Analysis of Polyaniline Oligomers by Laser Desorption Ionization and Solventless MALDI

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While direct laser desorption ionization of soluble polyaniline dried onto metal sample plates results in mass spectra that are similar to previously shown electrospray ionization data of similar samples, laser desorption of unsolubilized solid polyaniline results in major fragmentation of the phenyl rings. Solventless MALDI, a recently developed technique for insoluble or slightly soluble species, involves the use of only solid analyte and matrix during sample preparation. Solventless MALDI of solid polyaniline results in mass spectra that are similar to the direct laser desorption ionization spectra of the soluble oligomers with some larger molecular weight oligomers also being detected. Based on the matrix used, different series of polyaniline with dissimilar end groups are detected. The matrix also affects the percentages of benzenoid and quinoid units in the oligomers. Thus, solventless MALDI appears to be a promising new technique for the mass spectrometric analysis of low solubility, but industrially important, polyanilines. (J Am Soc Mass Spectrom 2004, 15, 893–899) © 2004 American Society for Mass Spectrometry

Matrix assisted laser desorption (MALDI) coupled to time-of-flight (TOF) has become the major method of analyzing synthetic polymers with mass spectrometry [1, 2]. This analytical technique generates a mass spectrum that can give information about repeat units, end groups, and the molecular weight distribution of the polymer [3, 4]. Intact, singly charged gas-phase ions of high molecular weight analytes are generated with this technique when utilizing proper sample preparation methods. The most important aspect of this experiment is the sample preparation process. An appropriate matrix must isolate the analyte molecules and absorb the high intensity laser fluence. There have been many sample preparation techniques for synthetic polymers developed in order to optimize the mass spectral quality [5–7]. In the most commonly employed technique, the "dried droplet method" [8], the polymer is dissolved in a few microliters of a suitable solvent and then diluted with excess matrix solution. Approximately one microliter of this final solution is spotted onto the sample plate and allowed to air dry. One of the major problems with this technique involves sample and matrix solubility and compatibility with each other. In order for them to co-crystallize on the sample plate, they must both be uniformly dissolved in the solvent system. For insoluble or slightly soluble samples, this becomes a major problem that leads to sensitivity, selectivity, and reproducibility issues.

Currently, only a few mass spectrometry techniques are available for the analysis of insoluble samples. Some of these techniques include electron ionization, chemical ionization, field ionization, and direct laser desorption ionization [9–11]. The major drawback with these techniques is the lack of intact molecular ions, especially when there are phenyl rings present along the backbone of the polymer. Other techniques involve the use of chemical modifications in order to make the analyte soluble in a particular solvent [12–14]. However, these modifications are time consuming and alter the molecular structure of the analyte of interest. A recently developed technique, solventless MALDI, has been described which eliminates these problems from a typical experiment [15–19]. Essentially, the sample, the matrix, and the salt are all mixed and ground together with either a mortar and pestle or a ball mill. After the initial grinding, the sample can be further diluted with the matrix to get the appropriate analyte:matrix:salt ratio. The mixture can then be applied to the sample plate using double-sided sticky tape [18, 20], through the use of excess heat on both the sample plate and a spatula [19], a conducting carbon disk [16], as a pressed pellet [15], or through the use of gentle pressure affixing the mixture directly to the plate [17, 20, 21]. Some of the polymers that have been analyzed by this technique include poly(ethylene glycol) [16], poly(9,9-diphenyl-2,7-fluorene) [21], polyamides [15], hydrocarbon oligomers [19], polystyrenes [20], and polymethylmethacrylate [20]. These reports show that the mass spectra that are generated by this technique compare favorably with conventional MALDI prepared mass spectra. This technique also opens the door for a wide variety of new

matrices such as 7,7,8,8-tetracyanoquino-dimethane [17, 20, 21] that were not compatible with soluble samples previously.

