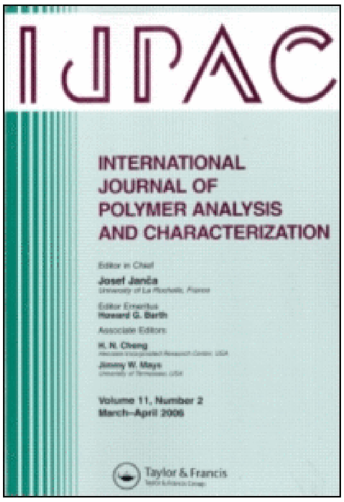

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Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry Analysis of Poly(para-phenyleneethynylene)s

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Abstract: For the first time, MALDI-TOF MS was utilized for the determination of the structures of four partially soluble poly(*p*-phenyleneethynylene)s (PPEs) used to disperse single-walled carbon nanotubes in polymers. The spectra obtained indicated that the synthesis of the PPEs resulted in the formation of a co-oligomer with two different repeat groups. Various methods were employed to obtain an optimum spectrum. The evaporation-grinding sample preparation method (E-G method) combined with dithranol as matrix and KTFA as cationizing agent appeared to be the best method for obtaining a MALDI-TOF MS spectrum. AgTFA was the most effective cationizing agent for one sample that contained a high carbon-to-oxygen ratio.

Keywords: MALDI-TOF MS; PPE; Poly (para-phenyleneethynylene)s; Evaporation-grinding method

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INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are dispersed in commercial polymers in order to achieve conductivity levels required for electrical applications. Due to the smooth surfaces of the SWNTs, they are often difficult to disperse in common solvents and polymers.[1] Two approaches have been used in the past to disperse the SWNTs in a host polymer: (1) lengthy sonication that can damage/cut the SWNTs and (2) in situ polymerization in the presence of SWNTs, which are highly dependent on the specific polymer. A versatile, non-damaging third approach has recently been introduced that preserves almost all of the intrinsic properties of the SWNTs utilizing poly(*p*-phenyleneethynylene)s (PPEs).[1] These are short, rigid conjugated polymers that allow SWNTs to be solubilized by a polymeric material by adhering to the SWNT's surface. The basis of this adherence is a π-stacking interaction between the pi ring systems.[1–3] By interacting with the SWNTs, the variations in the PPE backbone can control the distance between functional groups on the PPE and hence on the carbon nanotube surface.[4] By varying the distance between the functional groups, the solubility of the SWNTs will change for each specific host polymer.

In order to determine the optimal distance of functional groups for each host polymer, one must be able to synthesize a variety of PPEs with highly characterized structures and molecular weights. The products and impurities from each synthesis of PPE must be identified. The difficulty in doing this lies in the low solubility of PPEs in most solvents.[5]

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) yields a wealth of information on the mass, structure, and end groups of large molecules generated in chemical reactions, and this information can provide insight into the reactions and side reactions taking place in their creation.[6,7] This laboratory recently developed the Evaporation-Grinding (E-G) method, which is specifically used to analyze synthetic polymers with low solubility.[8,9] This method allows us to determine the major and minor products of the synthesis of PPEs, which, in turn, will aid others in engineering these molecules for future use in solubilizing SWNTs in polymers.

EXPERIMENTAL SECTION

Poly(*p*-phenyleneethynylene) Synthesis

Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers (Aldrich, Fluka, Acros, Lancaster) and were used without further purification. All chemicals were of reagent grade.

Tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$), (trimethylsilyl) acetylene, and trans-dichlorobis(triphenylphosphine)palladium (II) ($(PPh_3)_2 PdCl_2$) were purchased from Aldrich and used as received. Dimethylformamide (DMF) and pyridine were purchased as dry solvents, stored over molecular sieves, and used as received. Diisopropylamine was dried over solid KOH pellets, distilled under argon atmosphere, and degassed by three freeze-pump-thaw cycles. Transfer of air-sensitive chemicals was achieved by using double-ended needles under argon pressure or by graduated syringes. Preparation for the polymerization was conducted in a glovebox, and all polymerizations were carried out by using standard vacuum-line techniques. All monomers were prepared and characterized according to published procedures.[10]

Oligomer A

Monomer **1** (0.350 g, 0.238 mmol), monomer **2** (1,4-bis((triethylene glycol monomethyl ether)oxy)-2,5-diethynylbenzene) (0.235 g, 0.524 mmol), monomer **3** (1,4-diiodo-2,5-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene) (0.155 g, 0.238 mmol), and iodobenzene (0.010 g, 0.05 mmol) as end group were polymerized to give oligomer A by using the Sonogashira coupling reaction in the presence of $(PPh_3)_4Pd$ (28 mg, 0.024 mmol) and CuI (5.0 mg, 0.024 mmol) in DMF (35 mL) and diisopropylamine (10 mL) at 60°C for 24 hours. An additional amount of iodobenzene (0.030 g, 0.15 mmol) was added to the mixture, which reacted for another 3 hours. The oligomer was precipitated in ethanol, filtered, washed with acetone, and dried under vacuum at room temperature.

Oligomer B

Monomer **1** (0.5 equ.), (1,4-diethynylbenzene) (**5**) (1.1 equ.), and monomer 1,4-diiodobenzene (**6**) (0.5 equ.) were polymerized to give oligomer B in a way similar to oligomer A.

Oligomer C

Monomer **4** (0.5 equ.), (1,4-diethynylbenzene) (**5**) (1.1 equ.), and 1,4-diiodobenzene (**6**) (0.5 equ.) were polymerized to give oligomer C in a way similar to oligomer A except using toluene as reaction solvent.

Oligomer D

Monomer **4** (0.35 g, 0.237 mmol), 1,4-bis-dodecyloxy-2,5-diiodo-benzene (**8**) (0.166 g, 0.237 mmol), 1,4-bis-dodecyloxy-2,5-diethynyl-benzene (0.258 g, 0.521 mmol) (**7**), and iodobenzene (0.010 g, 0.05 mmol) as end groups were polymerized to give oligomer D by using the Sonogashira coupling reaction in the presence of $(PPh_3)_2PdCl_2$ (17 mg, 0.024 mmol) and CuI (5.0 mg, 0.024 mmol) in toluene (35 mL) and diisopropylamine (10 mL) at 60°C for 24 hours. An additional amount of iodobenzene (0.030 g, 0.15 mmol) was added to the mixture, which reacted for another 3 hours. The oligomer was precipitated in ethanol, filtered, washed with acetone, and dried under vacuum at room temperature.

All syntheses were performed in the laboratory of coauthor Liu at Michigan Technological University.

