Chain-Length Dependence of Electrochemical and Electronic Properties of Neutral and Oxidized Soluble α,α-Coupled Thiophene Oligomers

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The electrooxidation of α,α-coupled thiophene oligomers with terminal α-$(CH_3)_3Si$ groups (α-TMS) and β-CH_3 groups was studied in methylene chloride at room temperature. The oligomers with four, five, six, seven, and eight thiophene rings undergo two stepwise oxidations to produce the radical cation and dication, respectively, as confirmed by the ESR spectra. The redox waves are chemically reversible and separated by 180 mV for the hexamer, heptamer, and octamer, suggesting that the same electrochemical behavior should be observed with the next higher oligomers or with the π-conjugated segments of polythiophene. Thus it is proposed that the broad, featureless voltammogram observed with films of polythiophene is not an inherent property of the polymer segments but may reflect complications from the solid-state nature of the film. Radical cations and dications of some of the oligomers were succesively generated with stoichiometric amounts of $FeCl_3$ in CH_2Cl_2 and characterized by vis-near-IR. The energies of the sharp absorption bands in the visible and near-infrared of the neutral and oxidized oligomers are found to scale linearly with the inverse of the oligomer size. Extrapolation of the absorption energy to infinite chain length leads to excellent agreement with the values for neutral poly(methylthiophene), but significant differences are observed with those for the oxidized forms. The implications of this difference on the delocalization length of the polymer radical cation and dication are discussed. Some of the electronic transition assigments for the oxidized thiophene oligomers which appear in previous reports are reinterpreted.

Introduction

Electroactive polymer coatings on electrode surfaces have generated a great deal of interest because they can be tailor-made to exhibit specific properties.[1] Among them, electronically conducting polymers such as polypyrrole,[2] polyaniline,[3] and polythiophene[4] are in a class of their own due to their electrochemically tunable electrical, optical, and chemical properties,[5,6] which, in principle, makes them good candidates for applications in batteries,[7] display devices,[8] and transistors.[9] Crucial to the successful development of these materials for technology is a good understanding of the factors controlling the electrochemical charging and discharging processes. Although appreciable progress has been realized, the details of the electrochemical processes are not fully understood and are still a subject of debate.[10-14]

In particular, the study of the charging/discharging process of polythiophene and some of its derivatives is further complicated by the odd electrochemical behavior reported in the literature. The electrooxidation of thin films of this polymer sometimes leads to one wave followed by a large current plateau[15-18] and in some cases a "prewave" appears as a peak or a shoulder.[6,19-23] A big oxidation current appears at the more anodic potentials and is often related to degradation of the polymer.[24-27] The reverse reduction half-cycle usually displays two ill-resolved broad processes. The oxidation "prewave or prepeak" has been attributed to the presence of different conjugation lengths[20] and to the presence of two conformers.[28] Unfortunately, there is no experimental support for either hypothesis. More recently, it has been demonstrated that the shape of the current peaks of some polythiophene films is related to a relaxation effect[21-23] which may indicate reversible swelling effects[21] as observed for poly(vinylferrocene).[29] In addition, resistivity changes within

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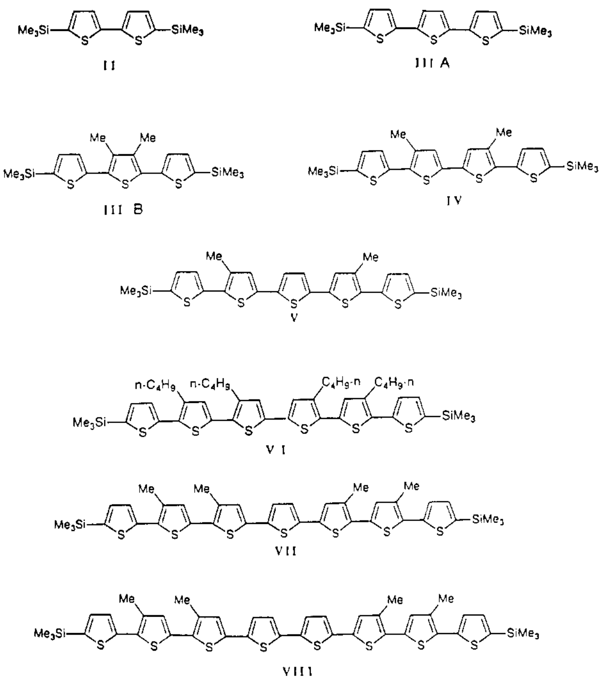
Chart I



the polymer film on the electrode have been shown to affect the shape of the voltammogram sometimes producing an additional peak or shoulder.[30] Capacitive and lattice interaction effects in the polythiophene films can also influence the shape of the peaks.[1,11,31] The nature of charge storage in polythiophene polymers is also unsettled where bipolarons only, polarons plus bipolarons,[32-35] and π-dimers[36,37] have all been proposed to describe the electronic structure of the oxidized polythiophenes.[36,37]

Because the properties of conducting polymers are often difficult to interpret due to the unavailability of well-characterized polymers, well-defined oligomeric compounds have been used to predict or explain polymer behavior.[38-48] Previous electrochemical studies of thiophene oligomers (monomer to hexamer) were, however, limited to determining oxidation peak potentials because of the instability of the oxidized forms.[38,49,50] The chemical oxidation of unsubstituted thiophene oligomers having three to six units has also been reported, but only the oxidized pentamer and hexamer were stable enough to be adequately characterized,[45-48] even though the oxidized pentamer is known to be reactive and leads to insoluble dimerization products.[50]

In this study, the redox properties of α,α-coupled thiophene oligomers (Th_n, $n = 2$–8) with terminal α-$(CH_3)_3Si$ (α-TMS) and β-CH_3 groups are examined and related to the polymer segments in polythiophene (Chart I). These oligomers provide more definitive results because they are free of some of the problems with the polymer, such as, irregular couplings,[18] molecular weight distributions,[20] plus lattice interactions,[1] swelling,[21] capacitance,[11,31] and resistance[30] as may occur in films. In contrast with the previous studies,[38,49,50] the oxidized forms of these substituted thiophene oligomers are sufficiently stable and soluble at room temperature to permit (1) the determination of the diffusion coefficents (D) and the electrochemical stoichiometry (n), (2) assessment of the single broad oxidation peak in the voltammogram of the polymer, (3) the characterization of the electronic spectra and to revisit the electronic transition assigments of the oligomers, and (4) the estimation of the delocalization lengths in the oxidized polymer.

