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

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ABSTRACT: A combination of the evaporation-grinding MALDI-TOF MS sample preparation method with surface-modification techniques is presented for the characterization of intractable poly(*p*-phenylene sulfide)s (PPS). Studies focus on the relationships between the following experiments: (1) effects of MALDI laser fluence and area of irradiation on model PPS phenyl-capped trimers and cyclics; (2) modification of PPS synthesis conditions; (3) thermal curing of PPS under various atmospheric (N_2 and air) and thermal (100−300 °C) conditions; and (4) heated *N*-methyl-2-pyrrolidone fractionation of high MW PPS (25, 50, 75, and 100 °C). These studies yielded a wealth of information on the mass, structure, and end groups of species generated in the synthesis, postsynthesis modification, and thermal curing of PPS. Furthermore, surface-modified MALDI sample preparation techniques were shown to selectively isolate cyclic species from high-molecular-weight PPS.

Introduction

Edmonds and Hill developed the first commercially viable process for the synthesis of poly(*p*-phenylene sulfide) (PPS) in the 1960s,[1] involving the reaction of a "polymerizable" sulfur source derived from sodium sulfide and *p*-dichlorobenzene in *N*-methyl-2-pyrrolidone (NMP) at elevated temperature and pressure. The Edmonds−Hill polymer, as received from the reactor, is a low-molecular-weight "linear" polymer having $M_n \approx 20\,000$. When subjected to thermal curing, a process in which the polymer is heated in an oxidizing environment, several changes occur: (1) toughness increases, (2) melt viscosity increases, (3) kinetics and extent of crystallization decrease, and (4) the color becomes darker. Despite the significant time that has elapsed since the initial discovery, aspects of the Edmonds−Hill process are not well understood, specifically, the nature of the thermal curing reactions, the special role of NMP, and end-group chemistry.

PPS polymers are virtually insoluble in most solvents at ambient temperatures and are therefore difficult to characterize. Traditionally, these intractable polymers have been characterized by infrared spectrometry and thermal methods of analysis, most notably pyrolysis.[2−9] Until the development of the evaporation-grinding method (E-G method),[10] MALDI-TOF MS had only limited capabilities for examining intractable materials and obtaining information such as the nature of end groups and molecular mass distributions. The current study reports a combination of MALDI-TOF MS and surface treatment techniques that permit the examination of synthesis, postsynthesis modification, and thermal curing of intractable PPSs.

Experimental Section

Materials. The commercial PPS used in this study was Ryton powder, produced by the Edmonds−Hill process[1] and supplied by Chevron Phillips Chemical Company, LP, Bartlesville, Oklahoma. The structure of the polymer repeat unit was assumed to be that shown for the cyclic and linear species (1-1 and 1-2) in Table 1.

Model phenyl-capped PPS trimers were synthesized via solution polymerization.[11] All reagents were obtained from commercial sources and used as received. The structure of the oligomers produced is shown as species 1-4 in Table 1.

MALDI-TOF MS Measurements. All 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 > 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 Angiotensin 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 (M_n = 2000; Polymer Source) to yield monoisotopic masses exhibiting a mass accuracy better than $\Delta m = \pm 0.05$ Da. The instrument was calibrated before every measurement to ensure constant experimental conditions.

All samples were run in Dithranol (Aldrich) doped with silver trifluoroacetate (AgTFA, Aldrich), copper(II) chloride ($CuCl_2$, Aldrich), or with no cationization agent added. All spectra displayed the expected mass shifts for the respective cationizing agent; AgTFA was the reagent of choice because it yielded spectra with the best signal-to-noise ratios. Samples were prepared using the evaporation-grinding method (E-G method)[10,12,13] in which a 2 mg sample of PPS was ground to a fine powder using an agate mortar and pestle. Molar ratios (with respect to moles of the polymer) of 25 parts matrix and 1 part cationizing agent were added to the finely ground polymer along with 60 μL 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

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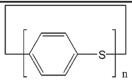
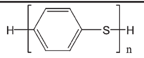
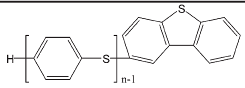
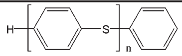
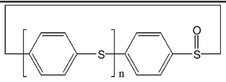
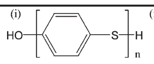
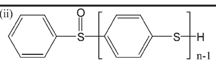
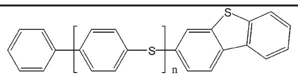
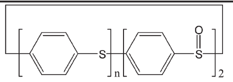
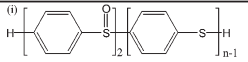
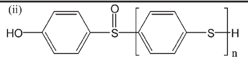
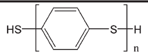
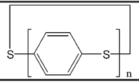
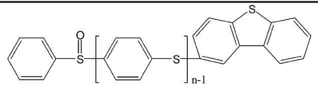
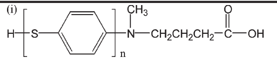
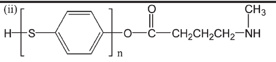
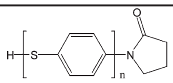
Table 1. Structural Assignments for Peaks in the MALDI-TOF Mass Spectra Reported in Figures 1−7,[a]