MALDI-TOF MS Measurements

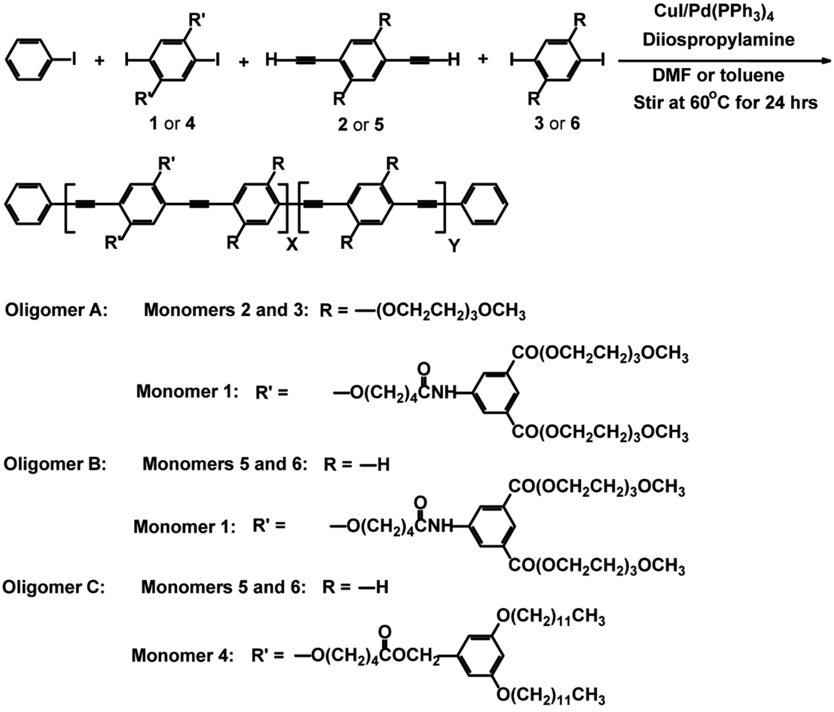
All poly(*p*-phenyleneethynylene)s (PPEs) samples were analyzed using a Voyager Elite MALDI-TOF MS (Applied Biosystems, Framingham, Mass., USA) equipped with a 337 nm N_2 laser. All the spectra were obtained in the positive ion mode using an accelerating voltage of 20 kV and a laser intensity of ~10% greater than threshold. The grid voltage, guide wire voltage, delay time, and mode were optimized or chosen for each spectrum to achieve as high a signal-to-noise (S/N) ratio as possible. Mass calibration was performed using protein standards from a Sequazyme peptide mass standard kit (Applied Biosystems) and a two-point calibration method using ACTH (clip 1–17) ($m = 2094$) and insulin (bovine) ($m = 5735$). The instrument was calibrated immediately after each spectrum was obtained to keep the experimental conditions constant. All PPE samples were obtained using the matrix dithranol doped with potassium trifluoroacetate (KTFA), cesium trifluoroacetate (CsTFA), and silver trifluoroacetate (AgTFA) salt (all obtained from Aldrich).

These samples were prepared using the Evaporation-Grinding method (E-G method). A molar mixing ratio of 25:1:1 matrix:PPE:salt ratio and ~60 μL tetrahydrofuran (THF; Fisher) was ground with an agate mortis and pestle (Fischer) until the THF evaporated and the matrix and cationizing agent precipitated. After evaporation of the THF, the mixture was ground again to insure homogeneity. A sample size of 5 mg was pressed into a sample well by a spatula on the MALDI sample plate.

All MALDI analyses were performed in the laboratory of William K. Nonidez at the University of Alabama at Birmingham.

RESULTS AND DISCUSSIONS

Poly(*p*-phenyleneethynylene)s are typically synthesized by a Sonogashira coupling polymerization under Sonogashira conditions of a diiodaryl monomer with diethynyl monomer. Oligomers A, B, and C were prepared using $(PPh_3)_4Pd$ as a catalyst and CuI as a cocatalyst (Scheme 1). Iodobenzene was used as an endgroup. Oligomer D was prepared using

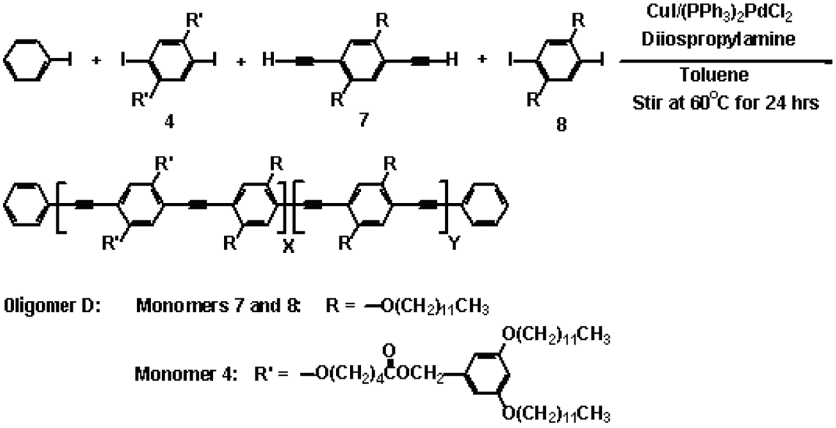


Scheme 1. Generic PPE synthesis of A, B, and C.

the same methods, except $(PPh_3)_2PdCl_2$ was used as a precatalyst instead of $Pd(PPh_3)_4$ (Scheme 2).

