Characterization of Synthetic Polyamides by MALDI-TOF Mass Spectrometry

Haeyoung Choi,[†] Eun Kyung Choe,[‡] Eun Kyung Yang, Sungwoo Jang, and Chan Ryang Park[*]

Department of Chemistry, Kookmin University, Seoul 136-702, Korea. [*]E-mail: crpark@kookmin.ac.kr
[†]Medical Device Research Center, Korea Electrotechnology Research Institute, Ansan 426-901, Korea
[‡]Textile Ecology Laboratory, Korea Institute of Industrial Technology, Chonan 330-825, Korea
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MALDI-TOF-MS technique was applied to obtain structural and compositional information of synthetic polyamides, Nylon6 and Nylon66. Mass spectra of both the original and the hydrolyzed polyamide samples were analyzed using the self calibration method as well as the internal calibration method with the standard materials of known masses. The MALDI-TOF mass spectra of Nylon6 samples showed the presence of protonated, sodiated, and potassiated ions that were assigned to cyclic and NH_2/COOH terminated linear oligomers. From the MALDI-TOF mass spectra of Nylon66 samples, the potassiated linear oligomers with three different end groups are identified as well as the cyclic oligomers, *i.e.*, NH_2/COOH terminated oligomers, NH_2/NH_2 terminated oligomers, and COOH/COOH terminated oligomers. Full characterization of the molecular species and end groups present in the polyamide samples has been achieved, and also the changes in mass spectral patterns after the hydrolysis of the samples are presented.

Key Words : MALDI-TOF MS, Polyamide, End group, Hydrolysis, Oligomer

Introduction

A complex polymer is characterized by its molar mass, chemical composition, the sequence of the monomer units in the polymer chain, and the functionality. Mass spectrometry has been known to be very powerful for the fast and accurate determination of molar masses, the sequence of repeat units, the polymer additives, and etc. The main obstacles for mass spectrometry of polymer compounds, which arise mainly from the low volatility and thermal instability of polymers, have been surmounted by the development of soft ionization technique, so called, matrix-assisted laser desorption/ionization (MALDI) technique.

MALDI-TOF technique allows desorption and ionization of very large molecules even in complex mixtures, which is one of great advantages over the conventional methods of characterization in polymer analysis. It gives information on the masses of individual oligomers, which allows a lot of important information on the polymers to be derived, including the repeat units, end-groups, the presence of rings, molar mass distributions, and other information.[1]

It was, however, not until 1992 that it was demonstrated that synthetic polymers of molar masses above 10^5 $gmol^{-1}$ can be analyzed using MALDI-TOF method,[2] probably due to the difference in sample preparation method compared with biopolymers. Furthermore, MALDI-TOF method sometimes suffers from the lower signal-to-noise ratio due the fact that synthetic polymers often shows a high polydispersity, which results in the spreads of signal intensity over a number of oligomers having different degrees of polymerization. During the last decade, however, MALDI-TOF mass spectrometry has become an essential tool for the characterization of synthetic polymers.[3-5] This technique made possible direct determination of the composition of species contained in each polymer sample and also different end groups present in the oligomer series. It was also demonstrated recently that MALDI-TOF is superior to all other techniques in analyzing functionally heterogeneous polymers with respect to the degree of polymerization and the type of functional end groups in one experiment.[6,7]

Mass accuracy and mass resolution obtainable in MALDI-TOF mass spectrometry often allows the direct structural determination of the species contained in each polymer sample and also of the end-groups that are present. Chemical structures and end-groups of polyamides such as Nylon6 (repeat unit = 113.1 Da), Nylon12 (repeat unit = 197.3 Da) have been characterized by the MALDI-TOF mass spectrometry.[8,9] Other types of polyamides (repeat unit = 197.3 Da and 246 Da) have also been used to study the sample preparation methods, in which they compared solid mixture pallet method with common dried droplet sample preparation method.[10]

