The Cationization Mechanism Study of Novel Oligo (*p*-phenyleneethynylene)s

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Two series of new oligo(*p*-phenyleneethynylene)s (OPEs) **O1–O4** and **O5–O8**, which have been proven to be one of the chief classes of molecules mainly used as the wires and other potential backbones of molecular electronic devices, have been synthesized by stepwise synthetic approach. The characterization of these oligomers was performed on MALDI TOF MS. Different cationization salts have been applied to investigate the ionization processes of these series of oligomers under MALDI conditions. The experimental results show that these oligomers display a strong tendency to undergo radical cationization and varied ionization efficiency with different cationization agents attributable to their difference in cationic diameters. Furthermore, we found that these two series of oligomers differed in ionization properties because of their different end-groups even when the same cationization agent was used. (J Am Soc Mass Spectrom 2005, 16, 1695–1701) © 2005 American Society for Mass Spectrometry

During the past two decades, π -conjugated polymers [1–3] and their oligomers [4–6] are subjects of rising interest to both academia and industries because of their wide applications as advanced materials for electronics and photonics. They are promising candidates for these applications because of the inherent synthetic flexibility, potential ease of processing, and the possibility of tailoring characteristic properties to accomplish a desired function. Recently, research on monodisperse conjugated oligomers has dramatically expanded as this class of compounds serve as model systems to generate useful and predictive structure–property relationships which aid in rationalizing the properties of the parent polydisperse polymeric materials [7]. In addition, oligomeric materials with defined length and constitution have become important subjects of their own [8]. One of the emerging and most challenging areas for monodisperse conjugated oligomers is molecular scale electronics, in which single or small packets of molecules function as the active channels for information transportation, processing, and storage [9, 10]. Constructing electronic devices with organic molecules can overcome the fundamental physical restraints in traditional Si-based technologies and can also result in a rapid and low-cost bottom-up manufacturing process for electronic device fabrication.

At present, the common characterization techniques for most of the newly synthesized oligomers are NMR,

IR, and UV [11–13]. The spectroscopic techniques ^1H and ^{13}C NMR can provide the main structural information of the oligomers. The absorption and emission properties of the oligomers can then be investigated by UV and PL spectrophotometric techniques. Molecular weight, which is one of the most important properties, cannot be obtained directly from the above-mentioned methods. In addition, molecular weight determination of oligomer is met with several problems. This is attributed to the inherent feature of oligomers, which hinders the results of mass analyses using common mass spectrometers. These features include their relatively high molecular weight (normally beyond 1 k), low or nonpolarity due to the symmetrical conjugated structure posing difficulties to FAB mass spectrometer, and the poor aqueous solubility of most of the oligomers making it hard for ESI analysis.

Since its introduction in 1988 [14], MALDI TOF MS has been considered to be an ideal tool for analyzing polymers [15–19] because of the simplicity of the mass spectra which show mainly singly-charged molecular ions with hardly any fragmentation. The time-of-flight (TOF) analyzer makes the analysis of high molecular weight polymers possible; the reflectron instruments equipped with delayed extraction ion source offer fairly high-resolution permitting the characterization of the repeat-unit mass and the mass residue of the polymers [20]. Taking advantage of these benefits, MALDI TOF MS proves to be a useful tool for the analysis of oligomers. Although MALDI is widely used in the characterization of polymers now, the ionization/desorption process of MALDI is not yet fully understood.

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Scheme 1. Structures of samples O1–O8.

Therefore, the selection of matrix and cationization agent for different classes of polymers has become the key subject of research for MALDI analysts. Herein, we present the MALDI TOF MS characterization of a series of monodisperse and shape-persistent oligomers comprising of eight newly developed oligo(*p*-phenyleneethynylene)s (OPEs) **O1–O8** (structures shown in Scheme 1). They form the main class of molecules that have been proposed and demonstrated for use as the wires and other potential backbones of molecular electronic devices. In most of the MALDI studies, protonization $[M + H]^+$ and alkali-cationization, e.g., $[M + Na]^+$, $[M + K]^+$ are the dominant formation of analyte even though no alkali cations are added. In the characterization of these eight oligomers, the analyte molecular radical cations $[M]^+$ are the only observed ions in the spectra. To investigate the ionization/desorption process of these interesting oligomers under MALDI conditions, we applied several regular cationization agents, including the alkali salts (from Li to Cs), silver, and copper salts, to our study. Interestingly, the radical cations still showed very strong signal in the spectra even when large excess of the above cationization agents were added. Similar observation of radical cations was reported by McCarley and Limbach [21]. In McCarley and Limbach's study on metallocenes, they believed that analyte molecular radical cations were produced by the electron-transfer reactions between matrix radical cations and neutral analytes. However, our oligomers did display good radical cation signals in the spectra without the addition of any matrix or cationization salts. Furthermore, we found that the structures of the end-groups influence the ionization properties of these oligomers.

