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MALDI-TOF MS Study of Poly(*p*-phenylene Terephthalamide) Fibers

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ABSTRACT: MALDI-TOF MS was used to study the end group distribution of a series of poly(*p*-phenylene terephthalamide) and Kevlar fibers. Poly(*p*-phenylene terephthalamide) fibers were synthesized using various percent mole ratios of diamine-to-diacid chloride (70:30, 51:49, 50:50, 49:51, and 30:70), and their resulting MALDI-TOF mass spectra were compared with the mass spectra of Kevlar fibers. Oligomers synthesized with excess diamine or excess diacid chloride were found to contain abundances of amine or carboxylate end groups, respectively, along with side products that were specific to their synthesis. Oligomers synthesized with near equimolar ratios of reactants produced dominant species with amine-carboxyl end groups along with small quantities of cyclic and imine branched species, which were also found in the oligomeric portion of commercially produced Kevlar. Experimental results from this study indicate that mass spectra derived from the oligomeric portion of high molecular weight polymers can yield useful information about their synthesis.

Introduction

Historically and commercially, polyamides occupy an important place in the world of synthetic polymers. The early work of Carothers at DuPont (in the early 1930s) dealt with aliphatic polyamides and led to the first commercial development of synthetic fibers (in 1934), known commonly as nylons.[1] Some of the most important recent developments in polyamide synthesis have been in the field of wholly aromatic polyamides (aramids). The first commercially available aramid containing predominantly para-oriented linkages was marketed in 1972 under the name Kevlar fiber by DuPont.[2] The rigid totally aromatic structures of the aramid polymers give them exceptional heat and flame resistance, melting points above their decomposition temperature of 500 °C, ultrahigh strength, and better resistance to solvents and oxidizing agents as compared to aliphatic polyamides.[3]

The greatest obstacle in characterizing aramids with MALDI-TOF MS has been their poor solubility in common solvents due to strong intermolecular hydrogen bonding and crystallinity.[2,4] Even when a suitable solvent is found for the aramids, there is the problem of finding a matrix and cationizing agent that are also soluble in that solvent. Therefore, the evaporation-grinding method[5−7] (E−G method) was investigated for use in MALDI-TOF MS analysis of these aramids.

The application of MALDI-TOF MS to the study of synthetic polymer reactions is quite recent and involves the collection of MALDI-TOF mass spectra at different time/reaction intervals to observe the structural/mass distribution changes that occur in the synthetic process.[7−10] MALDI−TOF mass spectra yield a wealth of information on the molecular mass, structure, and end groups of species generated in the reaction process and provide great insight about the reaction mechanisms of synthetic polymers. It should be noted that end group identification and determination of the actual composition of a polymer sample are of the utmost importance in polymer analysis.[3,11−14] Conventional methods of analysis (i.e., viscometry, TGA, DSC, GPC, NMR, IR, and Py-GC/MS) have proven to be inadequate in providing exhaustive information on the mass distribution, chemical distribution, and structural heterogeneities present in these aramid fibers.

In previous work, we reported the MALDI-TOF MS characterization of low molecular mass oligomers of commercially available Nomex and Kevlar fibers.[6] In this prior work, only low molecular weight species were found in the Kevlar fibers. This work raised the question as to whether amide protons were capable of hydrogen/sodium exchange, were our methods selectively extracting species and not capable of observing all expected end groups, and was it possible to extract synthesis information about high MW aramid fibers by examining the low MW portion of these materials that exhibit a bimodal distribution of molecular weights.[2]

In our present work, we attempt to answer these questions by analyzing, using the MALDI-TOF MS evaporative grinding method (E−G method) previously described,[5−7] five samples of low molecular mass poly(*p*-phenylene terephthalamide) (PPD-T) fibers that were synthesized using various percent mole ratios of diamine-to-diacid chloride (70:30, 51:49, 50:50, 49:51, and 30:70). After polymerization was completed, the products were reacted with either distilled H_2O, ethanol, 2-propanol, or tertiary-butyl alcohol (*t*-butyl alcohol) to convert any remaining acid chloride groups to end groups (e.g., carboxyl groups in the case of H_2O or ester groups in the case of the alcohols). The mass spectra obtained indicate that the method described in our previous work[6] (and further refined in this work) is capable of resolving all expected oligomeric species. This work also indicates that the end group distribution observed in the mass spectra can be used as a quick and dirty method for determining the ratio of reactants used in the synthesis. However, it is the abundance of the minor side products such as fully cyclic, decarboxylated, deaminated, aldehyde, and branched species that are most decisive in determining the percent molar ratios of reactants used in their synthesis. Additionally, this work suggests that careful inspection of the end group and side product

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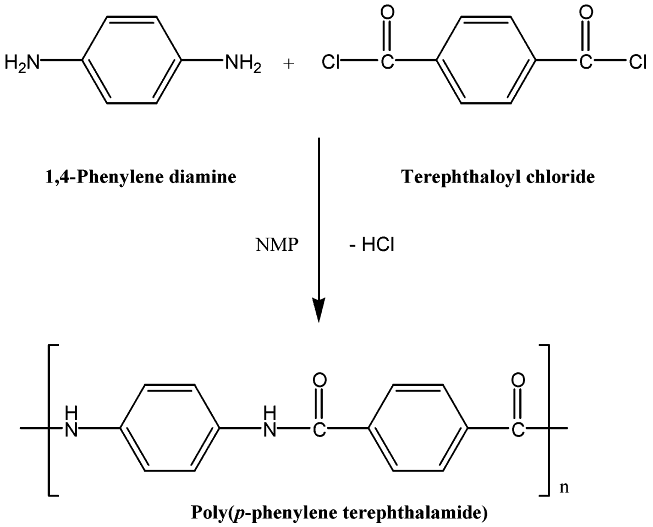
Scheme 1. Poly(*p*-phenylene Terephthalamide) Synthesis



distributions present in the oligomeric portion of high molecular weight step-growth polymers may yield fingerprint identification of the molar ratios of reactants used in their synthesis.

