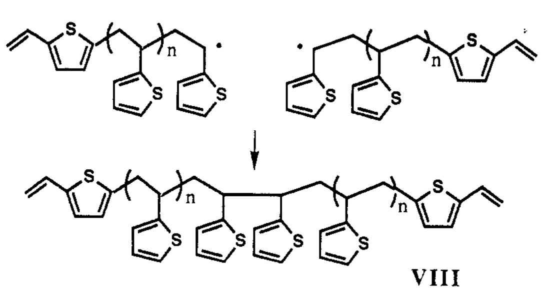
The radical cation can then react in at least two ways:

Mechanism 1. Free radical chain propagation involving loss of a proton after the initiation step:



VII

The propagating radical **VII** can terminate by combination, disproportionation, or chain transfer. Termination by combination will lead to product **VIII**, which would be expected to give rise to peaks in the series $m/z = [n(110) - 2 + 23]$:



VIII

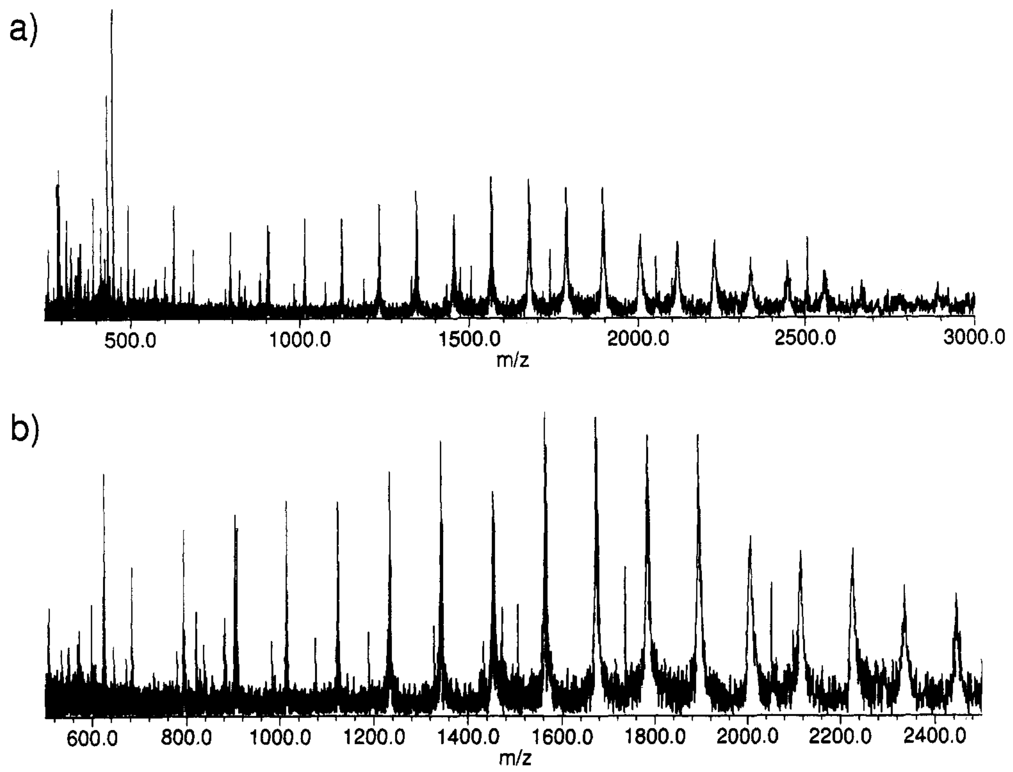
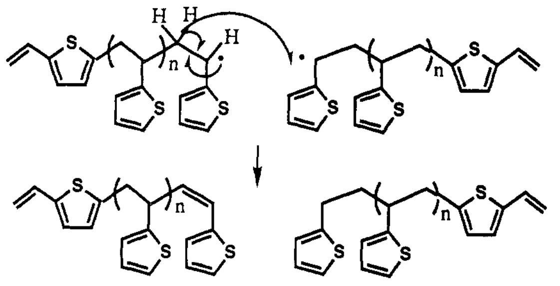


Figure 4. (a) FTMS laser desorption spectrum of polymer C. (b) Expanded portion of spectrum shown in (a).

