

# Characterization of Polyesters Prepared from Three Different Phthalic Acid Isomers by CID-ESI-FT-ICR and PSD-MALDI-TOF Mass Spectrometry

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**Polyesters prepared from the same diol, 2-butyl-2-ethyl-1,3-propanediol, but different phthalic acid isomers, phthalic, isophthalic, and terephthalic acid, were characterized by collision-induced dissociation electrospray ionization Fourier transform ion cyclotron resonance (CID-ESI-FT-ICR) and postsource-decay matrix-assisted laser desorption/ionization time-of-flight (PSD-MALDI-TOF) mass spectrometry. Sodiated dihydroxyl-terminated polyester oligomers containing five repeating units at  $m/z$  1634 were selected as precursor ions for dissociation studies. Two main mechanisms occurred in the fragmentation of all of the polyesters, since dissociation of the oligomers was initiated by hydrogen rearrangement or transesterification reactions. Polyesters prepared from different phthalic acid isomers could be distinguished by their fragmentation behavior. Polyester prepared from phthalic acid was easily identified by using both CID-ESI-FT-ICR and PSD-MALDI-TOF mass spectrometry. However, distinguishing between the polyesters prepared from isophthalic and terephthalic acid succeeded marginally only with CID-ESI-FT-ICR mass spectrometry. Molecular dynamics calculations were used to obtain an idea of the fragmentation behavior of the polyesters. The low-energy structures of the precursor ions were determined, and the coordination of the oxygen atoms of the polyester oligomers to the sodium cation was examined more closely. Both the experimental and the theoretical studies showed that the sodium ion affinity of polyester changed with the phthalic acid isomer.**

Polyesters are polymers with a number of different applications. They are used in fibers and films as well as in composite materials. Polyesters are also widely applied as coating materials and, in addition, many of the biodegradable polymers are polyesters. Polyesters are conventionally prepared from polyols and from polyacids or derivatives of polyacids by step-growth polymerization. Different phthalic acid isomers—phthalic, isophthalic, and terephthalic acid—are some of the most commonly used feedstocks of polyesters. These aromatic diacids improve the hydrolytic stability, durability, and viscosity of the final polyester material, for instance.<sup>1</sup>

The chemical compositions of the polyesters that are prepared from phthalic acid isomers may be characterized by spectroscopic methods such as Raman<sup>2</sup> and NMR<sup>3,4</sup> spectroscopy. Phthalic acid isomers are readily distinguished by their characteristic Raman bands and chemical shifts. In addition, both analytical methods enable quantification of the amounts of acid components in the polyester, which is highly useful in the determination of the compositions of copolyesters.<sup>2,4</sup> A limitation of spectroscopic analyses is, however, that only the average structures of the polyesters may be determined. More detailed information about the polyester samples can be obtained by means of mass spectrometry, since this can be used to characterize the individual polyester chains. In recent years, matrix-assisted laser desorption/ionization (MALDI)<sup>5–24</sup> and electrospray ionization (ESI)<sup>10,17,19,25–29</sup>

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have been found to be the most convenient ionization techniques for the mass spectrometric analysis of polyesters. They have been successfully used to study the polyesters based on phthalic,<sup>14,19,22</sup> isophthalic,<sup>9,10,12,19,22,24,28</sup> and terephthalic acid,<sup>8,12,15,16,18,20</sup> in addition to the aliphatic polyesters.

When the peaks of the different polyester chains are separated in the mass spectrum, the structures of the end groups and repeating units may be concluded from the masses of the chains. In addition to the homopolyesters, the compositions of the copolyesters<sup>5,11,18,20,23</sup> have been estimated by means of normal mass spectra. However, a structural characterization of the polyester chains using molecular masses requires that the starting materials of the polyester should be known or the character of the polyester should have also been defined by some other method. Determination of the structure of an unknown polyester may be assisted by the chemical treatment<sup>15,6,10,17,21,22,24</sup> or pyrolysis<sup>6</sup> of the sample. Furthermore, closer examination can be performed by means of a mass spectrometric fragmentation technique, such as collision-induced dissociation (CID),<sup>25–30</sup> which also makes it possible to characterize the sequence of an entire polyester chain.

CID studies of polyesters have been carried out on samples ionized by ESI by using Fourier transform ion cyclotron resonance (FT-ICR),<sup>28</sup> ion-trap,<sup>26,27,29</sup> and triple quadrupole<sup>25</sup> mass spectrometers and on a sample ionized by MALDI by using a hybrid magnetic-sector time-of-flight (TOF) instrument.<sup>30</sup> Another mass spectrometric fragmentation technique is postsorce decay (PSD), which has not been used previously for the characterization of polyesters but has been used for investigating polycarbonate,<sup>31</sup> poly(methyl methacrylate),<sup>32</sup> polystyrene,<sup>32,33</sup> and poly(ethylene oxide)-*b*-poly(*p*-phenylene ethynylene) diblock copolymer.<sup>34</sup> PSD

studies have been performed on the polymers ionized by MALDI using TOF<sup>31–34</sup> and magnetic-sector-TOF<sup>32</sup> mass spectrometers.

Our interest was in whether the polyesters prepared from different phthalic acid isomers could be identified by mass spectrometry. Such information would, for example, assist in the characterization of copolyesters prepared from different phthalic acid isomers.<sup>12</sup> The polyesters attracting our attention were poly-(2-butyl-2-ethyl-1,3-propylene phthalate) (PA-BEPD), poly(2-butyl-2-ethyl-1,3-propylene isophthalate) (IPA-BEPD), and poly(2-butyl-2-ethyl-1,3-propylene terephthalate) (TPA-BEPD). These were prepared from phthalic anhydride (PA), isophthalic acid (IPA), terephthalic acid (TPA), and 2-butyl-2-ethyl-1,3-propanediol (BEPD). In an earlier study of isomeric dihydroxybenzene phthalate polyesters, the monomeric structures of poly(1,2-dihydroxybenzene phthalate), poly(1,3-dihydroxybenzene phthalate), and poly(1,4-dihydroxybenzene phthalate) have been distinguished by mass spectrometric analysis of their pyrolysis products.<sup>35</sup> However, pyrolysis is not a sufficiently selective method for determining the whole sequence of an individual polyester chain.