Experimental Procedures

Materials. The commercial aromatic polyamide used in this study was commercial Kevlar aramid fiber supplied by E. I. du Pont de Nemours and Company, Wilmington, DE. The structures of the polymers were assumed to be those shown in Scheme 1.

Solution Polymerization of Poly(*p*-phenylene Terephthalamide) Fibers. Poly(*p*-phenylene terephthalamide) fibers were synthesized via solution polymerization.[14] All reagents were obtained from commercial sources and used as received after analysis by Py-GC/MS to verify their purity. To a well-dried, 250 mL three-necked flask, with nitrogen inlet/outlets and magnetic stirrers, 24.0 g of finely ground (and dried) calcium chloride and 196.9 mL of dry 1-methyl-2-pyrrolidinone (NMP, Fisher) were added. To this suspension, 7.3 g of powered 1,4-phenylenediamine (Aldrich), 26.5 mL of triethylamine (Aldrich), and 18.9 g of triethylamine hydrochloride (Aldrich) were added with stirring. The resulting mixture was cooled to 0 °C. Subsequently, with continued cooling and rigorous stirring, an appropriate amount of terephthaloyl chloride (Aldrich) was added to achieve diamine-to-diacid chloride percent molar ratios of 70:30, 51:49, 50:50, 49:51, and 30:70. Stirring was continued for 60 min while the temperature rose to 28 °C. A crumbled mass formed at the bottom of the flasks, which was the poly(*p*-phenylene terephthalamide) that had precipitated. The reaction mixtures were each terminated with large volumes of distilled water, ethanol, 2-propanol, or *t*-butyl alcohol yielding a fibrous precipitate. Each precipitate was filtered and washed thoroughly with the appropriate terminating solution. The experimental conditions (i.e., NMP as the solvent) were chosen to ensure that the reactions would yield low molecular weight PPD-T fibers.[2] The structures of the oligomers were assumed to be as shown in Scheme 1.

MALDI-TOF MS Measurements. Poly(*p*-phenylene terephthalamide) and Kevlar samples were analyzed using a Voyager Elite DE STR MALDI-TOF MS (Applied Biosystems, Framingham, MA) equipped with a 337 nm N_2 laser. All spectra were obtained in the positive ion mode using an accelerating voltage of 20 kV and a laser intensity of ~10% greater than the threshold. The grid voltage, guide wire voltage, and delay time were optimized for each spectrum to achieve the best signal-to-noise ratio. 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. External mass calibration was performed using protein standards from a Sequazyme Peptide Mass Standard Kit (Applied Biosystems) and a three-point calibration method using Angiotension I (m = 1296.69 Da), ACTH (clip 1−17) (m = 2093.09 Da), and ACTH (clip 18−39) (m = 2465.20 Da). Internal mass calibration was subsequently performed using a PEG standard (Polymer Source, Inc.) to yield monoisotopic masses exhibiting a mass accuracy better than D_m = 0.1 Da. The instrument was calibrated before every measurement to ensure constant experimental conditions. All polyamide samples were run in 3-aminoquinoline (3AQ, Aldrich) doped with sodium trifluoroacetate (NaTFA, Aldrich), potassium trifluoroacetate (KTFA, Aldrich), or cesium trifluoroacetate (CsTFA, Aldrich) salt. All spectra displayed the expected mass shifts for the respective cationizing agent and were used for interpretation of the spectra. However, NaTFA was chosen for explanation in this paper since it yielded spectra with the greatest S/N ratios. The samples were prepared using the evaporation−grinding method (E−G method)[5] in which a 2 mg sample of aramid fiber was ground to a fine powder using an agate mortar and pestle. Then, molar ratios (with respect to the mol of polymer) of 25 parts matrix and 1 part cationizing agent (NaTFA, KTFA, or CsTFA) were added to the finely ground polymer along with 60 mL of distilled tetrahydrofuran (THF, Fisher). The mixture was ground until the THF evaporated after which the residue that accumulated on the sides of the mortar was pushed down to the bottom of the vessel. The mixture was then ground again to ensure homogeneity. A sample of the mixture was then pressed into a sample well by a spatula on the MALDI sample plate. Kevlar fibers required extra steps in which the fibers were first treated with concentrated sulfuric acid (Fisher) to aid in the grinding and to wash away any finish oil that may be present.[2] The Kevlar fiber was immersed in enough acid to cover it completely for 5 min or until it became soft. The container was then tilted, and the sulfuric acid was allowed to drain from the sample and container for 24 h. The sample was then washed thoroughly with ethanol and ground to fine particles for 5 min with an agate mortar and pestle. None of the observed mass spectra detected the presence of sulfonated species as possible side products.

