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MALDI-MS Evaluation of Poly(3-hexylthiophene) Synthesized by Chemical Oxidation with $FeCl_3$

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ABSTRACT: Poly(3-hexylthiophene) synthesized by chemical oxidation with $FeCl_3$ was investigated with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) using either dithranol or the electron-transfer matrices terthiophene and anthracene. Two to three series of ions were observed in the MALDI mass spectra. These series all have hexylthiophene repeat groups, and the end groups/modifications were identified as two or more chlorine atoms through the analysis of isotopic distributions and exact mass measurements. The chlorine atoms may be end groups (on α- or β-carbons of terminal thiophenes) or substituents on the β-carbons of the thiophene groups along the polymer backbone. Although poly(3-alkylthiophenes) synthesized by this method have been reported to contain iron or chlorine impurities, this is the first demonstration that the polymeric product actually contains chlorine atoms that are covalently bound to the polymer chain (vs residual $FeCl_3$). The $FeCl_3$ oxidizing agent—*not* the chlorinated solvent—is found to be responsible for halogenating the polymer, as determined by experiments with $FeBr_3$ as the oxidant. In addition, we have demonstrated that when using either dithranol or the electron-transfer matrices, the ion series represent radical molecular cations, $M^{\bullet +}$, rather than the protonated molecules or salt adducts that are typically observed in MALDI-MS.

Introduction

Soluble polymers with the ability to conduct electricity have been of great interest for the past two decades due to their use in nonlinear optical devices, light-emitting diodes, transistors, smart windows, sensors, batteries, and nanoscopic electronic structures.[1] Of the soluble conducting polymers investigated thus far, substituted poly(thiophenes), particularly poly(3-alkylthiophenes), are by far the most thoroughly investigated due to their ease of being processed using various thermal and solution means and the fact that such polymers are stable under a variety of conditions.[2] Structural characterization of these systems has led to a greater understanding of how one can manipulate the electrical and physical properties of poly(3-alkylthiophenes) by making changes in the structure of the monomer or the synthetic conditions for polymerization.

There are a variety of methods that can be used to synthesize poly(3-alkylthiophenes), but in the current study, we have investigated a poly(3-alkythiophene) synthesized by chemical oxidation of monomer with $FeCl_3$ due to the widespread use of this preparative technique for the polymer.[1] There have been reports that poly(3-alkythiophenes) produced by $FeCl_3$ oxidation may contain iron or chlorine impurities.[3−5] These impurities may have a great impact on the electrical or physical properties of the polymer. However, the nature of these impurities (covalently bound vs residual $FeCl_3$) has not been fully elucidated. Information regarding end-group identity of these polymers, as well as other modifications, would be helpful in gaining a better understanding of the mechanism of polymer formation and in applications where modifying the end groups may be useful so that tethering polymer chains to surfaces or to other molecules may be possible.

Since the introduction of MALDI-MS by Karas et al. in 1987[6] and Tanaka et al. in 1988,[7] this technique has been used widely for the characterization of polar organic molecules and biopolymers (proteins[8,9] and oligonucleotides,[10,11] for example). The application of MALDI-MS to synthetic polymers has also proven successful,[12,13] although for a more limited variety of polymer classes. The synthetic polymers that currently can be characterized most successfully by MALDI-MS are the more polar or polarizable polymers such as poly(glycols), poly(styrenes), and poly(methyl methacrylates). The most commonly used MALDI matrices are low molecular weight, acidic organic molecules such as 2,5-dihydroxybenzoic acid (DHB), α-cyano-4-hydroxycinnamic acid, and 3,5-dimethoxy-4-hydroxycinnamic acid (sinapinic acid) for biopolymers and indoleacrylic acid and dithranol for synthetic polymers.