Experimental

General Instrumentation and Conditions

MALDI experiments were carried out using a Bruker BIFLEX III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument is equipped with a N_2 laser emitting at 337 nm (Laser Sciences Inc., Cambridge, MA), a 1-GHz sampling rate digitizer, a pulsed ion extraction source, and an electrostatic reflectron. The laser pulse width is 3 ns, and the maximum power is 200 μ J. The spectra were acquired in the reflection positive-ion mode. The acceleration voltage was 19 kV. Typically, 200 single-shot mass spectra were summed to give a composite spectrum. All data were reprocessed using Bruker XTOF software. The mass scale was calibrated externally, using the peptides angiotensin II and bovine insulin B-chain (Sigma, St. Louis, MO) as mass standards. MALDI analysis of the polymers utilized dithranol (DI) (Aldrich) as the matrix.

Samples and Reagents

Oligomers **O1–O8** were synthesized by Pd/Cu-catalyzed coupling reaction and the synthetic details were reported previously [22]. The solvent, inhibitor-free tetrahydrofuran (Aldrich, Milwaukee, WI), stored in a Sure/Seal bottle, was used as received. The oligomers were dissolved in THF at a concentration of 3×10^{-5} mol/L, and the matrix DI had a concentration in THF of 30 g/L. When alkali salts (LiCl, NaCl, KCl, RbCl, and CsCl) were purchased from Acros) were used as ionization agent, a mixed solvent was used ($CH_3OH/H_2O/TFA$, 2:1:0.03) with a concentration of 5 mg/mL. Anhy-

Figure 1. Typical MALDI spectra of oligomers O2 (a) and O6 (b).

drous methanol and trifluoroacetic acid (TFA) were purchased from Acros. Silver trifluoroacetate (AgTFA, bought from Acros) and copper (II) acetylacetonate (CuAAT, purchased from Aldrich) dissolved in THF at the concentration of 5 mg/mL. We used the dried droplet method to prepare the sample target: 1.5 μ L of sample mixture was applied to the sample target and air-dried for 5 min.

Results and Discussion

Characterization of Oligomers

Before MALDI TOF MS analyses, elemental analyses, and NMR are commonly used for the characterization of the monodisperse oligomers. High-field NMR instruments can easily provide analyzable signals of the samples. By identifying the ^1H and ^{13}C chemical shifts and calculating the signal integration, the backbone structure of a compound is determined. Along with elemental composition information by elemental determination, the main general characterization of a sample can be performed. The quality of the results from elemental analyses and NMR depends on the purity of the sample. Without high purity, elemental determination will be inaccurate and useful information will be obscured in the NMR spectra from impurity peaks. Compared with NMR and elemental analysis, MALDI TOF MS has its own advantage, which is higher sensitivity and less influence from sample purity.

Results from elemental analysis and NMR demonstrated that the eight new oligomers used in this study are of high purity. We conducted the characterization of

eight new oligomers using MALDI-TOF MS. Some of the MALDI spectra in reflectron mode are shown in Figure 1. Radical ions were found to be molecular ions in the spectra of the eight oligomers while no protonated molecular ions $[\text{M} + \text{H}]^+$ were observed. Table 1 displays the observed molecular weights and the calculated ones of the eight analytes. The values agree well with each other and, hence, the expected target molecules were obtained. For further confirmation, the theoretical isotopic distribution simulated by software is compared with the observed one. The theoretical one and the experimental one are so identical that they confirm the structures of the synthetic compounds. The consistency in the results show that MALDI TOF MS is a good analyzing tool for this series of oligomers.

Study of Cationization

It is well known that alkali salts are highly-efficient cationization agents for polymers. In many cases, sodium and potassium cationized ions were found in the spectra even when no salts were added [18, 23]. The data listed in Table 1 were obtained through the MALDI spectra without the addition of any cationization agents. We are interested in the outcome upon the addition of cationization agents, for instance, commonly used alkali salts. Oligomer O2 was chosen as the model compound to illustrate this effect. The alkali chlorides from LiCl to CsCl were used as cationization agents. The MALDI spectra were obtained in reflectron mode (shown in Figure 2). Both radical ions and alkali cationized ions were observed in the spectra. From the

Table 1. The observed and the calculated molecular weights of the eight oligomers

Oligomer	O1	O2	O3	O4	O5	O6	O7	O8
Observed MW (m/z)	1070.8	1671.0	2271.3	2871.6	626.2	1226.4	1827.0	2427.4
Calculated MW (m/z)	1070.8	1671.1	2271.5	2871.9	626.3	1226.6	1827.1	2427.5

Figure 2. The MALDI spectra of cationized analytes.

