

Hydrolytic Degradation of Synthetic Polytrimethylene Terephthalate and Characterization by MALDI-TOF Mass Spectrometry

Eun Kyung Yang, Sungwoo Jang, Young Dal Cho,[†] Eun Kyung Choe,[†] and Chan Ryang Park*

Department of Chemistry, Kookmin University, Seoul 136-702, Korea. *E-mail: crpark@kookmin.ac.kr

[†]Textile Ecology Laboratory, Korea Institute of Industrial Technology, Ansan, Korea

Received November 26, 2010, Accepted November 30, 2010

The structural analysis of polytrimethylene terephthalate (PTT) and characterization of the hydrolytic degradation products after acid hydrolysis were performed using MALDI-TOF mass spectrometry. Mass spectra of the PTT samples were analyzed using a self-calibration method as well as an internal calibration method with standard materials of known masses. PTT structures constituting the samples were determined from the analyses of the spectra, and their relative compositions were estimated. The MALDI-TOF mass spectra of the acid-hydrolyzed PTT sample showed three main series of oligomer products with different end groups in accordance with the hydrolysis schemes. From the spectra of both Na⁺ and K⁺ adducts, it was concluded that the PTT samples have higher affinity for Na⁺ compared with K⁺ and therefore show higher ionization efficiency with sodium ions when dithranol is used as a matrix. Two different wavelength laser beams ($\lambda = 337$ nm and 355 nm) were tested and it was observed that the 355 nm beam was more efficient in obtaining the MALDI spectra of PTT using dithranol as a matrix under our experimental conditions.

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

Introduction

Development of a soft ionization technique, referred to as matrix-assisted laser desorption/ionization (MALDI), enabled us to overcome the main obstacles for mass spectrometry of polymer compounds, which arise mainly from the low volatility and thermal instability of polymers. MALDI-TOF allows desorption and ionization of very large molecules even in complex mixtures, which is an advantage over conventional methods for 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 repeat units, end groups, presence of rings, molar mass distributions, and other information.¹

In 1992, it was demonstrated that synthetic polymers of molar masses above 10^5 g mol⁻¹ can be analyzed using the MALDI-TOF method.² During the last decade, MALDI-TOF mass spectrometry has become an essential tool for the characterization of synthetic polymers.³⁻⁵ It was also demonstrated recently that MALDI-TOF is superior to other techniques in analyzing functionally heterogeneous polymers with respect to the degree of polymerization and type of functional end groups in a single experiment.^{6,7}

Recently, chemical structures and end groups,⁸⁻¹⁰ thermal degradation^{11,12} and photo-oxidation^{13,14} of synthetic polymers were extensively studied by Montaudo and co-workers using MALDI-TOF mass spectrometry. Mass accuracy and mass resolution in MALDI-TOF mass spectrometry permitted the direct structural determination of the species and end groups contained in each polymer. The most plausible mechanisms for the degradation processes of synthetic polymers were consequently proposed.

Hydrolysis of synthetic polymers through alkaline or enzymatic treatment is often used for surface modification of polymeric textiles in the textile industry. Through the hydrolytic

weight reduction processes, the textiles are known to become softer and more hydrophilic. Structural identifications of the hydrolyzed oligomer products of various polymers including polyamides and polyesters were reported by several groups using MALDI-TOF mass spectrometry, where they focused on the characterization of different end groups present in the oligomer chains.^{9,15}

Polytrimethylene terephthalate (PTT) has been commercially available for nearly 50 years. It is known to be produced through a condensation or transesterification process from the two monomer units, which are 1,3-propanediol and terephthalic acid or dimethyl terephthalate. Similar to polyethylene terephthalate (PET), the polyester PTT is used to make carpet fibers.

Here, we report the structural analyses of polytrimethylene terephthalate (PTT) supplied by DuPont and the characterization of the hydrolytic degradation products after acid hydrolysis by means of MALDI-TOF mass spectrometry. Self-calibration and internal calibration methods for the MALDI-TOF mass spectra enabled us to determine the accurate mass values and to distinguish all the oligomers with different end groups. Wavelength and power dependence of the laser pulse on the generation of MALDI ions of PTT, and the relative affinity of metal adducts to PTT oligomers are also discussed.