Experimental Section

The soluble α,α-coupled thiophene oligomers with the terminal α-TMS groups and β-methyl groups were prepared by Ni- and Pd-catalyzed coupling reactions of the corresponding halide, stannane, or Grignard derivatives.[51]

The cyclic voltammetry and chronocoulometry experiments were performed with a potentiostat/galvanostat EG&G model 273 and recorded on an *X–Y* IBM recorder. The working, counter, and reference electrodes were an 0.5 cm² Pt disk, a gold wire, and a SCE double junction containing the electrolyte, respectively. Solutions containing 10^{-4} M of the oligomers (10^{-5} for the octamer) and 0.1 M Bu_4NBF_4/CH_2Cl_2 were used in all the electrochemical experiments, and no *iR* compensation was applied to the cell. Oxidation peak potentials were determined from voltammograms recorded at a scanning rate of 25 mV/s, while rates from 10 to 100 mV/s were used to determine the current peak dependence on the sweep rate. Chronocoulometry measurements were made by stepping the potential of the Pt disk to 25 mV passed the peak potentials of the oligomers and recording the intergrated current response with time. The initial potential was 0.7 V for the trimer and 0.5 V for the other oligomers. The n values were then calculated using the slopes of the i_{pa} vs $\nu^{1/2}$ plot from cyclic voltammetry (Randles–Sevick equation) and of the q vs $t^{1/2}$ plot from the chronocoulometry (Cottrel equation).

Chemical oxidation of the thiophene oligomers was performed using a procedure similar to that of Fichou et al.[45-47] Solutions of oligomers (1.0×10^{-4}) and anhydrous $FeCl_3$ (2.0×10^{-4}) were prepared in HPLC grade dichloromethane. For the vis–near-IR and ESR measurements, $FeCl_3$ solution was added stepwise to a quartz cell and a capillary tube each containing a solution of the oligomer, and the spectra were recorded immediately. The oxidation reaction occurs spontanously as indicated by the rapid color change of the solution which ranges from pink to dark blue depending on the oligomer and the amount of $FeCl_3$ added. The oxidation potential of $FeCl_3$ in dichloromethane is estimated to be 1.22 V (vs SCE) using the Nernst equation, $E = E° + (0.059/n) \log (C_{ox}/C_{red})$, where the formal potential $E°$ was found equal to 1.1 V (vs SCE) from the cyclic voltammogram of $FeCl_3$ in dichloromethane. The C_{ox}/C_{red} ratio was obtained from the labeled

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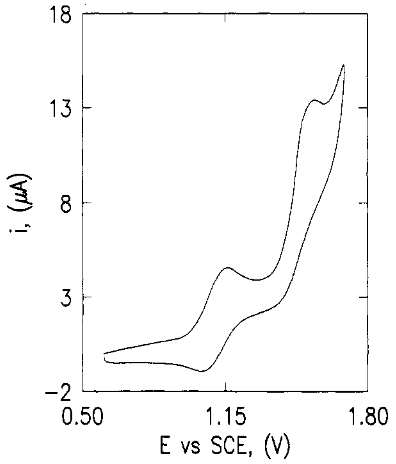

Figure 1. Cyclic voltammogram for IIIb (10^{-4} M) at a Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution (sweep rate = 50 mV/s).

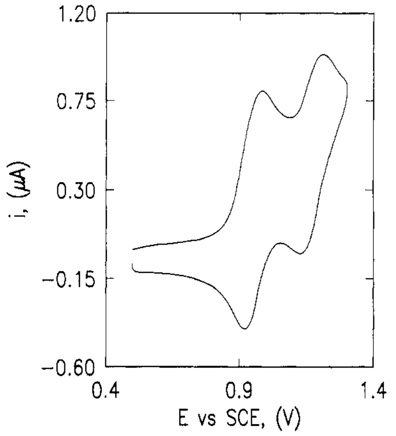

Figure 2. Cyclic voltammogram for V (10^{-4} M) at a Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution (sweep rate = 50 mV/s).

purity of the reagent grade $FeCl_3$ which gives a $FeCl_3/FeCl_2$ ratio of 100.

ESR measurements were performed with an X-band spectrometer ER100D (IBM instruments) at room temperature, at a frequency of 9.26 MHz, with a 1-G modulation amplitude and the magnetic field centered at 3.3 kG. Electronic spectra were obtained with a Perkin-Elmer UV-vis-near-IR Lambda 9 spectrophotometer at room temperature. All spectra are corrected for the solvent absorption.

Results

Electrochemistry and UV-Vis Spectroscopy of the Neutral Oligomers. The cyclic voltammograms for the substituted thiophene oligomers II-VIII were obtained in 0.1 M Bu_4NBF_4/CH_2Cl_2 solutions with a scanning rate of 25 mV/s. The voltammograms for IIIb and V (10^{-4} M) are shown in Figures 1 and 2, respectively. The voltammogram for IIIb reveals two defined oxidation waves and only one reduction wave in the cathodic sweep. The current at 1.7 V is from the oxidation of the electrolyte. The voltammogram for V (Figure 2) displays two well-defined anodic and cathodic processes. Electrochemical oxidation of bithiophene, II and IIIa, shows only one chemically irreversible oxidation wave which is similar to the second anodic current peak observed for IIIb (Figure 1). The voltammograms for IV, VI, and VII also show two well-defined consecutive oxidation and reduction reactions as is observed for V, but the spectra are not shown here. With all the oligomers, the oxidation current peak values (i_{pa}) scale linearly with the square root of the sweep rate ($\nu^{1/2}$) for ν between 10 and 100 mV/s, as expected for a diffusion-limited reaction at the surface of an electrode.

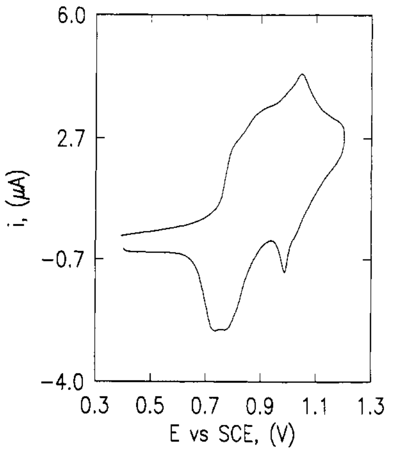

Figure 3. Cyclic voltammogram for VIII (10^{-4} M) at a Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution (sweep rate = 50 mV/s).