Species	Structure (M)	$^{\cdot+}$ M (Da)	Ag^{+} M (Da)
1-1		**540.0** (n = 5) **648.0** (n = 6) **756.0** (n = 7) **864.0** (n = 8) **972.0** (n = 9) .... **2160.0** (n = 20)	**646.9** (n = 5) **754.9** (n = 6) **862.9** (n = 7) **970.9** (n = 8) **1078.9** (n = 9) .... **1618.9** (n = 14) **1726.9** (n = 15) **1834.9** (n = 16) **1942.9** (n = 17) **2050.9** (n = 18) **2158.9** (n = 19) .... **3994.9** (n = 36)
1-2		**542.0** (n = 5) **650.0** (n = 6) **758.0** (n = 7) **866.0** (n = 8) **974.0** (n = 9) .... **2162.0** (n = 20)	**648.9** (n = 5) **756.9** (n = 6) **864.9** (n = 7) **972.9** (n = 8) **1080.9** (n = 9) .... **1944.9** (n = 17) **2052.9** (n = 18) **2160.9** (n = 19) .... **3996.9** (n = 36)
1-3		**616.0** (n = 4) **724.0** (n = 5) **832.0** (n = 6) **940.0** (n = 7) .... **2344.0** (n = 20)	**722.9** (n = 4) **830.9** (n = 5) **938.9** (n = 6) .... **1694.9** (n = 13) **1802.9** (n = 14) **1910.9** (n = 15) **2018.9** (n = 16) **2126.9** (n = 17) .... **2450.9** (n = 20)
1-4		**510.1** (n = 4) .... **942.1** (n = 8) **1050.0** (n = 9) **1158.1** (n = 10)	**509.0** (n = 3) .... **941.0** (n = 7) **1049.0** (n = 8) **1157.0** (n = 9)
1-5		**556.0** (n = 4) .... **880.0** (n = 7) **988.0** (n = 8) **1096.0** (n = 9) .... **2284.0** (n = 20)	**554.9** (n = 3) .... **878.9** (n = 6) **986.9** (n = 7) **1094.9** (n = 8) .... **2290.9** (n = 19)
1-6	(i)  (ii) 	**558.0** (n = 5) **666.0** (n = 6) **774.0** (n = 7) **882.0** (n = 8) **990.0** (n = 9) **1098.0** (n = 10) .... **2178.0** (n = 20)	**556.9** (n = 4) **664.9** (n = 5) **772.9** (n = 6) **880.9** (n = 7) **988.9** (n = 8) **1096.9** (n = 9) .... **2284.9** (n = 20)
1-7		**584.1** (n = 3) .... **2096.1** (n = 17)	**583.0** (n = 2) .... **2095.0** (n = 16)
1-8		**788.0** (n = 5) **896.0** (n = 6) **1004.0** (n = 7) .... **1652.0** (n = 13) **1760.0** (n = 14) **1868.0** (n = 15) **1976.0** (n = 16) **2084.0** (n = 17) .... **2408.0** (n = 20)	**786.9** (n = 4) **894.9** (n = 5) **1002.9** (n = 6) .... **1650.9** (n = 12) **1758.9** (n = 13) **1866.9** (n = 14) **1974.9** (n = 15) **2082.9** (n = 16) .... **2514.9** (n = 20)
1-9	(i)  (ii) 	**574.0** (n = 4) .... **898.0** (n = 7) **1006.0** (n = 8) .... **2302.0** (n = 20)	**572.9** (n = 3) .... **896.9** (n = 6) **1004.9** (n = 7) .... **2408.9** (n = 20)
1-10		**574.0** (n = 5) **682.0** (n = 6) **790.0** (n = 7) **898.0** (n = 8) **1006.0** (n = 9) .... **2194.0** (n = 20)	**572.9** (n = 5) **680.9** (n = 5) **788.9** (n = 6) **896.9** (n = 7) **1004.9** (n = 8) .... **2300.9** (n = 20)
1-11		**572.0** (n = 5) .... **1544.0** (n = 14)	**570.9** (n = 4) .... **1650.9** (n = 14)
1-12		**524.0** (n = 3) .... **848.0** (n = 6) **956.0** (n = 7) .... **1604.0** (n = 13)	**630.9** (n = 3) .... **846.9** (n = 5) **954.9** (n = 6) .... **1710.9** (n = 13)
1-13	(i)  (ii) 	**765.1** (n = 6) .... **1629.1** (n = 14) **1737.1** (n = 15) **1845.1** (n = 16) **1953.1** (n = 17) **2061.1** (n = 18) **2169.1** (n = 19) **2277.1** (n = 20)	**872.0** (n = 6) .... **1628.0** (n = 13) **1736.0** (n = 14) **1844.0** (n = 15) **1952.0** (n = 16) **2060.0** (n = 17) **2168.0** (n = 18) **2276.0** (n = 19) .... **2384.0** (n = 20)
1-14		**517.1** (n = 4) .... **841.1** (n = 7) **949.1** (n = 8) **1057.1** (n = 9) .... **2029.1** (n = 18) **2137.1** (n = 19) .... **2245.1** (n = 20)	**516.0** (n = 3) .... **840.0** (n = 6) **948.0** (n = 7) **1056.0** (n = 8) .... **2028.0** (n = 17) **2136.0** (n = 18) .... **2352.0** (n = 20)

[a] Underlined masses correspond to the highest mass peaks observed for a given series.

