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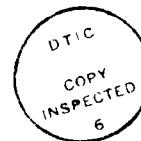
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"FAST ATOM BOMBARDMENT MASS SPECTROMETRIC
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by

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in press

Fast Atom Bombardment Mass Spectrometric Characterization of Poly(*o*-toluidine)^a

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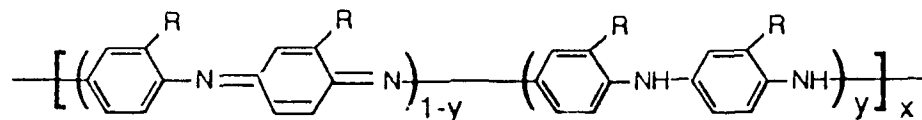
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ABSTRACT

Fast atom bombardment (FAB) mass spectrometry has been used to analyze chemically prepared and fractionated poly(*o*-toluidine) of low molecular weight ($m/z < 5800$) to evaluate its potential for the characterization of polymers of similar structure. In the lower mass range (m/z 400-1800) ionic species detected are separated by the mass of a toluidine monomer unit ($m/z = 105$). An interesting feature of the mass spectra is the observation that the apparent main component of poly(*o*-toluidine) contains one oxygen atom per chain. This is further confirmed by MS/MS analysis of selected ions. Several possible reasons for the presence of oxygen in the polymer are discussed. All results support the proposed structure of the polymer and demonstrate that FAB-MS can provide detailed structural information on the electrically conductive poly(*o*-toluidine) and related compounds.

Introduction

Polyaniline and alkyl ring-substituted polyanilines have been extensively investigated recently because of their moderately high electrical conductivity on doping with nonoxidizing Brönsted acids¹⁻³. These polymers, which can be synthesized by chemical or electrochemical oxidation of aniline or ring substituted anilines, possess interesting electrochemical behavior⁴⁻⁵ as well as environmental stability. Polyaniline is one of the first conductive polymers to be commercialized and it is now used as the electrode material in rechargeable batteries⁶. Techniques have also been reported to process films and fibers of polyanilines with relatively high conductivity and enhanced mechanical properties⁷. Numerous potential commercial applications of polyanilines and other conductive polymers are discussed in detail in recent articles⁸. The proposed structure of the base form of polyaniline and alkyl ring-substituted anilines can be schematically represented by the following general formula:



where R=H for polyaniline and R= CH₃ for poly(*o*-toluidine); the value of *y* represents the oxidation state of the polymers². The polymers are completely oxidized when *y* = 0 or completely reduced when *y* = 1. The "emeraldine" oxidation state (*y* = 0.5) consists of an equal number of reduced and oxidized units.

Most of the properties of polymers depend on their chemical structure, molecular weight, and molecular weight distribution⁹⁻¹⁰. In general, characterization of the conductive polymers is a rather difficult task because many of these polymer materials are insoluble in common organic solvents and may be sensitive to air, radiation, and heat. Thus, there is a great need for suitable techniques to determine the molecular weight and molecular weight distribution

along with other structural information to facilitate understanding the electrical properties of these polymers.

There are many conventional techniques used for molecular weight determination¹¹. Among them, gel permeation chromatography (GPC) and viscometry are widely used. However, most of these conventional techniques do not provide accurate molecular weight information. For example, the accuracy of the determination of molecular weights by GPC is severely limited by the availability of suitable calibration standards, which must be structurally similar to those polymers of unknown molecular weight¹².

Mass spectrometry has become a viable technique for determining the molecular weight distribution and chemical structure of polymers with minimal sample preparation. Various mass spectrometric techniques such as field desorption (FD)¹³, laser desorption (LD)¹⁴⁻¹⁵, fast atom bombardment (FAB)¹⁶, electrohydrodynamic ionization (EH)¹⁷ and secondary ionization mass spectrometry (SIMS)¹⁸ have been used with varying degrees of effectiveness. Attempts have been reported for the characterization of polyaniline and ring-substituted polyanilines using FD¹⁹, laser desorption Fourier-Transform mass spectrometry (LD/FTMS)²⁰ and SIMS²¹. Unfortunately, both LD/FTMS²⁰ and FDMS¹⁹ provided little information on the chemical structure these polymers. In SIMS, the highest ion mass detected in the negative ion spectrum of polyaniline contained only two monomer (aniline) units; no direct information on polymer chain structure was obtained from the positive ion spectrum²¹.