Recently, thermal degradation[11,12] and photo-oxidation[13,14] of polyamides were extensively studied by Montaudo group using MALDI-TOF mass spectrometry. They observed that the MALDI spectra of photo-oxidized polyamide samples showed the presence of over 40 compounds, as compared to 3 or 4 peaks in the original polyamide samples. They were able to assign all the peaks in the spectra based on the molecular masses and to propose the most plausible mechanisms for the degradation processes of polyamides. In these works, they proved that MALDI-TOF technique could be a powerful tool in analyzing the products of polymer reactions, even though some of the structural assignments of MALDI peaks are based on the speculations for molecular masses of predicted chemical structures.

Hydrolysis of polymer through alkaline treatment or enzymolysis is often used for surface modification of polymeric textiles in the textile industries. Through this hydrolytic weight reduction processes, the textile fabrics are known to

become more hydrophilic and softer. Structural identification of oligomer products of hydrolyzed Nylon6 was partly reported by Montaudo group using MALDI-TOF mass spectrometry, where they focused on the characterization of different end groups present in the oligomer chains.[9] From MALDI-TOF mass spectra, they were able to show the presence of protonated, sodiated, and potassiated ions that were assigned to Nylon6 chains terminated with the expected end groups, as well as the presence of the cyclic oligomers contained in the samples.

In this study, we report the results of structural analyses of two different synthetic polyamides (Nylon6 and Nylon66) and the mass spectral changes observed after hydrolysis by means of MALDI-TOF mass spectrometry. Linear time-of-flight mass spectrometer has been constructed to detect matrix-assisted laser desorption/ionization generated ions. A self-calibration method for the MALDI-TOF mass spectra of polymeric materials enabled us to determine accurate mass values and to distinguish all the oligomers with different end groups.

Experimental Section

The linear time-of-flight mass spectrometer (partly manufactured by R. M. Jordan Co., Grass Valley, CA) used in these studies was a modified type of Wiley-McLaren design working in positive ion mode with the capability for high-voltage acceleration up to ± 30 kV. The high voltages were supplied by Spellman's two separate high voltage power supplies (CZE 1000R). The TOF chamber was equipped with a microchannel plate (MCP) at one end of 1.2 m-long flight tube to detect the ions generated from matrix-assisted laser desorption/ionization process.

A nitrogen laser (Spectra Physics, VSL-337ND-S) delivering 337 nm radiation was used for desorption of analytes. The laser beam of 10 ns pulse width, 10 Hz repetition rate, 10-30 μJ/pulse power was loosely focused on to the 1/4 inch diameter probe tip at a 45° angle to the probe surface with a single quartz lens of 50 cm focal length. A CCD camera was attached to the TOF chamber to facilitate alignment and focusing of the laser beam. Although the laser irradiance was not measured directly, it was, however, estimated as *ca.* 10^6-10^7 W/cm^2 from the focused laser spot size on the probe tip.

Spectral resolution was optimized using standard polystyrene samples (Sigma Aldrich, M_w = 4,000 and M_w = 13,200) and the best resolution was achieved with the repeller and extractor voltages of 27 kV and 16 kV, respectively. Dithranol and silver trifluoroacetate were used as a matrix and a cationization agent, respectively. The resolution was about 400 at 3500 Da and 300 at 10,000 Da. Data were recorded by summing 1,000 transients using a LeCroy digital oscilloscope (LT372, 500 MHz bandwidth, 4G sampling rate) and subsequently transferred to an IBM PC for further processing.

The materials used in MALDI sample preparation such as matrixes, solvents, and metal adducts were purchased from Aldrich Chemical Co. 2-(4-hydroxyphenylazo)-benzoic acid (HABA), α-cyano-4-hydroxy cinnamic acid (CHCA), dithranol, 2,2,2-trifluoroethanol (TFE), trifluoroacetic acid (TFA), tetrahydrofuran (THF), potassium Iodide (KI), silver trifluoroacetate (AgTFA) were used as supplied. Angiotensin, $P_{14}R$ (synthetic polymer) and polystyrenes were also purchased from Aldrich for mass calibration and optimization of spectral resolution.