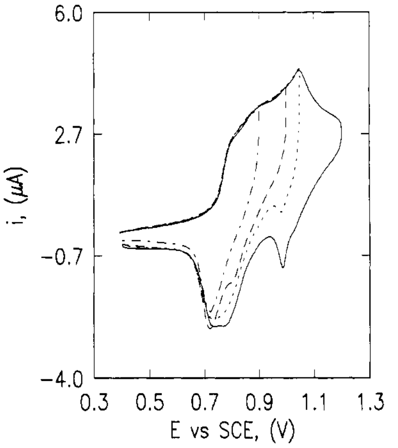

Figure 4. Cyclic voltammogram for VIII (10^{-4} M) at a Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution at different potential limits (sweep rate = 50 mV/s).

The cyclic voltammogram of a 10^{-4} M solution of VIII is shown in Figure 3. In marked contrast with the previous voltammograms (Figures 1 and 2), multiple poorly resolved oxidation and reduction waves are observed. In addition, sharp anodic and cathodic current peaks appear at ca. 1.0 V which are superimposed on the broader ones. Figure 4 shows the cyclic voltammograms for the octamer at 25 mV/s between 0.4 V and different anodic limits. The scan to 0.9 V shows the two ill-resolved peaks and only one reduction peak. A second reduction process appears on scanning to 0.95 V, while a third cathodic wave appears in the scans to 1.04 V. The complicated voltammogram is not due to the nature of the working electrode because a similar shape was obtained with a graphite electrode. The shape of the voltammogram for VIII is quite unusual for a species in solution, although complicated voltammograms often result from adsorption, precipitation, chemical instability, conformational changes, slow electron transfer, and interactions between the electroactive centers.[52,53] Figure 5 shows the cyclic voltammograms of a solution containing 9 × 10^{-6} M VIII recorded on a platinum electrode at 25 mV/s, before (A) and after (B) the correction for the current of the electrolyte. With the correction, the two peaks becomes clearer. Thus, VIII undergoes two stepwise redox reactions just like V. The

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Table I. Summary of Electrochemical Data

compound	E_{pa1}, E_{pa2} (V vs SCE)	ΔE_p (mV)	10^5D (cm^2/s)	n_1, n_2	$h\nu_{max}$ (eV)	$h\nu_{min}$ (eV)
ferrocene	0.59	70	2.55	0.99		
bithiophene	1.50				4.1	
II	1.46				3.87	3.43
IIIa	1.21				3.37	2.94
IIIb	1.16, 1.53	80	1.9	0.95	3.56	3.04
IV	1.04, 1.36	70, 90			3.15	2.68
V	0.98, 1.20	60, 70	2.0	1.04, 0.95	2.94	2.52
VI	0.93, 1.08	70, 70			2.94	2.49
VII	0.86, 1.04	60, 80	1.2	1.06, 0.99	2.78	2.36
VIII	0.85, 1.03	60, 60			2.72	2.29

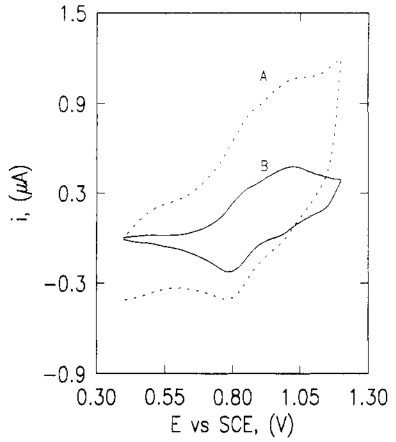

Figure 5. Cyclic voltammogram for VIII (9×10^{-6} M) at a Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution (A) before and (B) after background substraction (sweep rate = 50 mV/s).

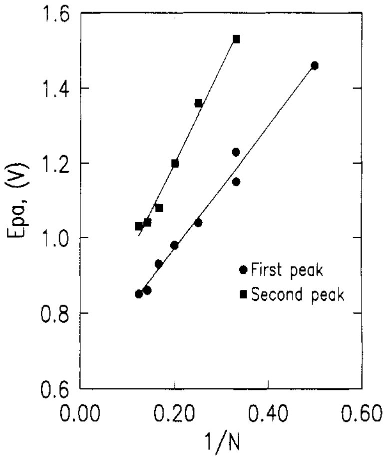

Figure 6. Variation of the oxidation peak potential (E_{pa}) with the reciprocal of the number of rings (N).

electrochemical data obtained from the cyclic voltammetry along with the n and D values obtained from the chronocoulometry experiments are summarized in Table I. Ferrocene is used here as a reference molecule.

As seen from Table I, the electrochemical oxidation of bithiophene, II and IIIa is chemically irreversible, which is not surprising since bithiophene and II are known to dimerize via the α positions when oxidized.[50,54] Accordingly, the vis–near-IR absorption bands of the resulting ion from IIIa closely resemble those of the oxidized VI (Figure 13). The unsubstituted thiophene trimer, tetramer, and pentamer are also known to dimerize when oxidized.[50] This probably explains the lack of reported electrochemical data (beside the first oxidation wave) at room temperature on unsubstituted and substituted thiophene oligomers.[38,49,50] In this study, however, the results show that the trimer to octamer series (IIIb, IV, V, VI, VII, and VIII) can be oxidized reversibly at room temperature. The electrodonating properties of the β-CH_3 and α-TMS groups produce a cathodic shift in the oxidation waves of the oligomers IIIb to VIII and must reflect some stabilization of the cations by these groups. This can be seen in Table I by comparing the E_{pa} values of bithiophene with II, and IIIa with IIIb. These substituents also improve the chemical reversibility of the oxidation reactions, and give the materials excellent solubility. Note that more recently, oxidized α,α'-*tert*-butyl-substituted α-linked tetrathiophene was found to be stable.[55] Although the oxidation reactions of the oligomers IIIb–VIII are chemically reversible, only the first oxidation process of IV–VIII is electrochemically reversible. For the latter, the anodic and cathodic peak separation, ΔE_p, equals 60 ± 10 mV and is invariant to the scan rate between 10 and 100 mV/s, and the i_{pc}/i_{pa} ratio is close of the unity.