spectra, we can obviously find that the signal intensities of alkali adducts display a weakening tendency from $[M + \text{Li}]^+$ to $[M + \text{Cs}]^+$. The $[M + \text{Li}]^+$ ions present the strongest signal shown in Figure 2a while we could hardly find an $[M + \text{Cs}]^+$ signal in Figure 2e. The signal intensities of the alkali metal adducts decrease as the metal atomic radius increase from lithium to potassium. The signal intensities of cationic adducts of potassium, rubidium, and cesium are hardly observed in the spectra. In MALDI, one of the vital factors that affect the signal intensity is the cationization efficiency. The success of the attachment of the cation to the analyte molecule directly associates with the signal intensity. We ascribe the weak signals of $[M + \text{K}]^+$, $[M + \text{Rb}]^+$, and $[M + \text{Cs}]^+$ to the poor cationization efficiency.

Considering the fact that the interaction of alkali metal ions with polymers is mainly electrostatic in nature, the possible sites where alkali ions attach to the analytes are expected to be located on the oxygen of

$-\text{OC}_6\text{H}_{13}$ group, the phenyl group, or the alkynyl group in the oligomers. These three places are rich electron sites where the metal ions attach easily. As the classic electronegative atom, oxygen is favorably attached by the positive metal ions. Some groups have reported their studies on the metal ions attaching to oxygen in polymers [24, 25]. The π -conjugated electron system renders the benzene rings readily attached to the alkali ions by forming a sandwich structure between two benzene rings [26]. Bonding metal ions to unsaturated hydrocarbon has long been a subject in organometallic chemistry, catalysis, and surface chemistry. The generally accepted point is that the interactions between metal ions and unsaturated hydrocarbon involve electrostatic forces as well as covalent forces [27]. In previous reports, metal ion is always bound to oxygen by the coordination of several oxygen donors in the complex. The backbone is expected to fold to facilitate the coordination. In our case, good rigidity of the large π -con-

Table 2. The cationic diameters and the bond length of alkyne

Ion	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ag ⁺	Cu ²⁺	C≡C
Diameter/length (pm)	80	100	160	180	210	150	114	120

jugated system of the oligomers resulting from the phenyl groups and triple bonds prevent the backbone folding. In addition, the long, rigid chain also hinders the association of metal ion to the oligomers by sandwich formation. Hence, the most possible attachment site of cations to the oligomers is the alkynyl group.

Table 2 lists the data of cationic diameters in aqueous solutions [28] and the bond length of alkyne. It is interesting to find that the bond length of alkyne (120 pm) lies between the size of sodium ion (100 pm) and that of potassium (160 pm). If the oligomers were cationized by inserting the cation into alkyne, this can provide possible explanation why sodium can cationize the analyte successfully while potassium cannot. The key is the comparison between the cationic diameter and the triple bond length. The diameters of lithium and sodium ions are smaller than the length of the triple bond, so they can insert into the triple bond. Meanwhile, it is easier for lithium ions to insert than sodium ions due to the smaller size of the former which is reflected by the higher relative signal intensity of $[M + Li]^+$ than $[M + Na]^+$.

The other widely used cationization agents in MALDI, silver and copper, are considered to be more efficient in cationizing most of the synthetic polymers. The MALDI spectra of **O2** with silver and copper addition are shown in Figure 2f and g, respectively. The peaks of radical ions dominate the silver spectrum, although the weak signals of silver adducts are observed. This phenomenon indicates that the silver does not cationize the oligomer as efficiently as it does for most of the polymers, for instance, polystyrenes [29], while in the spectrum of copper, the signals of copper adducts are much stronger than those of silver. The ionic diameters of silver (I) and copper (II) are 150 pm and 114 pm, respectively. The results agree with our above speculation. Silver can hardly attach to the oligomers while copper did it successfully because of the difference of their cationic diameters. Similar results were observed in the case of the other oligomers in our study.

No matter what cationization agents were added, the radical cations always dominated the MALDI spectra. The oligomers demonstrated very strong tendency on its radical cationization. In fact, radical cationization has been reported before, e.g., McCarley and Limbach's study on metallocenes, Räder and coworkers on poly(*p*-phenylene)sä [30], Janssenä et al. onä poly(3-alkylthiophene)sä andä poly(thienylene-phenylene)sä [31,ä32]. In McCarley and Limbach's study, terthiophene and anthracene were used as matrices, which are known as good electron-transfer matrices for their large extinction coefficient at 337 nm, the wavelength of the laser in

MALDI. These matrices can absorb laser radiation and become radical cations by photoionization. Subsequently, the matrix radical cations and the neutral analytes yield analyte radical cations by the electron-transfer reaction instead of the regular protonated or metalized cations in the majority of MALDI analysis.