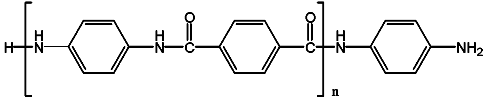
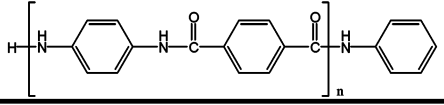
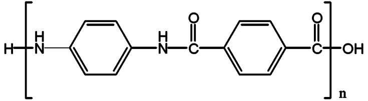
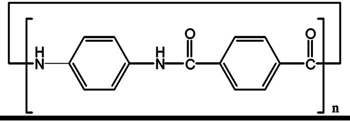
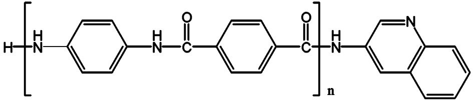
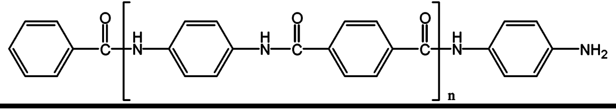
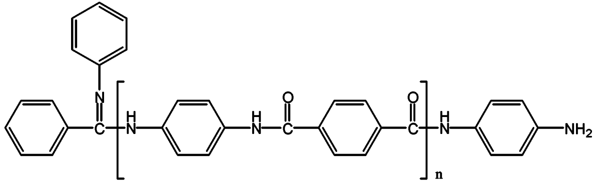
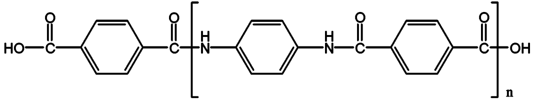
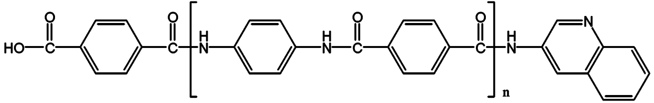
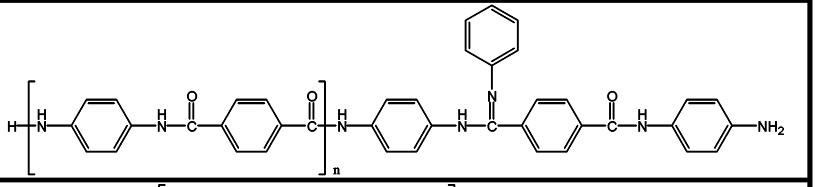
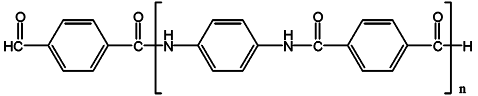
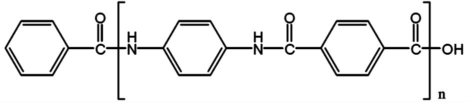
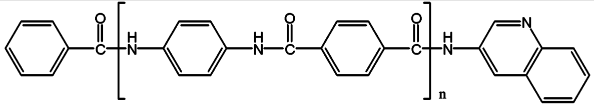
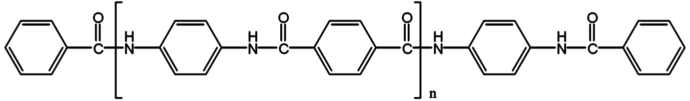
Results and Discussion

To answer questions about selectivity of the E−G method for certain species, five samples of PPD-T oligomer were synthesized each using different diamine-to-diacid chloride percent mole ratios (70:30, 51:49, 50:50, 49:51, and 30:70). It was envisioned that each of these oligomer samples would have end group distributions characteristic of their synthesis (e.g., the samples produced with excess diamine should produce oligomers in which amine−amine end groups predominate as seen in structure 1-1 in Table 1). The sample produced with excess diacid chloride should alternatively produce oligomers with carboxyl−carboxyl end groups after hydrolysis as shown in Table 1, structure 1-8. Samples produced with 50:50 mol ratios of diamine-to-diacid chloride should produce oligomers with 50% amine−carboxyl end groups, as depicted in structure 1-3 in Table 1, and 25% amine−amine and 25% carboxyl−carboxyl end groups.

Figures 1−5 show expanded regions (900−1150 Da) of spectra obtained from PPD-T fibers synthesized using various molar ratios of diamine/diacid chloride. They show peaks labeled in the *x*-*y* format (x = table number, y = structure number) followed by the atom and/or ion which has been added to the oligomers during the MALDI process. For instance, a peak labeled 1-1 NaNa$^+$ would arise from a structure found in Table 1, structure 1-1, which substituted a sodium ion for a hydrogen ion and is ionized by an additional sodium ion during the MALDI process. In cases discussed previously, peaks having ambiguous identification were further identified from the oligomers formed from the acid chloride esterification reaction with ethanol and noting the mass shifts occurring in the spectra.

Figure 1 shows a spectrum of PPD-T synthesized using a 51:49 molar ratio of diamine/diacid chloride and displays the

Table 1. Structural Assignments for Peaks in the MALDI-TOF Mass Spectra Reported in Figures 1−5

Species	Structure (M)
1-1	
1-2	
1-3	
1-4	
1-5	
1-6	
1-7	
1-8	
1-9	
1-10	
1-11	
1-12	
1-13	
1-14	

expected predominance of amine−amine end groups throughout the entire mass spectrum, along with large quantities of a side product representative of a decarboxylated amine−carboxyl end group (structure 1-6, Table 1) at masses of 949.3 Da (1-6 Na$^+$) and 971.3 Da (1-6 NaNa$^+$). Small amounts of aldehyde side products are present (structure 1-11, Table 1) at masses of 915.3