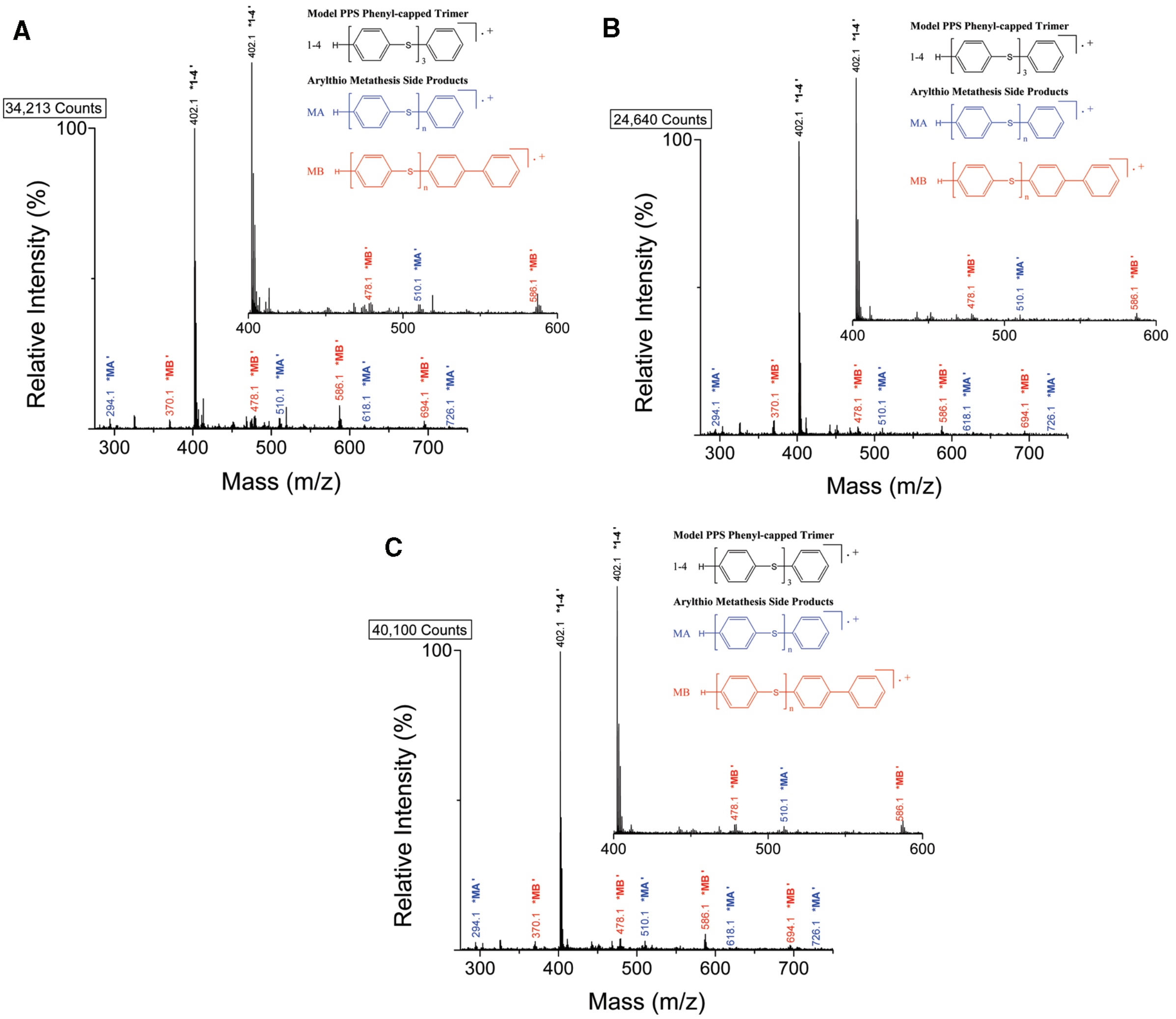


Figure 1. MALDI-TOF mass spectra of a model poly(*p*-phenylene sulfide) trimer oligomers showing the effects of MALDI laser fluence (A) 10% above threshold and 30 s of grinding (“normal” MALDI preparation and analysis), (B) 10% above threshold and four additional 30 s grinding steps (“excessive” grinding time and “normal” MALDI analysis), and (C) 30% above threshold (“normal” grinding time and “excessive” laser fluence).

ground again to ensure homogeneity. A sample of the mixture was then pressed into a sample well by spatula on the MALDI sample plate. The weight-average molecular weights (M_w) of all PPS samples were determined with the Data Explorer 4.9 software supplied by Applied Biosystems.

Results and Discussion

The present study reports a series of experiments, which were conducted to evaluate the usefulness of mass spectrometry for studying high-MW PPS produced by the Edmonds–Hill process. The focus of this article will be on PPS characterization learned from the following experiments: (1) effects of sample grinding times, MALDI laser fluence, and area of irradiation on model PPS tetramers and cyclics; (2) synthesis modification of PPS; (3) thermal curing of PPS under various atmospheric (N_2 and air) and thermal (100–300 °C) conditions; and (4) heated NMP fractionation of high MW PPS (25, 50, 75, and 100 °C). The MALDI-TOF MS data presented will examine the selectively extracted low-molecular-weight (end-group rich) portion of PPS.[14] Comparisons between MALDI-TOF MS and PPS synthesis and curing conditions will be presented to support proposed synthesis mechanisms leading to high-MW PPS polymers.

MALDI-TOF MS. *MALDI Studies on Model Poly(p-phenylene sulfide) Phenyl-Capped Trimers and Cyclics.* Our previous MALDI-TOF MS studies of poly(*p*-phenylene terephthalamide) (PPD-T)[14] and polybenzoxazole (PBO)[15] fibers raised the question about possible mass spectral artifacts produced by analysis-induced chain fragmentation. To address this question for PPS, we considered two possible sources of analysis-induced artifacts: (1) grinding-induced fragmentation resulting from the E-G MALDI sample preparation method[10] and (2) in-source fragmentation induced by the MALDI laser.

Model PPS phenyl-capped trimers (structure 1-4, $n = 3$, in Table 1) were examined to study the effect of MALDI laser fluence on a PPS trimer. Figure 1A shows a MALDI spectrum of the trimer obtained with the effective laser area as large as possible (the “fanned-out” setting with an observed fluorescence of 10% of the sample well area) and the laser fluence that is normally used (ca. 8 μJ). The most intense peak in Figure 1 at $m/z = 402.1$ is due to the trimer, structure 1-4. Figure 1B shows a spectrum using the same laser fluence but with four additional 30 s grinding steps used in sample preparation. Figure 1C shows a spectrum obtained using the normal grinding time but with a laser fluence 30% above threshold (ca. 10 μJ). Clearly, there is no significant difference in the intensities of the MA and MB peaks, relative to the 402.1 Da peak, in either Figure 1B or 1C compared with 1A. It is important to note that no cationizating agent was used to obtain the spectra shown in Figure 1. Similar mass

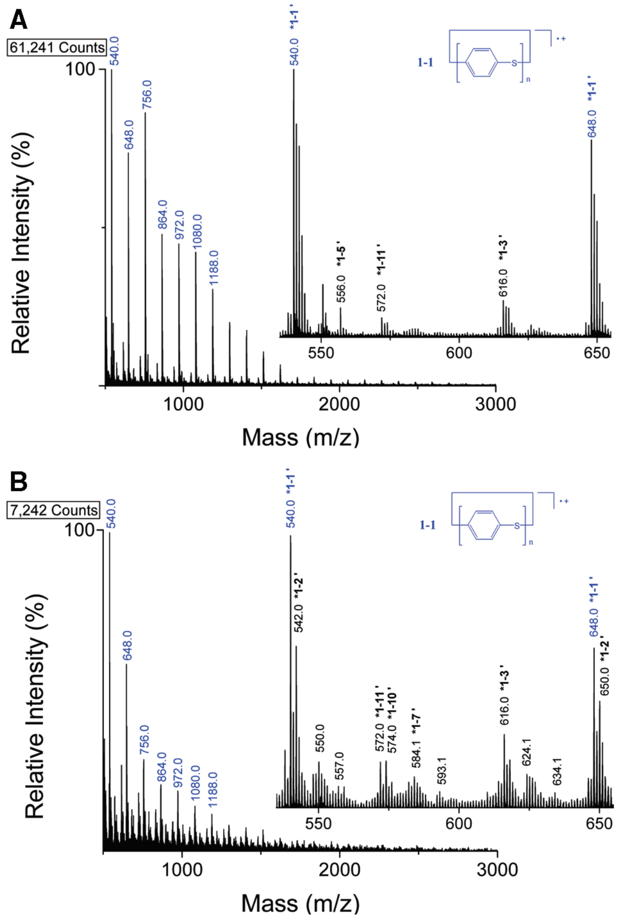


Figure 2. MALDI-TOF mass spectra of a model poly(*p*-phenylene sulfide) cyclic oligomers showing the effects of (A) a "fanned-out" laser area setting and (B) a "pin-point" laser area setting.

spectra were obtained when the laser was rastered across the surface of the MALDI sample mixture or held at a specific point. A series of weak peaks is also observed, labeled MA and MB. The structures are also shown and are presumably due to metathesis side reactions.