On the supposition that the above explanation about electron-transfer is true for our oligomers, we sought to probe the effect on the oligomers without matrix. The results revealed that under the conditions identical to those of the experiments in which matrix was used, the analyte radical cations were still detected when no matrix was added. Hence, these oligomers did desorb and photoionize directly but not through the electron-transfer process by the matrix described in literature. Actually, the oligomers have strong absorption at the wavelength of nitrogen laser (337 nm) although the maximum is at a higher wavelength (UV spectra of **O1–O4** shown inä Figureä3)ä [22].ä Thus,ä theä oligomers undergo electron-transfer reactions yielding considerable amounts of radical cations. These multi-aromatic oligomers are good electron-transfer materials themselves.

To our knowledge, matrix has as an important role in MALDI process. It dilutes the sample to prevent association of analyte molecules; absorbs the majority of laser power to protect the analytes from decomposition by excessive laser energy; and increases the ion formation of analyte through proton transfer to analyte molecules by photoexcitation and photoionization of matrix moleculesä [33].ä However,ä theä resultsä describedä above showed that these oligomers still generated good signals without matrix. The oligomers acted as both analyte and matrix in the experiments. By comparison of

Figure 3. UV spectra of **O1–O4** in THF solution (300 nm to 500 nm).

Figure 4. The MALDI spectra of **O2** and **O7**. (a) **O7** cationized by Li without matrix; (b) **O7** cationized by Li with matrix; (c) **O2** cationized by Li with matrix.

the MALDI spectra shown in Figure 4a and b, we can find the real difference between the nonmatrix assisted LDI and matrix assisted LDI. These are the spectra of oligomer **O6** under the identical conditions except that in Figure 4a no matrix was used. The absolute intensity of a radical cation of Figure 4a ($<1.5\text{ k}$) was much lower than that of Figure 4b ($\sim 3\text{ k}$). In addition, there were much more fragment signals observed in the lower mass range when matrix was not applied. The evidence proves that matrix still works by diluting the analytes and protecting the analyte molecules from fragmentation even when the analytes photoionize directly without the aid of matrix radical cations. For the oligomers with higher tolerance of laser energy, the MALDI experiments may be much easier because the selection of matrix will not pose a problem.

Although the signals of analyte radical cations were strong in the MALDI spectra of both series of oligomers, some difference still existed. The spectra of oligomer **O2** and **O6** under the same experimental conditions are shown in Figure 4c and d, respectively. Lithium was used as cationization salt. Obviously, the intensity of **O6** radical cations $[M]^+$ was lower than that of lithium adducts $[M + \text{Li}]^+$ which was in a reverse condition to **O2**. This phenomenon occurred in the other six oligomers of the two series. These eight oligomers were all OPEs categorized in two series by the terminals (**O1–O4** with trimethylsilyl (TMS) terminal, **O5–O8** with thioacetyl (SAC) terminal). With the same matrix used, laser power applied, analyte/matrix ratio and shoot times accumulated, the possible explanation for the totally reversed results of ionization properties of these two series of oligomers with identical monomer structure is the influence of end-groups. It was reported by Montaudo and coworkers in their study on polymer blends that the peak intensity of analyte depended on the nature of the end-groups [34]. As a nonpolar functional group, TMS has no sites for metal cation undergoing cation-attaching reaction. In the case of SAC, there are more polar atoms of S and O for metal attachment.

Thus, the oligomer-SAC cationized by metal cation by inserting into the triple bond of alkyne can, in addition, be cationized by metal cation attaching to the polar sites of SAC group. The possibility of two pathways to cationization renders oligomer-SAC higher ionization efficiency than oligomer-TMS. In the meantime, the highly efficient cationization of oligomer-SAC suppresses the analyte radical ionization during the gas-phase ionization process.

Conclusions

Eight new oligo(*p*-phenyleneethynylene)s (OPEs) of two series (**O1–O4** and **O5–O8**) synthesized by stepwise synthetic approach have been characterized by MALDI TOF MS. For all eight oligomers, the signals of radical cations dominated in the spectra. These interesting compounds offer us a good chance to carry out the study on MALDI ionization mechanism. First, to investigate ionization property of these oligomers, alkali salts (from LiCl to CsCl), silver salt, and copper salt were used as cationization agents. The results showed that lithium, sodium, and copper successfully cationized the analytes while potassium, rubidium, cesium, and silver displayed poor cationization efficiency. Based on the experimental results and the data of cationic diameters and triple bond length, we propose a mechanism of cationization in which the cation inserts into triple bond of alkyne under MALDI condition. Second, the multiaromatic nature of these oligomers makes them such good electron-transfer materials that they prefer radical cationization to metal cationization, which also allows them independence from matrix. Furthermore, by comparing the MALDI spectra of two series of oligomers, we found that the end-group did affect the ionization properties of the oligomers because of the possibility of cation attachment.

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