Most of the analyte ions generated by MALDI appear to be the result of proton-transfer reactions between the matrix and analyte (forming $[M + H]^+$ or $[M - H]^-$) or cation adduction (forming $[M + Na]^+$ or $[M + Ag]^+$ if silver salt is added), yet several authors have reported the possible formation of analyte radical molecular cations.[14−17] This led us to investigate the possibility that in certain cases matrix ions may be able to assist in the ionization process by undergoing electron-transfer reactions with an analyte, forming radical molecular cations or anions ($M^{\bullet +}$ or $M^{\bullet -}$) rather than protonated or deprotonated analytes.[18,19] We suspected that *electron-transfer MALDI-MS might lead to superior ion formation for electroactive analytes which do not have functional groups that can obviously become protonated or deprotonated but have relatively low ionization energies.* Our initial study demonstrated that anthracene and terthiophene can be used as MALDI matrices for small, electroactive compounds such as ferrocenes and a

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bisphenol and that the resulting analyte ions are in fact radical cations.[18,19]

Since the time that our initial study of electron-transfer MALDI-MS was performed, we have found the electron-transfer MALDI matrices superior to the more common proton-transfer matrices for the MALDI-MS analysis of a variety of molecules including ferrocenes, resorcinarenes, poly(vinylferrocene), other ferrocene-based oligomers, and calixarenes.[20-23] Due to the success we experienced with electron-transfer matrices in the MALDI-MS analysis of a variety of electroactive compounds, we felt that the electron-transfer matrices would be ideal for the MALDI-MS analysis of conducting polymers, such as poly(3-alkylthiophenes).

We have used matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) to characterize poly(3-hexylthiophene) synthesized by chemical oxidation with $FeCl_3$, and we have taken a particular interest in identifying end groups, modifications, and the nature of the molecular ions that are formed by MALDI.[24] In a concurrent study, McCullough used MALDI-MS to successfully characterize the molecular weight and end groups of regioregular poly(3-alkylthiophenes) synthesized by a modified Grignard cross-coupling method.[25]

Experimental Section

Monomers. The monomer 3-hexylthiophene was either synthesized as previously described[26] or used as received from Aldrich Chemical Co. (99+%). The monomer 3,4-dihexylthiophene was prepared by a Grignard cross-coupling reaction between hexylmagnesium bromide and 3,4-dibromothiophene in dry diethyl ether containing a nickel catalyst, following the procedure of Kumada et al.[27]

Synthesis of Poly(alkylthiophenes). Poly(3-hexylthiophene) and poly(3,4-dihexylthiophene) were synthesized by chemical oxidation following the synthetic method described by Leclerc et al.[3] Either 3-hexylthiophene or 3,4-dihexylthiophene monomer was dissolved in dry chloroform and added dropwise to a suspension of $FeCl_3$, also in dry chloroform, and stirred under argon for 24 h at room temperature. The polymer was precipitated by addition of the reaction mixture to methanol. The precipitate was washed with copious amounts of methanol and then further washed by Soxhlet extractions with methanol and then acetone. The resulting polymer was then dried in vacuo and stored under argon. Alternatively, poly(3-hexylthiophene) was synthesized by chemical oxidation using $FeBr_3$ rather than $FeCl_3$ (*Caution: $FeBr_3$ reacts violently with water. Therefore, it must be handled in an inert environment.*) The $FeBr_3$ dissolved in dry chloroform was added to a dry chloroform solution of 3-hexylthiophene in a glovebox and stirred for 24 h. The reaction mixture was transferred to a fume hood where the excess $FeBr_3$ was quenched by exposure to air followed by the same procedure used to isolate the polymer synthesized by $FeCl_3$ oxidation.

MALDI-MS. Poly(3-hexylthiophene) and matrix were both dissolved in tetrahydrofuran and mixed, typically in a ratio of 2000:1 (w/w). Matrices used were terthiophene, anthracene, and dithranol. In some cases, silver trifluoroacetate was also added to the matrix/polymer mixture to investigate the formation of silver adducts. A Bruker ProFLEX III MALDI-TOF mass spectrometer was used in reflectron mode with pulsed ion extraction (250 μs delay) and a low mass gate set at m/z 500. Typically, the mass spectrometer was calibrated with a standard mixture of peptides/proteins (4-hydroxy-α-cyanocinnamic acid matrix) which bracketed the mass range of the polymers studied. Mass calibrations with internal standards are described in the Results and Discussion section.

