



Matrix-assisted laser desorption/ionization-time-of-flight/time-of-flight collision-induced dissociation study of poly(*p*-phenylenediamine terephthalamide) fragmentation reactions

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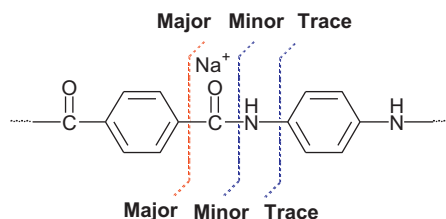
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HIGHLIGHTS

- This represents the first detailed MS/MS study of aramid polymers.
- MALDI-TOF/TOF collision-induced dissociation experiments are reported on model PPD-T polymers.
- Diamine-terminated oligomers were the major product of synthesis using excess amine.
- Di-carboxylic acid oligomers were the major product for excess acid.

GRAPHICAL ABSTRACT

Collision-Induced Dissociation of Aramids



ARTICLE INFO

Article history:

Received 20 June 2013

Received in revised form 2 September 2013

Accepted 5 September 2013

Available online 10 September 2013

Keywords:

MALDI

Collision-induced dissociation

Polymers

Aramids

Fragmentation mechanisms

ABSTRACT

MALDI-TOF/TOF collision-induced dissociation (CID) experiments are reported on model poly(*p*-phenylenediamine terephthalamide) (PPD-T) polymers, revealing a variety of synthesis reaction products. Diamine-terminated oligomers were the major product of synthesis using excess amine, and di-carboxylic acid oligomers were the major product for excess acid. Structures of major reaction products were confirmed by CID fragmentation studies, along with detailed studies of MS/MS decomposition pathways. Apparent fracture of the phenyl-carbonyl bond was the major fragmentation pathway (independent of end groups), resulting from initial NH-CO bond cleavage with subsequent CO loss. Hydrogen-transfer reactions play an important role in fragmentation, involving both cross-chain abstraction of NH hydrogen and long-range H-transfer. End-group and main-chain modifications produce fingerprint CID fragmentation patterns that can be used to identify end groups and branching patterns; the structure of an unanticipated synthesis product was established using CID. The effect of synthesis conditions on polymer composition was studied using the analysis of variance, specifically, the amine-to-acid ratio used and post-synthesis addition of CaO. Of particular interest is oligomer end-group modification by the solvent (*N*-methyl pyrrolidone) induced by addition of CaO.

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1. Introduction

In previous studies of poly(*p*-phenylenediamine terephthalamide) (PPD-T) and polybenzoxazoles, we discussed the limits of MALDI-TOF MS, using the evaporation-grinding MALDI sample preparation method (E-G method), for aramid analysis [1,2]. Briefly, comparisons were made between the mass spectra obtained from low molecular mass PPD-T, synthesized using various molar ratios

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of reactants, and high molecular mass Kevlar® fibers. Observed PPD-T end groups were primarily in agreement with the monomer ratios used during synthesis. However, small quantities of cyclic and imine branched species were also found in the oligomeric portion of model PPD-T oligomers and Kevlar®. Also, “unexpected” mass peaks were observed in the MALDI spectra which could not be explained on the basis of aramid metathesis reactions; it could not be confirmed that they were not produced by the MALDI process. Also, the degree of branching was difficult to predict and more definitive information was necessary to confirm the chemical structures of the observed PPD-T mass peaks.

Following the above study, we combined the use of the evaporation-grinding MALDI sample preparation method with ion mobility (IM) separations to overcome some of the problems associated with mass spectral analysis of complex polymeric mixtures [3]. In these studies [3], MALDI-IM/MS provided clear separation of linear and branched aramid species, and distinction was made between the branched meta-para-aramid (MP-amide) trendline and the branched Kevlar® (para-para-aramid) trendline. However, “fingerprint” identification of PPD-T chemical structures was still unattainable with this technique.

In the present study, we combine the E-G method with TOF/TOF collision-induced dissociation (CID) to examine the chemical structures of aramids, and suspected arylamide metathesis products found in model PPD-T oligomers. Based on CID identification of predominant PPD-T main-chain apparent cleavage at the phenyl–carbonyl bond (Ph–CO), we were able to develop a general aramid fragmentation scheme and obtain “fingerprint” identification of “suspect” species. This work presents evidence for the existence of PPD-T branching and NMP side reactions, during synthesis and post-synthesis treatment, which lead to PPD-T end group modifications. It also presents arguments for arylamide metathesis reactions being the origin of the “unexpected” PPD-T structures.