Experimental Section

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

Depending on the samples and matrices, N₂ laser (337 nm,

4 ns pulse width, Spectra Physics) or Nd:YAG laser (355 nm, 6~7 ns pulse width, Continuum) were used for desorption and ionization of the analytes. The laser beam was loosely focused onto the 1/4 inch diameter probe tip at a 45° angle to the probe surface with a 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 estimated as *ca.* $10^6 \sim 10^7 \text{ W/cm}^2$ by measuring the spot size of the beam on the probe tip.

Spectral resolution was optimized using standard polystyrene samples ($M_w = 4,000$ and $M_w = 13,200$) and the best resolution was achieved with the repeller and extractor voltages of 26 kV and 16 kV, respectively. The resolution was estimated as ~400 at 3500 Da and ~300 at 10,000 Da, respectively. Normally, data were recorded by summing 700~1,000 transients using a LeCroy digital oscilloscope (LT372, 500 MHz bandwidth, 4 G sampling rate) and subsequently transferred to an IBM PC for further processing.

The materials used in MALDI sample preparation such as matrices, solvents, and metal adducts were purchased from Aldrich Chemical Co. α -cyano-4-hydroxy cinnamic acid (CHCA), dithranol, acetonitrile (ACN), trifluoroacetic acid (TFA), tetrahydrofuran (THF), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), potassium Iodide (KI), sodium trifluoroacetate (NaTFA), silver trifluoroacetate (AgTFA) were used as supplied. Angiotensin II, P₁₄R (synthetic peptide), ACTH fragment 18 - 39, insulin oxidized B chain, and polystyrenes were also purchased from Aldrich for mass calibration and optimization of spectral resolution.

The PTT sample provided from DuPont was used without any structural information. The PTT chips were ground to powder and dried under vacuum at 60 °C for 3 days before use. Hydrolysis of the PTT sample was carried out with water in TFA following the same procedures as described in previous work.¹⁵ Typically, 1.2 g of PTT was refluxed with 200 mL of TFA at 85 °C under nitrogen. Hydrolysis was carried out for 29 hours by slowly adding 50 mL of distilled water while constantly stirring. The mixture was then added to aqueous ammonia solution to neutralize TFA. 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 dried under vacuum at 80 °C for 3 days before MALDI analysis.

The original or acid-hydrolyzed PTT samples for MALDI analysis were prepared as follows; polymer solution (1.8 mg/mL in HFIP), dithranol matrix solution (10 mg/mL in HFIP), and metal adduct (NaTFA or KI) solution (3 mg/mL in HFIP) were mixed in 5:5:1 volume ratio. Using a micropipette, 2~3 μL of the mixture was loaded on the MALDI sample probe tip and slowly dried to allow co-crystallization of the analyte and matrix. This procedure is referred to as the dried droplet method.

Results and Discussion

From the simple relationship between m/z and time-of-flight t , i.e., $m/z = at^2 + b$,¹⁶ the absolute masses were determined by applying internal or external calibration procedures using standard samples with well defined masses. Four standard mass

samples were selected to cover the mass range of interest in this study; angiotensin (1,046 Da), P₁₄R (1,533 Da), ACTH fragment 18 - 39 (2,465 Da), and insulin oxidized (3,494 Da). The calibration sample mixture was prepared by mixing the standard mass solution (each mass standard in concentration of 20 nmole/mL in TFA) with matrix solution (10 mg of CHCA in 1 mL of TFA/ACN) at 1:1 volume ratio. A MALDI probe tip was designed such that two different samples could be loaded and analyzed consecutively without breaking the vacuum or changing the experimental conditions by simply rotating the probe tip by 180 degree. Spotting the analyte sample on one side of the split probe tip and the standard sample on the other half side, MALDI-TOF mass spectra of both analyte and standard sample were obtained without changing high voltages, laser powers, or flight length of the ions.