To study individual polyester oligomers, we employed CID-ESI-FT-ICR and PSD-MALDI-TOF mass spectrometry as the tools for analyzing our samples. Earlier fragmentation studies of polyesters using the CID method have been performed on samples whose components differed in their masses. The present study is the first reported attempt in which an attempt has been made to identify the structural isomers located in a particular polymer chain. In our CID experiments, we used a sustained off-resonance irradiation (SORI)<sup>36</sup> technique, which increases the upper mass limit of the ions that can be studied by means of CID with a particular FT-ICR instrument. SORI-CID has been previously applied in the characterization of poly(ethylene glycol), polyisoprene, and polystyrene with MALDI-FT-ICR<sup>37</sup> and also in the characterization of polyesters with ESI-FT-ICR.<sup>28</sup> In the present CID and PSD experiments, sodium adduct cations of dihydroxyl-terminated oligomers of PA-BEPD, IPA-BEPD, and TPA-BEPD were selected as the parent ions.

Molecular dynamics calculations were used to obtain an idea of the fragmentation behavior of the PA-BEPD, IPA-BEPD, and TPA-BEPD polyesters. The minimum energy structures of the parent ions were determined. Similar calculations were made earlier for the alkali metal adduct ions of poly(ethylene glycol),<sup>38</sup> poly(ethylene terephthalate),<sup>39</sup> and poly(methyl methacrylate).<sup>40</sup>

## EXPERIMENTAL SECTION

**Materials.** The polyesters PA-BEPD, IPA-BEPD, and TPA-BEPD were prepared by melt polycondensation from PA, IPA, and TPA with an excess of BEPD, as described elsewhere.<sup>24</sup> NaI used in the ESI studies was obtained from Merck (Darmstadt, Germany), and NaI used in the MALDI experiments was obtained

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from Aldrich (Steinheim, Germany). MALDI matrix 2,5-dihydroxybenzoic acid (DHB) was purchased from Aldrich (Gillingham, U.K.).

**ESI Sample Preparation.** Stock solutions of polyesters and NaI were prepared by dissolving the polyesters in acetone and NaI in water at a concentration of 1 mg/mL. For the ESI measurements, a diluted solution of polyester and NaI was prepared by mixing 5  $\mu$ L of the polyester solution and 1  $\mu$ L of the NaI solution with 1 mL of methanol.

**ESI-FT-ICR Mass Spectrometry.** The ESI studies were carried out using a Bruker BioAPEX II 47e Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a 4.7 T superconducting magnet (MagneX Scientific, Abingdon, U.K.) and an infinity ICR cell. Ions were generated in an external ESI source (Analytica of Branford, Branford, CT) and guided into the ICR cell with an rf-only hexapole ion guide. Sample solutions were introduced using a syringe pump at a flow rate of 50  $\mu$ L/h, and nitrogen was used as a drying gas at 250 °C. The ionization voltage was  $-3.3$  kV.

Argon was used as a collision gas in the CID experiments. The sample ions that were trapped in the ICR cell were at first collisionally cooled using an argon pulse followed by a 2-s reaction delay. The precursor ions that were isolated by the correlated harmonic excitation fields (CHEF) technique<sup>41</sup> were excited using a SORI excitation pulse with an off-resonance frequency of 500 Hz and a duration of 250 ms. The excitation energy was adjusted by changing the peak-to-peak voltage,  $V_{pp}$ . The reaction delay after excitation was 5 s, after which a spectrum was recorded. A total of 64 spectra were accumulated in each CID experiment.

**MALDI Sample Preparation.** Polyester samples were dissolved in tetrahydrofuran at a concentration of 2 mg/mL. NaI was dissolved in methanol at a concentration of 4 mg/mL, and DHB matrix was dissolved in methanol at a concentration of 20 mg/mL. Separate solutions of the sample, salt, and matrix were mixed in a volume ratio of 5:1:15. An  $\sim 0.5$ - $\mu$ L portion of the mixture was applied to the target plate and allowed to air-dry.

**MALDI-TOF Mass Spectrometry.** MALDI studies were performed with a Bruker Reflex II time-of-flight mass spectrometer (Bruker-Franzen Analytik, Bremen, Germany) equipped with a nitrogen laser ( $\lambda = 337$  nm) and a microchannel plate detector. Measurements were carried out in reflectron mode using delayed extraction. The length of the flight tube was 145 cm; and the delay time, 50 ns. The acceleration voltage was 28.5 kV; the extraction voltage, 20 kV; the lens voltage, 10 kV; and the detector voltage,  $-1.5$  kV.

The precursor ions were selected by the ion gate situated in the linear tube after the ion source. To collect PSD data, the reflector voltage was decreased in 15 steps from 30 to 0.95 kV. The segments acquired for each reflectron voltage were pasted together to produce a complete MALDI-PSD spectrum. An optimal value of the laser irradiance was tested for every segment of each sample so that the fragments detected had a signal intensity as high as possible. A total of 200 laser shots were employed to obtain a spectrum of each segment.

**Molecular Modeling.** The AMBER 5.0 suite of molecular mechanics/dynamics programs<sup>42</sup> was used to obtain further

structural information on the precursor ions selected for the dissociation studies. Because of the large number of different conformations available for polymers, a series of annealings and energy minimizations were employed to obtain the possible structures of the sodium adducts of polyester oligomers. The initial structure of each sodium adduct was energy-minimized, and the molecular dynamics simulation was started by raising the temperature in 5 ps from 0 K to the high temperature, which was 800 K for PA-BEPD, 750 K for IPA-BEPD, and 700 K for TPA-BEPD. The temperature was maintained at a high value for 20 ps and then reduced back to 0 K in another 20 ps, where it was maintained for 5 ps. The final structure was energy-minimized and used as a starting point for another molecular dynamics run. This procedure was repeated until 100 low-energy structures were obtained for each precursor ion. The highest temperature for each polyester was selected so that the sodium cation was not ejected from the system during heating.

## RESULTS AND DISCUSSION

All three polyesters, PA-BEPD, IPA-BEPD, and TPA-BEPD, were found to contain mainly dihydroxyl-terminated oligomers, which appeared as the most abundant peak series in both the ESI and MALDI spectra. This was expected, since the polyesters were synthesized using an excess of BEPD. In addition, doping the samples with NaI caused most of the peaks appearing in the ESI and MALDI spectra to correspond to sodiated oligomers. The mass of the repeating unit, 290 Da, was seen as the difference of similarly terminated oligomers in the spectra.

For the CID-ESI-FT-ICR and PSD-MALDI-TOF studies, the sodium adduct ions of the dihydroxyl-terminated oligomers of PA-BEPD (1), IPA-BEPD (2), and TPA-BEPD (3) at  $m/z$  1634, consisting of five repeating units, were selected as precursor ions. The structures of the oligomers that were selected for the fragmentation studies are presented in Scheme 1.