Polyamide samples (Nylon6 and Nylon66) purchased from Aldrich were ground to powder and dried under vacuum at 60 °C for 3 days before use. The original polyamide samples purchased are expected to consist of oligomers with each chain terminated mostly with NH_2 and COOH as informed from Aldrich Co. Chemical structures of polyamide samples are shown below.

Nylon6 (repeat unit = 113.1 Da):

$$H\text{-}[\text{-}NH\text{-}(\text{-}CH_2\text{-})_5\text{-}CO\text{-}]_n\text{-}OH$$

Nylon66 (repeat unit = 226.3 Da):

$$H\text{-}[\text{-}NH\text{-}(\text{-}CH_2\text{-})_6\text{-}NH\text{-}CO\text{-}(\text{-}CH_2\text{-})_4\text{-}CO\text{-}]_n\text{-}OH$$

The hydrolyses of polyamide samples were carried out with water in methanesulfonic acid following the same procedures as described in previous work.[9] Typically, each of 5 g of Nylon6 (M_w = 10,000 Da) and 5 g of Nylon66 (M_w = 22,000) was refluxed under stirring at 85 °C with 195 mL of methanesulfonic acid under nitrogen. Hydrolysis was carried out for 10 minutes by adding 60 mL of distilled water while stirring the solution. The mixture was then added to 1.2 liters of 2 M aqueous ammonia solution to neutralize methanesulfonic acid. The precipitated polymer was filtered and washed several times with water to remove unwanted impurities. The filtered polymer was refluxed with methanol for 12 hours and was dried under vacuum at 80 °C for 3 days, to yield about 4.5 g of low molecular weight polyamides.

Samples for the MALDI analytes were prepared as follows. Each 10 mL polymer solution (10 mg/mL in TFE) was mixed with the same volume of HABA matrix solution (20 mg/mL in TFE), and 1-2 μL of 0.05 N KI solution in TFE/H_2O (1:1 v/v) was added to the mixture as cationization salt (KI) if necessary. The samples were prepared with crystalline MALDI matrixes using dried droplet method. Using micropipette, 2-3 μL of each mixture was loaded on the MALDI sample probe tip and slowly dried to allow analyte/matrix co-crystalization. The layered sample preparation technique was also tried to improve the quality of MALDI spectra, *i.e.*, a layer of matrix solution was applied to the sample target, dried in air, and covered by a second layer of sample solution.

Results and Discussion

Time-to-mass conversion of time-of-flight mass spectra was achieved using the self-calibration method developed by M. S. Montaudo group.[15-17] Basically, the method allows one to obtain absolute mass values in MALDI-TOF mass spectra of polymeric materials. This calibration procedure can be applied to mixtures of polymers and to copolymers

when the repeat unit of at least one component in the polymeric material to be analyzed is known. The absolute masses were also confirmed by applying internal calibration procedure using standard samples that have well known masses (Angiotensin (1046 Da) and $P_{14}R$ (1533 Da)). The sample for the internal mass calibration was prepared by mixing standard mass solution in TFA with matrix solution (α-cyano-4-hydroxy cinnamic acid (CHCA) in TFA) to obtain 1:1 volume ratio. Spotting analyte samples on one half side of the probe tip and standard samples on the other half side of the same probe tip, MALDI-TOF mass spectra of both analyte and standard samples were obtained without changing the high voltages, laser powers, or flight length of the ions by simply rotating the probe tip.