The effect of laser irradiation area on the MALDI spectra of model PPS cyclic oligomers was examined, as shown in Figure 2. Again, no cationizing agent was added to obtain the spectra in Figure 2. Cyclic PPS was chosen for this study because it lacks end groups, making it an ideal model compound for the study of polymer backbone fragmentation. Spectra were obtained using two laser settings for comparison. In the first, the laser was defocused as widely as possible in the "fanned-out" mode (observed fluorescence area was 10% of the sample well area) for Figure 2A, and in the second, the laser was focused as narrowly as possible in the "pin-pointed" setting (observed fluorescence area was 5% of the sample well area), still being able to obtain a MALDI spectrum. Figure 2A shows the MALDI spectrum obtained using the "fanned-out" laser setting with laser fluencies at 10% above threshold (ca. 8 μJ).[14,15] As in the laser fluence studies of model PPS phenyl-capped trimers, no fragmentation of the model PPS cyclic oligomers was observed in the fanned-out mode, regardless of the laser fluence or extra grinding steps introduced in the sample preparation. Also, similar mass spectra were obtained when the laser was rastered across the surface of the MALDI sample mixture or held at a specific location. However, the "pin-pointed" laser setting shown in Figure 2B shows three notable effects. First, the absolute intensity drastically decreases from ca. 61K counts in Figure 2A for the "fanned-out" setting to ca. 7K counts in Figure 2B, the "pin-pointed" setting. Second, the "grass" (chemical noise) in the mass spectrum is significantly greater in Figure 2B, and weak peaks from free radicals are observed. Third, the shape of the polymer peak intensity distribution changes from partial Gaussian in Figure 2A to a ski-slope-shaped distribution in Figure 2B, indicating that relatively more low-mass species are produced in the latter. Both of these effects are characteristic of polymer decomposition. However, even under the extreme conditions, polymer decomposition is not at the level where it would greatly bias the identification of the major species. For example, the relative intensities of species 1-3 and 1-11 are essentially constant in Figure 2A,B. If these species were degradation products, then their peak intensities should be far greater in Figure 2B than in Figure 2A. However, using the pinpoint laser setting for MALDI certainly would affect the measurement of M_n and M_w for the polymer. In summary, MALDI done with near threshold settings does not contribute to decomposition, and artifacts due to laser fluence or sample grinding do not appear in the mass spectra when the "fanned-out" mode is used.

Synthesis Modification of Poly(p-phenylene sulfide). These experiments examined the effects of synthesis modification of PPS by the addition of NaOH to the reaction mixture. We sought to identify the chemical processes that produced changes in the physical properties of the polymers that have been previously observed.[3,16,17]

Three samples of PPS were examined by MALDI-TOF MS, one with no added NaOH and others with the addition of 5 or 10% of NaOH versus PPS. Figure 3 shows that as the amount of NaOH added to the reaction is increased the peak intensities of the hydroxylated linear species (1−6; 556.9 et seq. Da) increase with respect to the cyclic species (1-1; 754.9 et seq. Da) and the mass distribution of species 1-1 changes. For example, when no NaOH is added to the reaction (Figure 3A), the species 1-6 peak at 556.9 Da is approximately equal in intensity to the species 1-1 peak at 754.9 Da, the lowest mass cyclic species observed, and the base peak (1-1) is at 1078.9 Da. As shown in Figure 3B, when 5% NaOH was added to the reaction mixture, the PPS peak at 556.9 Da has increased to 85% of the base peak, which is now at 970.9 Da, and the peak at 754.9 Da (species 1-1) is 65% of the base peak. In addition, the intensity ratio of the 556.9 Da peak to the 754.9 Da peak has increased from approximately 1.0 to 1.3. Also, additional peaks from species 1-6 are seen, for example, 772.9 Da. When 10% NaOH was added, as shown in Figure 3C, the species 1-6 peak at 556.9 Da became the base peak, and the peak at 754.9 Da (species 1-1) was 55% of the base peak, a ratio of ~2.0. Also, the peak maximum for the 1−1 series has shifted to 862.9 Da.

During the MALDI study, it was discovered that the addition of 1 μL of THF to the surface of the dithranol/PPS MALDI sample after it was affixed to the MALDI sample plate selectively extracted cyclic (1-1) and hydroxylated linear (species 1-6) species from the complex PPS mixture. (Essentially, it drew them closer to the MALDI sample surface for selective ionization from the PPS mixture.) This permitted easy comparison of the two species. This MALDI surface-modified sample preparation potentially should be useful for constructing calibration curves to monitor quantitatively the amount of linear-hydroxyl-containing species versus cyclic species produced during synthesis.