For the preparation of the polystyrene sample, dithranol (20 mg in 1 mL of THF) and silver trifluoroacetate (3 mg in 1 mL of THF) solutions were used as the matrix and cationization agent, respectively. The polystyrene solution (10 mg in 1 mL of THF) was mixed with dithranol and silver trifluoroacetate solutions at 5:5:1 volume ratio. The samples were loaded and crystallized using the dried droplet method. With this configuration, the MALDI spectrum of polystyrene ($M_w = 4,000$, repeat unit 104.15 Da) was acquired (Figure 1) along with that of the

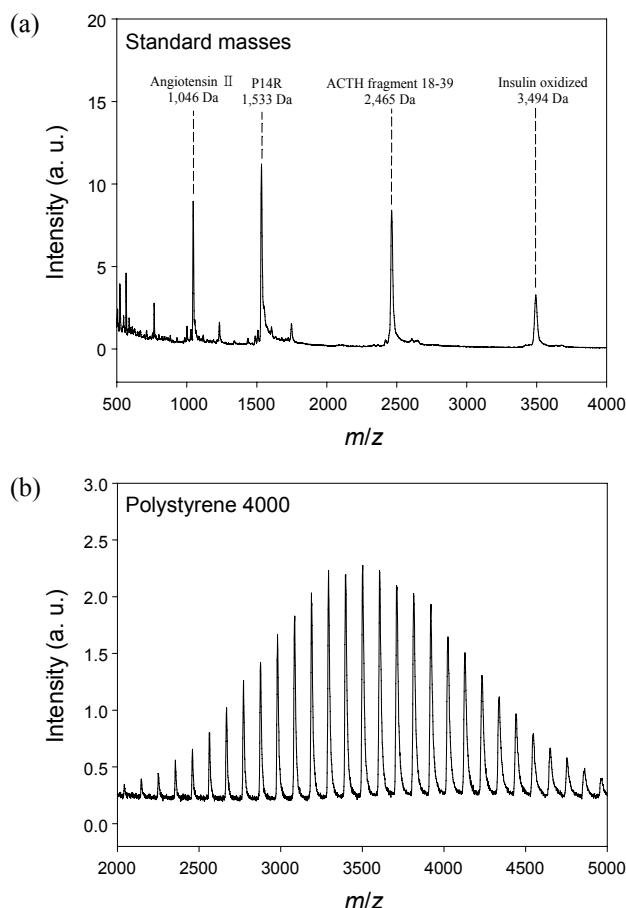


Figure 1. MALDI-TOF mass spectra of (a) four standard mass compounds; angiotensin II (1,046 Da), P₁₄R (1,533 Da), ACTH fragment 18-39 (2,465 Da), insulin oxidized (3,494 Da) and (b) polystyrene ($M_w = 4,000$, unit mass 104.15 Da).