The MALDI-TOF mass spectrum of original Nylon6 sample is presented in Figure 1(a). While the previous work failed to obtain a MALDI-TOF spectrum of original Nylon6 due to the high molecular weight distribution (M_w = 43,000),[9] we were able to obtain the spectrum of original sample with moderately high molecular weight sample (M_w = 10,000). The spectrum shows distribution of oligomers which is typical for a polymer of polydispersity higher than 3.[1] The M_w values of this sample used in this experiment is around 10,000 Da with the lower molar mass tail reaching down to around 1,000 Da. Since MALDI-TOF mass spectrometer records only the low molar mass tail of the distribution, the molar mass distribution reproduced in the spectrum seems to be incorrect although the repetition unit and different end groups can be determined. One of the possible solutions for this problem is to produce samples with sufficiently low polydispersity by fractionation method such as size exclusion chromatography.[18]

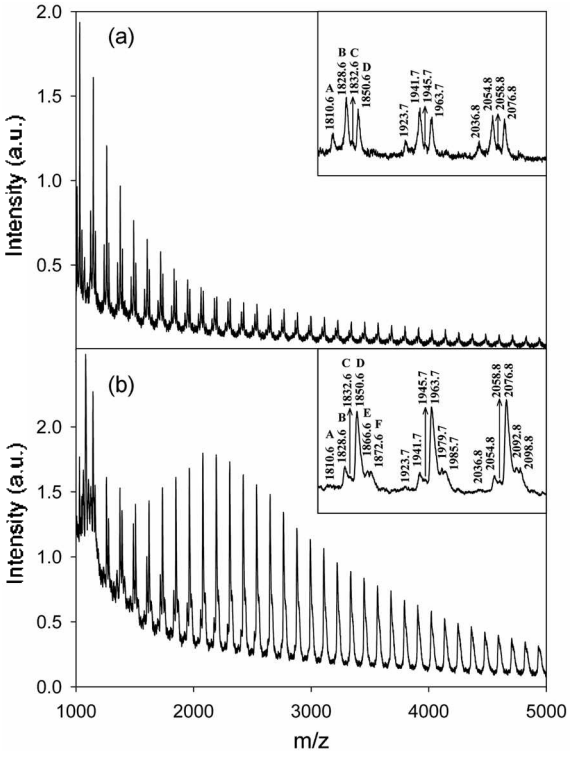

Figure 1. MALDI-TOF mass spectra of (a) original Nylon6 sample (M_w = 10,000) and (b) hydrolyzed Nylon6 sample. Structural assignments are described in the text.

From Figure 1(a), the original Nylon6 sample is expected to be composed of cyclic oligomers and linear oligomers with each chain terminated with NH_2 and COOH as can be seen from structural assignments below. The MALDI-TOF mass spectrum of Nylon6 hydrolyzed with water in methanesulfonic acid (CH_3SO_3H) was presented in Figure 1(b). As can be seen clearly from the spectrum, the hydrolyzed sample exhibit average molar masses of about 2,500 Da and homogeneous oligomer distributions. For the oligomer distributions and structural assignments, we obtained basically the same results compared with the previous result[9] except the mass distribution of the hydrolyzed oligomers shifted to higher mass side by *ca.* 600 Da, probably due to the difference in the degree of hydrolysis.

The main mass spectral features of the MALDI spectrum is contributed by a series of intense peaks (series D) ranging from 1,000 to 7,000 Da. From mass analyses, those peaks are assigned to the ions of the type H-[-NH(CH_2)5CO-]$_n$-OH $\cdots Na^+$ (113.1 × n + 18 + 23), where n ranges from 8 to 60. Part of the peaks associated with this series (peaks at 1850.6, 1963.7, 2076.8 Da), which corresponds to oligomers with n = 16, 17, and 18, are enlarged and presented in the inset.