Another type of polymer that would be an excellent candidate for the solventless MALDI technique is polyaniline. Polyaniline is one of the most widely studied conducting polymers to date because of its electrical conductivity [22–26]. It consists of both benzenoid and quinoid units throughout the backbone of the polymer. The conductivity of the polymer can be changed through simple acid/base chemistry and the protonation/deprotonation of an amine along the backbone of the polymer. The fully reduced form of polyaniline, leucoemeraldine, consists entirely of benzenoid units, while the fully oxidized form, pernigraniline, is comprised of all quinoid units. The emeraldine base form has an equal number of benzenoid and quinoid units. The conductive form of polyaniline, the emeraldine salt, is the protonated form of the emeraldine base in which the nitrogens on the quinoid units are protonated with the counter-ion from the acid balancing the charge. However, there is still some debate over the exact structural composition of the various oxidation states of polyaniline because of positively charged nitrogens in the emeraldine base form and oxygen being detected in ESCA studies [27, 28]. Some of the uses of polyaniline include rechargeable batteries [29], antistatic materials [30], corrosion protection [31], sensors [32, 33], and recently as a conductive coating for nanospray emitters [34], just to name a few. The major drawback to polyaniline is its insolubility in conventional solvents. This has especially deterred structural analysis by mass spectrometry, as is evidenced by the limited numbers of MS studies of polyaniline [35–43]. Recently, we reported a synthetic procedure for polymerizing low molecular weight oligomers of polyaniline that were slightly soluble in acetonitrile and tetrahydrofuran [44]. This allowed for their detection by electrospray ionization triple quadrupole mass spectrometry, and four different end groups were found to be present on the various types of soluble oligomers.

Here we report the analysis of the same polyaniline using the solventless MALDI technique. We compare and contrast the results with direct laser desorption ionization of soluble samples, both in the presence and absence of acid. The utilization of various matrices will be shown in order to analyze the various end groups that are detected by each, as well as the number of quinoid units present in each oligomer. Comparison will also be made to direct laser desorption of finely ground solid polyaniline without the presence of any matrix material.

Experimental

Reagents

Aniline was purchased from Fisher Scientific Co. (Fair Lawn, NJ) and was distilled prior to use. Ammonium persulfate, ammonium hydroxide, tetrahydrofuran (THF), and glacial acetic acid (GAA) were purchased from J. T. Baker Chemical Co. (Phillipsburg, NJ), acetonitrile (ACN) was purchased from Aldrich (Milwaukee, WI) and was of HPLC grade, while hydrochloric acid was also obtained from Fisher Scientific Co. The matrices gentisic acid (2,5-dihydroxybenzoic acid) (DHB) and dithranol (1,8-dihydroxy-9[10H]-anthracenone) were both purchased from Sigma (St. Louis, MO) while 7,7,8,8-tetracyano-quinodimethane (TCNQ) was purchased from Aldrich. The MALDI-TOF peptide mass calibrants, angiotensin II and gramacidin D, were both purchased from Sigma as well. All solvents and chemicals were used as received unless otherwise stated, and aqueous solutions were prepared using doubly distilled-deionized water.

Sample Preparation

The synthesis of polyaniline was the same as previously described [44]. This method of synthesis was a procedure adopted from Chiang et al. [45] in order to optimize the generation of low molecular weight oligomers of polyaniline. For the direct laser desorption experiments, 5 mg of polyaniline was dissolved in either acetonitrile or tetrahydrofuran. After 10 min, the samples were centrifuged and the solid polyaniline that had not dissolved was decanted off. This procedure only analyzes the soluble, low molecular weight oligomers of polyaniline, since the higher molecular weight oligomers did not dissolve in solution and were discarded prior to analysis. In some samples, glacial acetic acid was added in order to change the oxidation state of the polymer. In these cases, two percent acid by volume was added to the solution. The samples were then directly spotted onto the sample plate and allowed to air dry.