Termination by disproportionation leads to products **IX** and **X**, which would give rise to peaks in the two series $[n(110) - 2 + 23]$ and $[n(110) + 23]$:

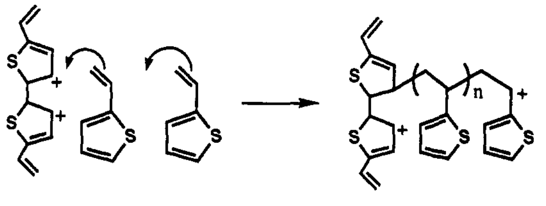


IX X

Termination of **VII** by chain transfer to monomer also leads to product **IX** (an additional contribution to the series $m/z = [n(110) - 2 + 23]$) plus monomer radical. Once formed, the monomer radical can initiate propagation via **IV** as described for polymer **A**. Subsequent termination by disproportionation would lead to peaks in two series: $m/z = [n(110) + 23]$ (**V**) and $m/z = [n(110) + 2 + 23]$ (**VI**). Termination by chain transfer would lead to peaks in the series $m/z = [n(110) + 23]$ (**V**). This mechanism accounts for experimental observation of the three series of peaks: $m/z = [n(110) + 2 + 23]$, $[n(110) + 23]$, and $[n(110) - 2 + 23]$. However, it does not allow us to predict the relative contributions of each step to the overall process.

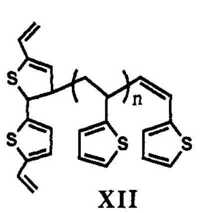
Another possible first step in the overall polymerization process involves dimerization of the initially formed radicals. The coupling of cation radicals to themselves, rather than initiating polymerization of monomer, has been shown to be involved in the first step of the carbon–carbon bond forming process in the electrochemical polymerization of substituted pyrroles.[15]

Mechanism 2. Two initially formed radical cations combine to give a dication which then propagates through a cationic mechanism:



XI

Termination of **XI** involving the loss of two protons overall leads to product **XII**, which would give rise to peaks in the series $m/z = [n(110) - 2 + 23]$:

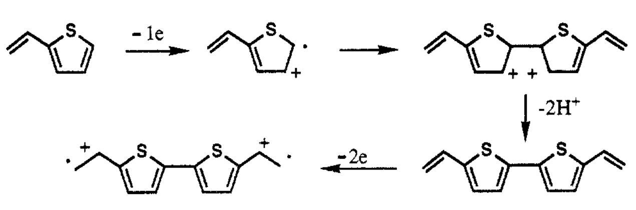


XII

The mass spectrometric data do not allow us to distinguish between the two proposed mechanisms, although mechanism 2 by itself does not adequately explain the data as it is expected to lead only to peaks in the $m/z = [n(110) - 2 + 23]$ series.

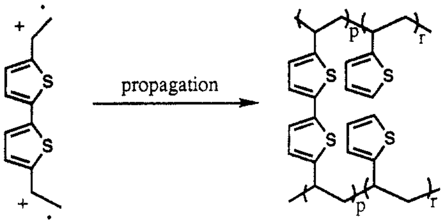
The DP of polymer **B** runs from $n = 11$ ($m/z = 1233$) to $n = 33$ ($m/z = 3653$). Using the intensities from the appropriate peaks, polymer **B** was calculated to have $M_n = 2244$, $M_w = 2535$, and a polydispersity index of 1.04.