The spectrum also contains other series of lower intensity peaks corresponding to the linear oligomers terminated with NH_2/COOH, which are ionized by the attachment of a proton (series B, peaks at 1828.6, 1941.7, 2054.8 Da) and a potassium ions (series E, peaks at 1866.6, 1979.9, 2092. 8 Da). The Peaks at 1810.6, 1923.7, 2036.8 Da can be assigned to protonated cyclic oligomers (series A), since they exhibit mass differences of 18 Da and 40 Da to series B and D. For the same reason, the small peaks at 1832.6, 1945.7, 2058.8 Da are assigned to sodiated cyclic oligomers (series C). Finally, the peaks at 1872.6, 1985.7, 2098.8 Da can be assigned to the sodium salt of the NH_2/COOH-terminated Nylon6 chains, which are desorbed as sodium adducts (series F).

Structural assignments of MALDI generated ions of Nylon6 samples in the Figure 1(a) and Figure 1(b) are summarized below.

A. cyclic -[-NH-(-CH_2-)$_5$-CO-]$_n$-$\cdots H^+$
B. H-[-NH-(-CH_2-)$_5$-CO-]$_n$-OH$\cdots H^+$
C. cyclic -[-NH-(-CH_2-)$_5$-CO-]$_n$-$\cdots Na^+$
D. H-[-NH-(-CH_2-)$_5$-CO-]$_n$-OH$\cdots Na^+$
E. H-[-NH-(-CH_2-)$_5$-CO-]$_n$-OH$\cdots K^+$
F. H-[-NH-(-CH_2-)$_5$-CO-]$_n$-ONa$\cdots Na^+$

In contrast to biopolymers, the ionization of synthetic polymers is usually known to occur through cationization rather than protonation. In relatively polar polymers, however, sodium and/or potassium adduct ions could be observed in the MALDI spectrum even though they are not added to mixture of matrix and analyte due to the fact that these cations are present as impurities in matrix, reagents, solvents, and glassware.[1] Most of the synthetic polymers having

heteroatoms like polyamides are cationized by the addition of sodium or potassium salts.[19,20]

As seen above, the MALDI-TOF mass spectra in Figure 1(a) and Figure 1(b) display peaks due to cyclic oligomers of Nylon6. The detection of cyclic oligomers in Figure 1(a) implies that they are contained in the original Nylon6 polymer sample. Relative amount of cyclic oligomers in the original sample is non negligible compared to that of linear oligomers assuming the same proton affinity for both types of oligomers. It can be seen, however, from Figure 1(b) that cyclic oligomers are almost completely hydrolyzed and only trace amounts are detected after hydrolysis in contrast to the case of Nylon66 presented below.

For Nylon66, on the other hand, attempts to obtain a complete MALDI-TOF mass spectrum of the original Nylon66, sample (M_w = 22,000) has not been very successful probably due to relatively high molecular weight distribution, and one of the spectra of original Nylon66 sample is presented in Figure 2(a). Overall shape of the oligomer distribution turns out to resemble that of Nylon6, and shows oligomer distribution characteristic of high polydispersity polymers. The MALDI-TOF mass spectrum of original sample reveals that the cyclic form of the Nylon66 oligomers is predominant below the mass range of 2,000 Da compared to the linear ones, according to the structural assignment below. The original Nylon66 sample is, as informed from Aldrich Co., expected to be formed by oligomers mostly with each chain terminated with NH_2 and COOH. Other oligomer chains, however, with end groups of NH_2/NH_2 and COOH/COOH are clearly discernible from the spectrum even though the signal intensity is not high.

The MALDI-TOF mass spectrum of Nylon66 hydrolyzed with water in methanesulfonic acid is presented in Figure 2(b). The MALDI spectrum shows a series of the most intense peaks (series B) ranging from 1,000 to 5,000 Da, corresponding to ions of the type H-[-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n$-OH$\cdots K^+$ (226.3 × n + 18 + 39), where n ranges from 5 to 22. Part of the spectrum containing two peaks belonging to this series (peaks at 1641.1, 1867.4 Da), which correspond to oligomers with n = 7 and 8, are enlarged and displayed in the inset.