For solventless MALDI, samples were all prepared in a similar manner as that previously reported [17, 20, 21]. Polyaniline and matrix (either DHB, dithranol, or TCNQ) were mixed and ground in a mortar with a pestle for 15 min in order to reduce the size of the polyaniline particles. A molar ratio of analyte to matrix of 1:50 was used (assuming a molecular weight of 1000 Da for polyaniline, as calculated from previous studies on these samples [44]) with approximately 2 mg of polyaniline being used for each sample. In order to adhere the ground sample to the plate, approximately 0.5 mg of the sample was spread out over several spots on the plate, giving a minimal amount of surface coverage. Gentle pressure was applied to the top of the polyaniline in order to compress the solid with a spatula that was slowly slid across the plate. Excess solid was then blown off of the sample plate with a gentle stream of air to avoid contamination prior to insertion of the sample stage in the mass spectrometer. These resulting sample "films" were kept very thin in order to prevent any calibration errors and losses in sensitivity. For the direct laser desorption of solid
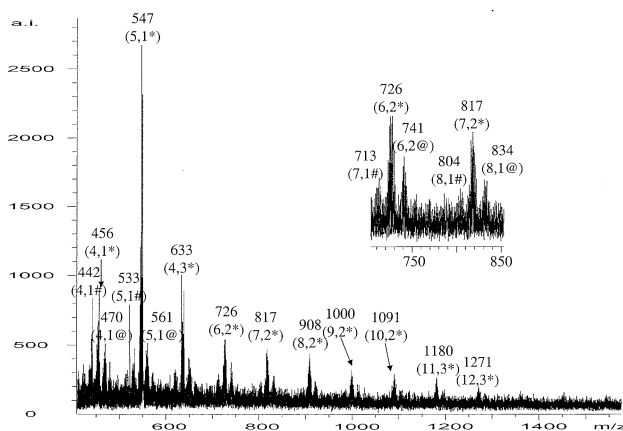
Figure 1. A direct laser desorption ionization mass spectrum of polyaniline that is soluble in THF. This spectrum contains three different end groups on the oligomeric chains, containing chiefly one or two quinoid units per oligomer. The inset of this figure contains an expanded region of the spectrum showing the presence of these different end groups around the 8-mer and 9-mer.
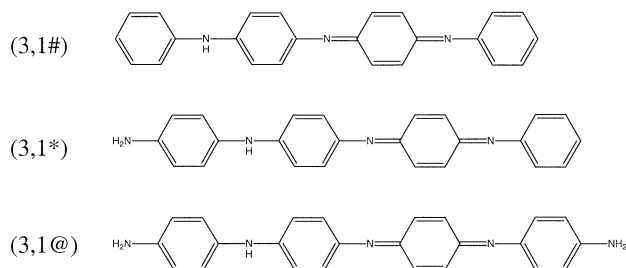

Figure 2. Structures for the three different types of end groups on polyaniline that are shown in the accompanying figures. The first is designated with the (number) symbol which corresponds to polyaniline which is terminated by a phenyl group on both ends. The second set contains equal numbers of six-membered rings and nitrogen containing groups and is given the (asterisk) symbol. The third series is given the (at) symbol, which contains an additional nitrogen containing group. All of these structures contain one quinoid unit as is designated by the number preceding the symbol. The sum of the two numbers in parentheses indicates the degree of polymerization.

polyaniline, the same procedure was used except that no matrix was added to the mortar and pestle prior to grinding the sample.

Mass Spectrometry

All LD-TOF and MALDI-TOF spectra were acquired on a commercially available Bruker Biflex IV (Billerica, MA) MALDI mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). The analyzer was operated in the reflectron mode with a mass range of 100–5000 m/z. External calibration was performed prior to the experiments using a one or two point calibration utilizing angiotensin II and/or gramicidin D. The laser fluence was kept at a value of 50–60 percent depending on the minimal percentage necessary for the generation of signal. All spectra were generated with an acceleration voltage of 19 kV and were the average of 200 laser shots. Data acquisition was done using the Flex Control program, while data processing was performed with Bruker's XTOF software.