In the present work, FAB-MS is used to analyze poly(*o*-toluidine) of low molecular weight ($m/z < 5800$) to evaluate its potential for the characterization of electrically conductive polymers of similar structure. Poly(*o*-toluidine) used in this work was synthesized by chemical oxidation of toluidine, followed by extraction with acetonitrile. The polymer was also characterized by GPC and

elemental analysis. The FAB-MS results obtained are interesting, showing oligomer ions in the mass range of $m/z = 400-2000$; only matrix ions are observed below $m/z = 400$. Ionic species detected in the mass range of $m/z = 400-1800$, are separated by the mass of a toluidine monomer ($m/z = 105$).

Experimental

Synthesis and Chemical Characterization

Poly(*o*-toluidine) was synthesized by chemical oxidation of the monomer in an acidic (1.0 M HCl) aqueous solution using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant (0.25 molar ratio to monomer). It was then converted to its base form by treating with an excess amount of 0.1 M aqueous ammonia solution, based on previously reported procedures². Elemental analysis of the polymer sample showed it to consist of C: 80.0%, H: 6.4%, and N: 13.2%, adding to a total analysis of 99.6%. Taking the accuracy (± 0.2 % for carbon) of the elemental analysis into account, these results are consistent with the empirical formula of the emeraldine base form of poly(*o*-toluidine): $[\text{C}_{14}\text{N}_2\text{H}_{13}]$ with calculated values of C: 80.35%, H: 6.26%, and N:13.39%.

Extraction of the crude poly(*o*-toluidine) product was carried out on a Soxhlet extractor using acetonitrile as solvent for 48 hr. The soluble portion (POTI) of the polymer was recovered (7.1% by weight) by rotatory evaporation of the acetonitrile solvent. Elemental analyses of this soluble fraction gave C: 80.6%, H: 6.2%, N:13.4%, which again agrees with the empirical formula of the emeraldine base form of poly(*o*-toluidine). The residue retrieved after this extraction (POTII) and the original product were also analyzed by mass spectrometry.

Gel-permeation chromatography was performed on a Waters GPC Model IIA equipped with a Model 590 programmable solvent delivery module, a differential refractometer detector (Waters 410), and a Ultrastyrigel linear THF-packed column. For a typical procedure, 50 mg of poly(*o*-toluidine) base was dissolved in 25 mL of

1-methyl-2-pyrrolidinone (NMP, HPLC grade from Aldrich) followed by filtering through a 0.5 mm teflon filter. Temperatures of both the GPC column and detector were kept at 35°C. NMP was used as the eluent at a flow rate of 1.0 mL/min. The chromatogram of the polymer in NMP showed a bimodal elution pattern¹². With polystyrene calibration, the number average molecular weight (M_N) of the lower molecular weight fraction of poly(o-toluidine) before the extraction was ca. 5800, with a polydispersity of 2.1. For the poly(o-toluidine) recovered from acetonitrile extracts, molecular weight was ca. 1600, with a polydispersity of 2.3.

Mass spectrometry

All FAB mass spectra were recorded on a Finnigan TSQ70 triple quadrupole mass spectrometer at Sterling Research Group, Malvern, PA, equipped with a continuous-flow FAB ionization source and 20kV conversion dynode electron multiplier detection system from Finnigan MAT. The conversion dynode was set to 10kV during both the MS and MS/MS analyses. Mass calibration of both Q1 and Q3 was performed using cesium iodide clusters to 4000 daltons.