Fragmentation of the sodiated polyester oligomers under CID and PSD conditions was found to take place with similar mechanisms. Two main fragmentation mechanisms occurred in the experiments, and series of fragment ion peaks were observed in all of the product ion spectra. The fragmentation mechanisms were considered to be similar to those reported in an earlier CID-ESI-FT-ICR study of polyesters.<sup>28</sup> All of the fragments consisting of at least two repeating units were sodiated, but smaller fragments were mostly protonated instead, although the precursor ion was the sodium adduct cation. The main fragmentation pathways and the types of fragments are presented in Scheme 2. Sodium cation may remain for both of the fragments formed in the dissociation reactions, but the sodium affinities of the fragments affect the distribution of the sodium cations between the different fragments.

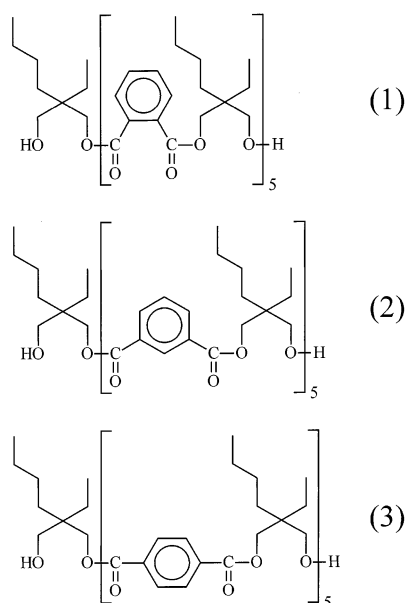
In mechanism 1, the rearrangement of the hydrogen leads to cleavage of the ester bond between the diol and diacid units. The rearranged hydrogen most probably originates from somewhere in the alkyl chains of the diol, and it is attached to the carbonyl oxygen of the diacid. Mechanism 1 produces two fragment ions that are a sodiated molecule with acid and alcohol end groups,

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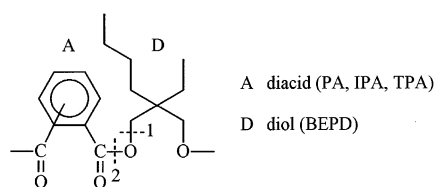
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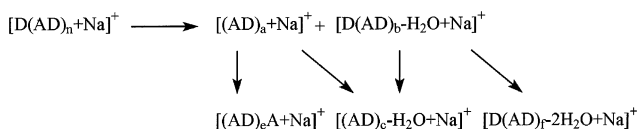
Scheme 1



Scheme 2



## 1. Hydrogen rearrangement



## 2. Transesterification



$[(AD)_a + Na]^+$ , and a sodiated molecule containing two alcohol end groups from which one water molecule has been cleaved,  $[D(AD)_b - H_2O + Na]^+$ . In mechanism 2, an alcohol end group of the sodiated oligomer reacts with an ester group in the same chain, leading to the cyclic structure  $[(AD)_c - H_2O + Na]^+$  and a fragment ion with two alcohol end groups,  $[D(AD)_d + Na]^+$ .

In addition, some fragment ions presumably originating from the primary fragments were observed. A fragment ion with two acid end groups,  $[(AD)_e A + Na]^+$ , is most probably formed from  $[(AD)_a + Na]^+$  via a secondary hydrogen rearrangement reaction. Another clear secondary dissociation product is  $[D(AD)_f - 2H_2O + Na]^+$ , which is formed as a consequence of an additional hydrogen rearrangement reaction in  $[D(AD)_b - H_2O + Na]^+$ . Fragment ions of the type  $[(AD)_c - H_2O + Na]^+$  are not necessarily sodiated cyclic molecules, since the linear fragment ions with the same elemental composition may also be formed from both  $[(AD)_a + Na]^+$  and  $[D(AD)_b - H_2O + Na]^+$  via a hydrogen rearrangement. The mass-to-charge values of the

Table 1. Sodiated Fragments Formed by Mechanisms 1 and 2

symbol	fragment ion	$m/z$
A	$[(AD)_a + Na]^+$	$a \times 290.15 + 18.01 + 22.99$
B	$[D(AD)_b - H_2O + Na]^+$	$b \times 290.15 + 160.15 - 18.01 + 22.99$
C	$[(AD)_c - H_2O + Na]^+$	$c \times 290.15 + 22.99$
D	$[D(AD)_d + Na]^+$	$d \times 290.15 + 160.15 + 22.99$
E	$[(AD)_e A + Na]^+$	$e \times 290.15 + 166.03 + 22.99$
F	$[D(AD)_f - 2H_2O + Na]^+$	$f \times 290.15 + 160.15 - 2 \times 18.01 + 22.99$

Table 2. Abundance Ratio of  $m/z$  23–1634 as a Function of Peak-to-Peak Voltage for the Different Polyesters

$V_{pp}$ (V)	PA-BEPD	IPA-BEPD	TPA-BEPD
10	0.01	0.02	0.07
12	0.03	0.11	0.34
14	1.71	5.54	19.4

fragment ions formed by mechanisms 1 and 2 can be calculated as shown in Table 1.

**CID-ESI-FT-ICR Mass Spectrometry.** SORI-CID experiments were carried out using three different values of peak-to-peak voltage  $V_{pp}$ , 10, 12, and 14 V, which corresponded to different collision energies, in which the higher the voltage was, the higher the energy was.<sup>36</sup> The intensities of the sodium cation and precursor ion peaks in the CID spectra were compared as a function of  $V_{pp}$ , since the loss of the adduct cation from the precursor ion was found to be a competing reaction for the fragmentation of the precursor ion, as in an earlier CID study of poly(methyl methacrylate) oligomers.<sup>40</sup> The abundance ratios of  $m/z$  23–1634 are presented for different polyesters in Table 2. The results clearly show that the sodium ion affinity of the polyester increases with the phthalic acid isomer in the order of TPA < IPA < PA. Measuring the CID spectra as a function of the collision energy also showed that changing  $V_{pp}$  did not affect the fragmentation mechanisms of the different polyesters. However, the abundance of low-mass fragments increased in comparison to that of the high-mass fragments, and furthermore, the relative abundance of some of the fragment ions changed as the collision energy increased.