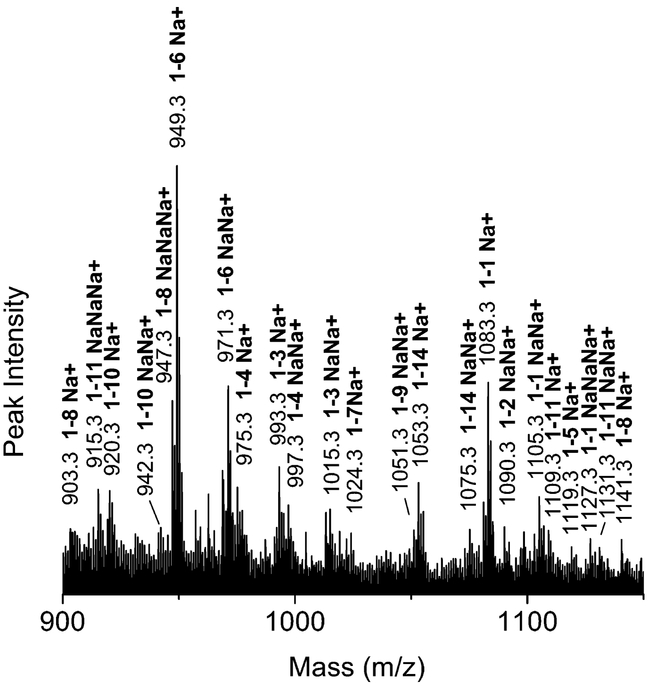


Figure 1. MALDI-TOF mass spectrum (900−1150 Da) of H_2O terminated PPD-T 51:49 diamine/diacid chloride. Sample prepared by the E−G method in 3AQ and cationized with NaTFA.

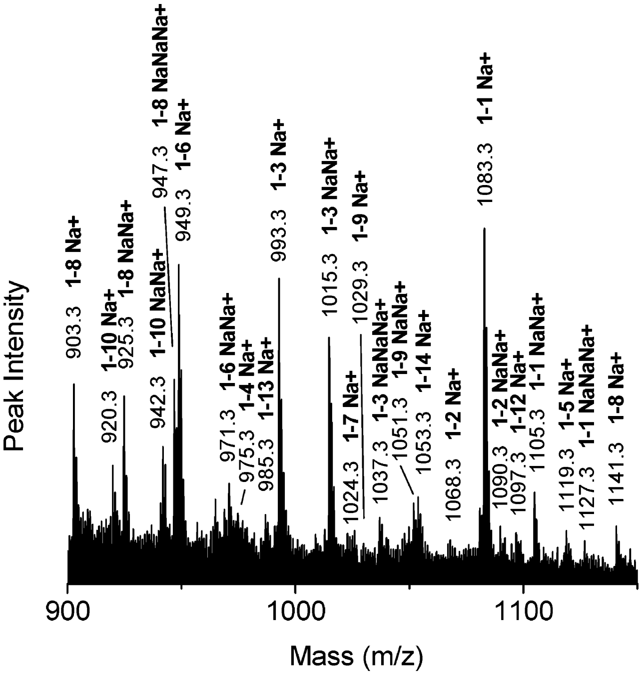


Figure 2. MALDI-TOF mass spectrum (900−1150 Da) of H_2O terminated PPD-T 50:50 diamine/diacid chloride. Sample prepared by the E−G method in 3AQ and cationized with NaTFA.

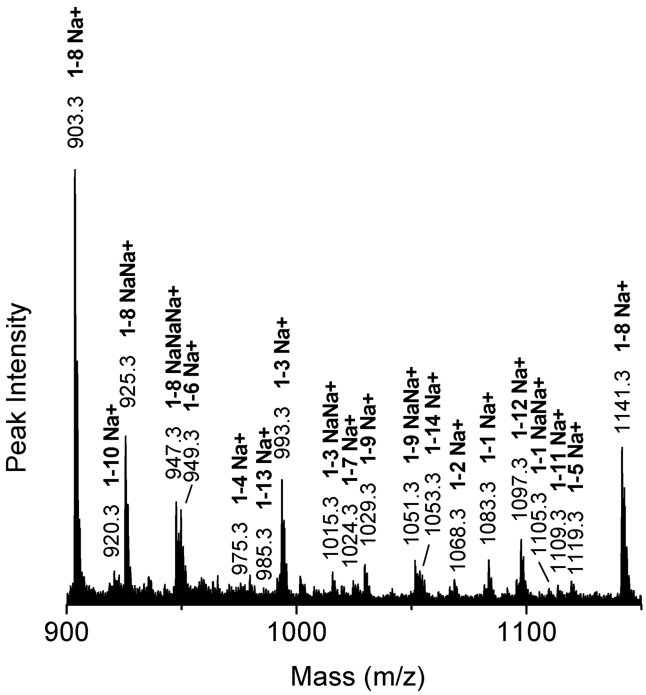


Figure 3. MALDI-TOF mass spectrum (900−1150 Da) of H_2O terminated PPD-T 49:51 diamine/diacid chloride. Sample prepared by the E−G method in 3AQ and cationized with NaTFA.