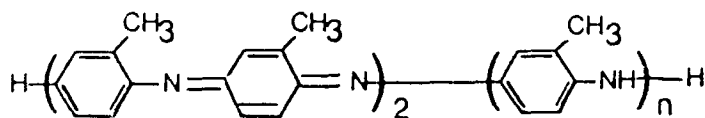
Samples for analysis were prepared by adding a minimum volume of NMP solvent to solubilize a small granule of polymer sample. All samples were prepared just prior to mass spectral analysis. Approximately 1 μ l of solubilized polymer was added to 2 μ l of either glycerol (Aldrich)/5% acetic acid (Baker) or (1:1) glycerol/thioglycerol matrix (v/v) and mixed directly on a copper FAB target. The resulting mixture was then subjected to FAB analysis using a FAB11NF Saddle Field Fast Atom Bombardment Source (Ion Tech Limited, Teddington, England). The FAB source was operated at 0.35mA ion current, 1.0mA current with an 8kV output using Xenon gas (Cryogenic Rare Gases) as the source of high energy atoms. Single quadrupole mass spectra were typically obtained on Q3, in the positive ion scanning mode, from 100 daltons to 3000 daltons with a quadrupole scan rate of approximately 1second/1000daltons. Spectral addition was typically performed on all data collected

(usually the first 10 to 15 scans) and these summed scans are presented.

MS/MS collisionally activated dissociation (CAD) was performed by filling Q2 with Xenon gas to a pressure of 1-4 mtorr operated in the rf only mode. Daughter ion experiments were performed, in the positive ion scanning mode, on $m/z = 747$ with a collision cell offset voltage of -20v and a daughter quadrupole offset voltage of -30 or -40v. The parent ion $m/z = 747$ was allowed to pass unimpeded to optimize ion transmission before pressurizing the collision cell. Daughter ion mass data was collected and summed scans are presented.

Results and Discussion:

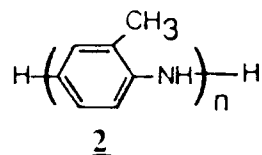
The positive ion FAB mass spectrum of POTI is shown in Figure 1. Molecular oligomer ions in the partially oxidized¹³ form (containing imine double bonds), 1, are observed in the mass range of m/z 500-1300. This is not surprising since this is the main product expected from the synthesis¹⁹. Note that the distribution sequence of imine double bonds within the polymer chain may vary depending on the chain length and the stability of the isomer. The ion mass of the highest intensity contains seven monomer units ($n=3$) in this series. If one assumes equal probability of ionization, no volatility or solubility discrimination for all oligomers, and no fragmentation during the FAB analysis, then it is fair to say from the observed results that the major component of this oligomer series has seven monomer units.



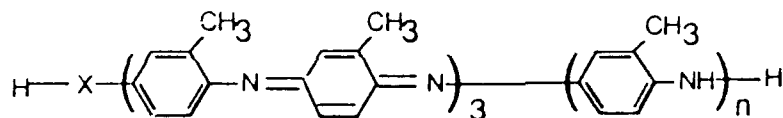
1, where $n=2-8$ and $m/z=628-1259$ (Figure 1).

However, no oligomers having less than 5 monomer units were observed. The mass difference between two adjacent peaks corresponds to $m/z=105$, indicating that the polymer backbone is

composed solely of toluidine repeat units. It is also important to note that no ions corresponding to the fully reduced (no imine double bonds) form of the polymer **2**, was observed for this sample.



An interesting feature of the spectrum shown in Figure 1 is the observation of ions of a polymer series, like **1**, in which an oligomer is either fifteen or sixteen mass units higher than that of the corresponding **1**. The following discussion and additional evidence from collisionally activated dissociation mass spectrometric analysis (see below) of some selected ions indicate that this polymer series has the following structure, **3**, containing either an oxygen atom or an additional -NH- group per oligomer.