The high-mass CID fragments from the sodiated PA-BEPD, IPA-BEPD, and TPA-BEPD oligomers at  $m/z$  1634 are presented in Figure 1. These spectra have been measured using a peak-to-peak voltage of 14 V, and only the fragment ions above  $m/z$  550 are displayed. The polyester PA-BEPD was evidently fragmented by both mechanisms 1 and 2, but the fragmentation of the polyesters IPA-BEPD and TPA-BEPD clearly occurred only with mechanism 1. Previous CID studies of the polyesters of adipic acid,<sup>28</sup> isophthalic acid,<sup>28</sup> and 3-hydroxybutanoic acid<sup>26,27</sup> have shown that hydrogen rearrangement is the main reaction that induces the fragmentation of these polyesters. On the other hand, the fragmentation behavior of polyesters in CID was found to be similar to that in pyrolysis, since pyrolysis of phthalic acid polyesters readily produces cyclic molecules.<sup>35</sup>

The most abundant fragments of PA-BEPD were of the type  $[D(AD)_d + Na]^+$  ions. These fragments were observed at  $m/z$

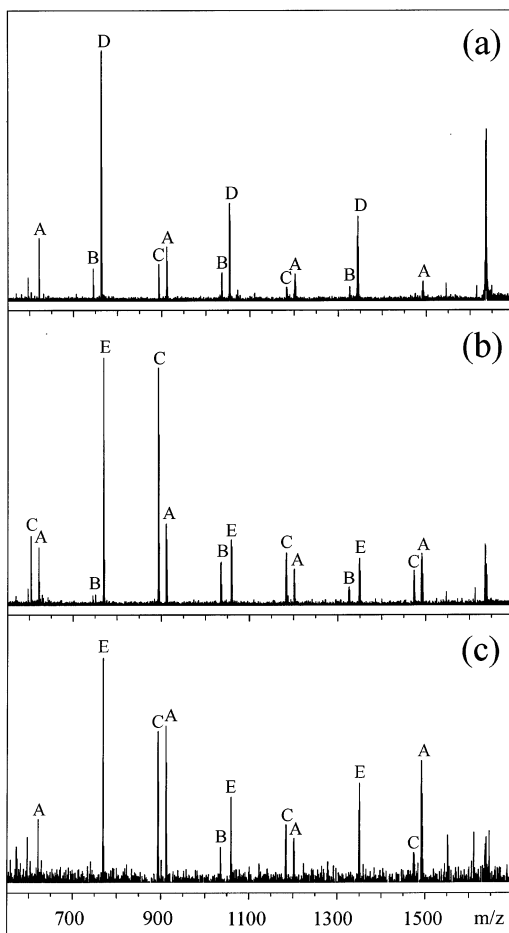


Figure 1. High-mass CID fragments from the sodiated PA-BEPD (a), IPA-BEPD (b), and TPA-BEPD (c) oligomers at  $m/z$  1634. Fragment ions of the type  $[(AD)_a + Na]^+$  (A),  $[D(AD)_b - H_2O + Na]^+$  (B),  $[(AD)_c - H_2O + Na]^+$  (C),  $[D(AD)_d + Na]^+$  (D), and  $[(AD)_eA + Na]^+$  (E) are shown.

763.4, 1053.5, and 1343.5. They can be formed only by an intramolecular transesterification reaction when the cyclic molecules have also been produced. The fragment ions at  $m/z$  893.4 and 1183.5 whose compositions are  $[(AD)_3 - H_2O + Na]^+$  and  $[(AD)_4 - H_2O + Na]^+$  may be sodiated cyclic molecules, but another possibility is that they are linear molecules that have been formed via hydrogen rearrangement reactions, as described earlier. However, the series of fragment ions of the type  $[(AD)_a + Na]^+$  and  $[D(AD)_b - H_2O + Na]^+$  was clear evidence of the hydrogen rearrangement. The ions of the type  $[(AD)_a + Na]^+$  were seen at  $m/z$  621.3, 911.3, 1201.5, and 1491.4, whereas the  $[D(AD)_b - H_2O + Na]^+$  ions were observed at  $m/z$  745.4, 1035.5, and 1325.5. When the peak-to-peak voltage was reduced from 14 to 10 V, the relative abundance of  $[(AD)_a + Na]^+$  ions had clearly increased, whereas that of the  $[D(AD)_d + Na]^+$  ions had decreased.

The two most abundant fragment ions originating from IPA-BEPD were  $[(AD)_2A + Na]^+$  at  $m/z$  769.2 and  $[(AD)_3 - H_2O + Na]^+$  at  $m/z$  893.3. The rest of the fragment ions had a much lower intensity in the spectrum, and their relative abundances were close to each other. Sodium adduct ions of the type  $[(AD)_eA + Na]^+$  also appeared at  $m/z$  1059.3 and 1349.3. The formation of  $[(AD)_eA + Na]^+$  fragment ions from IPA-BEPD was noticeably

different from the fragmentation behavior of PA-BEPD. Another important finding was the absence of  $[D(AD)_d + Na]^+$  fragment ions in the CID spectrum of IPA-BEPD. However, IPA-BEPD produced the series of  $[(AD)_a + Na]^+$ ,  $[D(AD)_b - H_2O + Na]^+$ , and  $[(AD)_c - H_2O + Na]^+$  fragment ions, as did PA-BEPD.  $[(AD)_a + Na]^+$  ions were seen at  $m/z$  621.2, 911.3, 1201.4, and 1491.4, whereas two peaks of  $[D(AD)_b - H_2O + Na]^+$  ions were at  $m/z$  1035.4 and 1325.4. In addition to the abundant  $[(AD)_3 - H_2O + Na]^+$  ion, the other  $[(AD)_c - H_2O + Na]^+$  fragment ions were observed at  $m/z$  603.2, 1183.4, and 1473.5. Reducing the peak-to-peak voltage from 14 to 10 V again increased the relative abundance of  $[(AD)_a + Na]^+$  ions and, in addition, reduced that of the  $[(AD)_c - H_2O + Na]^+$  and  $[(AD)_eA + Na]^+$  ions.

Fragment ions from TPA-BEPD were much less abundant than those from PA-BEPD and IPA-BEPD. The high intensity of the sodium cation peak, compared to the intensities of the fragment peaks in the CID spectrum, suggested that the sodium cation is more readily lost from the precursor ion than retained for the fragments under CID conditions. However, TPA-BEPD produced types of fragments similar to those produced by IPA-BEPD, and the fragmentation behavior of TPA-BEPD differed from that of PA-BEPD. Sodiated fragments of the type  $[(AD)_a + Na]^+$ ,  $[D(AD)_b - H_2O + Na]^+$ ,  $[(AD)_c - H_2O + Na]^+$ , and  $[(AD)_eA + Na]^+$  were formed from TPA-BEPD and were seen at  $m/z$  621.2, 769.2, 893.3, 911.3, 1035.4, 1059.3, 1183.5, 1201.4, 1349.3, 1473.5, and 1491.4. A reduction of the peak-to-peak voltage from 14 to 10 increased the relative abundance of the  $[(AD)_a + Na]^+$  ions and reduced that of the  $[(AD)_c - H_2O + Na]^+$  and  $[(AD)_eA + Na]^+$  ions.