The dried-droplet method (D-D method) was initially used for the sample preparation, but it either yielded no spectra or spectra of such poor quality that they were of little use. Since some of the oligomers appeared not to be very soluble, we chose to try the E-G method, which produced serviceable spectra for each oligomer. Various matrices were also used (dithranol, 3-aminoquinoline (3AQ) and dihydroxybenzoic acid (DHB)), with dithranol producing the best overall spectra. KTFA, AgTFA, and CsTFA were used as cationizing agents and were selectively used to generate the spectra with the highest S/N ratios for purposes of identifying each polymer.

Through the course of the experiments, oligomers A and B gave superior spectra when cationized with KTFA, while C responded better to AgTFA. Structures proposed by our MALDI-TOF MS technique demonstrate that oligomers A and B have carbon-to-oxygen ratios of 119:40 and 92:24 respectively, and oligomer C has a carbon-to-oxygen ratio of 110:10. The well-known ability of the potassium ion to cationize



Scheme 2. Generic PPE synthesis of D.

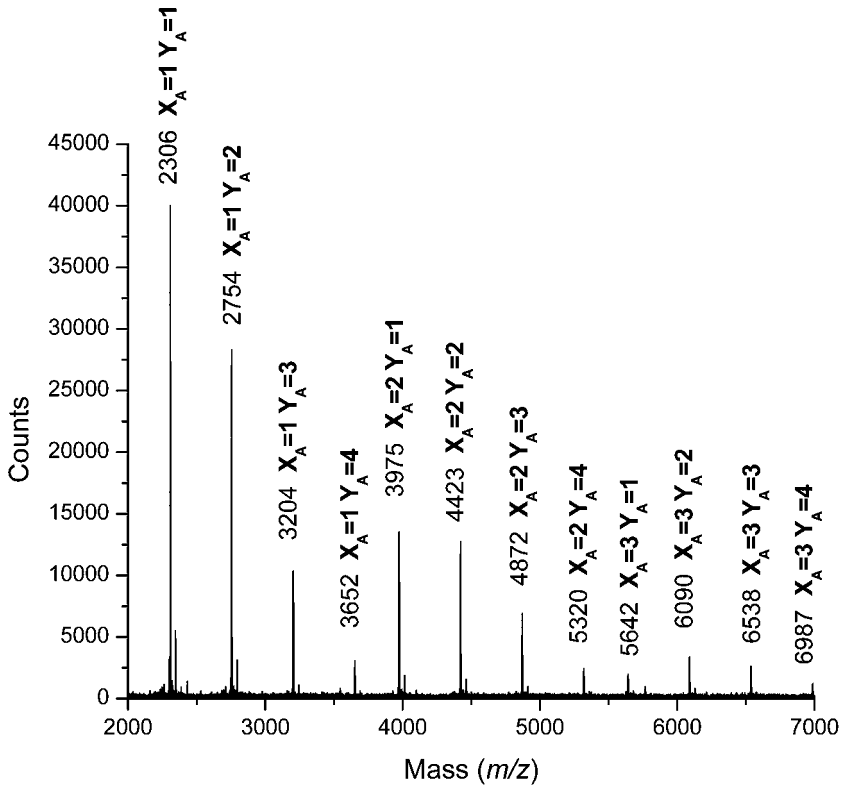


Figure 1. MALDI-TOF mass spectrum of PPE A prepared by the E-G method in dithranol, cationized with KTFA.

large molecules with numerous atoms with unshared electrons such as oxygen or nitrogen and the well-known ability of the silver ion to cationize large molecules containing numerous bonds well explains this observation. Oligomer C with its relatively small amount of oxygen is