GPC Analysis. The molecular weight of poly(3-hexylthiophene) in tetrahydrofuran was measured using a Waters gel permeation chromatograph (GPC) with a differential refractive index detector and a Phenogel 10 μm column (Phenomenex), operated by Wyatt Astra software. The instrument was calibrated using poly(styrene) standards.

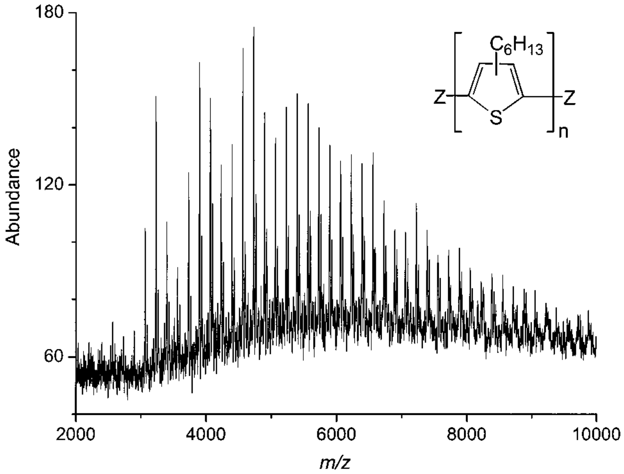

Figure 1. MALDI mass spectrum of poly(3-hexylthiophene) synthesized by $FeCl_3$ oxidation. Terthiophene was used as the matrix (200 scans averaged, 19-point Savitzky−Golay smooth).

Results and Discussion

To analyze ions of intact poly(3-hexylthiophene) by mass spectrometry, the polymer must be ionized by *matrix-assisted* laser desorption/ionization.[24] *Direct* laser desorption/ionization (no matrix) of poly(3-hexylthiophene) prepared by $FeCl_3$ oxidation produces only very weak-intensity, low-mass ions ($< m/z$ 2000) which may correspond to fragments resulting from photoionization of the polymer. Thus, poly(3-hexylthiophene) synthesized by $FeCl_3$ oxidation was analyzed by MALDI-MS. Several MALDI matrices were evaluated in order to achieve the highest quality poly(3-hexylthiophene) spectra and also to compare the spectra obtained with a traditional proton-transfer matrix vs matrices that we have introduced as electron-transfer agents.[18,19] Dithranol, terthiophene, and anthracene matrices produced spectra with similar ions and molecular weight averages and distributions, but the terthiophene matrix was preferred because of the higher signal-to-noise ratio and resolution routinely attained with its use. The addition of silver salt to the dithranol and terthiophene matrices did not result in higher quality spectra when compared to those acquired with dithranol or terthiophene alone, and the resulting ion series were not shifted by a mass that would be indicative of polymer−silver or other adducts. Incidentally, our data do not show evidence that alkyl side chains are eliminated as fragments during ionization, as has been reported in the MALDI-MS analysis of poly(n-octylperylene).[28]

End-Group Analysis and Nature of Molecular Ions. The mass spectrum of poly(3-hexylthiophene) employing terthiophene as the matrix is displayed in Figure 1. Two ion series are present in the spectrum: $(166_n + 70)^+$ and $(166_n + 104)^+$. The repeat groups correspond to 3-hexylthiophene units ($HT = C_{10}H_{14}S_1$, 166 u), and the residual masses correspond to the combined end-group masses or possible polymer modifications. On the basis of the oxidative route used for this polymer synthesis, we expected that the end groups would be hydrogens and that there would be no modifications. If so, the residual mass would be 2 u, but neither of the observed ion series supports this prediction. In addition, the presence of two ion series indicates