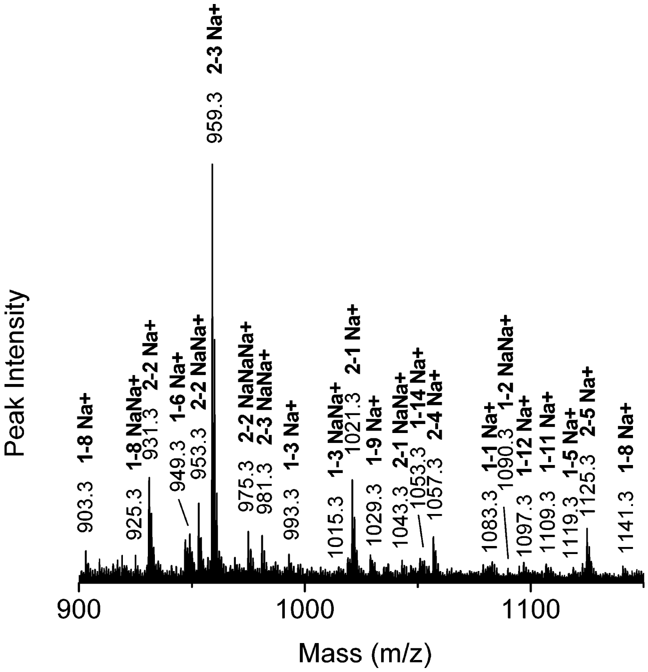


Figure 4. MALDI-TOF mass spectrum (900−1150 Da) of ethanol terminated PPD-T 30:70 diamine/diacid chloride. Sample prepared by the E−G method in 3AQ and cationized with NaTFA.

Da (1-11 NaNaNa$^+$), 1109.3 Da (1-11 Na$^+$), and 1131.3 Da (1-11 NaNa$^+$). Figure 2 shows the spectrum of the 50:50 molar ratio reaction, in which all three expected end groups are found with amine−carboxyl end groups being the predominant species in the mass spectrum and notable quantities of decarboxylated side products representative of amine−carboxyl (structure 1-6, Table 1) at masses of 949.3 Da (1-6 Na$^+$) and 971.3 Da (1-6 NaNa$^+$). There are also trace quantities decarboxylated side products representative of carboxyl−carboxyl end groups (structures 1-12 and -13, Table 1) at masses of 1097.3 Da (1-12 Na$^+$) and 985.3 Da (1-13 Na$^+$). Overall, very few side products are observed. Figure 3 displays the spectrum of the 49:51 molar ratio reaction, in which all three expected end groups are found with carboxyl−carboxyl end groups being the predominant species in the mass spectrum and small quantities of decarboxylated side products representative of amine−carboxyl (structure 1-6, Table 1) at a mass of 949.3 Da (1-6 Na$^+$). There are also small quantities of decarboxylated side products representative of carboxyl−carboxyl end groups (structures 1-12 and -13, Table 1) at masses of 1097.3 Da (1-12 Na+) and 985.3 Da (1-13 Na$^+$). Only trace amounts of

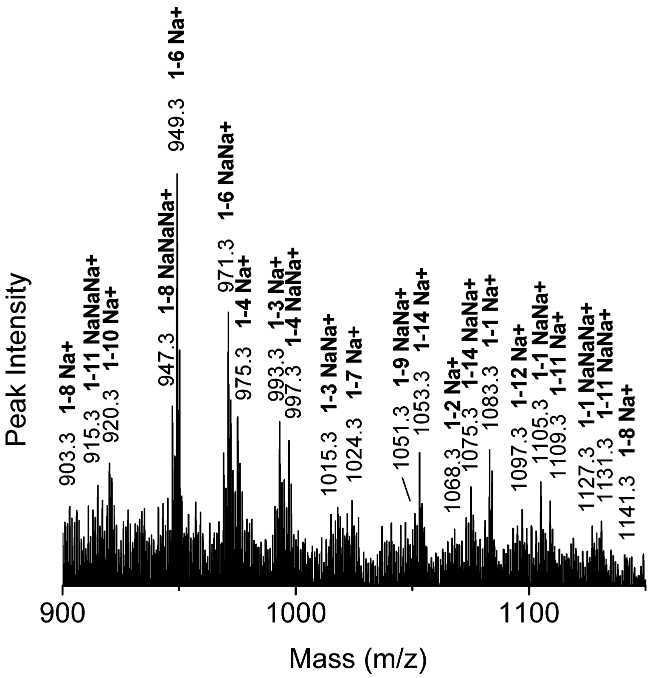


Figure 5. MALDI-TOF mass spectrum (900−1150 Da) of Kevlar fibers prepared by the E−G method in 3AQ and cationized with NaTFA.

aldehyde side products are present (structure 1-11, Table 1) at mass 1109.3 Da (1-11 Na^+).

PPD-T fibers synthesized using 30:70 molar ratios show a predominance of carboxyl−carboxyl end groups in the mass spectrum (Figure 4: ethanol terminated PPD-T) and no evidence of branching. There are also trace quantities of an aldehyde terminated side product of a carboxyl−carboxyl end group (structure 1-11, Table 1) at mass 1109.3 Da (1-11 Na^+) and trace quantities of decarboxylated side products representative of carboxyl−carboxyl end groups (structures 1-12 and 2-5, Table 1) at masses of 1097.3 Da (1-12 Na^+) and 1125.3 Da (2-5 Na^+). Mass spectra of PPD-T fibers synthesized using 70:30 molar ratios show a predominance of amine−amine end groups complicated by extensive imine branching throughout the spectra as shown in Scheme 2 (structure 1-7, Table 1).