Polymer C. The laser desorption mass spectrum of polymer C is shown in Figure 4a. This spectrum also shows a fragment ion region ($m/z < 800$) and a molecular weight region (m/z = 800–2700). The expanded spectrum of the molecular weight region (Figure 4b) shows there are no end groups other than those corresponding to the monomer molecule. The main series of peaks appears to correspond to $m/z = [n(110) + 23]$ with n running from 6 (m/z = 683) to 22 (m/z = 2443). As in the case of polymer **B**, each of the peaks in Figure 4b is actually a cluster of peaks and might consist of a number of overlapping series of the type $n(110) + 23$ plus or minus a small number of H atoms. However, in this case the experimental data were not as well resolved, and we were unable to arrive at a "best" fit between calculated and experimental clusters. Higher-mass oligomers appear to have components that correspond to $n(110)$ minus one or more hydrogen atoms. A possible formation mechanism involves a first step linking of the initially formed radical cations with the elimination of two protons to form a dimer, **XIII**. Because polymer **C** is formed in close proximity to the electrode (as a coating), this dimer would be expected to be easily oxidized with the loss of one or possibly two electrons to give (**XIV**):



XIV XIII

XIV could then initiate polymerization (radical or cation initiated) to give a polymer containing some cross-linking, **XV**:



XV

This is consistent with IR and solid state NMR data showing some cross-linking in polymer **C**.[10,11] In this case the mass spectrometric data give us no information on the termination process.

The DP of polymer **C** runs from n = 5 (m/z = 573) to n = 24 (m/z = 2663). Calculations using the appropriate peak intensities give M_n = 1564, M_w = 1685, and a polydispersity index of 1.08.

Conclusions

We have used laser desorption mass spectrometry to determine the molecular weight distributions of three forms of poly(2-vinylthiophene). These are the classic, free radical-initiated form, polymer **A**, and two polymeric products that arise from anodic oxidation of 2-vinylthiophene. One of these, polymer **B**, precipitates from the anolyte during the oxidation. The other, polymer **C**, forms as an insoluble film on the anode.

For all three of these products we have obtained oligomeric distributions in the form of Na^+-attached species. The high resolution data obtained using the FTMS technique, in conjunction with other experimental information (method of preparation, IR data), have allowed us to draw some conclusions about the different mechanisms involved in the production of the polymers.

For polymer **A** observation of oligomers containing benzoate groups and the nonobservation of oligomers containing phenyl groups allow us to conclude that the benzoate group initiates the polymerization and that the rate of this initiation step is greater than the rate of decomposition of benzoate radicals to phenyl radicals and carbon dioxide. Further the nonobservation of oligomers containing two benzoate groups allows us to conclude that termination does not take place by combination of propagating radicals. The mass spectral data indicate that termination takes place most probably by chain transfer to monomer with some contribution from disproportionation. Chain transfer to monomer initiates another polymerization process, and the data indicate that termination of this is most probably by chain transfer.

For polymer **B** the mass spectral data indicate that there are no end groups significantly different from the repeating unit. Specifically, the oligomers are made up of equal amounts of $[(C_6H_6S)_{15} + 2H + Na]^+$, $[(C_6H_6S)_{15} + Na]^+$, and $[(C_6H_6S)_{15} - 2H + Na]^+$. Two mechanisms can be proposed that are consistent with these data. The first involves free radical chain propagation with proton elimination by the initially formed radical cation. Termination in this case involves either combination of radicals, disproportionation, or chain transfer to monomer. Chain transfer to monomer can then lead to anotherpolymerization process similar to that proposed for polymer **A**. The second mechanism involves combination of the initially formed radical cations to give a dication which then propagates via a cationic mechanism. Termination in this case involves the loss of two protons. The second mechanism by itself does not adequately explain the data.

For polymer **C**, the mass spectral data are not inconsistent with a mechanism that involves an initial ring–ring radical coupling followed by deprotonation to form a neutral dimer. This is then further oxidized, possibly involving the loss of two electrons to give a diradical dication which can initiate polymerization either by a radical mechanism or by a cationic mechanism to produce a polymer containing some cross-linking. This is consistent with inferences drawn from the IR data.

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