2. Experimental

2.1. Materials

The aromatic polyamides used in this study were model poly(*p*-phenylenediamine terephthalamide) (PPD-T) oligomers supplied by Teijin Aramid, Arnhem, Netherlands. Model oligomers were prepared using diamine-to-diacid chloride molar ratios of 2:1, 6:5, 8:7, 8:9, and 1:2. PPD-T was synthesized using *N*-methyl pyrrolidone (NMP) as the solvent. CaO was added to one set of reaction mixtures (2:1, 6:5, 8:7, and 1:2) and compared with a second identical set that was not treated with CaO, to examine any reactions caused by the neutralization process. The reason for adding CaO to the synthesis is to neutralize the HCl produced during the reaction; otherwise the HCl reacts with the diamine and slows the reaction. The structures of the oligomers observed in the polymer spectra were those shown in Table 1; species 1-1 is the nominal structure of the polymer. Note that it is diamine terminated.

2.2. MALDI-TOF/TOF CID measurements

Aramid samples were analyzed using an Applied Biosystems 4700 Proteomics Analyzer MALDI-TOF/TOF instrument (Applied Biosystems, Framingham, MA) equipped with a 355 nm Nd:YAG laser. All spectra were obtained in the positive ion mode using an accelerating voltage of 8 kV for the first source and 15 kV for the second source and a laser intensity of ~10% greater than threshold. The grid voltage, guide wire voltage, and delay time were optimized for each spectrum to achieve the best signal-to-noise ratio. MALDI spectra were run in a 3-aminoquinoline (3AQ, Aldrich) matrix doped with sodium trifluoroacetate (NaTFA, Aldrich). Polymer

samples were prepared using the evaporation-grinding method (E-G method) [1] in which a 2 mg sample of aramid was ground to a fine powder with 60 μ L of distilled tetrahydrofuran (THF, Fisher) in an agate mortar and pestle. The molar ratios of matrix:NaTFA:polymer were 25:1:1. Next, using a fume hood, 100 μ L of trifluoroethanol (TFE, Fisher) were added to the ground sample and the mixture was ground a second time until the TFE evaporated. The mixture was then ground a third time to ensure homogeneity.

The collision energy in the TOF/TOF instrument is defined by the potential difference between the source acceleration voltage and the floating collision cell; in our experiments this voltage difference was set to 1 kV. Air was used as a collision gas at pressures of 1.5×10^{-6} and 5×10^{-6} Torr (which will later be referred to as “low” and “high” pressure). All spectra were acquired in the reflectron mode with a mass resolution greater than 3000 fwhm; isotopic resolution was observed throughout the entire mass range detected. Sample preparation and instrument calibration details were described previously [4].

2.3. Bond energy calculations

The bond energies for PPD-T were determined by two different approaches using Gaussian09 software. First, the parent structure was optimized followed by independent optimizations of the two fragment structures. In this approach the energies of the two independent structures were added together and then subtracted from the energy of the parent structure to give the energy of the broken bond. The independent fragments were determined to have doublet multiplicity due to the single radical on each fragment resulting from homolytic bond cleavage. The second approach consisted of optimizing the parent structures and then optimizing the two fragments resulting from the homolytic bond cleavage present together in the calculation. The two structures were placed ~15 Å apart to ensure that they would not interact with each other. The two fragments together were determined to have triplet multiplicity due to each of the two fragments having one radical from the homolytic bond cleavage. The total energy of the optimized two fragments was then subtracted from the energy of the parent structure to give the energy of the broken bond. The energies (kcal mol^{-1}) for both the doublet and triplet treatments of the homolytic bond cleavage agreed almost exactly with one another as can be seen in Fig. 1, giving credence to their numerical validity. DFT/B3LYP/6-31G* level of theory was used for all the calculations and they were performed in vacuo and in the ground state.

3. Results and discussion

We will first define the nomenclature to be used in this study and then present TOF/TOF CID fragmentation data for model PPD-T oligomers both with and without CaO neutralization. Additionally, we will present general aramid fragmentation mechanisms to explain the fragment species identified in the TOF/TOF CID mass spectra.

3.1. Nomenclature

3.1.1. Terminology

All figures will show structures and peaks labeled according to the following key:

- (i) precursor ion peaks are labeled in the *x*–*y* format (*x* = table number, *y* = structure number) for precursor ions observed in the MALDI spectra and structure letters for fragment ions observed in MS/MS. When needed the table and structure number are followed by the ion which provides the charge added to the

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