Our studies indicate that cyclization occurs in small quantities, in discreet mass ranges, with structural side reactions being heavily influenced by the molar mixing ratios of diamine-to-diacid chloride. An excess molar portion of diamine favors the production of imine branching along with other side reactions such as aldehyde formation and extensive decarboxylation to form side products representative of carboxyl−amine end groups. Equal molar ratios (or very slight excesses of diamine or diacid chloride) show moderate quantities of decarboxylation to form side products representative of carboxyl−amine and carboxyl−carboxyl end groups. A large excess of diacid chloride favors the production of moderate quantities of decarboxylation to form side products representative of carboxyl−carboxyl end groups with no evidence of imine branching. Fully cyclic species appear in very small quantities in all mass spectra, and their occurrence does not appear to show a dependence on the molar ratio of the reactants as was discovered in our previous studies with poly(*m*-phenylene isophthalamide) (MPD-I)[15], which found fully cyclic species being the predominant species observed when using equimolar ratios of reactants. The findings of the MPD-I studies were validated using ESI-MS and the dried-droplet MALDI sample preparation methods to ensure that the species we were detecting was not the result of fragmentation due to the ionization process.[15] Since MPD-I is structurally similar to PPD-T (yet in comparison, possesses lower strength and modulus properties),[3] it is safe to assume that the species we are detecting is the actual species present in the sample and not the result of fragmentation. It is well-known, in poly(amic acid)s and polyimides, that reactions using excess diamine monomers are hindered by side product formation and polymer deterioration, so it is not surprising to find increased levels of imine branched species along with deamination and decarboxylation of the end groups.[16,17] Additionally, acid chlorides are extremely reactive, and when present in near equal molar or excess quantities (relative to the diamine), they would be expected to produce exothermic conditions that lead to decar-

Scheme 2. Poly(*p*-phenylene Terephthalamide) Imine Branching

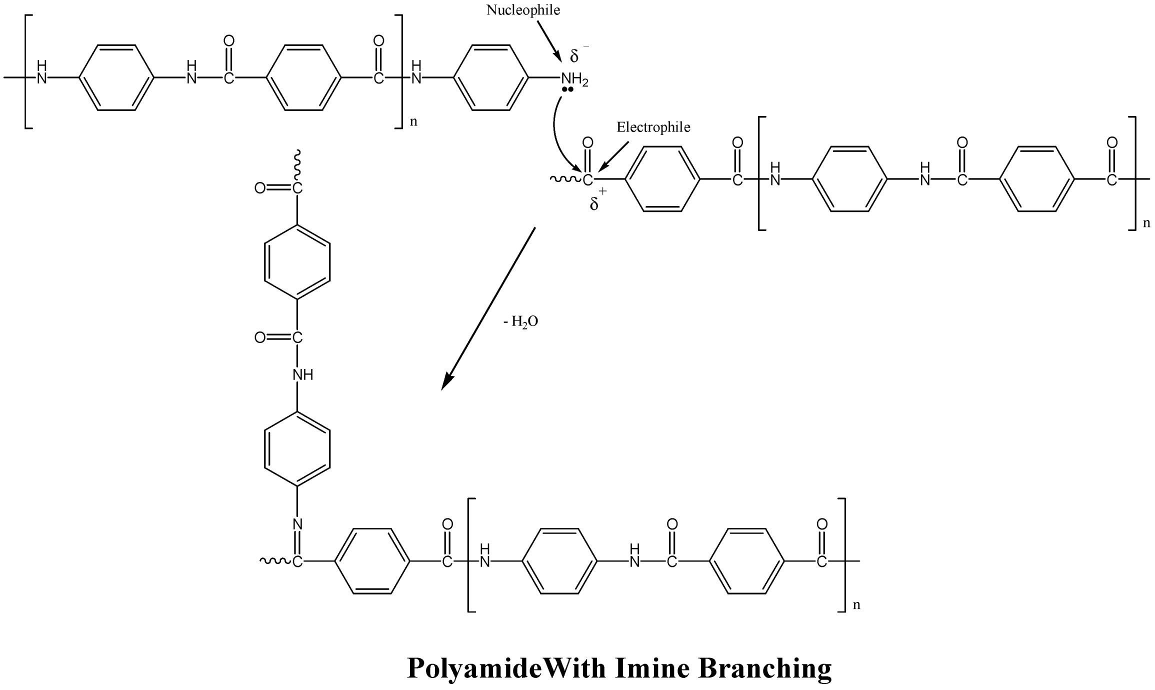


Table 2. Structural Assignments for Peaks in the MALDI-TOF Mass Spectra of Ethanol Terminated Polymers (Figure 4)

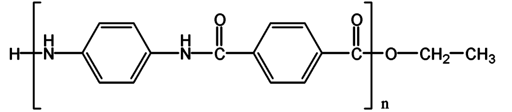
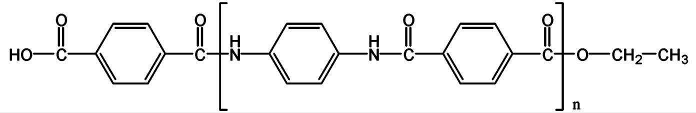
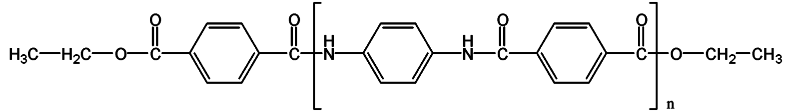
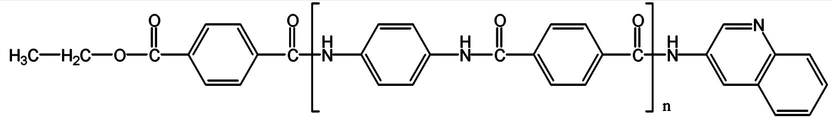
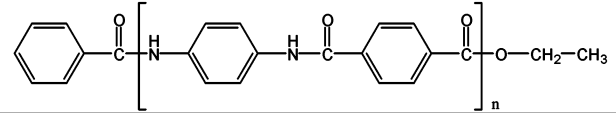
Species	Structure (M)
2-1	
2-2	
2-3	
2-4	
2-5	