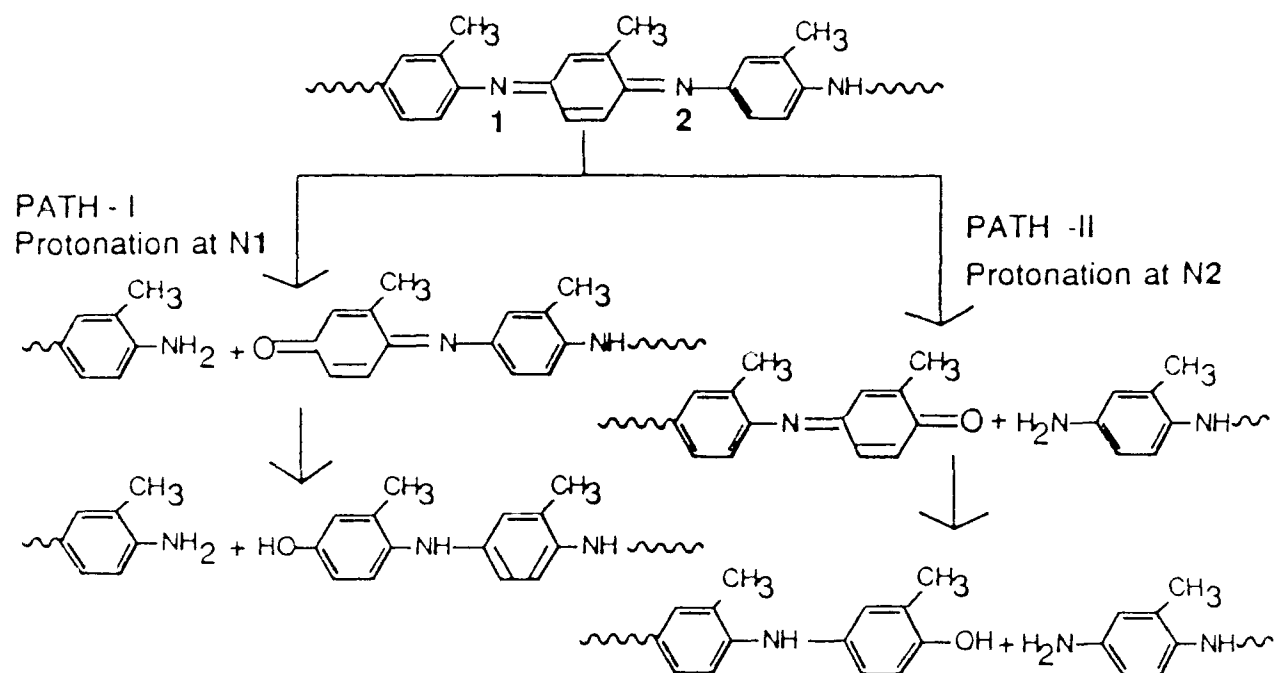


3 where X = O or -NH-, n=1-10 and m/z=747-1692 (Figure 1).

The relative intensity of the ions from **3** are higher (at least 2-3 times) than those from **1**. The above observation may or may not mean that the major component of the polymer sample is **3** for the following reason. The only structural difference between these oligomers (**1** and **3**) is the presence of an oxygen atom or an additional -NH- group in **3**. Therefore, it is possible that there is a difference in surface activity of the polymer with structure **3**, i.e., the oligomer **3** may be preferentially desorbed from the FAB matrix because of its higher surfactant properties. The measurement of such a difference in surface activity is not possible using our experimental facilities. Thus caution should be exercised in trying to use these data for any semi-quantitative purposes. Also note that the oligomers are partially oxidized, each having three pairs of imine double bonds (see

the structure **3**). The ion with the highest relative intensity corresponds to $n=1$ (i.e., it is composed of seven monomer units).

There are many possibilities by which an oxygen atom can be introduced into poly(*o*-toluidine). Imine double bonds are labile and can undergo hydrolysis in an acid medium. As the poly(*o*-toluidine) synthesis was carried out in 1 M HCl aqueous solution, it is possible that an oxygen is introduced into the oligomer by this hydrolysis process during the synthesis. This hydrolysis, as described below in Scheme I, may lead to an oligomer having either an oxygen (path I) atom or an additional -NH- group (path II) depending on the protonation site. This type of hydrolysis in an acid medium has already been reported for polyaniline²² with the detection of quinone as a byproduct. It is also interesting to note that an oligomer series having an additional -NH- group is one of the end products from the hydrolysis processes proposed by the same workers²². The presence of oxygen in polyaniline was also detected by X-ray photoelectron spectroscopy²³ and hydrolysis has been suggested for the production of the same. The mass spectrometric results obtained for poly(*o*-toluidine) presented here tend to support the hydrolysis processes reported, i.e., a polymer series (one like **1**) containing either an oxygen atom or an additional -NH- group per oligomer (**3**). This is the first mass spectrometric report to confirm the presence of such an oxygen atom or an additional -NH- group in a polyaniline analog, probably introduced by hydrolysis during the synthesis.