Post-Synthesis Thermal Curing of Poly(p-phenylene sulfide). The postsynthesis, thermally induced, chemical modification of PPS was examined as a function of curing

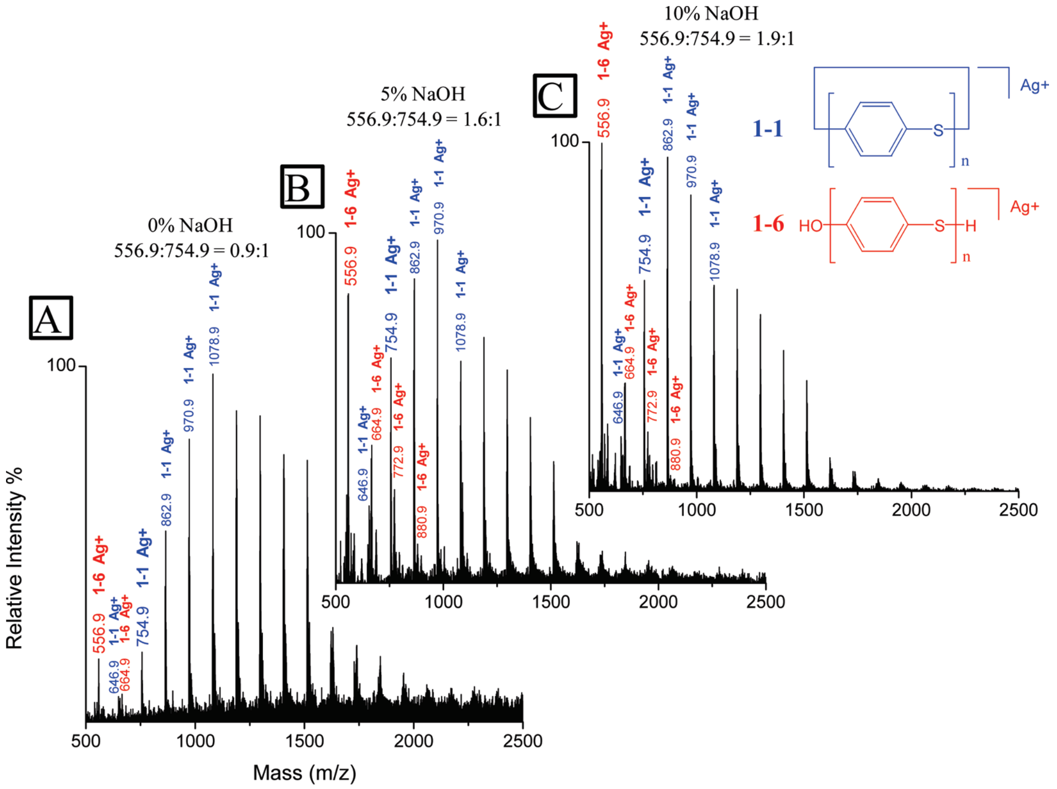


Figure 3. MALDI-TOF mass spectra (mass regions between 500−2500 Da) of Edmonds−Hill poly(*p*-phenylene sulfide) (Ryton) with the addition of (A) 0, (B) 5, and (C) 10% NaOH during the synthesis.

time, temperature, and atmosphere. In an effort to simplify the interpretation of MALDI spectra, we will focus our discussion on the narrow mass region of 950−1110 Da. Figure 4A shows the MALDI spectrum of an uncured PPS sample, two predominant species are observed; cyclic (1-1) and linear (1-2) PPS, the latter with benzenethiol end groups. Note that the region between the major peaks is quite clean. Figure 4B shows a mass spectrum of PPS cured at 230 °C for 12 h in air. Comparison with the uncured reference spectrum (Figure 4A) indicates that species 1-5 and 1-6 are produced as the major oxidation products during the thermal curing process. Smaller amounts of a sulfoxide species having both thiol and phenolic end groups (species 1-9) are also seen. PPS also was cured under the same conditions (230 °C, for 12 h) under a nitrogen atmosphere; the MALDI spectrum is shown in Figure 4C. The relative intensities of species 1-5 and 1-6 are drastically reduced relative to those in Figure 4B; species 1-1 and 1-2 are the major species. Small amounts of species 1-4, 1-8, and 1-9 are also seen. Although care was taken to eliminate oxygen from the nitrogen curing experiment, some “adventitious oxidation” must have occurred. Despite this, the study clearly indicates that air curing has profound effects on the backbone chemistry of PPS, resulting in the formation of sulfoxides. These could be intermediates in the formation of branched species in fully cured PPS, as speculated by Hawkins.[18] However, it was not possible to identify any structures indicative of significant branching.

Heated NMP Fractionation of Poly(*p-phenylene sulfide*). A sample of PPS was studied by fractional extraction at different temperatures with NMP. The purpose was to examine the solubility of different “cuts” of the PPS molecular weight distribution and chemical species contained therein as a function of solvent temperature. This experiment involved the introducing thoroughly degassed NMP into an enclosed glass column filled with high MW PPS, heating the mixture, and removing the solvent to yield polymeric material for MALDI analysis. Extractions were performed sequentially at different temperatures (25, 50, 75, and 100 °C) to ensure that each successive fraction would contain a higher MW fraction of PPS. The goals of this study were: (1) to examine the limits of MALDI-TOF MS for characterization of narrow MW PPS fractions, (2) to identify the PPS structures and end groups that are soluble at different temperatures, and (3) to examine changes in the PPS MALDI spectra as a function of polymer molecular weight.

The first fraction, taken at 25 °C, contained primarily low-MW cyclic species (1-1); their distribution is shown in Figure 5A. Figure 5B shows a spectral segment under higher resolution, revealing a significant presence of linear benzenethiols (1-2). Figure 5B also shows minor peaks identified as being from cyclics with one sulfoxide group (1-5), cyclics with two sulfoxide groups (1-8), cyclics with a biphenyl linkage (1-3), and cyclics with a biphenyl linkage and one sulfoxide group (1-12). Although these peaks are weak, they occur with higher intensity in subsequent spectra. The presence of copper-coordinated species in Figure 5B is the result of an impurity introduced during synthesis.

The high mass portion of the MALDI spectrum (Figure 5C) shows medium intensity peaks for linear PPS species having ring-opened NMP attached as an end group (1-13). As shown in Scheme 1A, when H_2O is added to PPS synthesis, it can react with Na_2S and NMP to form ring-opened sodium *N*-methyl-2-aminobutanoate (SMAB). SMAB is necessary for the solvation of NaSH during PPS synthesis. SMAB can then react with a phenyl chlorine (Scheme 1B) to form the ring-opened NMP end group; such a polymer is identified as species 1-13.