Table 3. Mass Assignments for Peaks in the MALDI-TOF Mass Spectra Reported in Figures 1−5

species	51:49 H_2O Na^+ M (Da)	50:50 H_2O Na^+ M (Da)	49:51 H_2O Na^+ M (Da)	30:70 EtOH Na^+ M (Da)	Kevlar Na^+ M (Da)
1-1	607.2 ($n = 2$)... 2274.7 ($n = 9$)	607.2 ($n = 2$)... 2750.8 ($n = 11$)	607.2 ($n = 2$)... 2512.8 ($n = 10$)	607.2 ($n = 2$)... 2036.6 ($n = 8$)	607.2 ($n = 2$)... 1798.6 ($n = 7$)
1-2	592.2 ($n = 2$)... 2259.7 ($n = 9$)	592.2 ($n = 2$)... 2735.8 ($n = 11$)	592.2 ($n = 2$)... 2735.8 ($n = 11$)	592.2 ($n = 2$)... 2497.8 ($n = 11$)	592.2 ($n = 2$)... 1783.5 ($n = 7$)
1-3	755.2 ($n = 3$)... 2184.6 ($n = 9$)	517.1 ($n = 2$)... 2660.8 ($n = 11$)	517.1 ($n = 2$)... 2184.6 ($n = 9$)	517.1 ($n = 2$)... 2184.6 ($n = 9$)	517.1 ($n = 2$)... 1946.5 ($n = 8$)
1-4	737.2 ($n = 3$)... 1928.6 ($n = 8$)	737.2 ($n = 3$)... 1928.6 ($n = 8$)	737.2 ($n = 3$)... 1928.6 ($n = 8$)	737.2 ($n = 3$)... 1928.6 ($n = 8$)	737.2 ($n = 3$)... 1928.6 ($n = 8$)
1-5	643.2 ($n = 2$)... 1834.6 ($n = 7$)	643.2 ($n = 2$)... 2548.8 ($n = 10$)	643.2 ($n = 2$)... 2786.8 ($n = 11$)	643.2 ($n = 2$)... 1357.4 ($n = 5$)	643.2 ($n = 2$)... 1834.6 ($n = 7$)
1-6	711.2 ($n = 2$)... 2378.7 ($n = 9$)	711.2 ($n = 2$)... 2616.8 ($n = 10$)	711.2 ($n = 2$)... 2616.8 ($n = 10$)	711.2 ($n = 2$)... 2140.7 ($n = 8$)	711.2 ($n = 2$)... 1902.6 ($n = 7$)
1-7	786.3 ($n = 2$)... 1500.5 ($n = 5$)	548.3 ($n = 1$)... 1500.5 ($n = 5$)	786.3 ($n = 2$)... 1500.5 ($n = 5$)		786.3 ($n = 2$)... 1500.5 ($n = 5$)
1-8	665.2 ($n = 2$)... 2094.6 ($n = 8$)	665.2 ($n = 2$)... 2570.7 ($n = 10$)	665.2 ($n = 2$)... 2808.8 ($n = 11$)	665.2 ($n = 2$)... 1856.5 ($n = 7$)	665.2 ($n = 2$)... 1617.4 ($n = 6$)
1-9	791.2 ($n = 2$)... 1505.4 ($n = 5$)	791.2 ($n = 2$)... 2458.7 ($n = 9$)	553.2 ($n = 1$)... 1505.4 ($n = 5$)	553.2 ($n = 1$)... 1982.6 ($n = 7$)	791.2 ($n = 2$)... 1505.4 ($n = 5$)
1-10	682.2 ($n = 1$)... 2349.7 ($n = 8$)	682.2 ($n = 1$)... 2587.8 ($n = 9$)	682.2 ($n = 1$)... 2587.8 ($n = 9$)	682.2 ($n = 1$)... 2349.7 ($n = 8$)	682.2 ($n = 1$)... 1873.6 ($n = 6$)
1-11	633.2 ($n = 2$)... 2300.7 ($n = 9$)	633.2 ($n = 2$)... 2300.7 ($n = 9$)	633.2 ($n = 2$)... 2300.7 ($n = 9$)	633.2 ($n = 2$)... 2776.8 ($n = 11$)	633.2 ($n = 2$)... 1824.5 ($n = 7$)
1-12		621.2 ($n = 2$)... 2526.7 ($n = 10$)	621.2 ($n = 2$)... 2764.8 ($n = 11$)	621.2 ($n = 2$)... 2526.7 ($n = 10$)	621.2 ($n = 2$)... 1097.3 ($n = 4$)
1-13		747.2 ($n = 2$)... 985.3 ($n = 3$)	747.2 ($n = 2$)... 1223.4 ($n = 4$)	747.2 ($n = 2$)... 1699.5 ($n = 6$)	747.2 ($n = 2$)... 985.3 ($n = 3$)
1-14	577.2 ($n = 1$)... 2244.7 ($n = 8$)	577.2 ($n = 1$)... 2244.7 ($n = 8$)	577.2 ($n = 1$)... 2720.8 ($n = 10$)	577.2 ($n = 1$)... 2482.8 ($n = 10$)	577.2 ($n = 1$)... 1768.5 ($n = 6$)
2-1				545.2 ($n = 2$)... 2688.8 ($n = 11$)	
2-2				693.2 ($n = 2$)... 2360.7 ($n = 9$)	
2-3				721.2 ($n = 2$)... 2864.9 ($n = 11$)	
2-4				581.2 ($n = 1$)... 2724.8 ($n = 10$)	
2-5				649.2 ($n = 2$)... 2554.8 ($n = 10$)	