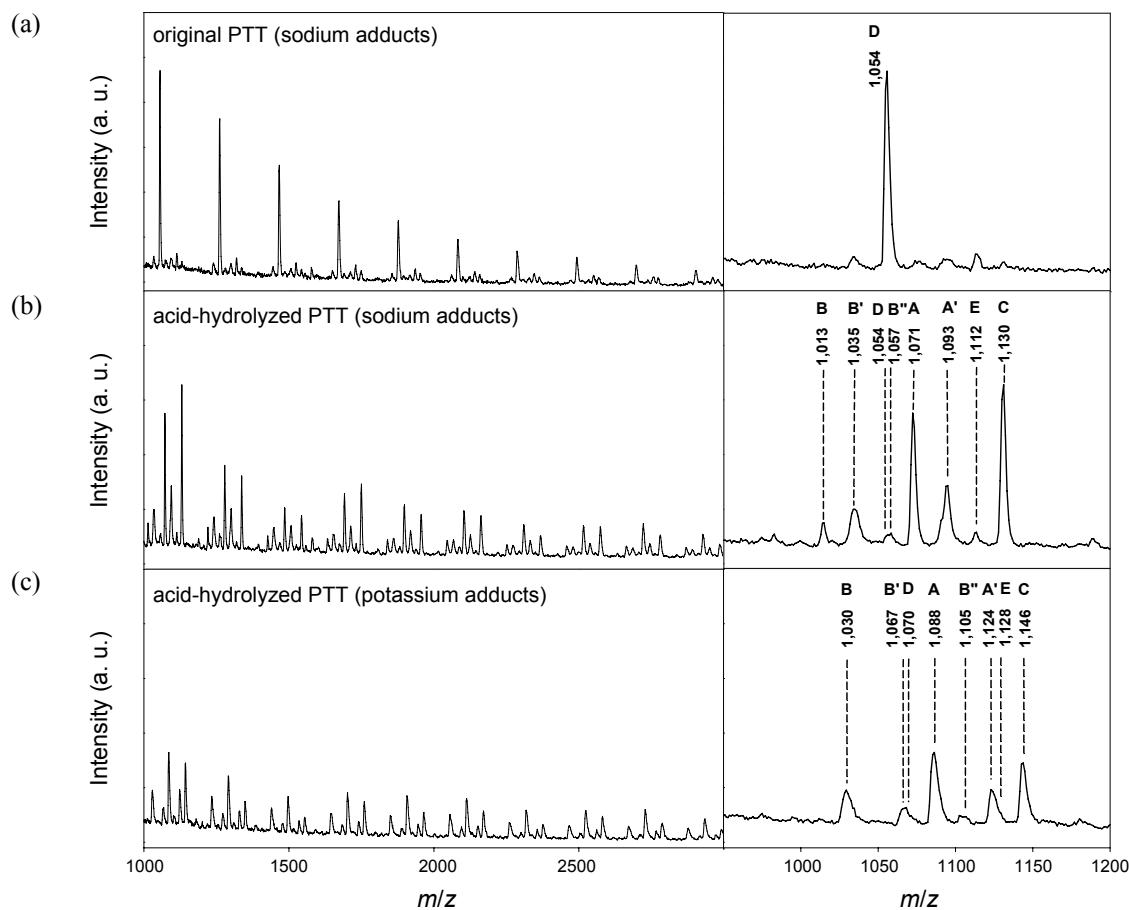


Figure 2. MALDI-TOF mass spectra of (a) original PTT (sodium adducts), (b) acid-hydrolyzed PTT (sodium adducts) and (c) acid-hydrolyzed PTT (potassium adducts). Structural assignments and labels of mass series are described in the text and Table 1.

standard sample comprised of four standard masses. From the optimized coefficients a and b determined from time-to-mass conversion of the standard mass sample, all the mass peaks produced from polystyrene were assigned with a discrepancy of less than 1 Da of absolute mass. The mass calibration of MALDI TOF spectra of the PTT samples were conducted in the same way. Time-to-mass conversion of time-of-flight mass spectra was also achieved using the self-calibration method developed previously.¹⁷⁻¹⁹ The method allows absolute mass values to be obtained in MALDI-TOF mass spectra of polymers when the repeat unit of at least one component in the polymer sample to be analyzed is known.

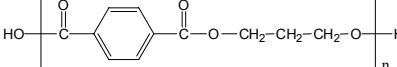
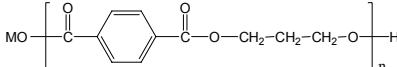
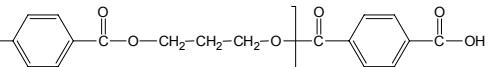
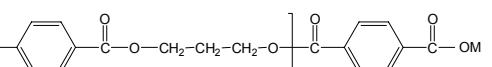
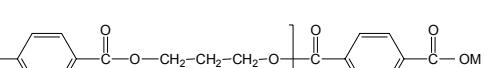
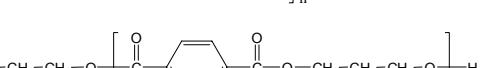
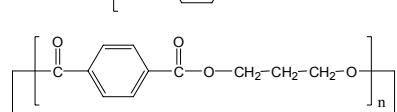
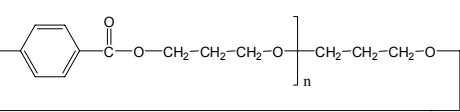
The PTT sample from Dupont is expected to be produced by a method called condensation polymerization or transesterification, where the two monomer units used in producing this polymer are 1,3-propanediol (PDO) and terephthalic acid (TPA) or dimethyl terephthalate (DMT). The MALDI-TOF mass spectrum of the untreated PTT sample as supplied is presented in Figure 2a. The spectrum shows molar-mass distribution of oligomers of moderate polydispersity.¹ The polydispersity index D is defined as $D = M_w/M_n$, where M_n is the number-average molar mass and M_w is the weight-average molar mass. Since $M_n < M_w$, the index D is always larger than 1. Narrow mass distributions are characterized by D values close to 1, whereas broad mass distributions are characterized by D values of 2 or higher.