The spectrum also includes other peaks of lower intensities corresponding to the oligomers in which both ends are terminated with two NH_2 groups or two COOH groups. Due to the unsymmetrical repeat unit, Nylon66 has two different sites of amide bonds that can be hydrolyzed to produce two different end groups, *i.e.*, oligomers terminated with two carboxyl groups at the ends or two amino groups at the ends. In addition to the linear oligomers, the spectrum also includes the peaks due to Nylon66 cyclic oligomers.

The MALDI peaks in Figure 2(b) are due to six series of oligomers, which are generated all in the form of potassiated ions since KI is added as a metal adduct to facilitate cationization of oligomers. Structural assignments of the ions generated from Nylon66 samples in the Figure 2(a) and Figure 2(b) are summarized below.

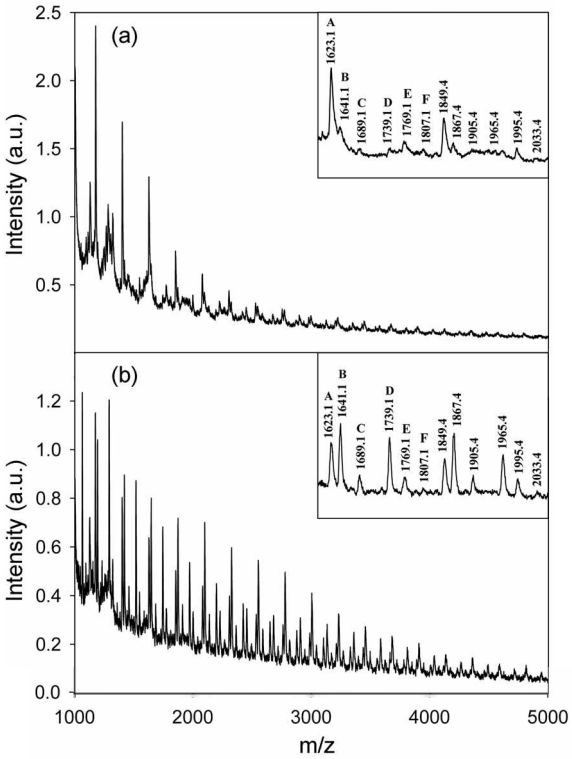

Figure 2. MALDI-TOF mass spectra of (a) original Nylon66 sample (M_w = 22,000) and (b) hydrolyzed Nylon66 sample. Structural assignments are described in the text.

A. cyclic [-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n\cdots K^+$,
B. H-[-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n$-OH$\cdots K^+$,
C. H-[-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n$-OK$\cdots K^+$,
D. H-[-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n$-NH-(-CH_2-)$_6$-$NH_2\cdots K^+$,
E. HO-CO(-CH_2-)$_4$-CO-[-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n$-OH$\cdots K^+$,
F. HO-CO(-CH_2-)$_4$-CO-[-NH-(-CH_2-)$_6$-NH-CO-(-CH_2-)$_4$-CO-]$_n$-OK$\cdots K^+$,

In addition to the most intense peaks at 1641.1, 1867.4 Da corresponding to NH_2/COOH terminated linear oligomers, which are ionized by the attachment of a potassium (series B), the peaks at 1689.1, 1905.4 Da can be assigned to their potassium salts (series C). Potassiated ions of linear oligomers terminated with two amino groups at the ends (series D) are found at 1739.1 and 1965.4 Da. The peaks at 1769.1, 1995.4 Da can be assigned to the potassiated ions of linear oligomers terminated with two carboxyl groups at the ends (series E), and the peaks due to their potassium salts are found at 1807.1 and 2033.4 Da (series F). Finally, the peaks at 1623.1, 1849.4 Da can be assigned to potassiated cyclic oligomers (series A), since they exhibit mass differences of 18 Da to series B as a water molecule is removed from the linear oligomer chain.