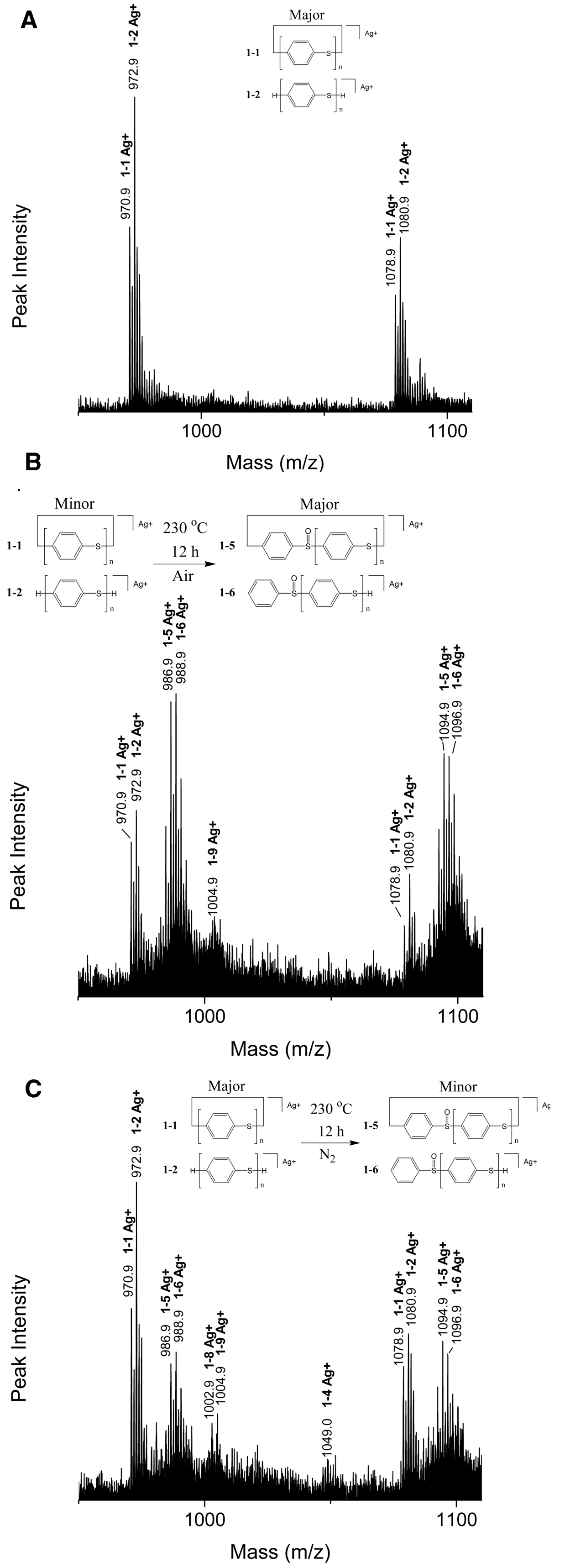


Figure 4. MALDI-TOF mass spectra (mass regions between 950−1110 Da) of (A) uncured poly(*p*-phenylene sulfide) (PPS), (B) PPS cured at 230 °C for 12 h under an atmosphere of air, and (C) PPS cured at 230 °C for 12 h under an atmosphere of nitrogen.

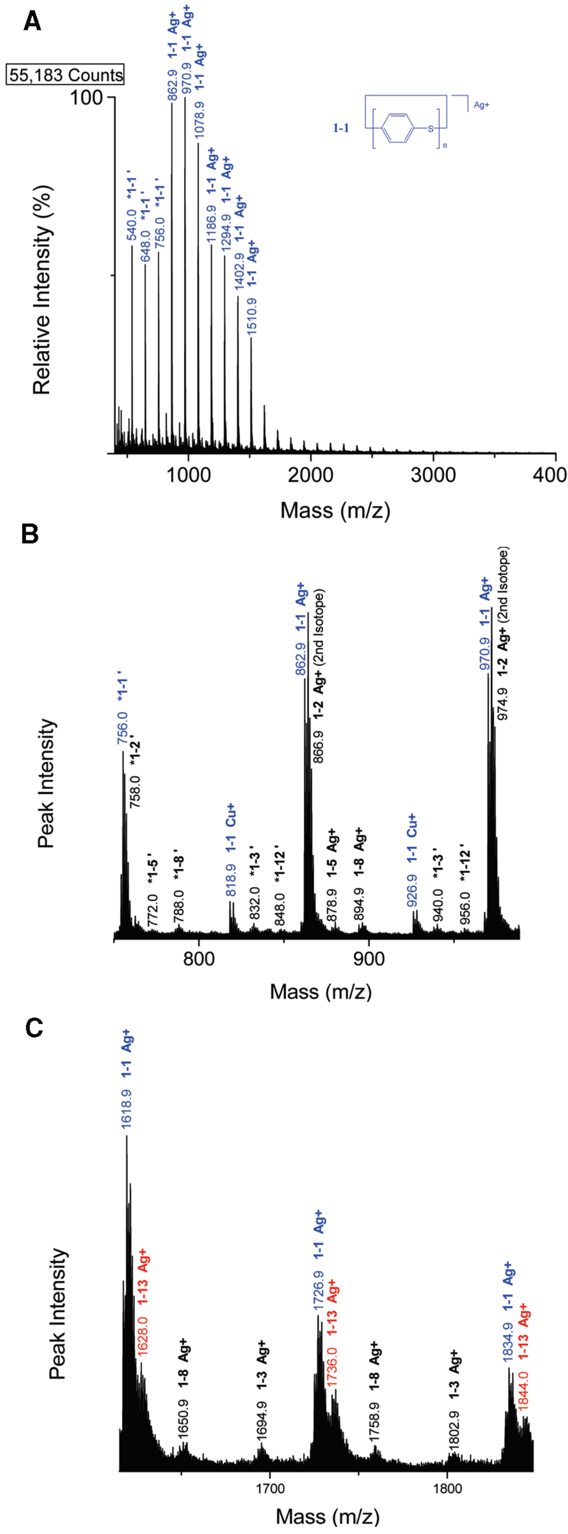
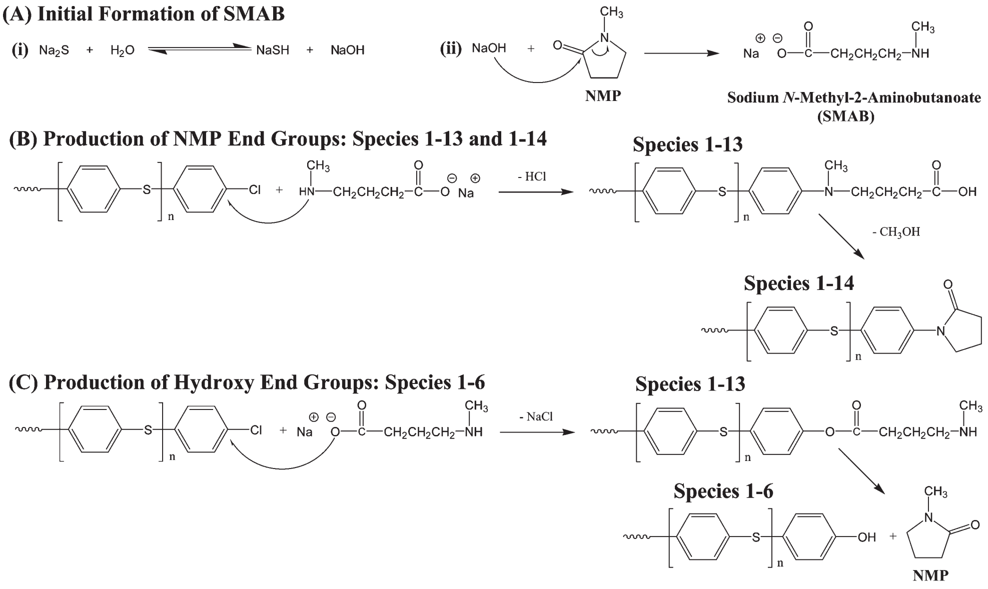