For our PTT sample, the D value was estimated to be approximately 1.3 ignoring the presence of a low mass tail.

From the mass conversion and structural assignment, we determined that the original PTT sample contains a dominant fraction of cyclic oligomers and a trace amount of several linear oligomers with different end groups. Assignment of the mass series with different end groups will be discussed below. The relative abundances of cyclic forms decreases drastically as the mass grows, which is a typical result often found in synthetic polymers containing cyclics.²⁰ Peaks due to the cyclic oligomers are stronger than those due to linear ones up to $n = 13$, whereas in the region above 3,000 Da the intensities due to both types of oligomers reach about the same level. For our PTT sample, it was estimated that about 85% of oligomers are present in cyclic forms in the mass range of 1,000~3,000 Da (repeat unit $n = 4 \sim 15$). The sodiated cyclic structure of PTT (unit mass 206.2 Da) is presented in Table 1.

The relative ion intensities may not correctly reflect the relative abundances of the molecules present in the sample due to the intrinsic problem of MALDI-TOF mass spectrometry, so called the mass discrimination effect. Although, to derive quantitative molar-mass distribution, the ionization yield of various oligomers must be independent of chain size and the detector should show a constant response to ions regardless of mass of the oligomers, the ion yield and the detector response usually

Table 1. Structural assignment of the peaks displayed in the MALDI-TOF mass spectra of PTT with sodium and potassium adducts reported in Figure 2

Species	Structure	n	$+Na^+$ (M=Na)	$+K^+$ (M=K)
A	M ⁺	5	1,071
A'	M ⁺	5	1,093
B	M ⁺	4	1,013
B'	M ⁺	4	1,035
B''	M ⁺	4	1,057
C	M ⁺	5	1,130
D	M ⁺	5	1,054
E	M ⁺	5	1,112

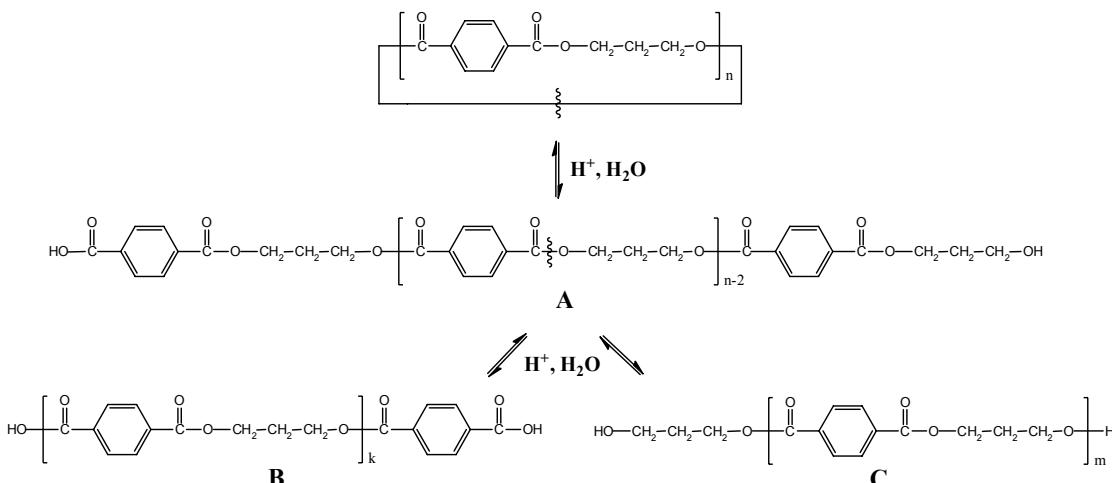
decrease with chain length in many cases.²¹ One solution for this problem is to produce samples with sufficiently low polydispersity close to 1 by a fractionation method such as size exclusion chromatography.²² However, since the mass range of the cyclic oligomers is relatively limited, the mass discrimination can be regarded not to be very severe in our case.