While we obtained six series of oligomers in the MALDI-TOF mass spectrum of Nylon66, the previous works,[14] in which sodium trifluoroacetate (NaTFA) was used as an

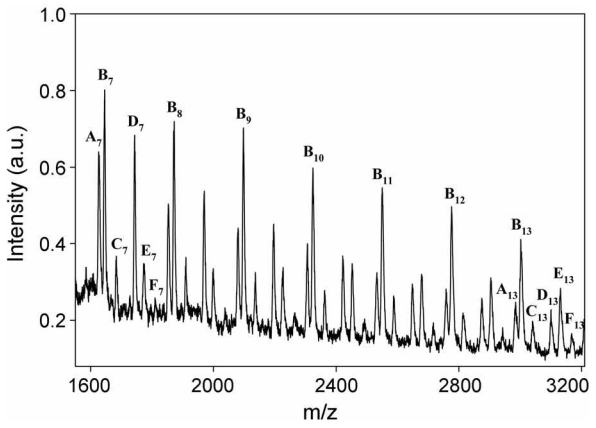

Figure 3. Enlarged MALDI-TOF mass spectra of hydrolyzed Nylon66 sample in the mass range of 1,600-3,200 Da corresponding to n = 7-13. Structural assignments are described in the text.

cationization agent instead of KI, reported four series of oligomers corresponding to series A, B, D, and E in our results. Peaks due to the formation of sodium salts, corresponding to series C and F in our results, were not observed. Another previous MALDI-TOF experiment on Nylon66,[12] where KI was used as a metal adduct, showed only three series of oligomers corresponding to series A, B, and E in our results. Even though the Nylon66 samples in their experiment contained higher concentration of amino end group than carboxyl end group, potassiated ions of linear oligomers terminated with two amino groups at the ends (series D) were not observed, while those terminated with two carboxyl groups at the ends (series E) appeared in the spectrum.

Enlarged MALDI-TOF mass spectrum of hydrolyzed Nylon66 in the mass range of 1,600-3,200 Da corresponding to n = 7-13 is presented in Figure 3. Intensities of potassiated ions of linear oligomers terminated with two amino groups at the ends (series D) decrease rapidly while those of linear oligomers terminated with two carboxyl groups at the ends (series E) does not change much throughout the mass range presented in the Figure 3. The relative peak intensities of series D and series E are reversed at around m/z = 2,700 (n = 11), which probably reflects the fact that the potassium ion affinities for both types of oligomers varies depending on the oligomer size. The spectrum also shows that the intensities of potassium salt ions (series C and F) did not change very much and stayed low throughout the spectrum.

Conclusions

A linear MALDI-TOF mass spectrometer is constructed to investigate the structures and the compositions of two synthetic polyamides, Nylon6 and Nylon66. Both the original samples and the hydrolyzed samples are analyzed using MALDI-TOF method. HABA is used as a matrix for both samples, and KI is added to aid cationization in case of Nylon66 samples while no metal adduct is added to Nylon6 samples.

The method turned out to be very efficient for direct determination of the composition of the species contained in each polymer sample and also of different end groups present in the oligomer series. The changes in mass spectral patterns after the hydrolysis of both polyamide samples are presented, and the characterization of molecular species and end groups are discussed.

For Nylon6 samples, six series of oligomer peaks were observed, each of which was assigned to protonated, sodiated, and potassiated ions of cyclic and NH_2/COOH terminated linear oligomers of Nylon6. For the oligomer distributions and structural assignments, we obtained basically the same results as the previously reported results except that cyclic oligomers are not observed in our hydrolyzed Nylon6 sample.

For Nyon66 samples, six series of oligomer peaks were observed on the contrary to three or four series reported in previous works. All those peaks were assigned to potassiated ions of cyclic Nylon66 oligomers, linear oligomers terminated with carboxyl group at one end and amino group at the other end, linear oligomers terminated with two amino groups, and linear oligomers terminated with two carboxyl groups.

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