The low-mass CID fragments originating from the sodiated PA-BEPD, IPA-BEPD, and TPA-BEPD oligomers at  $m/z$  1634 are presented in Figure 2. The spectra have been measured using a peak-to-peak voltage of 14 V, and the fragments between  $m/z$  100 and 550 are shown. The fragments displayed contain no more than one repeating unit, and in addition to the sodiated fragments, the protonated fragments and their decomposition products were also observed. The fragment ion at  $m/z$  149 was the most abundant of all the ions above  $m/z$  100 in every CID spectrum. Abundant fragment ions at  $m/z$  57, 69, and 83 were also observed in all of the spectra, and in the case of IPA-BEPD and TPA-BEPD, the abundance of these ions was almost the same as that of the  $m/z$  149. The abundance ratio of  $m/z$  149 to 1634 was 19:1 for PA-BEPD, 17:1 for IPA-BEPD, and 12:1 for TPA-BEPD. In addition, the fragment ions at  $m/z$  125, 167, 255, 273, 291, and 313 were seen in the CID spectra of all of the polyesters. Instead, the formation of other fragments varied with the polyester studied. The compositions of the low-mass fragment ions formed from the different polyesters are presented in Table 3.

In the CID spectrum of PA-BEPD, the fragment ion at  $m/z$  149 very probably corresponds to the protonated phthalic anhydride molecule, which is recognized as the most evident fragment ion originating from phthalates.<sup>43,44</sup> The fragment ion at  $m/z$  125 is thought to be a carbocation formed from the protonated BEPD molecule, whereas the ion at  $m/z$  167 corresponds to the protonated phthalic acid molecule. Furthermore, the fragment ions at  $m/z$  291 and 313 correspond to the protonated and sodiated forms of the  $AD - H_2O$  molecule, which is most probably a cyclic

(43) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980; pp 86–87.

(44) Yinon, J. *Org. Mass Spectrom.* **1988**, 23, 755–759.

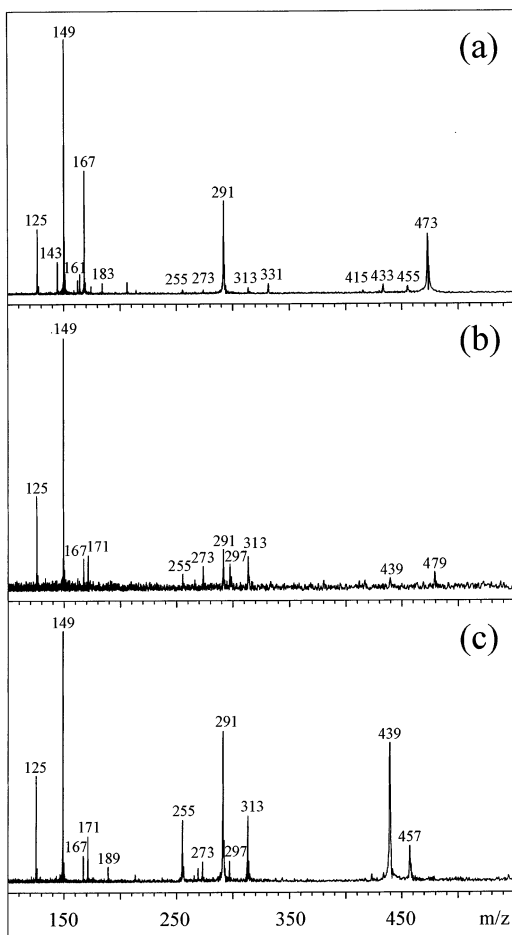


Figure 2. Low-mass CID fragments from the sodiated PA-BEPD (a), IPA-BEPD (b), and TPA-BEPD (c) oligomers at  $m/z$  1634.

Table 3. Low-Mass Fragment Ions Formed from the Different Polyesters

$m/z$	composition	$m/z$	composition
125	$[D - 2H_2O + H]^+$	297	$[AA - H_2O + H]^+$
143	$[D - H_2O + H]^+$	313	$[AD - H_2O + Na]^+$
149	$[A - H_2O + H]^+$	331	$[AD + Na]^+$
161	$[D + H]^+$	415	$[DAD - 2H_2O + H]^+$
167	$[A + H]^+$	433	$[DAD - H_2O + H]^+$
171	$[A - H_2O + Na]^+$	439	$[ADA - H_2O + H]^+$
183	$[D + Na]^+$	455	$[DAD - H_2O + Na]^+$
189	$[A + Na]^+$	457	$[ADA + H]^+$
255	$[AD - 3H_2O + H]^+$	473	$[DAD + Na]^+$
273	$[AD - 2H_2O + H]^+$	479	$[ADA + Na]^+$
291	$[AD - H_2O + H]^+$		

molecule with one BEPD and PA unit, since the polyesters based on phthalic acid very easily form cyclic structures as dissociation products.<sup>35</sup> Other low-mass fragment ions of PA-BEPD were observed at  $m/z$  143, 161, 183, 255, 273, 331, 415, 433, 455, and 473. The ions at  $m/z$  255 and 273 may be either cyclic or linear.

The low-mass CID fragments of IPA-BEPD partly differ from those of PA-BEPD. The ions at  $m/z$  125, 167, 255, and 273 were interpreted in a way similar to the corresponding ions in the PA-BEPD spectrum. The abundant ion at  $m/z$  149 has the same elemental composition as protonated phthalic anhydride, but its structure is probably different because of the *m*-substitution of the carboxyl groups in isophthalic acid. It is more likely that

the ion at  $m/z$  149 corresponds to the oxonium ion that is formed when a water molecule has been cleaved from protonated isophthalic acid.<sup>45</sup> The ions at  $m/z$  291 and 313 may have cyclic structures, as in the case of PA-BEPD, but they may also correspond to the linear molecule with the same elemental composition.