The MALDI-TOF mass spectra of PTT hydrolyzed with water in TFA were presented in Figure 2. The spectra of original PTT with Na adducts (Figure 2a), hydrolyzed PTT with Na adduct (Figure 2b) and with K adducts (Figure 2c) are plotted in the mass range of 1,000 ~ 3,000 Da along with the expanded spectra for comparison of three samples. Assigned oligomer structures corresponding to each series of peaks with various end groups are summarized in Table 1 for sodium and potassium adducts. Absolute ion masses of the assigned structures and the number of repeat units are also shown.

It is evident from Figure 2 that the cyclic oligomers (D series) are almost completely hydrolyzed and only trace amounts are detected after hydrolysis. The main mass spectral features of the MALDI spectra is contributed by 3 series of intense peaks, i.e., PTT containing carboxyl/OH end groups (series A), carboxyl/carboxyl end groups (series B), and OH/OH end groups (series C). The oligomers containing metal ions as salt forms are designated by single or double primes depending on the number of metal ions. Series A and B are capable of holding metal ions as salt forms due to the presence of acidic carboxyl end groups,

whereas series C and D can be present only as molecular forms. Another cyclic form is present in the PTT sample as a minor component and classified as series E. The corresponding structure for PET has been reported in previous work on thermal degradation of PET.²³ Part of the peaks associated with these series which correspond to oligomers of a mass range of 1,000 ~ 1,200 Da with repeat unit n = 4 or 5 are enlarged and presented in Figure 2. Assigned series of peaks are consistent with the expected products generated from the hydrolysis reaction of the original PTT which is cyclic as determined before and constitutes a majority of the untreated PTT sample. The hydrolysis reaction scheme which produces oligomers with different types of end groups is presented in Scheme 1.

The distributions of relative abundances of the main series of linear oligomer products (series A, B, and C) are plotted as a function of number of unit masses n in Figure 3 as well as those of cyclics before hydrolysis (series D). The molar mass distributions of the linear oligomer products produced from hydrolysis shows a tendency of a bimodal distribution, which results from the fact that the larger the size of the oligomer, the greater a chance it has to be hydrolyzed. According to Scheme 1, hydrolysis of the cyclic form must produce carboxyl/OH ended oligomers (series A), that are hydrolyzed into series B and C, or two A's. Further hydrolysis of series B always generates series A and B, whereas hydrolysis of series C generates series A and C. Hence series A will remain as the most abundant



Scheme 1. Hydrolytic process of cyclic PTT (series D) and expected products bearing different end groups (series A, B and C)

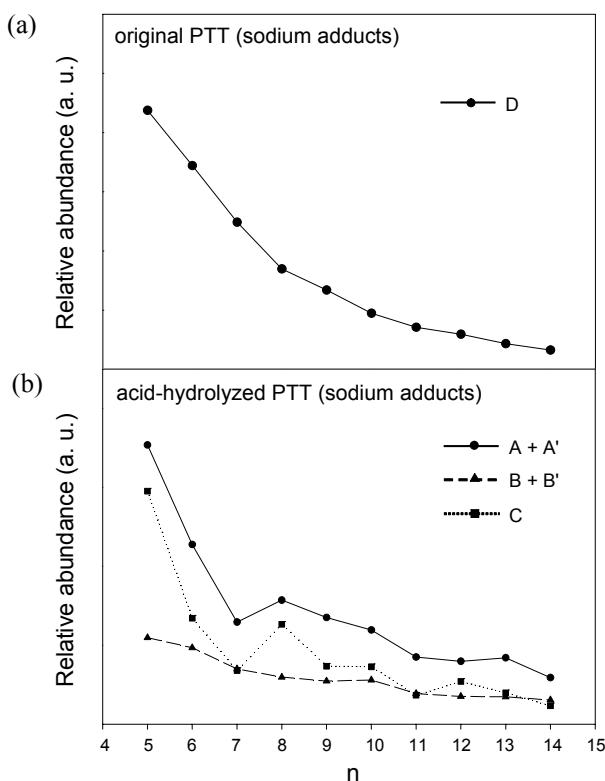


Figure 3. Distribution of relative abundance of the oligomers as a function of number of unit masses n : (a) before hydrolysis (Na^+ adducts of cyclics), (b) after hydrolysis (Na^+ adducts of linear forms).

species until the completion of the hydrolysis and the relative abundances of the species presented in Figure 3 are consistent with the hydrolysis scheme.