Table II. Comparison of Reported and Extrapolated Values for Poly(methylthiophene)

property	extrapolated	reported
E_{pa} (V vs SCE)	0.64	0.60–0.75
λ_{max} (eV)	2.3	2.20–2.45
λ_{max} polaron (eV)[a]	0.2	≃0.5
λ_{max} bipolaron (eV)[a]	0.1	≃0.6

[a] Transition of lowest energy.

As expected for a π-conjugated system, the E_{pa} values shift cathodically as the oligomer length increases and E_{pa1} and E_{pa2} both scale linearly with $1/N$ (Figure 6) with slopes of 1.6 and 2.6, respectively. The linearity holds for the oligomer series from trimer to octamer, which corresponds to a conjugation length involving from 12 to 32 carbon atoms. The slope of 1.6 for E_{pa1} is closed to the slope of 1.5 for the unsubstituted series.[38] Thus in solution, the β-CH_3 and α-TMS groups do not grossly affect the π-conjugation in the segments as observed with other substituents.[56] As seen in Table II, the extrapolated value of E_{pa1} to the infinite chain length is close to the values reported for poly(methylthiophene), which were obtained from those cyclic voltammograms displaying two oxidation peaks.[19,23,57] Such extrapolations have been used for conducting polymers.[38,39] From the slopes, it is clear that E_{pa2} is more sensitive to changes in the π-conjugation length than E_{pa1}. The E_{pa2} curve also has more scatter than E_{pa1} (from IV to VIII), probably reflecting some variation in the peak positions because the second oxidation reactions are not electrochemically reversible. The plot of the separation between these two oxidation peaks, ΔE_{pa}, is plotted against the number of repeating units in the oligomers (Figure 7). The two points for the hexamer are

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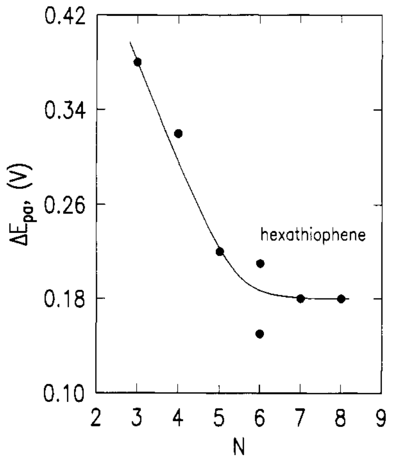

Figure 7. Variation of the oxidation peak separation (ΔE_{pa}) with the number of rings (N).

off the line and correspond to the unsubstituted[46] and butyl-substituted VI, while all the others are for the methyl-subsituted oligomers. Thus it is not surprising that for the hexamer, the two points fall on opposite sides of the line. ΔE_{pa} decreases with the size of the oligomer up to the hexamer (24 carbon atoms) and then becomes constant. This is in marked contrast with the case for the aniline oligomers where the peak separation continues to increase with the chain length.[58]

The changes in the HOMO and LUMO levels along the oligomer series can be monitored using the absorption spectra of the molecules. UV-visible spectra for each oligomer were also recorded in CH_2Cl_2, and the energies at the maximum, E_{max}, and at the edge, E_{min}, of the absorption band are reported in in Table I. As seen with the E_{pa} values, there is a corresponding decrease in the E_{max} and E_{min} of the π–π^* transition as the oligomer length increases, indicating that the HOMO and LUMO levels are merging. Furthermore, the energy of the fundamental transition scales linearly with $1/N$ (Figure 8) as is often seen for molecules with discrete energy levels,[59] and the slopes are 3.6 and 3.4, respectively. The corresponding plot for the unsubstituted thiophene series has the same slope of 3.6,[38] indicating a structural response similar to that found earlier with the oxidation potentials. The extrapolated E_{max} value for infinite size is close to the literature values for the polythiophene[17] (Table II), indicating that the polymer is a reasonable extension of the IIIb to VIII oligomer series. Finally, E_{pa1} scales linearly with both E_{max} and E_{min}, and the slopes are 0.52 and 0.48, respectively. The slope of ca. $^1/_2$ suggests that the HOMO and LUMO energies change symmetrically along the oligomer series.[36]

ESR and Vis–Near-IR of the Oxidized Oligomers. Chemical oxidation of thiophene oligomers (Th_n) and $FeCl_3$[47] can be used to control the stepwise production of the radical-cation (eq 1) and the dication (eq 2). Thus,

$$Th_n + 2FeCl_3 \rightarrow Th_n^{+} + FeCl_4^{-} + FeCl_2 \quad (1)$$

$$Th_n^{+} + 2FeCl_3 \rightarrow Th_n^{2+} + FeCl_4^{-} + FeCl_2 \quad (2)$$

the III–VIII oligomers were oxidized in CH_2Cl_2 by a stepwise addition of a $FeCl_3/CH_2Cl_2$ solution, and the ESR and vis–near-IR spectra of the cations were recorded. Figure 9 shows the ESR spectra of the IIIb (A), V (B), and VIII (C) after the addition of 2 and 4 equiv of the oxidizer. With the addition of 2 equiv of $FeCl_3$, each oligomer displays a strong and narrow ESR signal, ΔH_{pp} = 6–8 G, centered at g = 2.004, typical for organic radicals. The ESR signal has the predicted intensity for the quantitative conversion of the neutral oligomers to the mono radical cations species and grows with the additions of $FeCl_3$ to a maximum at 2 equiv of $FeCl_3$. The ESR spectrum of electrochemically generated radical cations of 2,5″-dimethylterthiophene was recently reported by Hill et al.[36] The reported spectrum revealed a hyperfine coupling interaction (hfc) of 5.0 G due to the six methyl protons, and the hfc interaction of 3.0 G with the 3′ and 4′ protons. Hyperfine structure is not present in the spectrum of radical cation of IIIb, and this is attributed to the presence of the TMS groups at positions 2 and 5″, and the methyl groups at positions 3′ and 4′. The changes in the ESR signal with the subsequent addition of 2 more equiv of $FeCl_3$ is, however, different for each oligomer. With IIIb, the ESR signal is unchanged, while with V it decreased significantly. With VIII, the ESR signal vanished almost completely and there is only a residual signal due to the resonant cavity (sharp signal) and to the paramagnetic $FeCl_4^-$ ions in solution. The latter has a much weaker and broader signal centered at g = 2 with ΔH_{pp} = 400–600 G. The residual signal is clearly observed in Figure 9C after the addition of 4 equiv of the oxidizer. It also appears superimposed on the ESR signal for the solutions of the other oligomers (Figure 9A,B). The changes in the ESR spectra of VI and VII upon addition of $FeCl_3$ were almost identical to those for VIII, while IIIa and IV produced an ESR spectra like the one for IIIb. Therefore, the neutral oligomers can be chemically oxidized to the radical cation as in eq 1, but only the readical cations of VI, VII, and VIII can be further oxidized to the dication as shown in eq 2.