Scheme I

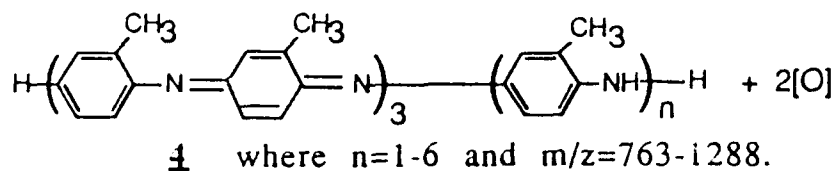
The polytoluidine was synthesized using an oxidizing agent, ammonium persulfate, in an open atmospheric environment. Thus oxidative processes involving either ammonium persulfate or aerial oxygen may have led to the insertion of an oxygen atom into the poly(*o*-toluidine). However, such processes can neither be confirmed or ruled out based upon our experiment results.

One other possibility is that the oxygen atom may be introduced by hydrolysis of the imine bonds during the FAB-MS analysis. If that is true, then one would expect a varying amount of imine double bonds per oligomer as a result of random process of hydrolysis influenced by kinetic effects, the extent of hydrolysis, and the stability of the end products. However, exactly three pairs of imine double bonds per oligomer (in the mass range of $m/z = 400-1800$) are detected for this series, supporting the supposition that there is no hydrolysis of imine double bonds occurring during FAB analysis. Furthermore, if random hydrolysis occurs during the FAB analysis, the reproducibility of the FAB spectra should also be affected

because the time taken for sample preparation and the mass spectral data acquisition were not kept constant, i.e., the relative intensity of the oligomer ions as well as the number of imine double bonds per oligomer should vary due to random hydrolysis from spectrum to spectrum for the same sample. No such irregularities were observed. The reproducibility of the spectrum was found to be excellent with respect to intensity and the number of imine double bonds present per oligomer. Thus these arguments indicate that the occurrence of hydrolysis of imine double bonds during FAB analysis is unlikely for this polymer sample.

The above discussion tends to support the hypothesis that the oxygen atom/-NH- group is most probably introduced by hydrolysis occurring during the synthesis. It is difficult to obtain any evidence for the presence of oxygen from the elemental analysis because of its lower percentage (which varies from 2.1-0.9 % over $n=7-16$ for structure **3**) compared to the other elements. The detection of the presence of an additional -NH- group using elemental analysis is also unlikely for the same reason, i.e., the increase in the percentage of nitrogen due to this additional -NH- group is too small to be detected.

In addition to the ionic species discussed above, expansion of the mass scale indicates that there are two more oligomer series present; one arises due to loss of methyl group from **3** and the other may have the following structure **4** with two oxygen atoms.

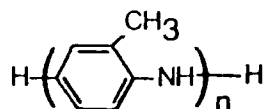


However, the intensities of the ions from **4** are extremely low with a signal to noise ratio of 1.5, limiting further experiments to confirm its structure and the location of the two oxygen atoms in the polymer chain.