Figure 5. MALDI-TOF mass spectra of the fraction of oligomers extracted from high MW poly(*p*-phenylene sulfide) (Ryton) at 25 °C. For inspection of identified mass peaks, the mass spectrum is presented as follows: (A) full mass spectrum (400−4000 Da), (B) low mass region (750−990 Da), and (C) high mass region (1615−1850 Da).

Both H_2O and NaOH are present in the wet basic synthesis of PPS. Fahey and Ash have previously reported the importance of SMAB formation in the production of high MW PPS:[19] it functions as a base and solublizes the NaSH.

Scheme 1. Poly(*p*-phenylene sulfide) Chemical Reactions for the Production of Unexpected End Groups: (A) Initial Formation of Sodium *N*-Methyl-2-aminobutanoate (SMAB); (B) Production of *N*-Methyl-2-pyrrolidone (NMP) End Groups (Species 1-13 and 1-14); and (C) an Alternative Mechanism of Production of Hydroxyl End Groups (Species 1-6)



The fraction extracted at 50 °C (Figure 6) showed increased presence of linear PPS species (1-2) along with higher MW cyclics, as can be seen by comparing Figures 5A and 6A. The 750−1000 Da portion of the MALDI spectrum (Figure 6B) shows an increased amount of cyclic PPS (species 1-1), and the linear benzenethiols (species 1-2) have become the predominant species in each peak cluster. The minor peaks cited earlier have become more intense: cyclic sulfoxides (species 1-5 and 1-8) and biphenyl-linked cyclic (species 1-3) and their respective sulfoxides (species 1-12). It should also be noted that a minor peak was identified as a PPS linear structure with cyclic NMP attached as an end group (species 1-14). Species 1-13 can undergo the loss of methanol to yield the cyclic NMP end group identified for species 1-14, further substantiating the importance of SMAB formation in the production of high MW PPS.[19]

Examination of the 1925−2200 Da portion of the mass spectrum (Figure 6C) shows that cyclic (species 1-1) are still predominant, but linear PPS species with a ring-opened NMP attached as an end group (species 1-13) have increased in peak intensity, as can be seen by comparing Figures 5C and 6C. Minor peaks are also observed for species 1-3 and 1-14.

The MALDI spectra of the 75 and 100 °C fractions (Figures 7 and S1, respectively) are quite similar, so only the 75 °C fraction MALDI spectrum will be discussed in detail. The 75 °C fraction (Figure 7A) shows the extraction of linear PPS along with higher MW cyclic species. Note particularly the very intense peaks at 1620.9 and 1728.9 Da. Inspection of the 750−1000 Da portion of the 75 °C fraction MALDI spectrum (Figure 7B) shows that an increasing amount of linear benzenethiols (species 1-2) is being extracted, fewer low MW cyclic species (1-1) are appearing, and linear PPS with cyclic NMP attached as an end group (species 1-14) is still a minor peak. The 1925−2200 Da portion of the 75 °C fraction spectrum (Figure 7C) shows that linear PPS with ring-opened NMP attached as an end group (species 1-13) has become a major species detected. Linear benzenethiol (species 1-2) and cyclic species (species 1-2) have become less intense at higher molecular weights. Linear PPS with a cyclic NMP attached as an end group (species 1-14) is observed as a minor peak. The increasing intensity of the 1-13 species provides further evidence of the importance of SMAB formation in the synthesis of PPS.

The NMP extraction experiment reveals a rather important finding in that Campbell had first theorized that NMP actively played a key role in the production of linear high MW Ryton, produced by the Campbell process,[20] which is capable of being spun into fibers. SMAB reactions with PPS have the potential for producing hydroxyl end groups on PPS (species 1-6 and 1-10). For example, the carboxyl end of ring-opened SMAB (instead of the amine group, as we have previously described) can react with a phenyl chlorine (Scheme 1C) to form an isobaric variation of the ring-opened NMP end group identified for species 1-13. This species can undergo the loss of an NMP group (thereby recycling NMP) to form hydroxylated linear PPS (species 1-6). The mechanisms shown in Scheme 1 illustrate the importance of NMP in SMAB formation, end group modification, and ultimately the quality of high MW PPS polymers.

Inspection of the broad-range MALDI spectra of the PPS fractions (Figures 5A−7A) reveals not only that different species are extracted as a function of temperature but also that the PPS molecular mass distributions are solubilized change as a function of NMP temperature. For example, cyclic species (1-1) with a peak mass distribution centered at 970.9 Da are the major species extracted at 25 °C (Figure 5A). However, when the extraction temperature is increased to 50 °C (Figure 6A), the distribution takes on bimodal character; the low mass and high mass distributions show both cyclics (1-1) and linears (1-2), but between 864.9 and 1512.9 Da, linear PPS is the major species. At temperatures of 75 and 100 °C, the PPS distribution is almost entirely linear species (1-2) centered at a higher molecular weight, 1620.9 Da. Also, at 100 °C, the high mass tail of the distribution consists of primarily of linear PPS with ring-opened NMP attached as an end group (species 1-13).