Results and Discussion

A direct laser desorption ionization spectrum of synthetic polyaniline soluble in tetrahydrofuran (THF), is shown in Figure 1. Oligomers up through the 15-mer are capable of dissolving in the solution and being detected. The ions that are generated are the result of either protonation of one of the nitrogens in the backbone of the oligomer, resulting in a quaternary nitrogen, or the formation of a radical cation. Due to the low mass resolution obtained by this technique, we are currently unable to determine which type of ions are actually generated. Unlike other laser desorption ionization MS experiments of polymers [2, 46], polyaniline does not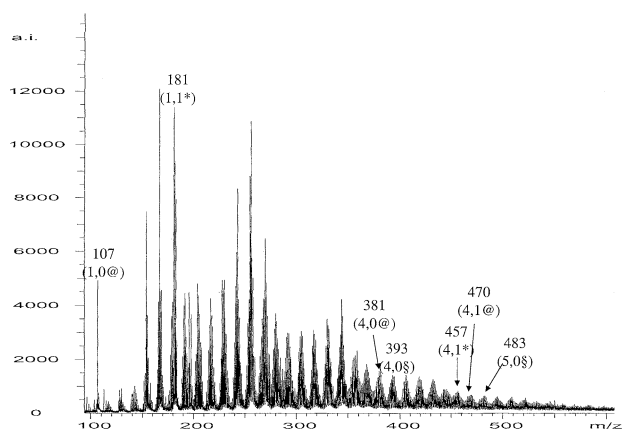 need an alkali metal present to covalently cationize the analyte, because of the presence of the amine groups in the backbone of the polymer. Each of the oligomers is present in the form of three series of ions in the mass spectrum. The two peaks that are present both 15 Da higher and lower than the main distribution are the result of different end groups on the oligomeric chain. These other products are the direct result of the synthetic procedure, and have been reported elsewhere [36, 38, 42, 44]. The general structures for the oligomers are shown in Figure 2. These general structures are representative of the higher molecular weight oligomers in the spectra shown and are only shown as a demonstration of the terminology used to designate the various types of oligomers. The lower mass oligomer is the result of a loss of the terminal amine group, leaving the oligomer terminated by two phenyl groups. This series of oligomers is designated as the symbol (#) preceeded by two numbers in brackets. The first number within a bracket represents the number of phenyl groups, while the second represents the number of quinoid units. A quinoid unit consists of one nitrogen atom involved in a double-bond to a six-membered ring. The main distribution of oligomers, or the most intense species for each set of oligomers, corresponds to an equal number of backbone nitrogen atoms and six-membered rings in the backbone of the oligomer. This distribution is given the (*) symbol. The third series, identified with the (@) symbol, represents oligomers which have an additional amine group present at the terminus of the chain. This series results in oligomeric chains that are terminated at both ends by an amine group. The inset in Figure 1 shows an expanded region of the spectrum showing these distributions. The laser desorption spectrum of THF-soluble polyaniline contains oligomers that predominantly contain only one set of quinoid units, for the low molecular weight oligomers. As the mass of the oligomers increases, the number of quinoid units also increases, up
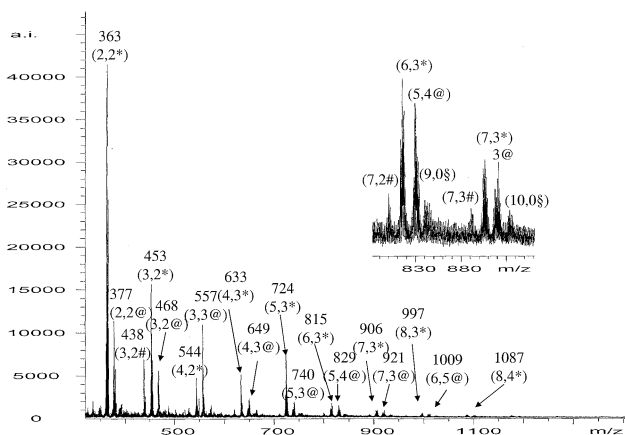
Figure 3. A direct laser desorption ionization mass spectrum of polyaniline that was dissolved in a 98:2 acetonitrile:glacial acetic acid solution. This spectrum shows the appearance of an additional end group (section symbol) that is a result of fragmentation of a terminal phenyl group. Also, as the molecular weight increases, the number of quinoid units in the chain also increases. The inset shows an expanded region around the 9-mer and 10-mer showing that all four of the series are present.