The ionization of synthetic polymers is generally known to occur through cationization rather than protonation in contrast to biopolymers, which is consistent with our results. Examination of the assigned structures of the ions listed in Table 1 reveals that the ions are produced *via* attachment of at least more than one metal ion. From Figure 2b and 3c, it is evident that the

peak intensities of sodium adducts are over two times stronger than those of potassium adducts. From this observation, the PTT samples seem to have a higher affinity for Na^+ than for K^+ , and as a consequence show higher ionization yield with Na^+ at least when dithranol is used as a matrix. Moreover, the MALDI spectrum of the mostly cyclic original PTT sample was hard to obtain using the potassium adducts. This also implies that the cyclic form of PTT has much lower affinity for K^+ than for Na^+ . There are some rough agreements on the rules for selection of the dopant most effective for a given polymers, but they are more or less empirical.²⁴ For example, polystyrene shows a higher affinity for Cu^+ than for K^+ , whereas polyethylene glycol shows a higher affinity for K^+ than for Cu^+ . These preferential attachments were discussed in terms of hard and soft acids in previous report.²⁴ In actuality, the ionization efficiency changes with the analyte even though ionization efficiency and cation attachment are closely connected. It has been reported previously that the relative ion yields of the hydroxyl-terminated oligomers of polyester decreased with dithranol on increasing the cation size from Na^+ to K^+ or Cs^+ .²⁵ The same trend has been observed in the present study as shown in Figure 1c. Since the cyclic form is lacking polar or ionizable end groups present in linear chains, it seems to be reasonable to state that the compositional estimate of 85% of cyclic forms in the original PTT sample can be regarded as a lower limit.

The threshold irradiance to obtain MALDI spectra mainly depends on the matrix among many other factors. Using dithranol as a common matrix, it was found that the threshold pulse power of a 355 nm laser beam for potassium adducts ($\sim 70 \mu\text{J}/\text{pulse}$) is higher than for sodium adducts ($\sim 50 \mu\text{J}/\text{pulse}$), which also could be related to the affinity difference between K^+ and Na^+ . The laser desorption/ionization was accomplished slightly above the threshold irradiance to minimize the saturation of detector and to increase the mass resolution. Finally, it is worthwhile to mention that 355 nm of the Nd:YAG laser was much superior to 337 nm of the N₂ laser in ionization efficiency and mass resolution. Even though the mechanisms of ion formation in MALDI process are still not fully understood, softer ionization with lower energy (longer wavelength) laser pulse was

more efficient in obtaining the MALDI spectra of PTT under our experimental conditions.

Conclusions

The structural analysis of polytrimethylene terephthalate (PTT) and the characterization of the hydrolytic degradation products after acid hydrolysis were conducted using a linear MALDI-TOF mass spectrometer constructed in our laboratory. Through time-to-mass conversion, we were able to determine accurate mass values and distinguish all oligomers with different end groups. The MALDI-TOF mass spectra of the original PTT sample showed a moderate polydispersity ($D \sim 1.3$) and the spectral analysis revealed that the sample was mainly composed of cyclic forms and the relative composition was estimated over 85%. MALDI-TOF mass spectra of the acid-hydrolyzed PTT sample showed three series of oligomer products with different end groups in accordance with the hydrolysis scheme of cyclic PTT, which were carboxyl/OH, carboxyl/carboxyl, and OH/OH end groups. Relative abundance and bimodal distribution of differently terminated oligomers with respect to the molar masses confirmed a random and statistical cleavage of ester bonds during hydrolysis.