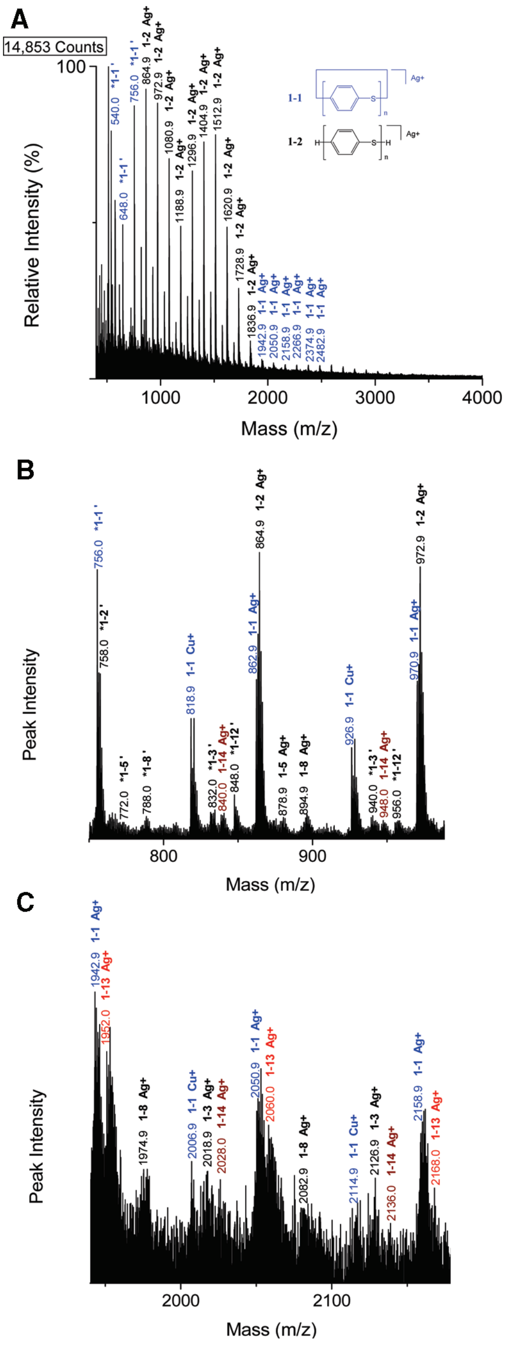


Figure 6. MALDI-TOF mass spectra of the fraction of oligomers extracted from high MW poly(*p*-phenylene sulfide) (Ryton) at 50 °C. For inspection of identified mass peaks, the mass spectrum is presented as follows: (A) full mass spectrum (400−4000 Da), (B) low mass region (750−990 Da), and (C) high mass region (1940−2180 Da).

Conclusions

The combination of MALDI-TOF MS and the evaporation grinding method was successfully exploited to examine the chemical modifications and chain growth mechanisms involved in the production of high-MW PPS. Findings indicate that (1) NMP plays a key role in the appearance of unexpected end groups and the production of high-MW PPS; (2) PPS thermal curing in the presence of oxygen, even at trace quantities, leads to oxygen uptake in the form of sulfoxides in the PPS backbone; and (3) the production of high-MW PPS involves linear chain extension, oxidative branching, and arylthio metathesis reactions, with the possibility of thermally induced free-radical chemical mechanisms. We believe that our study's reaction mechanisms are self-consistent with our observations in MALDI-TOF MS and another study we are completing on Py-GC/MS and MS/MS of PPS.

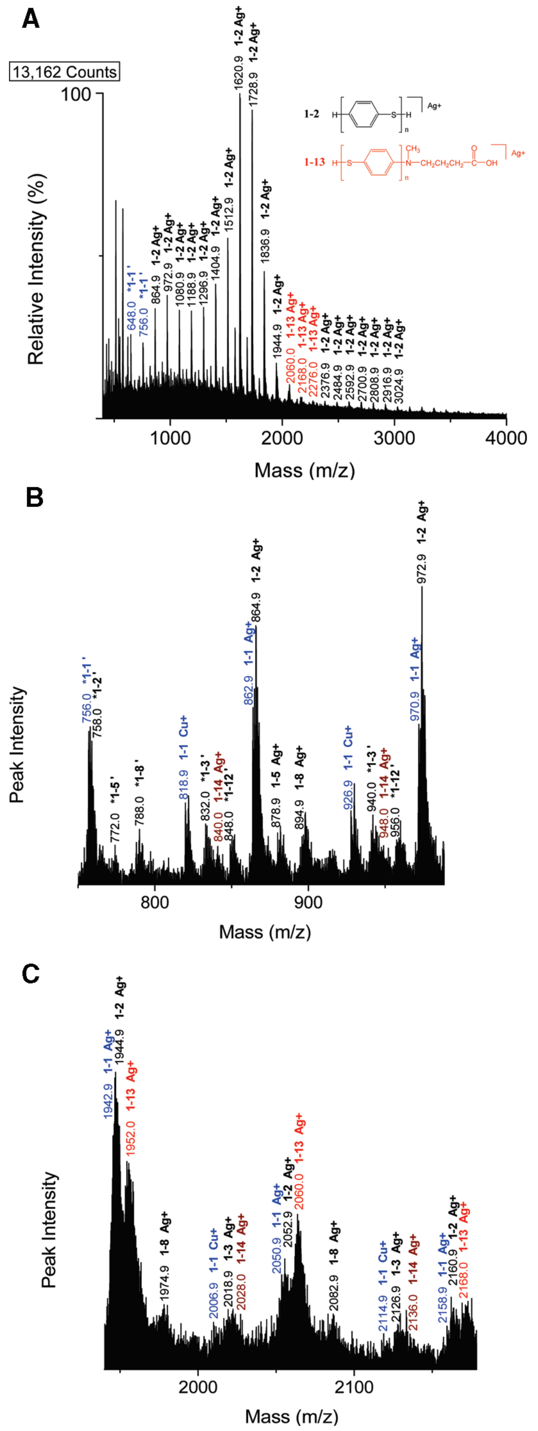


Figure 7. MALDI-TOF mass spectra of the fraction of oligomers extracted from high MW poly(*p*-phenylene sulfide) (Ryton) at 75 °C. For inspection of identified mass peaks, the mass spectrum is presented as follows: (A) full mass spectrum (400−4000 Da), (B) low mass region (750−990 Da), and (C) high mass region (1940−2180 Da).

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