Figure 4. A direct laser desorption ionization mass spectrum of finely ground polyaniline affixed to the sample plate. This mass spectrum contains many fragment ions which are separated from one another by 12–13 Da, many of which are relatively low mass fragments. There are only a few matching oligomers with conventional forms of polyaniline; however, the vinyl terminated series (section symbol) from Figure 3 is also observed in this mass spectrum.

to three for the highest molecular weight oligomers detected. Nonetheless, the isotope distributions are complex, suggesting that in addition to the different oxidation states of polyaniline, hydrogen losses or formation of odd-electron radical cations may also be contributing to the observed mass spectra. By dissolving the same polyaniline in a solution of 98/2 (vol/vol) acetonitrile:glacial acetic acid, a slightly different mass spectrum is obtained. A fourth set of oligomers are observed in the spectrum, as shown in Figure 3. The three distributions that were observed in the mass spectrum of polyaniline dissolved in THF are also observed in the mass spectrum of polyaniline dissolved in ACN, with the (*) series being the most intense of the oligomers. The new series is 26 Da higher in molecular weight than the main series, and is designated by the (§) symbol. This series has been tentatively given the assignment of an oligomeric chain that is terminated by a vinyl group; these oligomers also only contain phenyl groups but no presence of quinoids.

It is important to recognize that some of the oligomeric ions observed in the direct laser desorption ionization mass spectra could be generated through the fragmentation of the terminal phenyl ring upon laser desorption. Such types of fragmentations are the reasons for performing MALDI analysis so that the matrix absorbs the laser fluence (and the analyte molecules do not) resulting in much reduced fragmentation. This series and the (#) symbol series both give relatively weak intensity signals, but they are still present throughout the spectrum as can be seen in the inset of Figure 3, showing an expanded view of the 9-mer and 10-mer of polyaniline. Another interesting aspect of this mass spectrum is that even though there are more protons present in this sample solution because of the presence of acetic acid in the ACN solution, the number

of quinoid units is not less than those present in the THF spectrum. In fact, as the molecular weight increases, the number of quinoid units also increases. For this sample, the number of quinoid units ranges from zero to five, depending on the molecular weight of the oligomer.