The ions at  $m/z$  297 and 439 are most probably protonated anhydride molecules that have a cyclic structure. The ion at  $m/z$  439 corresponds to the molecule with one BEPD and two IPA units. BEPD and IPA units are normally bound by an ester bond, whereas an anhydride linkage exists between the IPA units. Instead, the ion at  $m/z$  297 corresponds to the molecule with two IPA units, both of which are linked by anhydride bonds. Other low-mass fragment ions that differed from those observed in PA-BEPD spectrum were seen at  $m/z$  171 and 479.

The low-mass fragments of TPA-BEPD were generally similar to the low-mass fragments of IPA-BEPD. The ions at  $m/z$  125, 167, 255, and 273 were interpreted as corresponding ions in both the PA-BEPD and the IPA-BEPD spectra, whereas the ions at  $m/z$  149, 171, 291, 297, 313, and 439 corresponded to the ions in the IPA-BEPD spectrum. The abundance of the cyclic anhydride fragments was much greater than in the IPA-BEPD spectrum. The fragment ions at  $m/z$  189 and 457 were seen only in the CID spectrum of TPA-BEPD. An interesting finding was that ADA fragment appeared in the IPA-BEPD spectrum as a sodiated molecule and in the TPA-BEPD spectrum, as a protonated molecule.

**PSD-MALDI-TOF Mass Spectrometry.** The PSD spectra of the sodiated PA-BEPD, IPA-BEPD, and TPA-BEPD oligomers at  $m/z$  1634 are presented in Figure 3, where the fragment ions above  $m/z$  550 are displayed. The abundance of the sodium cation was not examined, since the  $m/z$  scale of the PSD spectra was limited, with the result that the sodium cation could not be observed. As in the CID experiments, PA-BEPD was fragmented by both mechanisms 1 and 2, whereas IPA-BEPD and TPA-BEPD were definitely cleaved only by mechanism 1. Nevertheless, the fragment ions of type  $[(AD)_a + Na]^+$  dominated in the PSD spectra of all of the polyesters. Only the number of repeating units in the most abundant  $[(AD)_a + Na]^+$  fragment ion varied with the phthalic acid isomer.

The most abundant fragment ion of PA-BEPD was  $[(AD)_3 + Na]^+$ , followed by  $[(AD)_4 + Na]^+$  and  $[(AD)_5 + Na]^+$ . The fragment ions of type  $[D(AD)_b - H_2O + Na]^+$ ,  $[(AD)_c - H_2O + Na]^+$ , and  $[D(AD)_d + Na]^+$  were similar to those observed in the CID studies of PA-BEPD, but as an exception, the type  $[(AD)_eA + Na]^+$  ions were also formed in the PSD experiments. The most abundant fragment ions of the type  $[D(AD)_b - H_2O + Na]^+$ ,  $[(AD)_c - H_2O + Na]^+$ ,  $[D(AD)_d + Na]^+$ , and  $[(AD)_eA + Na]^+$  all contained three repeating units, as did the most abundant  $[(AD)_a + Na]^+$  fragment ion. In addition to other fragments formed via hydrogen rearrangement reactions, the  $[D(AD)_2 - 2H_2O + Na]^+$  fragment ion was observed in the PSD spectrum of PA-BEPD.

The two most abundant fragment ions of IPA-BEPD were  $[(AD)_4 + Na]^+$  and  $[(AD)_5 + Na]^+$ , which had almost the same intensities in the PSD spectrum.  $[(AD)_3 + Na]^+$  gave rise to the third most intense peak in the spectrum and, as in the CID

(45) Harrison, A. G. *Chemical Ionization Mass Spectrometry*, 2nd ed.; CRC Press: Boca Raton, FL, 1992; pp 131–137.

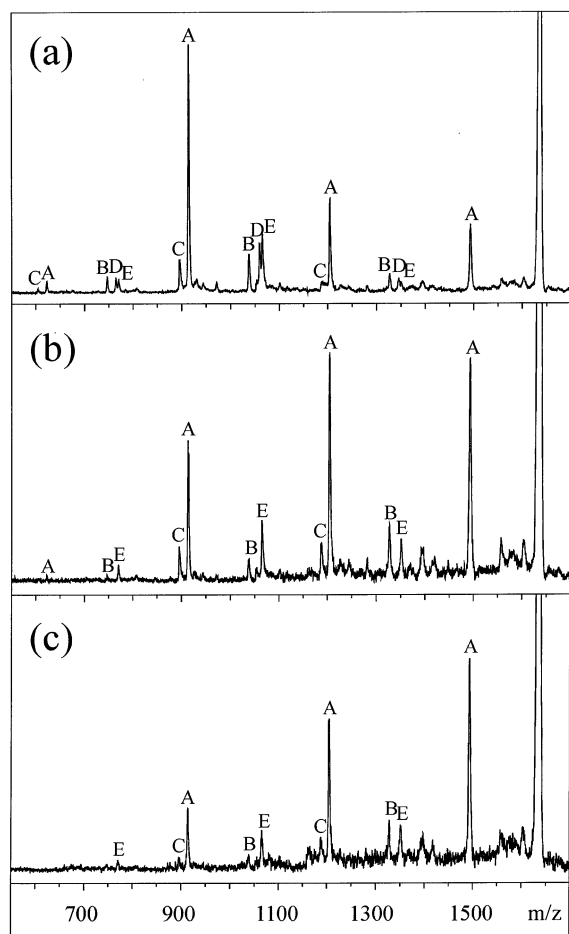


Figure 3. PSD spectra from the sodiated PA-BEPD (a), IPA-BEPD (b), and TPA-BEPD (c) oligomers at  $m/z$  1634. Fragment ions of the type  $[(AD)_a + Na]^+$  (A),  $[D(AD)_b - H_2O + Na]^+$  (B),  $[(AD)_c - H_2O + Na]^+$  (C),  $[D(AD)_d + Na]^+$  (D), and  $[(AD)_eA + Na]^+$  (E) are shown.

experiments, the  $[D(AD)_b - H_2O + Na]^+$ ,  $[(AD)_c - H_2O + Na]^+$ , and  $[(AD)_eA + Na]^+$  fragment ions were also observed. The most abundant  $[D(AD)_b - H_2O + Na]^+$  ion contained four repeating units, whereas the  $[(AD)_c - H_2O + Na]^+$  and  $[(AD)_eA + Na]^+$  ions, consisting of three and four repeating units, were together the most abundant fragment ions of that kind. The absence of  $[D(AD)_d + Na]^+$  ions in the PSD spectrum of IPA-BEPD again clearly distinguished IPA-BEPD from PA-BEPD.