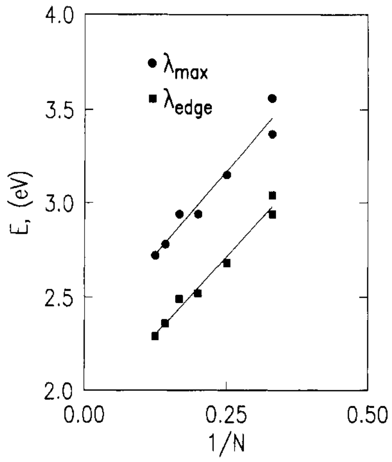

Figure 8. Variation of the absorption energy (E) with the reciprocal of the number of rings (N).

The chemical oxidation of the neutral oligomers produces a corresponding decrease of the π–π^* absorption and new transitions emerge in the vis–near-IR region as the radical cation and dication forms are generated. Figures 10–12 show the optical spectra between 400 and 2000 nm of the neutral and oxidized forms of IIIb, V, and VIII in CH_2Cl_2, respectively. The neutral spectrum of IIIb is not shown. The π–π^* bands for the neutral species completely disappear with all the oligomers studied when the stoichiometry of eq 1 is reached (except for IIIa). Every radical cation spectrum, including those of oligomer IV, VI, and VII, consists of two strong absorptions and shoulder transitions on the high-energy side. Radical cation IIIa has one strong absorption band in the visible region which was observed with a rapid spectrophotometer. The intensity of these absorption bands grows until 2 equiv of $FeCl_3$ are added to the solution which parallels the ESR

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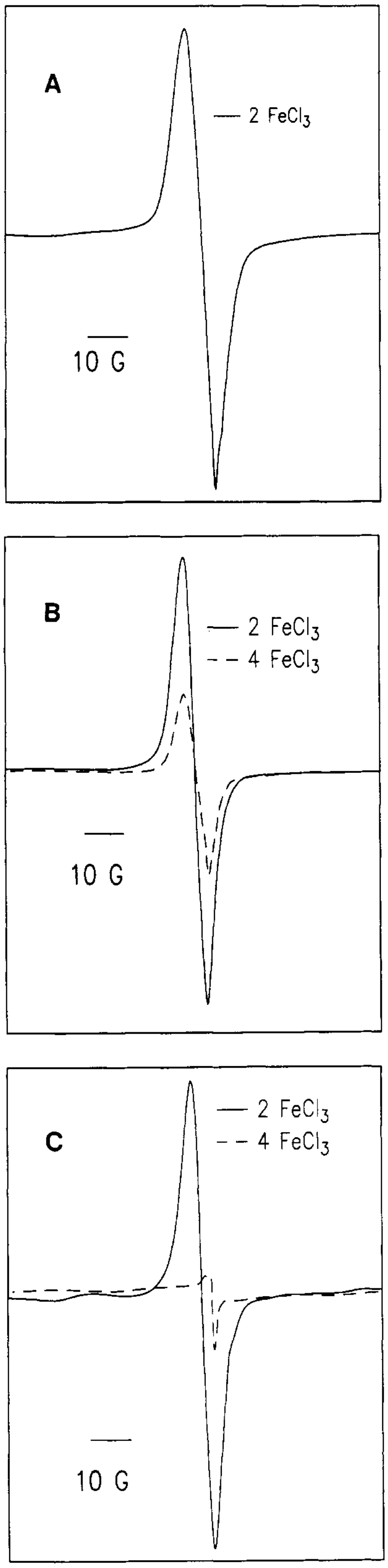

Figure 9. ESR spectra of the chemically oxidized (A) IIIb, (B) V, and (C) VIII using 2 and 4 equiv of $FeCl_3$.

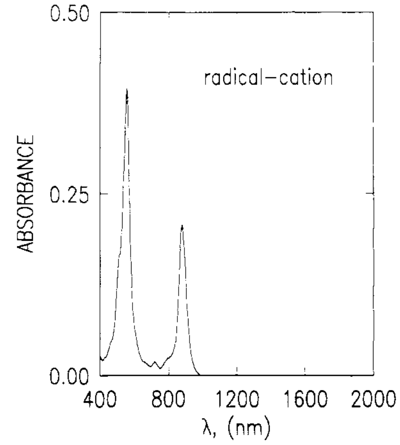

Figure 10. Vis–near-IR absorption spectrum of 10^{-5} M IIIb radical cation in CH_2Cl_2.

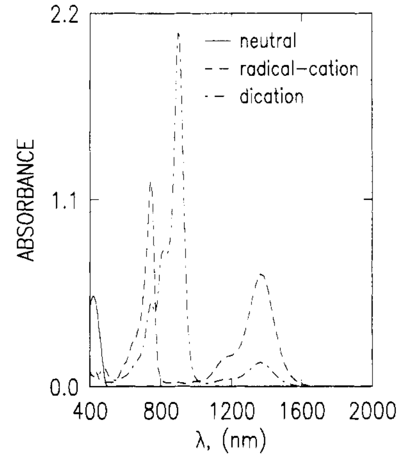

Figure 11. Vis–near-IR absorption spectrum of 2 × 10^{-5} M V in CH_2Cl_2 at different oxidation states.