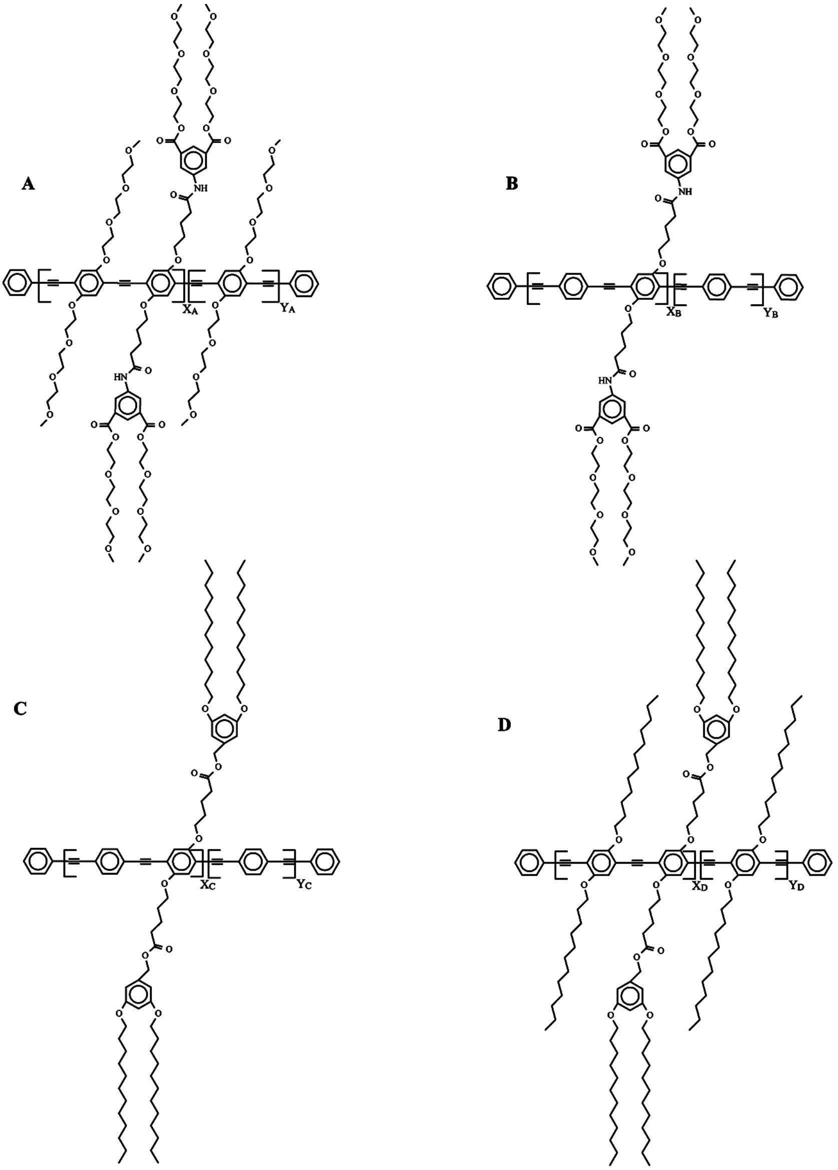


Figure 2. Structures of PPE A, B, C, and D.

more amenable to cationization with silver through interaction with its double bonds. Oligomer D showed little difference in S/N ratio with either cationizing agent.

Oligomer A

A representative spectrum of A, cationized with KTFA and prepared by the E-G method with dithranol as the matrix, appears in Figure 1. This spectrum contains a series of peaks found at masses of 2306 and 3975 Da, which are separated by 1669 Da. This is the expected mass for repeat unit X_A. A second series of peaks was identified whose masses, 2306, 2754, 3204, 3652, and 4100 Da, are separated by 449 Da. We propose that this second series corresponds to a second repeat unit Y_A, as shown in our proposed structure in Figure 2 making A a co-oligomer. Peaks with the same intervals above appeared in spectra cationized with AgTFA although these spectra had substantially lower signal-to-noise ratios. The masses of these peaks also appear in Table I and serve to verify the interpretation given above.