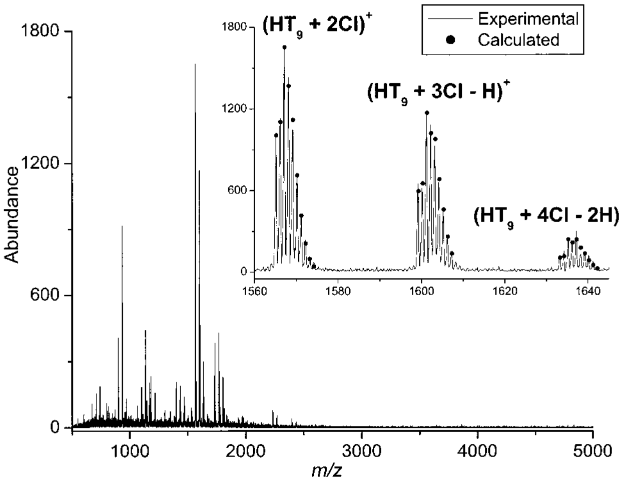

Figure 2. MALDI mass spectrum of acetone-soluble fraction of poly(3-hexylthiophene). The inset shows the region between *m*/*z* 1550 and *m*/*z* 1650. Terthiophene was used as the matrix (56 scans averaged, no smooth).

that two different sets of end groups and/or modifications must be present in the synthetic product.

We performed exact mass measurements with internal standards and used comparisons of observed and calculated isotopic abundances in order to identify the composition of the residual masses of low mass oligomers of the poly(3-hexylthiophene). The low mass fraction of the polymer in acetone (extracted from the Soxhlet purification of the polymeric synthetic product with acetone) was deemed most appropriate for this determination because the mass accuracy and resolution of our time-of-flight mass spectrometer are highest at lower masses. We have assumed that the low molecular weight fraction is representative of the higher mass polymers with respect to the residual masses. In these experiments we used the oligo(ferrocenyldimethylsilanes) $Fc[Si(CH_3)_2Fc]_5H$ and $Fc[Si(CH_3)_2Fc]_7H$[29] as internal standards. These oligomers have been characterized previously with electron-transfer MALDI matrices and were found to produce radical molecular cations.[20,21] In addition, they bracket the molecular weights of the most abundant ions observed in the MALDI mass spectrum of the acetone Soxhlet extract.

The MALDI mass spectrum of the acetone extract of poly(3-hexylthiophene) contains the ion series $[166_n + 70]^+$ and $[166_n + 104]^+$ as well as an additional ion series corresponding to $[166_n + 138]^+$ (Figure 2). In the MALDI mass spectra which were mass calibrated with the internal standards (not shown), poly(3-hexylthiophene) ions corresponding to $[166_9 + 70]^+$, $[166_9 + 104]^+$, and $[166_9 + 138]^+$ display mass-to-charge ratios of 1566.64, 1600.61, and 1634.58, respectively, agreeing well with the expected *m*/*z* for the ions $[HT_9 + 2Cl]^{+\bullet}$ (calculated *m*/*z* 1566.67), $[HT_9 + 3Cl - H]^{+\bullet}$ (calculated *m*/*z* 1600.63), and $[HT_9 + 4Cl - 2H]^{+\bullet}$ (calculated *m*/*z* 1634.59) (Table 1). The isotopic distributions of these ions also closely match the calculated abundances for these compositions (see inset, Figure 2). It should be noted that these compositions indicate that the ions are radical molecular cations, $M^{\bullet+}$, rather than protonated molecules, $[M + H]^+$, which is consistent with the results from our previous studies of MALDI-MS of electroactive compounds. This finding supports our prediction that *poly(3-hexylthiophene) is ionized by electron-transfer reactions with ions of the MALDI matrix terthiophene, rather than by proton transfer or salt addition.*