Instead of performing an initial MALDI experiment, the polyaniline alone was finely ground in order to reduce the particle size. The direct laser desorption of this sample when affixed to the sample plate using slight pressure is shown in Figure 4. Only extremely low molecular weight oligomers and fragments are present below 600 m/z. There appears to be a peak at just about every mass-to-charge unit, with a predominant series every 12–13 Da. These peaks are the result of absorption of the laser fluence by the phenyl rings in the oligomers followed by fragmentation that leads to the loss of individual carbon atoms. The first mass spectrometric analysis of polyaniline by Brown et al. in 1988 resulted in a mass spectrum which had a similar appearance [35]. There are some oligomers that correspond to intact polyaniline oligomers generally of the (@) symbol series. This could be the result of the terminal amine groups minimizing or inhibiting fragmentation of the oligomers. However, the majority of the major peaks cannot be assigned to conventional forms of polyaniline. The (§) fragmentation series that was evident in Figure 3, can also be detected in the laser desorption of the solid polyaniline, thus showing that indeed fragmentation is occurring in all of these types of laser desorption experiments. Thus, in order to obtain intact ions without the extensive fragmentation exhibited by direct laser desorption ionization, the solventless MALDI technique was then performed as a means of confirming whether or not the end groups
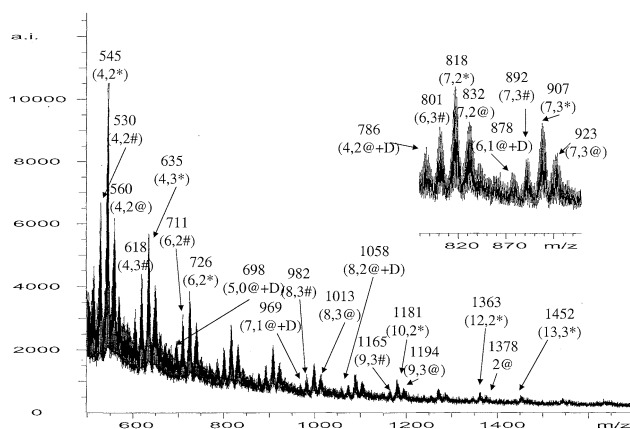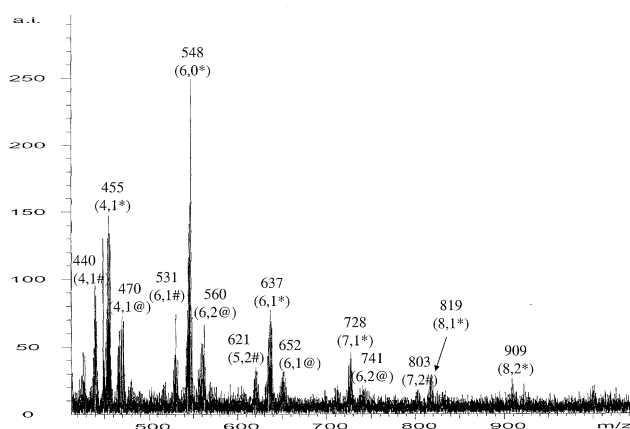
Figure 5. A solventless MALDI spectrum of polyaniline in a 1:50 molar ratio with dithranol. The spectrum contains the three different end groups along with dithranol adducts, which are symbolized as the oligomer + D. These oligomers contain either two or three quinoid units each. The inset shows all four of the series of oligomers for the 8-mer and 9-mer of polyaniline.

Figure 6. A solventless MALDI spectrum of polyaniline in a 1:50 molar ratio with DHB. This spectrum is less intense than Figure 4 but contains the same types of end groups with mostly one set of quinoid units per oligomer.

present are the result of synthesis, and not the result of fragmentation following the ionization process.

A solventless MALDI spectrum of polyaniline and dithranol is shown in Figure 5. This spectrum shows all three of the original end groups up through 1400 Da, with the (*) distribution still being the most prominent series. There is also another distribution present in this mass spectrum that is not the result of fragmentation of the backbone of the oligomers. In fact, these ions are shifted 226 Da higher than the (@) series, which corresponds to the molecular weight of dithranol. Thus, these ions are designated in the spectrum as @ + D, in order to symbolize the adduction of the dithranol unit. For the remaining sets of oligomers in the mass spectrum, the number of quinoid units is either two or three depending on the molecular weight range of interest. The oligomers less than 900 Da mostly contain two quinoid units, while higher molecular weight oligomers contain three. In the inset of this figure, it can be noted that there are four distinctly different types of oligomers for both the 8-mer and the 9-mer. The presence of all of these oligomers, and the lack of the (§) series, shows that the solventless MALDI approach to analyzing polyaniline is an ideal method for analyzing this slightly soluble polymer. Except for the presence of the adduct groups, this mass spectrum is very similar to the mass spectrum of the polyaniline that is dissolved in THF and is shown in Figure 1.