Oligomer B

A spectrum of oligomer B prepared via the E-G method with dithranol as the matrix appears in Figure 3. In this spectrum, the oligomer is cationized by the addition of KTFA. Once again, the spectrum has two

Table I. Mass assignments of the peaks displayed in the MALDI-TOF mass spectrum reported in Figure 1

N	M	Calculated K^+	Experimental K^+
1	1	2309	2306
1	2	2758	2754
1	3	3206	3204
1	4	3654	3652
1	5	4102	4100
2	1	3977	3975
2	2	4425	4423
2	3	4874	4872
2	4	5322	5320
2	5	5770	5769
3	1	5645	5642
3	2	6093	6090
3	3	6542	6538
3	4	6990	6987

Table II. Mass assignments of the peaks displayed in the MALDI-TOF mass spectrum reported in Figure 3

N	M	Calculated K^+	Experimental K^+
1	1	1661	—
1	2	1785	1782
1	3	1909	1906
1	4	2033	—
2	1	3004	3002
2	2	3128	3126
2	3	3252	3251
2	4	3377	3376
3	1	4348	4345
3	2	4472	4470
3	3	4596	4594
3	4	4720	4718
4	1	5691	5689
4	2	5815	5813
4	3	5939	5937
4	4	6063	6060
4	5	6188	6486

Table III. Mass assignments of the peaks displayed in the MALDI-TOF mass spectrum reported in Figure 4

N	M	Calculated Ag^+	Experimental Ag^+
1	1	1734	1736
1	2	1858	1860
1	3	1983	1984
1	4	2107	2108
1	5	2231	2234
2	1	3083	3086
2	2	3207	3210
2	3	3332	3334
2	4	3456	3458
2	5	3580	3582
2	6	3704	3705
3	1	4432	—
3	2	4556	4559
3	3	4681	4683
3	4	4805	4808
3	5	4929	4931
3	6	5053	5057

Table IV. Mass assignments of the peaks displayed in the MALDI-TOF mass spectrum reported in Figure 5

N	M	Calculated K^+	Experimental K^+
1	1	2405	2402
1	2	2897	2896
1	3	3390	3388
1	4	3883	3881
1	5	4376	4374
1	6	4868	4867
2	1	4123	4122
2	2	4616	4614
2	3	5109	5108
2	4	5602	5600
2	5	6094	—

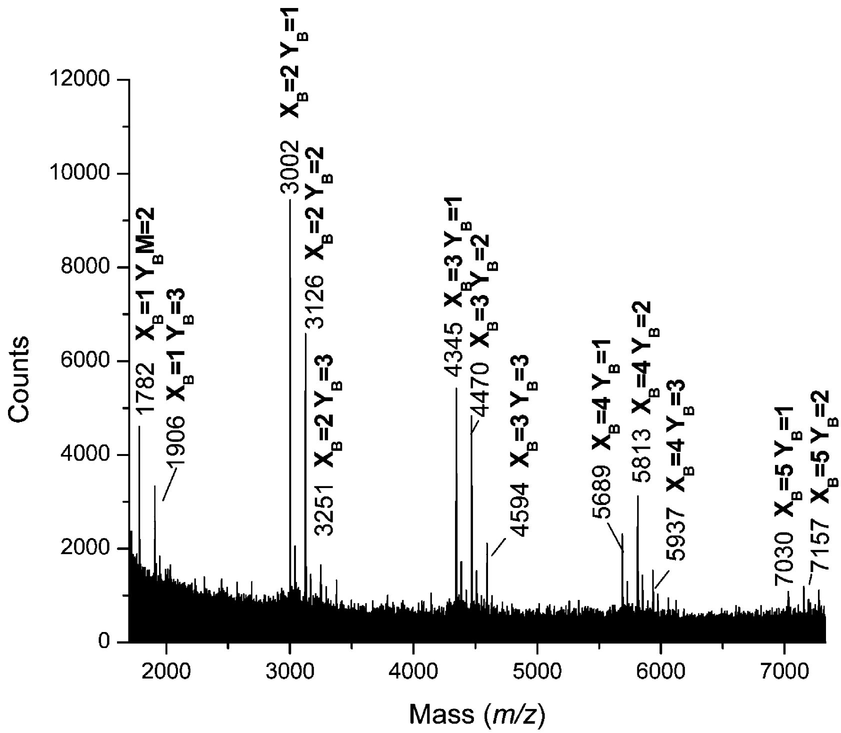


Figure 3. MALDI-TOF mass spectrum of PPE B prepared by the E-G method in dithranol, cationized with KTFA.