The exact mass measurements of the $[166_9 + 70]^+$, $[166_9 + 104]^+$, and $[166_9 + 138]^+$ ions of the acetone Soxhlet extract were repeated using anthracene as the MALDI matrix, also shown to be an electron-transfer matrix, as well as with dithranol, commonly thought to be a proton-transfer matrix but speculated by McCullough to ionize poly(3-hexylthiophene) by electron transfer.[25] The results (Table 1) reveal that *both anthracene and dithranol produce radical molecular cations, $M^{\bullet+}$, rather than protonated molecules, $[M + H]^+$.*

The location of the chlorine atoms in the poly(3-hexylthiophene) studied here cannot be determined unequivocally from the MALDI mass spectra. For the first ion series, $[HT_n + 2Cl]^{\bullet+}$, we tentatively have assigned the two chlorine atoms as end groups (on α- or β-carbons of the two terminal thiophenes), but they could alternatively be positioned on β-carbons of the thiophene groups along the polymer backbone. As a test to determine whether the two chlorine atoms could be end groups on the poly(3-hexylthiophene), we synthesized and analyzed poly(3,4-dihexylthiophene). In this polymer, all β-carbons of the poly(thiophene) backbone are blocked by identical moieties, so the only reasonable positions for the chlorine substituents are the end groups (on α-carbons of terminal thiophenes). The MALDI mass spectrum of poly(3,4-dihexylthiophene) is shown in Figure 3. The lower mass distribution of ions relative to that of poly(3-hexylthiophene) may be a reflection of the fact that the monomer is more sterically hindered than 3-hexylthiophene, and as a result, shorter length oligomers are formed. Nevertheless, the main ion series observed in the MALDI mass spectrum of poly(3,4-dihexylthiophene), $(250_n + 70)^+$, corresponds to a polymer with dihexylthiophene repeat units and two residual chlorine atoms. There are no other ion series that correspond to a polymer that has more or less than two chlorine atoms. The two chlorine atoms must be located on the α-carbons of the terminal thiophenes due to the fact that the thiophene rings along the backbone are completely blocked, preventing further substitution. The implication of these data for the poly(3-hexylthiophene) $[HT_n + 2Cl]^{\bullet+}$ ion series is that the two chlorine atoms are more than likely end groups located on α-carbons of the terminal thiophenes.

In the case of the poly(3-hexylthiophene) $[HT_n + 3Cl - H]^{\bullet+}$ and $[HT_n + 4Cl - 2H]^{\bullet+}$ ion series, the three or four chlorine atoms may be positioned along the polymer chain on the β-carbons of the thiophene groups (along the backbone) or on a combination of α-carbons and β-carbons. The scenario wherein all of the chlorine atoms could reside entirely on α-carbon chain ends would be possible only if poly(3-hexylthiophenes) have branch points that add to the total number of end groups per polymer chain, but poly(3-hexylthiophenes) are generally thought to be linear conducting polymers with no branch points. If the polymers were branched, the ratio of the ion series containing more than two chlorine atoms to the ion series with only two chlorine atoms would be expected to increase with repeat number, because as the polymer chain becomes longer, the amount of branching would be expected to increase due to the statistical nature of branching. In addition, ion series with higher numbers of substituted chlorine atoms would be expected for longer chain lengths.