Another matrix dihydroxybenzoic acid (DHB), or gentistic acid, was also tested as a solventless MALDI matrix. The resulting spectrum is shown in Figure 6. This mass spectrum is much weaker in intensity than the other mass spectra recorded for polyaniline. However, the main peaks are still present up through 900 Da, corresponding to all three of the intact series discussed previously. The interesting aspect of this mass spectrum is that the main peaks all predominantly

contain only one quinoid unit. Since this matrix is more acidic than dithranol, the presence of the gentisic acid will shift the oxidation state of the oligomers to more reduced states, corresponding to fewer quinoid units. This is the opposite effect that was seen with the direct laser desorption of the 98/2 acetonitrile:glacial acetic acid sample which is shown in Figure 3. The same polyaniline solid was used for each of the two solventless MALDI experiments, so any differences in their mass spectra are the result of different matrix-polyaniline interactions. Even though the analyte and the matrix are not dissolved together and then recrystallized onto the sample plate, they do indeed interact with each other as is evident by the shift in the number of quinoid units between the two mass spectra.

After noticing the interaction between polyaniline and the matrix, 7,7,8,8-tetracyano-quinodimethane (TCNQ), another matrix that has been utilized previously for solventless MALDI [17, 20, 21], was acquired. This matrix was used because of the notion that TCNQ is an electron acceptor, and thus would scavenge any radicals that are produced. This might simplify the spectra of the radical cations and only generate protonated species. Indeed, this is the case as is evident is Figure 7. This mass spectrum consists of only doublets that correspond to the two series (*) and (@). There are no oligomers that are doubly-terminated by phenyl groups; such ions are generally formed as radical cations. Like the other solventless MALDI spectra, there is no fragmentation of the oligomers. Apparently TCNQ does not form any adducts with the polyaniline oligomers, as can be seen in the inset of this figure showing an expanded region around the higher molecular weight oligomers. In fact, this matrix detected the highest molecular weight oligomers of polyaniline—up through 1700 Da. The number of quinoid units per oligomer ranged from two to four depending on the molecular weight. Oligomers lower than 1100 Da contained on average two quinoid units while the higher molecular weight oligomers contained three or four.
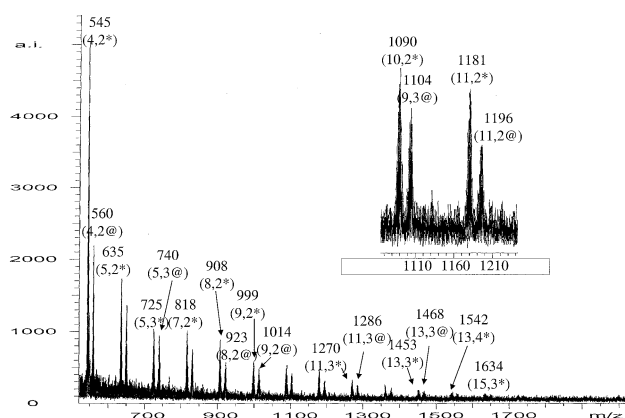
Figure 7. A solventless MALDI spectrum of polyaniline in a 1:50 molar ratio with TCNQ. This spectrum contains only two different series of polyaniline with differing end groups. The series of polyaniline oligomers doubly-terminated by phenyl groups have been suppressed by the matrix. Also, the highest molecular weight polyaniline oligomers are detected using this matrix. The inset is an expanded region around the 12-mer and 13-mer showing the presence of only two series of different end groups.

Conclusions

Regular laser desorption ionization of the soluble species gives similar spectra to those previously reported with varying end groups present on the oligomers. However, direct laser desorption ionization of just the solid polyaniline results in extensive phenyl ring fragmentation, leading to virtually uninterpretable mass spectra. With the addition of a matrix material, the solventless MALDI system produces mass spectra that are similar to the direct laser desorption mass spectra of the soluble samples. These MALDI spectra result in the detection of higher molecular weight oligomers of polyaniline than that which is detected with the direct laser desorption approach. The spectral output in terms of various end groups that are detected is influenced by the nature of the matrix that is utilized. With DHB and dithranol, all three different types of end groups are detected, while with TCNQ, only two of the end groups are present in the mass spectrum. Also, the number of quinoid units in the oligomeric chains is affected by the presence of the matrix.

Acknowledgments

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