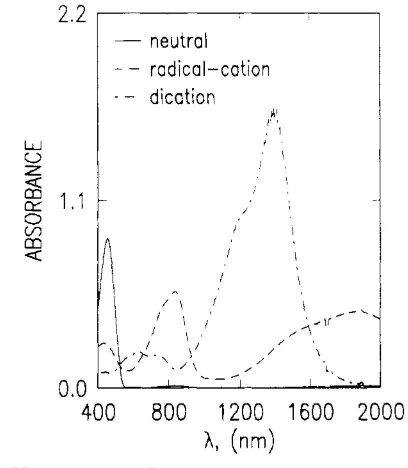

Figure 12. Vis–near-IR absorption spectrum of 2 × 10^{-5} M VIII in CH_2Cl_2 at different oxidation states.

signal. The low-temperature UV–visible spectra of electrochemically generated radical cations of three thiophene trimers recently reported by Hill et al.[36,37] show three well-defined absorption bands between 400 and 800 nm. One is attrituted to the mono radical cation and the others to radical cation dimers (π-dimers).[36,37] The two strong additional bands seen by Hill et al. are not present in the visible spectra of IIIa and IIIb radical cations, indicating that π-dimer formation is not important here. The absence of diamagnetic π-dimers is corroborated by the ESR results where the signal has the expected intensity for the quantitative conversion of neutral oligomers to their corresponding mono radical cations. π-dimer formation in these compounds may be unfavorable due to the steric encumberence of the subsitutents. On the other hand, the room-temperature vis–near-IR spectra of the mono radical cations of unsubstituted 2,5-linked thiophene pentamer and hexamer[47] also do not show evidence of π-dimer formation. We should mention that the reported π-dimeri-

Table III. Summary of Vis-Near-IR Data

	$h\nu_{max}$, $e\nu/(\lambda_{max}$, nm) radical cation				dictation	
oligomer	1	2	3	4	1	2
IIIa			2.16 (574)	2.37 (522)		
IIIb	1.41 (879)	1.59 (781)	2.24 (554)	2.42 (516)		
IV	1.10 (1123)	1.28 (971)	1.86 (666)			
V	0.90 (1373)	1.07 (1156)	1.67 (743)	1.84 (675)	1.38 (897)	1.53 (811)
VI	0.79 (1566)	0.97 (1274)	1.59 (779)	1.78 (693)	1.14 (1086)	1.30 (954)
VII	0.69 (1785)	0.87 (1427)	1.49 (834)	1.66 (740)	1.01 (1231)	1.16 (1068)
VIII	0.65 (1897)	0.83 (1500)	1.46 (848)	1.63 (762)	0.89 (1396)	1.04 (1189)

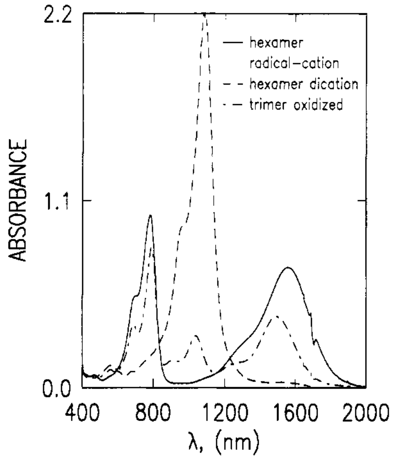

Figure 13. Vis–near-IR absorption spectrum of a 10^{-5} M oxidized IIIa and VI in CH_2Cl_2.

zation of the mono radical cations are associated with the electrochemical oxidation of the trimers in acetonitrile with 0.1 M Bu_4NBF_4, and the evidence for the π-dimers is seen between −30 and +5°.[36,37] More recently, the bands attributed to π-dimer formation have been observed in the room-temperature photooxidation of the trimers in the presence of oxygen in acetonitrile–trifluoroacetic acid (15%) solution.[37] These experimental conditions are completely different from the conditions used by us and by Fichou,[47] which are dichloromethane with ca. 10^{-5} M of $FeCl_3$ at room temperature.

The absorption bands in the spectra of Figures 10–12 are much sharper than those of the corresponding polymer film[19,60] because the electronic structure of oligomers can be represented by discrete molecular energy levels, while that of the polymer are better described by band structure.[61] The radical cation spectrum for IIIa, shown in Figure 13, is peculiar because the absorption band energies are close to those for the oxidized hexamer. This implies that the IIIa radical cation dimerizes to the VI cation even though the end α positions have TMS groups. This is not a new observation and there are reports of the coupling reaction of thiophene and bithiophene with α,α′-TMS groups[54] and of the dimerization of oxidized dimer, trimer, tetramer, and pentamer of thiophene.[50] As expected, the transitions for the radical cation undergo a bathochromic shift as the oligomer size increases. The energy for the absorption maxima scales linearly with $1/N$ and have near equal slopes of 3.7 and 3.8. This is seen in Figure 14. The radical cation and the neutral species have similar slopes, indicating similar sensitivity to incremental structural changes. Extrapolation to infinite size leads to a value of 0.2 eV, which is lower than the 0.5-eV value reported for a poly(methylthiophene) film.[62] This is listed in Table II. Figure 15 shows the linear relationship with similar slopes between E_{pa2} and E_{max} for the four electronic transitions for the radical cations. The slopes are 0.71, 0.73, 0.68, and 0.73 for the first, second, third, and fourth transitions, respectively. The slope of ca. 0.7 suggests that the HOMO level is more sensitive than the LUMO level to structural changes along the oligomer series.

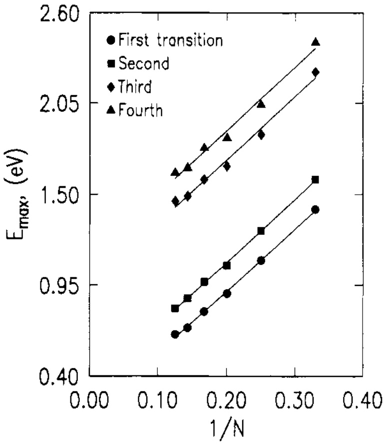

Figure 14. Variation of the maximum absorption energy (E_{max}) of the radical cation form with the reciprocal of the number of rings (N).