Table 1. Exact Mass Measurements of Poly(3-hexylthiophene) Nonamer Species

matrix	species	molecular formula	calcd m/z of $\mathrm{M}^{\bullet+}$ (A + 2) isotope[a]	measd $m/z \pm$ SD	error, ppm
terthiophene	$[\mathrm{HT}_9 + 2\mathrm{Cl}]^{\bullet+}$	$\mathrm{C_{90}H_{126}S_9Cl_2}$	1566.67	1566.64 ± 0.02	−19.1
	$[\mathrm{HT}_9 + 3\mathrm{Cl} - \mathrm{H}]^{\bullet+}$	$\mathrm{C_{90}H_{125}S_9Cl_3}$	1600.63	1600.61 ± 0.02	−12.5
	$[\mathrm{HT}_9 + 4\mathrm{Cl} - 2\mathrm{H}]^{\bullet+}$	$\mathrm{C_{90}H_{124}S_9Cl_4}$	1634.59	1634.58 ± 0.02	−6.1
anthracene	$[\mathrm{HT}_9 + 2\mathrm{Cl}]^{\bullet+}$	$\mathrm{C_{90}H_{126}S_9Cl_2}$	1566.67	1566.69 ± 0.04	12.8
	$[\mathrm{HT}_9 + 3\mathrm{Cl} - \mathrm{H}]^{\bullet+}$	$\mathrm{C_{90}H_{125}S_9Cl_3}$	1600.63	1600.68 ± 0.04	31.2
	$[\mathrm{HT}_9 + 4\mathrm{Cl} - 2\mathrm{H}]^{\bullet+}$	$\mathrm{C_{90}H_{124}S_9Cl_4}$	1634.59	N/A	N/A
dithranol	$[\mathrm{HT}_9 + 2\mathrm{Cl}]^{\bullet+}$	$\mathrm{C_{90}H_{126}S_9Cl_2}$	1566.67	1566.64 ± 0.02	−19.1
	$[\mathrm{HT}_9 + 3\mathrm{Cl} - \mathrm{H}]^{\bullet+}$	$\mathrm{C_{90}H_{125}S_9Cl_3}$	1600.63	1600.61 ± 0.03	−12.5
	$[\mathrm{HT}_9 + 4\mathrm{Cl} - 2\mathrm{H}]^{\bullet+}$	$\mathrm{C_{90}H_{124}S_9Cl_4}$	1634.59	1634.59 ± 0.02	0.0

[a] The (A + 2) isotopes were used due to their relatively high abundances. This was particularly important in the $[\mathrm{HT}_9 + 4\mathrm{Cl} - 2\mathrm{H}]^{\bullet+}$ ion series.

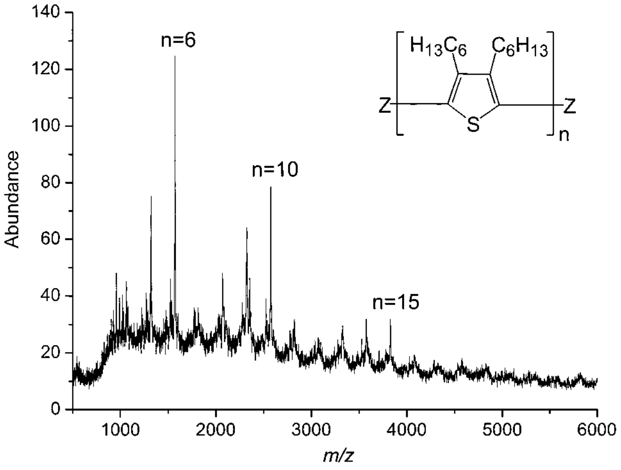

Figure 3. MALDI mass spectrum of poly(3,4-dihexylthiophene) synthesized by $\mathrm{FeCl_3}$ oxidation. Terthiophene was used as the matrix (71 scans averaged, no smooth).

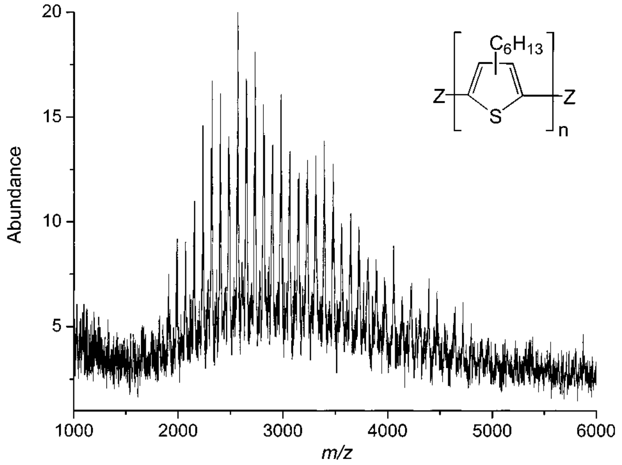

Figure 4. MALDI mass spectrum of poly(3-hexylthiophene) synthesized by $\mathrm{FeBr_3}$ oxidation. Terthiophene was used as the matrix (57 scans averaged, 19-point Savitzky−Golay smooth).