The collisionally activated dissociation (CAD) spectrum of an oligomer ion ($m/z = 747$ from the sample POTI) having the structure **3** is shown in Figure 2. There are many resonance structures possible for this oligomer with its imine double bonds at various positions²¹. The ionic species observed in the mass spectrum can be rationalized by all possible fragmentation paths of the parent ion from these resonance structures. Three such resonance structures for parent ions with possible fragmentation paths are shown in Scheme II. Ion masses arising due to successive loss of methane are given in the parentheses. One should also be aware of the fact that the loss of methyl radicals are equally possible and in fact, they are observed. Comparison of the CAD spectrum (Figure 2) with that of the sequential fragmentation (Scheme II) paths indicate that the proposed structure **3** for $m/z = 747$ with an oxygen atom/-NH- group present is in excellent agreement with the CAD spectrum. For example, ion masses at $m/z = 106, 121, 209, 314, 327, 417, 522, 536, 625, 640, 730$ and 731 can be rationalized as peaks resulted from the sequential fragmentation of the parent ions with various resonance structures (Figure 2, and Scheme II). The rest of the ions observed probably arise from the successive loss of either methane or methyl radicals from the species by sequential fragmentation. Ions detected at $m/z = 195, 283, 297, 311, 401, 416, 491, 505, 519$, and 609 (Figure 2 and Scheme II) are some of those expected due to loss of either methane or methyl radicals. The presence of imine double bonds are evident by the detection of ions at $m/z = 209, 224, 327, 432, 535$ and 640 which can only be rationalized with the association of these double bonds (Scheme II). A mass difference of either fifteen or sixteen between adjacent peaks [e.g., $m/z = (535, 519), (535, 520)$ in Figure 2] shows evidence for the presence of a methyl group. Loss of sixteen mass units may also indicate the presence of an -NH₂ group (e.g. $m/z = 747$ and 731). The peaks at $m/z = 747$ and 746 tend to support the proposed structure with the oxygen atom, since these peaks can not be rationalized without its presence. Alternatively, the same masses at $m/z = 747$ and 746 can be rationalized as the oligomer ion having an additional -NH- group with/without protonation; one would need high resolution mass spectral data from

a magnetic sector or Fourier-Transform instrument to distinguish the presence of an oxygen atom from that of a -NH- group. However, the CAD spectrum of $m/z = 747$ supports the presence of either one of them or both and provides a fair amount of evidence for the proposed structure **3** for the ion at $m/z=747$. The CAD mass spectrum of the selected ion at $m/z = 852$, which has one more monomer unit than that of $m/z = 747$, was also obtained. Comparison of the CAD mass spectra of ions at $m/z = 747$ and 852 indicate that the ions detected below $m/z = 747$ are identical, again supporting the proposed structure **3**.

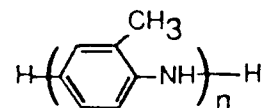
The reproducibility of the synthetic processes was checked by obtaining the positive ion FAB spectrum of a different batch of poly(*o*-toluidine) synthesized and fractionated under identical conditions. This spectrum is shown in Figure 3. All of the ionic species detected for the earlier sample (see the discussion above) are observed over the same mass range. The only difference observed was the detection of protonated molecular ions of poly(*o*-toluidine) in the fully reduced form **2**.



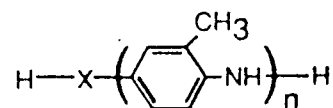
2 where $n=4-9$ and $m/z=423-948$ (Figure 3).

The intensities of these ions are much smaller than those arising from **3**; the intensities of the same may have been too low to be detected in the case of earlier sample. As the reproducibility of the mass spectrum is excellent these minor differences may be attributed to any unintended variation in the experimental operation during the synthetic processes. Thus it is important that one should exercise caution when comparing the spectra of two batches of samples synthesized under supposedly identical conditions.

The following series of oligomers **2** and **5** are detected for POTII in the positive ion FAB mass spectrum over the mass range of $m/z=500-2000$.



2 where $n=4-11$ and $m/z=423-1157$.



5 where $\text{X} = \text{O}$ or $-\text{NH}-$, $n=4-17$ and $m/z=431-1806$.

Both oligomer series are in the fully reduced form (no imine double bonds) and the ions with the highest relative intensities occur around $n=7-8$. The relative intensities of oligomer from **5** are higher than those of **2**, an observation which is similar to that made for POTI. In addition, the mass difference between two adjacent peaks corresponds to the mass of a toluidine monomer unit ($m/z=105$). The only difference in this case, compared to the spectrum of POTI, is the absence of peaks arising from the oligomer series **1** and **3**, which are the partially oxidized form (having imine double bonds) of **2** and **5**, respectively. Thus, it suggests that the partially oxidized form of the polymers of low mass ($m/z = 400-2000$) could be preferentially extracted into acetonitrile. The reasons for this process, i.e., the extraction of only the oxidized form into acetonitrile, is not clear. However, the results confirm again that the main portion of the lower mass polymers contains an oxygen atom/ $-\text{NH}-$ per oligomer, assuming that there is no preferential desorption.