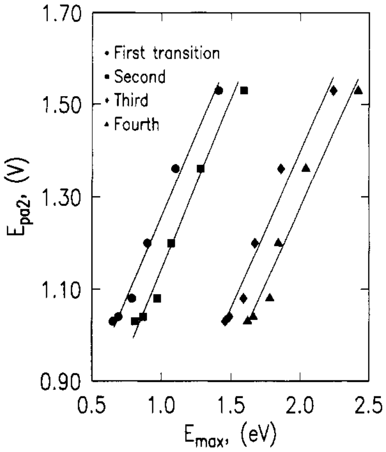

Figure 15. Variation of the second oxidation peak potential (E_{pa2}) with the energy of the maximum absorption (E_{max}) for the radical cation form.

When 2 equiv of $FeCl_3$ is added to each of the oligomer radical cation solutions, the vis–near-IR spectra for IIIb (Figure 10) and IV remain unchanged, but new absorption bands appear in the spectra of V (Figure 11), VI, VII, and VIII (Figure 12). For the latter, the intensity of the absorption bands for the radical cations decreases, and two new ill-resolved strong transitions appear as $FeCl_3$ is added incrementally. With VI, VII, and VIII, the intensity of the new peaks reach their maximum when a total of 4 equiv

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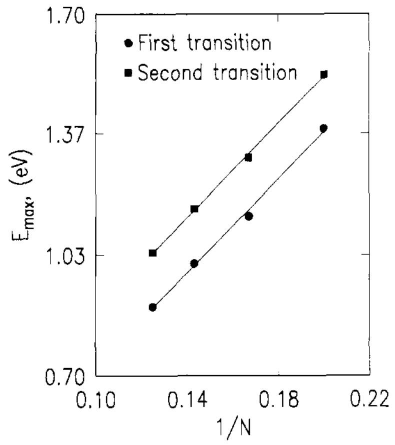

Figure 16. Variation of the maximum absorption energy (E_{max}) of the dication form with the reciprocal of the number of rings (N).

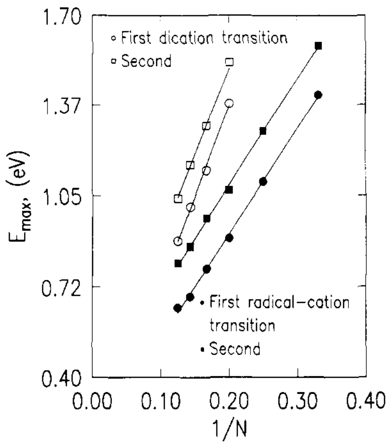

Figure 17. Variation of the maximum absorption energy (E_{max}) of the first and second transition of the radical cation and dication forms with the reciprocal of the number of rings (N).

of $FeCl_3$ has been added. This is seen in Figure 12. At this point, the radical cation absorptions have vanished as expected from the stoichiometry of eq 2. V behaves differently in that, as seen in Figure 11, the dication peak intensities reach their maximum after ca. 3 equiv of $FeCl_3$ total has been added, and the bands for the radical cation remain observable even when adding a greater excess of the oxidant. The absorption maxima of the oligomers are reported in Table III. Again, there is a linear relationship between E_{max} for the oligomer dications and $1/N$ and the slopes are 6.5. This is seen in Figure 16. The slope is almost twice that obtained for the neutral and radical cation forms and indicates a higher sensitivity of the ion to structural changes. The different slopes for the radical cations and the dications predict that the lowest energy transistions of these species should be close for long chains (Figure 17), which is actually the case for the poly(methylthiophene) film (and other thiophene polymers)[34,63] where the electronic transitions are at ca. 0.50 eV (polaron) and 0.65 eV (bipolaron).[33,62]

Discussion

The cyclic voltammograms of the thiophene oligomers show two oxidation processes. Chronocoulometry experiments show that the two successive oxidation waves of the oligomers involve one electron each. In addition, the ESR spectra of those oligomers that could be oxidized stepwise by $FeCl_3$ revealed that the first oxidation process yields a radical species, while further oxidation leads to a diamagnetic species. Therefore, the stepwise oxidations yield the radical cation and dication, successively. However, V radical cation ($E° = 1.16$ V) was partly oxidized while IIIb ($E° = 1.48$ V) and IV ($E° = 1.32$ V) radical cations were not oxidized by $FeCl_3$ to the dication as expected from their respective voltammograms. Likewise, neutral II (estimated $E° = 1.41$ V) could not be oxidized to the radical cation. These results make sense when comparing the E_{pa} values of the oligomers with the estimated oxidation potential of the $FeCl_3$/dichloromethane solution, 1.22 V, where only those oligomers with $E° < 1.22$ V will be oxidized. In addition, the decrease in the $FeCl_3/FeCl_2$ ratio during the oxidation reaction decreases the oxidation potential of the solution. This may account for the incomplete oxidation of the V radical cation.

Since ΔE_{pa} remains constant at 180 mV after the oligomer size reaches the hexamer (Figure 7), two separated oxidation reactions are expected for the next higher oligomers and for the large segments of the polythiophene chains. Accordingly, two oxidation waves separated by ca. 200–350 mV are observed in the voltammograms for polythiophene and poly(methylthiophene) obtained at room temperature and below.[6,19-23] The two peaks are not due to conformational changes in polythiophene[28] because of the two stable conformations known, rod and coil, only the rod has been identified in the solid state.[64] Furthermore, even if both conformations were present, the calculated bandgap (E_g) difference between the two conformations, 0.06 eV,[65] implies a small peak separation, ca. 30 mV (assuming that the HOMO and LUMO levels affect the gap similarly). This difference is far from the experimental differences, 200–350 mV.[6,19-23] Therefore, it is reasonable to assign the two oxidation peaks to two distinct anodic reactions. These results are in marked contrast with the conclusion that conducting polymers are expected to be electrochemically oxidized in one broad single step because of the interactions between the multiple redox sites in polymer chains.[28,43,66,67]

Therefore, the broad single oxidation peak voltammogram often obtained with polythiophene films does not appear to be an inherent property of the polymer segments but instead may reflect the complications caused by resistance[30] and swelling[21] of the polymer film, since both effects can shift the individual oxidation peaks and lead to the appearance of a single wave. Although it has been shown that when for two sequential electron-transfer reactions (reversible) have $E°$'s < ca. 100 mV, the waves merge into a single broad multiple-electron wave,[68] this effect does not apply to polythiophene because the $\Delta E°$'s are 200–350 mV.