The most abundant fragment ion originating from TPA-BEPD was  $[(AD)_5 + Na]^+$ , followed by  $[(AD)_4 + Na]^+$  and  $[(AD)_3 + Na]^+$ . Other types of fragment ions were again similar to those observed in the PSD study of IPA-BEPD, and the fragmentation behavior of TPA-BEPD also differed from that of PA-BEPD. The most abundant  $[D(AD)_b - H_2O + Na]^+$ ,  $[(AD)_c - H_2O + Na]^+$ , and  $[(AD)_eA + Na]^+$  ions all consisted of four repeating units.

**Comparison of CID and PSD Data.** The varying fragmentation behavior of polyesters in the CID and PSD experiments has to be due to differences in the CID and PSD conditions. For example, the reaction times in CID and PSD markedly differ from each other, since the time-scale of our CID experiments was on the order of seconds, but it was on the order of microseconds in the PSD studies. Another important factor is the amount of energy transferred for the precursor ion in the ESI-CID and MALDI-PSD processes. More energy is presumably delivered for the precursor

ion in CID than in PSD as a result of the different activation mechanisms. In CID, the precursor ion collides with a neutral collision gas, whereas in PSD, the precursor ion acquires energy only in the ionization process, resulting in metastable fragmentation.

The low activation energy of the hydrogen rearrangement reaction could explain why  $[(AD)_a + Na]^+$  fragment ions dominate in the PSD spectra, although they are not the most abundant fragment ions in any of the CID spectra. CID experiments in which reducing the amount of the excitation energy clearly increased the relative abundance of the  $[(AD)_a + Na]^+$  ions supports this conclusion. In contrast, reducing the amount of excitation energy in CID studies of PA-BEPD reduced the relative abundance of the  $[D(AD)_d + Na]^+$  fragment ions. This could explain why the  $[D(AD)_d + Na]^+$  ions are relatively low in intensity in the PSD spectrum of PA-BEPD.

On the other hand, some differences in the CID and PSD spectra could also be explained in terms of the reaction times. For example, intramolecular transesterification, which produces  $[D(AD)_d + Na]^+$  ions, is supposed to be a relatively slow reaction.<sup>28</sup> Likewise, multiple dissociation reactions probably require longer reaction times than single ones. This may at least partly explain the greater relative abundance of secondary fragments from IPA-BEPD and TPA-BEPD in the CID spectra than in the PSD spectra. In addition, the reaction times certainly affect the equilibrium between the dissociation products. This may explain why  $[(AD)_eA + Na]^+$  ions from PA-BEPD were observed only in the PSD spectrum, even though they would be formed under both CID and PSD conditions. The lifetime of the  $[(AD)_eA + Na]^+$  fragment ions may be very short if the sodium cation is rather shifted for another fragment or totally ejected from the  $[(AD)_eA + Na]^+$  ion.

**Molecular Modeling.** The AMBER 5.0 suite of programs was used to calculate 100 low-energy structures of precursor ions selected for mass spectrometric dissociation studies. A large distribution of different structures was obtained for each precursor ion, and the lowest-energy structures found among them are shown in Figure 4. As in earlier theoretical studies of the cationized oligomers of synthetic polymers, it was the oxygen atoms that coordinated to the sodium cation.<sup>38–40</sup> In the present study, the sodium cation was bound by both carbonyl and hydroxyl oxygens. The lowest-energy structures clearly show how the polyesters prepared from different phthalic acid isomers bind the sodium cation differently. More oxygen atoms were coordinated to the sodium cation in PA-BEPD than in IPA-BEPD and TPA-BEPD, which also resulted in a denser structure of the PA-BEPD precursor ion.

The coordination of oxygen atoms to the sodium cation was examined more closely by calculating the distances of all of the oxygen atoms from the sodium cation in each of the structures determined. Oxygen atoms that were closer than 2.5 Å to the sodium cation were assumed to be coordinated to it.<sup>40</sup> The number of polyester oligomers coordinated to a sodium cation with a certain number of oxygen atoms are presented in Table 4. The results show plainly that PA-BEPD oligomers can bind the sodium cation with more oxygen atoms than can the IPA-BEPD and TPA-BEPD oligomers. Up to seven oxygen atoms of the PA-BEPD oligomer may coordinate to the sodium cation, whereas the maximum number of binding oxygen atoms is five with IPA-BEPD



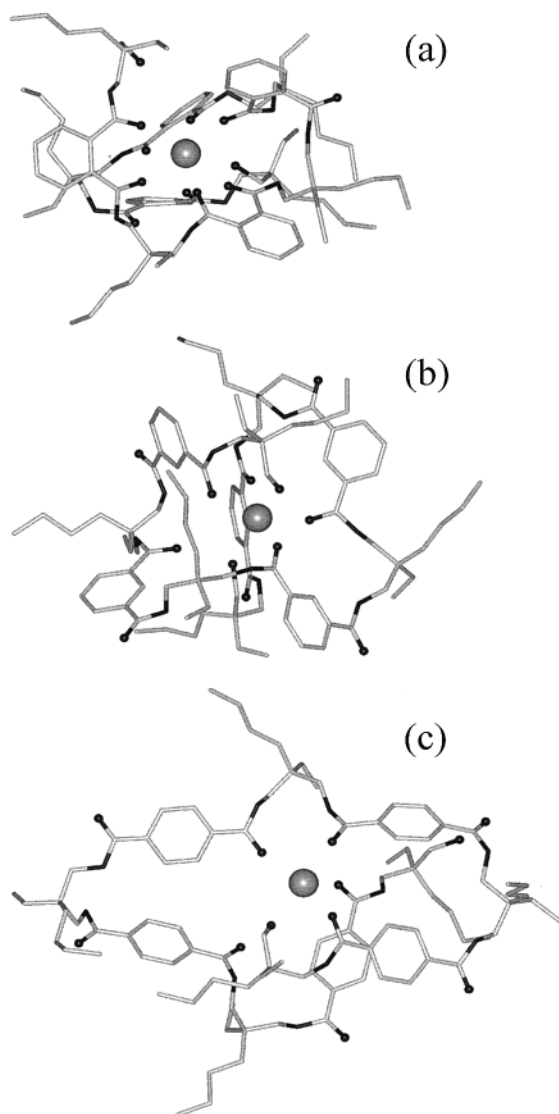


Figure 4. Lowest-energy structures of PA-BEPD (a), IPA-BEPD (b), and TPA-BEPD (c) precursor ions. Carbon atoms are shown as gray sticks, carbonyl and hydroxyl oxygens are shown as black sticks with small spheres, other oxygen atoms are shown as black sticks without spheres, and sodium cations are shown as large gray spheres. Hydrogen atoms are omitted for clarity.