boxylation and aldehydic side product formation of the carboxyl end groups as well.[17] However, the 0 °C synthesis conditions, along with the addition of triethylamine to complex the generated hydrochloric acid, seems to have limited their production of side products to decarboxylated species representative of carboxyl−carboxyl end groups. The constant production of small quantities of cyclic species (independent of the molar ratios of the reactants) would be due to the rigid nature of these oligomeric aramids. Very small amounts of these species do exist under these strained conditions but not to an appreciable extent as shown in MPD-I.[15] In addition, they only appear in the region between 737 and 1928 Da, which suggests that ring strain (for the low mass portion) and chain length (for the high mass portion) limit the likelihood of their formation.

Our previous studies with MPD-I fibers indicate that aromatic amide groups in the polymer chain undergo hydrogen/sodium exchanges as well as amine and carboxyl end groups.[15] This seems reasonable since hydrogen/deuterium exchange studies routinely report such exchanges occurring with aliphatic amide nitrogens. However, reviewers have pointed out that amide nitrogens of wholly aromatic polyamides are not expected to undergo such exchanges due to steric hindrance and stabilization from the aromatic ring. To address these questions, studies with the ethanol terminated PPD-T fibers were used to examine the ability of aramids to undergo hydrogen/sodium exchange. Figure 4 displays the mass spectrum of ethanol terminated PPD-T fibers. One can detect the presence of species 2-3 $NaNa^+$ (981.3 Da), which is a diester terminated oligomer ionized with a sodium cation and containing a sodium adduct (structure 2-3, Table 2). Inspection of the structure makes it apparent that the only functional group capable of hydrogen/sodium exchange is an amide nitrogen. These species are also detected in the mass spectra of 2-propanol and *t*-butyl alcohol terminated PPD-T fibers. These studies lead us to conclude that amide nitrogens in aramids are capable of hydrogen/sodium exchange as was seen in the fully cyclic species from our MPD-I studies.[15]

Kevlar fibers exhibit a bimodal distribution[2] of molecular weights, and initial studies were conducted to explore the possibility of using the low molecular mass distribution (accessible to MALDI-TOF MS) to derive synthesis information about the high molecular mass portion. As in our previous studies,[6] we could obtain mass spectra of the oligomeric portion of Kevlar, as shown in Figure 5. By observing the relatively even distribution of end groups, one can make a reasonable assumption (upon comparison with the mass spectra in Figures 1-3 and mass assignments in Table 3) that Kevlar fibers are synthesized using equimolar ratios of diamine and diacid chloride. However, when one closely examines the abundance of side products present (large quantities of a decarboxylated amine–carboxyl end group (structure 1-6, Table 1) at masses 949.3 Da (1-6 Na^+) and 971.3 Da (1-6 $NaNa^+$), small amounts of aldehyde side products are present (structure 1-11, Table 1) at masses of 915.3 Da (1-11 $NaNaNa^+$), 1109.3 Da (1-11 Na^+), and 1131.3 Da (1-11 $NaNa^+$) and small quantities of branched species (structure 1-7, Table 1) at a mass of 1024.3 (1-7 Na^+)), a signature pattern matches that of Figure 1 and indicates the use of a slight excess of diamine in the synthesis. This would be a good assumption since equimolar monomer ratios are necessary to achieve maximum polymer molecular weight in condensation polymerizations and to avoid/minimize side reactions.[2] As pointed out earlier in this paper, acid chlorides are extremely reactive and must be handled under anhydrous conditions or suffer a reduction in the amount of diacid chloride available for reaction. Furthermore, hydrochloric acid is a generated product of the condensation polymerization that will react with the diamine if not complexed by adequate quantities of triethylamine—additionally this can be countered by the addition of a slight excess of diamine. Either one of these conditions would explain the very slight excess of diamine present in our analysis of Kevlar fibers. Further studies are being conducted to refine this technique and to apply it to other polymeric materials.

Conclusions

The solution polymerization of low molecular mass PPD-T produces oligomeric species displaying end group distributions dependent on the ratio of reactants used in their synthesis. The evaporative grinding method is able to produce MALDI-TOF mass spectra of oligomers of all expected end group combinations including cyclic and branched species, which are minor species and are indicative of the percent molar ratios of the reactants.

We conclude that the oligomeric species, reported in our previous work are, in fact, the predominant species that are formed in commercial specimens due to the close to equimolar amounts of reactants in synthesis and were not species selectively extracted from the sample during the wet grinding process. Our work also suggests that the percent molar ratio of reactants in high molecular mass Kevlar-like polymers can be predicted from the distribution of end groups and, more importantly, the abundance of side products seen in the oligomeric portion are available for MALDI-TOF MS analysis. This information should be useful for polymer chemists in that it can assist them in adjusting their synthesis conditions when distinctive side products are being formed.

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