From the examination of peak intensities for both sodium and potassium adducts of PTT, it was concluded that the PTT samples show higher ionization efficiency with sodium adducts when dithranol is used as a matrix. Similarly, the threshold irradiance of the laser light for the sodium adducts was measured to be lower than that for the potassium adducts. In addition, compared with the 337 nm N_2 laser pulses, relatively soft ionization with the 355 nm YAG laser pulses was much more efficient in obtaining high quality MALDI spectra of the PTT samples using dithranol as a matrix.

Acknowledgments. This study was funded by the Korea Science and Engineering Foundation (Grant No. R01-2003-000-10886-0) and partly by the research program 2008 of Kookmin University in Korea. The authors gratefully acknowledge Prof. Montaudo for kindly providing the CALTOF program for mass calibration.

References

- (a) Montaudo, G.; Samperi, F.; Montaudo, M. S. *Prog. Polym. Sci.* **2006**, *31*, 277. (b) Montaudo, G.; Lattimer, R. P. *Mass Spectrometry of Polymers*; CRC Press: New York, 2002; Pasch, H.; Schrepp, W. *MALDI-TOF Mass Spectrometry of Synthetic Polymers*; Springer: New York, 2003.
- Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F. *Anal. Chem.* **1992**, *64*, 2866.
- Nielen, M. W. F. *Mass Spectrom. Rev.* **1999**, *18*, 309.
- Wu, K. J.; Odom, R. W. *Anal. Chem.* **1996**, *68*, 873.
- Thomson, B.; Suddaby, K.; Rudin, A.; Lajoie, G. *Eur. Polym. J.* **1996**, *32*, 239.
- Pasch, H.; Gores, F. *Polymer* **1995**, *36*, 1999.
- Braum, D.; Ghahary, R.; Pasch, H. *Polymer* **1996**, *37*, 777.
- Pasch, H.; Ghahary, R. *Macromol. Symp.* **2000**, *152*, 267.
- Montaudo, G.; Montaudo, M. S.; Puglisi, C. *Journal of Polymer Science, Part A: Polymer Chemistry* **1996**, *34*, 439.
- Skelton, R.; Dubois, F.; Zenobi, R. *Anal. Chem.* **2000**, *72*, 1707.
- Chionna, D.; Puglisi, C.; Samperi, F.; Montaudo, G.; Turturro, A. *Rapid Comm. Mass. Spectrom.* **2001**, *22*, 524.
- Puglisi, C.; Samperi, F.; Giorgi, S. D.; Montaudo, G. *Polymer Degradation and Stability* **2002**, *78*, 369.
- Carroccio, S.; Puglisi, C.; Montaudo, G. *Macromolecules* **2003**, *36*, 7499.
- Carroccio, S.; Puglisi, C.; Montaudo, G. *Macromolecules* **2004**, *37*, 6037.
- Choi, H.; Choe, E. K.; Yang, E. K.; Jang, S.; Park, C. R. *Bull. Korean Chem. Soc.* **2007**, *28*, 2354.
- Cotter, R. J. *Time-of-Flight Mass Spectrometry*, ACS Professional Reference Books; 1997.
- Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Rapid Comm. Mass. Spectrom.* **1994**, *8*, 981.
- Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Anal. Chem.* **1994**, *66*, 4366.
- Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Rapid Comm. Mass. Spectrom.* **1995**, *9*, 453.
- Spassky, N.; Platzgraf, H.; Simic, V.; Montaudo, M. S. *Macromol. Chem. Phys.* **2000**, *201*, 2432.
- Scamporrino, E.; Maravigna, P.; Vitalini, D.; Mineo, P. *Rapid Comm. Mass. Spectrom.* **1998**, *12*, 646.
- Montaudo, M.; Puglisi, C.; Samperi, F.; Montaudo, G. *Rapid Comm. Mass. Spectrom.* **1998**, *12*, 519.
- Samperi, F.; Puglisi, C.; Alicata, R.; Montaudo, G. *Polymer Degradation and Stability* **2004**, *83*, 3.
- Llenes, C. F.; O'Malley, R. M. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 564.
- Lainel, O.; Österholm, H.; Järvinen, H.; Wickström, K.; Vainiotalo, P. *Rapid Comm. Mass. Spectrom.* **2000**, *14*, 482.