^{1}H NMR (see Supporting Information) of the acetone extract of poly(3-hexylthiophene) was used in an alternate attempt to determine the location of the chlorine atoms. Previously, ^{1}H NMR spectroscopy has been used to determine the degree of regioregularity of poly(3-alkylthiophenes).[30−32] In those studies, signals associated with the backbone thiophene units were used to determine the degree of regioregularity. Proton signals in the aryl region for regiorandom material are upfield from those of regioregular polymer. However, for the purpose of end-group analysis, the aryl proton region of interest is both upfield and downfield from the regioregular signal from the aryl protons associated with the repeat groups; this is based on previous ^{1}H NMR data of 2-bromo-3-alkylthiophene monomers and low-molecular-weight, bromo-substituted alkylthiophene oligomers[30,31] and is suggested by ^{1}H NMR data of poly(3-alkylthiophenes) synthesized using a variety of methods.[33] However, upon evaluation of the NMR spectra of the bromo-substituted alkylthiophene oligomers and those of the poly(3-alkylthiophenes), it is clear that a definitive assignment of the various proton signals for our polymer in the end-group region is not possible at this time. Our NMR spectrum contained multiple signals in the 6.5−7.2 ppm region, indicative of a mixture of the various possible chlorine end-group positions on the terminal hexylthiophene groups.[31,33] Thus, at this time we cannot confirm the assignments made using MALDI-MS.

Source of Chlorine Atoms in Poly(3-hexylthiophene). We were curious about the source of chlorine atoms observed in poly(3-hexylthiophene). Two potential sources are the chlorinated solvent in which the monomer and chemical oxidant are dissolved during the synthesis and the $\mathrm{FeCl_3}$ oxidant itself. To test the possibility that the chlorine atoms are supplied by the $\mathrm{FeCl_3}$ oxidant, we synthesized poly(3-hexylthiophene) using $\mathrm{FeBr_3}$ as an alternative oxidant. If the source of the chlorine atoms in the polymer is due to the $\mathrm{FeCl_3}$, the use of $\mathrm{FeBr_3}$ should eliminate the incorporation of chlorine atoms and possibly produce polymer with incorporation of bromine atoms instead. The MALDI mass spectrum of the resulting polymer is displayed in Figure 4. A distribution of oligomer ions ranges from m/z 2000 to 5000, and it appears to be made up of two different ion series: $[\mathrm{HT}_n + 2\mathrm{Br}]^{\bullet+}$ and $[\mathrm{HT}_n + 3\mathrm{Br} - \mathrm{H}]^{\bullet+}$. Again, exact mass MALDI-MS analysis of the lower mass ions in these series extracted by the acetone Soxhlet purification of the polymer product confirms their molecular composition. Using terthiophene as a matrix and the same internal standards as mentioned above, the exact masses of the oligomer ions $[\mathrm{HT}_8 + 2\mathrm{Br}]^{\bullet+}$ (A + 2 isotope) and $[\mathrm{HT}_8 + 3\mathrm{Br} - \mathrm{H}]^{\bullet+}$ (A + 4 isotope) were measured to be m/z 1488.46 (SD = 0.03) and m/z 1568.36 (SD = 0.03), respectively (calculated values are 1488.49 and 1568.40). There were no ion series observed which correspond to poly(3-hexylthiophene) with chlorine atoms.