The positive ion FAB mass spectrum of the original product is shown in Figure 4 over the mass range of $m/z = 500-1500$. Ionic species observed here are almost identical to those obtained for POTII, i.e., only the oligomer series **2** and **5** (see the structures given above) are detected besides matrix ions in the lower mass range ($m/z < 500$). The relative intensities of oligomer ions of **5** are higher

than the corresponding ones of **2** under the experimental conditions used. However, ions corresponding to the oligomer series **1** and **3**, which were the main peaks in the case of POTI, were not observed as the major components. As indicated in the experimental section, the major component of the original product is POTII and this may be one of the reasons that the mass spectrum of the original product looks almost identical to that of POTII. The intensities of ionic species from the minor component, POTI, may be too low to be detected under these circumstances.

Conclusion:

The FABMS results indicate that a component of the low mass polytoluidine ($m/z=400-2000$) contains one oxygen atom/ $-NH-$ group per oligomer. One should exercise caution in using these results for quantitative purposes since the observed result is valid only if there is no preferential desorption due to surface activity differences. The mass difference between the adjacent peaks in the low mass polymers corresponds to the mass of a toluidine monomer unit ($m/z=105$), supporting expectations that the polymer consists solely of toluidine repeat units. Consideration of some of the possibilities for the introduction of oxygen/ $-NH-$ group into the polymer suggests that hydrolysis during the synthesis may be most likely. The molecular weight distribution can also be obtained from these results in addition to structural features (e.g. evidence for the presence of methyl and $-NH_2$ groups). The peak with the highest intensity is around $n=1$ (i.e., 7 monomer units) for the polymer containing the oxygen atom/ $-NH-$ group **3** and is also the same for the other series, **1**. Thus overall FAB results indicate that it has the potential for the analysis of polyaniline, providing more information, compared to the results for the same analogs obtained using various other techniques, which are already reported¹⁹⁻²¹.

The data described here supports the proposed structure for poly(*o*-toluidine)(i.e., **1**), which has been used to interpret its electrical conductivity. However, our results also indicate that the

relative intensity of this polymer component **1** is smaller than the one having the additional oxygen atom/-NH-group (i.e., **3**). This suggests that if various polymer components could be isolated, characterized and tested, a better understanding of the relationship between the structure and properties of the polymer may be developed and the conductivity of the polymer could be optimized.