repeating series, one for each repeat unit in the hypothesized co-oligomer. The peaks at masses 3002 and 4345 Da are separated by 1343 Da, which is the mass of repeat unit X_B. A series of additional peaks is also present with masses of 3126, 3251, and 3376 Da, separated by a nominal mass of 124.38 Da, which is the mass of repeat unit Y_B. Efforts to use other cationizing agents yielded spectra of such poor quality that they were of no use. The masses of this peaks also appear in Table II and serve to verify the interpretation given above.

Oligomer C

A representative spectrum of C prepared by the E-G method with dithranol as the matrix appears in Figure 4. In this spectrum, oligomer C is

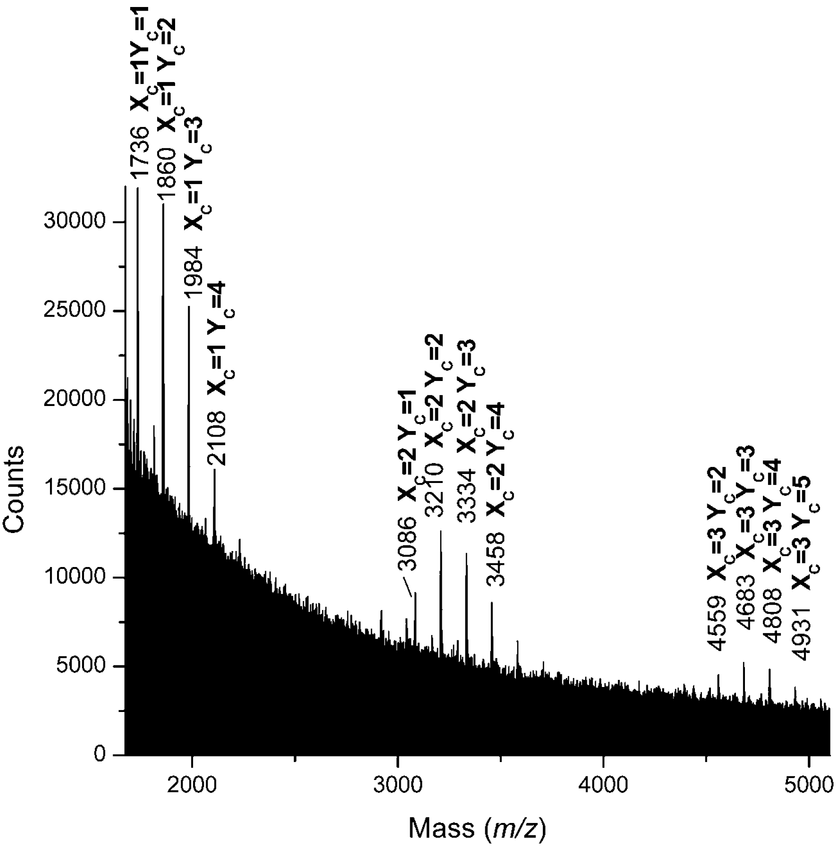


Figure 4. MALDI-TOF mass spectrum of PPE C prepared by the E-G method in dithranol, cationized with AgTFA.

cationized with the addition of AgTFA. This spectrum contains a series of peaks with masses that correlate to the repeat units of the respective co-oligomer. The peaks of this series found at masses of 1735 and 3084 Da are separated by 1349 Da, the expected repeat unit for X_C. A second series has peaks whose masses, 1858, 1983, and 2107 Da, are separated by a nominal mass of 124.03 Da, which corresponds to a second repeat unit Y_C. The masses of this peaks also appear in Table III and serve to verify the interpretation given above.