Table 4. Number of Polyester Oligomers Coordinated to Sodium Cation with a Particular Number of Oxygen Atoms for the Different Polyesters

no. O's	PA-BEPD	IPA-BEPD	TPA-BEPD
7	4		
6	29		
5	48	13	14
4	15	47	43
3	4	33	34
2		7	8
1			1

and TPA-BEPD. Instead, the majority of the PA-BEPD oligomers coordinate to the sodium cation with five oxygens, but the most common number with IPA-BEPD and TPA-BEPD is four. The binding energies of the sodium cation for the different oligomers were not determined, but on the basis of the number of oxygen

Table 5. Percentages of Carbonyl and Hydroxyl Oxygens Calculated from All of the Oxygen Atoms Coordinated to Sodium Cation for the Different Polyesters

type of O	PA-BEPD (%)	IPA-BEPD (%)	TPA-BEPD (%)
carbonyl	91	85	83
hydroxyl	9	15	17

Table 6. Number of Polyester Oligomers Coordinated to the Sodium Cation with a Certain Number of Hydroxyl Oxygens for the Different Polyesters

no. OH's	PA-BEPD	IPA-BEPD	TPA-BEPD
0	59	49	48
1	38	47	43
2	3	4	9

atoms coordinated to the sodium cation, it is thought that PA-BEPD possesses a higher sodium affinity than IPA-BEPD and TPA-BEPD.

Since both carbonyl and hydroxyl oxygens were found to bind the sodium cation, the ratios of the different types of binding oxygen atoms were determined for all of the precursor ions. The percentages of binding carbonyl and hydroxyl oxygens calculated from all of the binding oxygen atoms are presented in Table 5. These results show that the end-groups of IPA-BEPD and TPA-BEPD bind the sodium cation more easily than those of PA-BEPD. This also means that the sodium affinity of the PA-BEPD oligomers is not as dependent on the end groups as the sodium affinity of the IPA-BEPD and TPA-BEPD oligomers. In addition, the differences in the fragmentation behavior of the different polyesters might be partly explained by the coordination of the terminal hydroxyl oxygens to the sodium cation. A transesterification reaction in which a terminal hydroxyl group reacts with a polyester chain takes place with any certainly only in PA-BEPD, which is less likely to bind the sodium cation with hydroxyl oxygens than IPA-BEPD and TPA-BEPD are.

Closer examination of the coordination of the hydroxyl oxygens to the sodium cation is shown in Table 6, which presents the number of polyester oligomers coordinated to the sodium cation with a certain number of hydroxyl oxygens. Approximately one-half of the IPA-BEPD and TPA-BEPD oligomers do not bind the sodium cation with the hydroxyl oxygens at all, whereas it is over one-half of the PA-BEPD oligomers that do not bind. On the other hand, the number of PA-BEPD and IPA-BEPD oligomers that bind the sodium cation with both hydroxyl oxygens is almost the same, but the number of corresponding TPA-BEPD oligomers is much greater.

## CONCLUSIONS

CID-ESI-FT-ICR and PSD-MALDI-TOF mass spectrometry were used for the structural characterization of PA-BEPD, IPA-BEPD, and TPA-BEPD polyesters, which were prepared from the same diol but from different phthalic acid isomers. The fragmentation mechanisms of polyesters were similar in CID and PSD experiments, even though the CID and PSD conditions differ from each other. All of the polyesters were clearly fragmented through the hydrogen rearrangement reaction, but only PA-BEPD was



firmly fragmented via transesterification. The formation of  $[D(AD)_d + Na]^+$  fragment ions under both CID and PSD conditions only from PA-BEPD readily distinguished it from the IPA-BEPD and TPA-BEPD polyesters. In addition, the peaks of the  $[(AD)_eA + Na]^+$  fragment ions were not observed in the CID spectra of PA-BEPD. The IPA-BEPD and TPA-BEPD polyesters were solely distinguishable by some low-mass fragment ions, since the  $[A + Na]^+$  and  $[ADA + H]^+$  ions were seen only in the CID spectra of TPA-BEPD and the  $[ADA + Na]^+$  ions in the CID spectra of IPA-BEPD. In the analysis of copolyesters prepared from different phthalic acid isomers, the phthalic acid components along the polyester chain may be identified through their certain fragmentation behavior.

The different conditions in CID and PSD were thought to cause different abundances of some of the fragment ions in the CID and PSD spectra. For example,  $[(AD)_a + Na]^+$  fragment ions dominated in all of the PSD spectra, and their relative abundance in the CID spectra increased as the excitation energy decreased, which was probably the result of a relatively low activation energy in the hydrogen rearrangement reaction. In addition, the relative abundance of the  $[D(AD)_d + Na]^+$  fragment ions in the CID spectra of PA-BEPD decreased as the excitation energy decreased, which suggests that a transesterification reaction clearly requires more energy than a hydrogen rearrangement.

The ejection of the sodium cation from the precursor ion was found to be a competing reaction for the dissociation of the precursor ion. Comparison of the abundance ratios of the sodium cation to the precursor ion as a function of the activation energy revealed that the sodium affinity of the polyester increases with the phthalic acid isomer in the order of TPA < IPA < PA.

Molecular dynamics calculations were used to obtain the low-energy structures of the precursor ions selected for dissociation study. Carbonyl and hydroxyl oxygens were found to coordinate to the sodium cation in the sodiated polyester oligomer. PA-BEPD oligomers may coordinate to the sodium cation with more oxygen atoms than IPA-BEPD and TPA-BEPD, since the maximum number of oxygens coordinated to the sodium cation is seven for PA-BEPD and five for IPA-BEPD and TPA-BEPD. On the basis of the calculated structures, it can be claimed that PA-BEPD clearly possesses the highest sodium affinity of the polyesters studied. More efficient binding of the sodium cation in sodiated PA-BEPD than in sodiated IPA-BEPD and TPA-BEPD resulted in a denser structure of the lowest energy conformation of the sodiated PA-BEPD.

The terminal hydroxyl oxygens of the IPA-BEPD and TPA-BEPD oligomers were found to coordinate more readily to the sodium cation than those of the PA-BEPD oligomers. This may at least partly explain why a transesterification reaction occurs in PA-BEPD but not in IPA-BEPD and TPA-BEPD.

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