On the other hand, the observation of two oxidation waves in the cyclic voltammogram of polythiophene films (in particular the small prepeak or shoulder) may not necessarily indicate the presence of two distinct oxidation processes since they may result from complications associated with the film such as resistance,[30] capacitance,[11,31] MV distribution,[20] and irregular couplings.[18] However, showing that the separate waves prevail after repetitive cyclic scans[21,22,57] or electrolyte and temperature changes[21]

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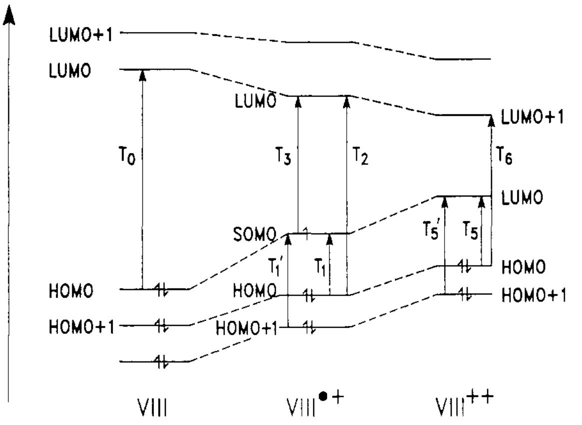

Figure 18. Molecular orbital diagram of the octamer in different oxidation states. Arrows represent possible transitions (see text).

helps dismiss these complicatons.

The MO diagrams of VIII in the neutral, radical cation, and dication states are shown Figure 18. By analogy to Fichou et al.,[46] the second highest occupied and lowest unoccupied molecular orbitals are dubbed (HOMO + 1) and (LUMO + 1), and the midgap singly occupied molecular orbital that appears for the radical cation is (SOMO). The lowest energy transition of neutral VIII (T0), located at 2.72 eV (Table II), is assigned to the fundamental π–π^* transition between the HOMO and LUMO levels. Upon oxidation, significant geometrical deformations of the molecule occur which lead to a major rearrangement of the MO energy levels as shown for the radical cation and dication. For the radical cation, the lowest energy absorption bands at 0.65 and 0.83 eV (Table III) may be due to transitions T1 (between HOMO and SOMO) and T1′ (between HOMO + 1 and SOMO). This interpretation is supported by first the recent theoretical calculations of noninteracting polarons in polythiophene which predicted these transitions; however, the band intensities are inverted compared to the experimental results.[61] Second, the calculated energy difference between these transitions, ca. 0.2 eV,[61] is very close to the experimental values for the oligomers, 0.17–0.18 eV (Table III). Finally, we find that the T2 − T1 = T3 rule is not observed for any oligomers which differs with the absorptions band assignments for the unsubstituted thiophene oligomers made by Fichou et al.[46] These assignments were made on the observation that the hexamer followed this rule, although (in the same paper) the pentamer did not adhere to the rule. Note that we observed that VI almost follows this rule which is in line with the observation by Fichou et al.[46] Another pair of absorption bands also separated by 0.17–0.19 eV appears at higher energies in the spectra of the oligomers. The electronic origin of the main bands is difficult to determine because it may involve transitions between the HOMO, SOMO, and LUMO levels. For the dication, the two bands at 0.89 and 1.04 eV may arise from transitions T5 (between HOMO and LUMO) and T5′ (between HOMO + 1 and LUMO), respectively, since the energy difference between the transitions, 0.15 eV, is close to that observed for the lowest absorption bands of the radical cation, 0.17 eV. It is interesting to note that the oxidized *p*-phenylene, 2,5-thienylenevinylene, *p*-phenylenevinylene, and other thiophene oligomers also display electronic absorption bands separated by ca. 0.15–0.30 eV.[44–47,69–72] On the other hand, sideband absorption may also be due to vibronic transitions. Indeed, it has recently been proposed that the ill-resolved absorption bands, separated by ca. 0.20 eV, observed in the solution- and solid-state visible spectrum of many neutral poly(alkylthiophenes)[73–75] is consistent with a C=C stretching mode that would strongly coupled to the electronic structure.[73]

The linear correlation obtained between $E_{\max}$ and $1/N$ for both the thiophene oligomer radical cations and dications implies that the charge encompasses the entire oligomer structure (Figures 15 and 16). Extrapolation of $E_{\max}$ to infinite chain length for the radical cation and dication yields values which do not match the experimental ones, unlike the case for the neutral species (Table I). This deviation suggests that the charges have a limited delocalization length involving 10 (dication)–12 (cation) thiophene units (40–48 carbons). This agrees with previous experimental estimations[38,76] and with the recent theoretical calculations which have shown good agreement between the calculated and experimental energy of the electronic transitions for polarons and bipolarons using a unit cell of 10 thiophene units for both.[61] From our results, 0.08 spin/ring is estimated, which is in the range of the reported experimental values of 0.04–0.10 spin/ring for polythiophene.[21,35,76]

In summary, thiophene oligomers with three or more units can be electrooxidized stepwise at room temperature to form the radical cation and dication forms. The peak separation between the first and second oxidation reaction remains constant at 180 mV with VI, VII, and VIII and suggests that two separate oxidation waves should also be visible in the room-temperature voltammogram for the next higher oligomers and for the π-conjugated segments of polythiophene. This is in marked contrast with the conclusion that conducting and conjugated polymers are expected to be oxidized in one broad single step.[28,43,66,67] Also, the cyclic voltammograms for the polythiophene films which do show the single broad wave may be reflecting complications associated with structural variations in the polymer and polymer chain interactions in the film. The soluble oligomers can be oxidized with stoichiometric amounts of $FeCl_3$ to the radical cation and dication. The vis–near-IR spectrum of the oxidized oligomers display multiple sharp absorption bands. We have shown that the previous assignments of the electronic transitions are inappropriate for the entire oligomer series. The correlation between the energy of the electronic transitions of the oxidized oligomers and the oligomer size enabled us to estimate the delocalization length of the radical cation (12 units) and the dication (10 units) in the polymer.

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Registry No. II, 127729-23-1; IIIA, 138983-69-4; IIIB, 138983-70-7; IV, 138983-73-0; V, 138983-74-1; VI, 143105-42-4; VII, 138983-79-6; VIII, 138983-81-0.

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