Oligomer D

A representative spectrum of D cationized with KTFA and prepared by the E-G method with dithranol as a matrix appears in Figure 5. The peaks of this series found at masses of 2402 and 4122 Da are separated

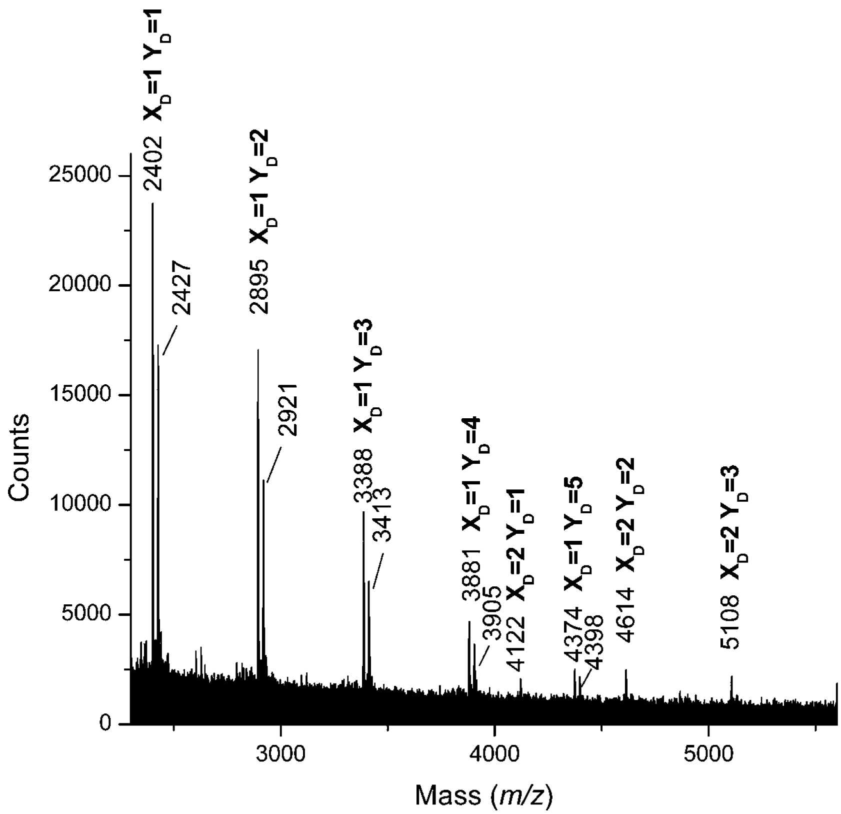


Figure 5. MALDI-TOF mass spectrum of PPE D prepared by the E-G method in dithranol, cationized with KTFA.

by 1719 Da – the repeat unit for X_D. A second series has peaks whose masses, 2402, 2896, 3388, and 3881 Da, are separated by 493 Da—the expected repeat unit for Y_D. There is a third series of peaks that appears, at masses approximately 24 Da more than the PPE oligomer. We believe that these peaks are side products containing extra acetyl linkages (C·C) and are the "butadiyne" defect reported previously by Ofer and coworkers, Zhou and Swager, and Steiger and coworkers.[11–13] The $(PPh_3)_2$ $PdCl_2$ precatalyst is activated by its oxidation of diyne, forming the butadiyne defects in the polymer. The masses of this peaks also appear in Table IV and serve to verify the interpretation given above.

CONCLUSION

For the first time, MALDI-TOF MS was utilized for the determination of the structures of four partially soluble PPEs used to disperse SWNTs in polymers. The spectra obtained indicated that the synthesis of the PPEs resulted in the formation of a co-oligomer with two different repeat groups. Various methods were employed to obtain an optimum spectrum. The E-G method combined with dithranol as matrix and KTFA as cationizing agent appeared to be the best method for obtaining a MALDI-TOF MS spectrum. AgTFA was the most effective cationizing agent for one sample that contained a high carbon-to-oxygen ratio.

We believe that this study demonstrates the power of MALDI-TOF MS as a tool for analysis of insoluble molecules of this type.

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