Acknowledgment

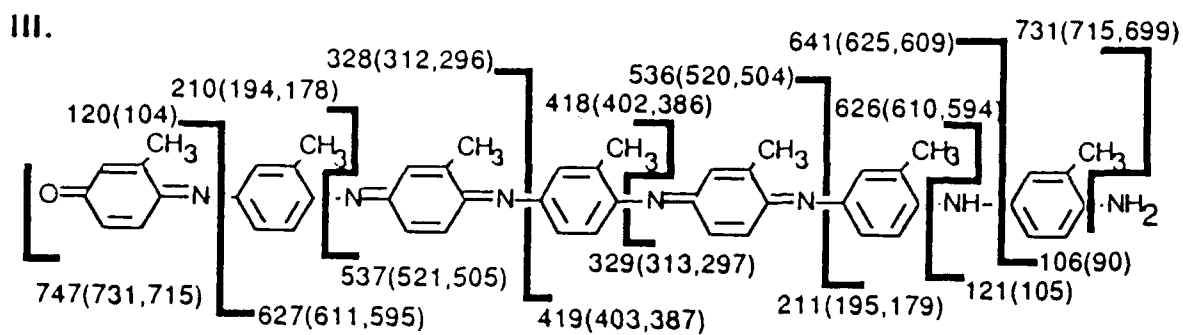
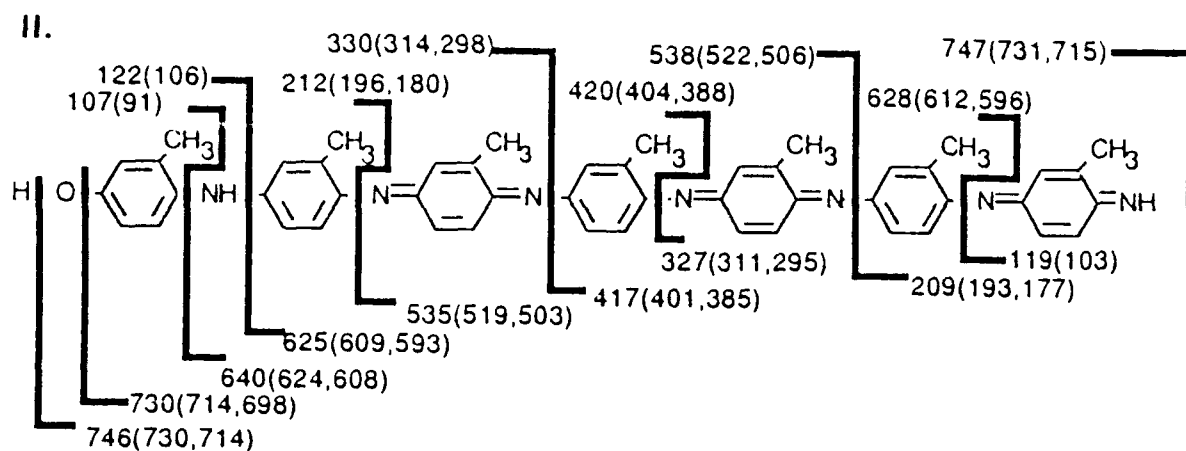
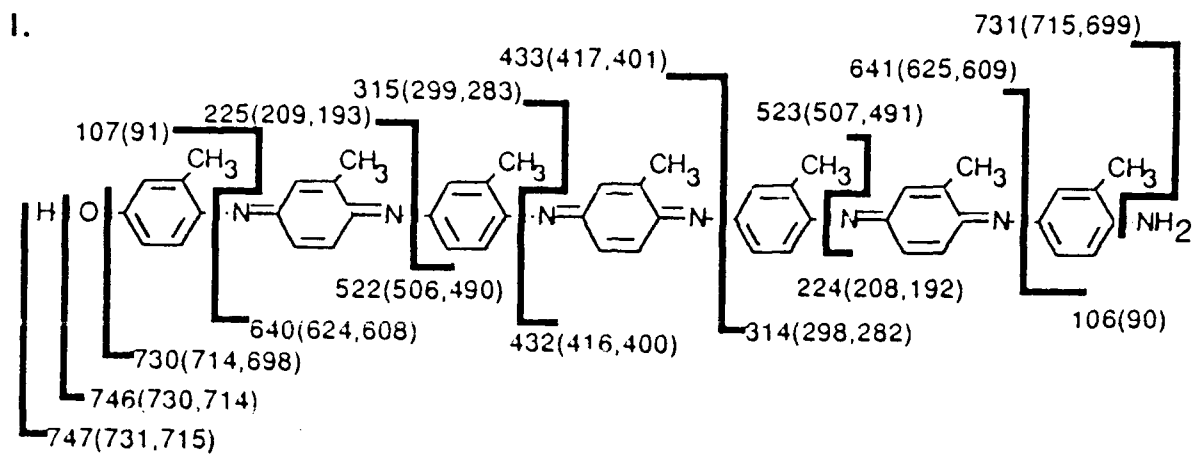
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SCHEME II

Figure Captions:

- Figure 1. Positive ion FAB mass spectrum of POT I, extracted using acetonitrile.
- Figure 2. Collisionally Activated Dissociation mass spectrum of $m/z = 747$.
- Figure 3. Positive ion FAB mass spectrum of POT I', extracted using acetonitrile. Samples for Figures 1 and 3 came from two different batches that were synthesized under identical conditions.
- Figure 4. Positive ion FAB mass spectrum of original POT.