The MALDI mass spectra of poly(3-hexylthiophene) synthesized by $\mathrm{FeBr_3}$ oxidation clearly show that the resulting polymer has covalently attached bromine atoms rather than chlorine atoms. This result indicates that the oxidizing agent—*not* the chlorinated solvent—is responsible for halogenating the polymer. To our knowledge, $\mathrm{FeBr_3}$ has not been mentioned in the literature as a suitable chemical oxidant for poly(3-

Table 2. Average Molecular Weights and Polydispersities of Poly(3-hexylthiophene)

	M_n	M_w	polydispersity
GPC	49048	70838	1.44
MALDI-MS	5491	6629	1.21

hexylthiophene), possibly because it is not as convenient to use as $FeCl_3$. However, poly(3-hexylthiophene) synthesized with bromine end groups could be useful for Grignard syntheses designed to further functionalize poly(3-hexylthiophene).

The covalent incorporation of one or two chlorine atoms into conjugated, conducting polymers as observed by laser desorption/mass spectrometry has been reported previously for poly(phenylene) synthesized by an oxidative route with $FeCl_3$[34] that is similar to the method we used to synthesize poly(3-hexylthiophene). In that study, the authors pointed out that $FeCl_3$ is known to react easily with carbon radicals and can halogenate aromatic nuclei. We suspect that reactions such as these may be responsible for the halogenation of poly(3-hexylthiophene) that we have observed.

Molecular Weight Analysis. A comparison of the average molecular weights and polydispersities obtained by MALDI-MS and GPC for poly(3-hexylthiophene) synthesized by $FeCl_3$ oxidation reveals that the values obtained by GPC are significantly higher that those obtained by MALDI-MS (Table 2). The number-average molecular weight as measured by MALDI-MS is 5500, whereas GPC yields a number-average molecular weight of 49 000. This trend is consistent with McCullough's study of the MALDI-MS and GPC analysis of poly(3-hexylthiophene) synthesized by a modified Grignard cross-coupling method.[25] As they point out, GPC tends to overestimate the molecular weights of rigid-rod polymers because their intrinsic viscosities are much different than those of the polystyrenes used for calibration in GPC.[35] In addition, MALDI-MS tends to discriminate against the high-mass ions for polymer systems with polydispersities over 1.2 due to desorption/ionization and detection issues.[36–39] Finally, larger discrepancies between the GPC- and MALDI-MS-determined molecular weights may exist for regiorandom polymers vs regioregular polymers. We are currently investigating the degree of high-mass discrimination observed in the MALDI-MS analysis of poly(3-hexylthiophene) synthesized by $FeCl_3$ oxidation.

Conclusions

We have used MALDI-MS to demonstrate that poly(3-hexylthiophene) synthesized by chemical oxidation with $FeCl_3$ consists of two to three different series of ions, each with hexylthiophene repeat groups and containing two or more chlorine atoms. The chlorine atoms originate from the oxidizing agent—*not* the chlorinated solvent—and they may be end groups on α-carbons of terminal thiophenes or substituents on the β-position of thiophene repeats along the polymer backbone. Recognition of the presence of covalently bound chlorine atoms is important because they may have an impact on the physical or electronic properties of the polymer. They should be considered when trying to understand the relationship between polymer structure and properties.

When using dithranol or electron-transfer matrices, the ion series represent radical molecular cations, $M^{\bullet+}$, rather than the protonated molecules or salt adducts that are typically observed in MALDI-MS. Although the difference in mass between the radical molecular cation and protonated molecule is only 1 u, this knowledge has an impact on our ability to identify end groups or structural modifications, particularly when one considers the improved mass accuracy available in the modern generation of pulsed ion extraction and reflectron time-of-flight mass spectrometers.

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Supporting Information Available: ^1H NMR spectrum of the acetone extract of poly(3-hexylthiophene) that was synthesized with $FeCl_3$ and MALDI mass spectrum of the acetone extract of poly(3-hexylthiophene) that was synthesized with $FeBr_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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