Characterization of Polyimides by Combining Mass Spectrometry and Selective Chemical Reaction

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Received November 10, 2003; Revised Manuscript Received May 4, 2004

ABSTRACT: Selective chemical reaction was employed to overcome problems related to molecular characterization of polyimides due to their insolubility. *N*-Methylethanolamine was used to induce ring opening, and chain cleavage was carried out by reaction with hydrazine. These reactions were used to enhance solubility of poly(trimellitic anhydride-*co*-4,4′-methylenedianiline), poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline), and its amic acid form in MALDI and ESI friendly solvents, thus enabling their qualitative analysis by these techniques for the first time. Derivatives of poly(trimellitic anhydride-*co*-4,4′-methylenedianiline), made with 2-fluoro-1-methylpyridinium *p*-toluenesulfonate to introduce charge on the polymer, were used to increase ionization efficiency and intensity in positive ion MALDI spectra.

Introduction

Polyimides, an important class of condensation polymers, have an excellent combination of thermal stability and mechanical, electrical, and chemical properties.[1] These properties derive from the imide repeat unit and the aromaticity of the polymer. Polyimides can also be made from aliphatic monomers, but this significantly lowers overall performance and high-temperature properties. Because their properties naturally result from their highly rigid main-chain structure, these materials are utilized in many demanding industrial applications.

Since polyimides are often insoluble in their fully imidized form, their processing is typically done by casting solutions of polyamic acid intermediates in organic solvents. The final ring closure to the imide form is accomplished by thermal or chemical dehydration and is generally referred to as "cure" (see Scheme 1).[2] Because of their complexity and insolubility in most solvents, characterization of the composition and structure of polyimides has always been a challenge for analytical chemists. Therefore, definitive studies of structure−properties relationships for these materials are scarce. Early work by Wallach[3] on poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline) consisted of first characterizing the dilute solution properties of its poly(amic acid) precursor. The number-average (M_n) and weight-average (M_w) molecular weights were then correlated to viscosities in concentrated sulfuric acid and to film properties of corresponding polyimides. Elegant dilute solution viscosity work has since been carried out by Cotts.[4] Additionally, a size exclusion chromatographic method has been developed by Walker,[5] which allows measurement of M_w/M_n for poly(amic acid)s in a single analysis.

Because of its high sensitivity, broad dynamic range, specificity, and selectivity, mass spectrometry (MS) has become an indispensable tool for determination of the structure of organic and inorganic polymeric materials. Hyphenation of thermal techniques to MS such as thermogravimetry (TG)[6] and pyrolysis−gas chromatography[7] has been frequently applied to the analysis of thermal degradation products of polyimides. Positive and negative SIMS have been used to study the imidization of polymers based on pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA).[8] Laser ablation followed by Fourier transform (FT)[9] and time-of-flight mass spectrometry[10] have been carried out to identify polyimides as well as to provide information on the laser ablation process itself. The curing chemistry involved in polyimide formation was pursued with combined TG/FT infrared/MS.[11]

Although the above-mentioned MS techniques provide considerable information about the chemical structure of the polyimides, their thermal stability, processing chemistry, impurities present in the material, etc., they do not allow the chain length and the chain length distribution to be determined from the spectra of fragmented polymers. Knowledge of these parameters is important as they determine the desired properties of a polyimide.

Two significant developments in ionization techniques in the late 1980s−matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI)−greatly affected the use of mass spectrometry for polymer characterization.[12] Although the entire area of ESI MS polymer molar mass and structural analysis has been less fruitful compared to MALDI MS, the technique shows promising results for the characterization of synthetic polymers.[13−15] The unique ability of ESI to produce multiply charged ions extends this extremely soft technique to a higher mass range even for the limited operating mass range of some analyzers. Another distinguishing feature of ESI MS is its natural compatibility with many types of separation techniques.[16,17] Both MS techniques, however, generally require sample solubilization in MALDI and ESI MS friendly solvents prior to analysis.

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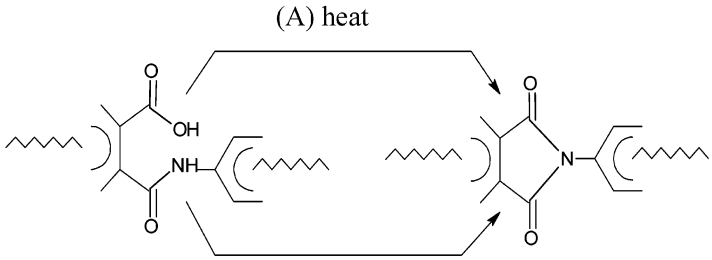
10.1021/ma030555p CCC: $27.50
Published on Web 07/02/2004

Scheme 1. Formation of Polyimides from Poly(amic acid)s: (A) Thermal Cyclodehydration, (B) Chemical Cyclodehydration



In some cases, derivatization reactions can be used to enhance the selectivity and/or sensitivity of ionization processes. This technique has been used widely in other analytical methods such as gas chromatography−MS and secondary ion mass spectrometry (SIMS)[18,19] but has not been used extensively with soft ionization MS techniques.[20] This is due to the fact that the soft ionization techniques often provide the required information from underivatized samples. However, regardless of the mechanism of ion formation, molecules that carry a preformed charge seem to be analyzed more efficiently than those which do not.

Recently, much research effort has been focused on synthesis of soluble and processable polyimides in the fully imidized form.[21] Most of the approaches for soluble polyimides are aimed at reduction of several types of chain−chain interaction, such as chain packing (e.g., crystallinity), charge transfer, and electronic polarization reactions. It should be noted, however, that the preparation of soluble polyimides without deterioration of their own excellent properties is not an easy task.

In the present article we report an approach for molecular characterization of insoluble polyimides, which is based on using selective ring-opening and chain-breaking reactions. These solubilization reactions make it possible to investigate polyimides by methods traditionally used for investigation of polymers. At this stage, the objective of our work is to overcome polyimide insolubility and to determine whether MALDI and ESI MS analysis can provide information about polyimide structure. This work should be considered as a first step in our ongoing research, which is directed toward the development of an analytical protocol for molecular characterization of insoluble polyimides.

Experimental Section

Materials. Poly(trimellitic anhydride-*co*-4,4′-methylenedianiline) (ca. 50% amic acid form) sample, PI-PAA, was supplied by Aldrich Chemical Co. (Milwaukee, WI).

Poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline), amic acid sample, PAA, and poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline) imide sample, PI (Kapton H film), were supplied by Dupont *i*-Technologies (Circleville, OH).

Ring-Opening Reaction. *N*-Methylethanolamine (NME) (Aldrich Chemical Co., Milwaukee, WI) was used to perform the PI-PAA ring-opening reaction. 0.257 mL of NME was added to 1 g of PI-PAA partially dissolved in 30 mL of *N*,*N*-dimethylformamide (DMF) in a three-neck flask. The reaction proceeded in an inert atmosphere (N_2) at room temperature for 10 h. The bright yellow PI-PAA powder was completely dissolved in the course of the ring-opening reaction. The solution was evaporated under vacuum overnight.

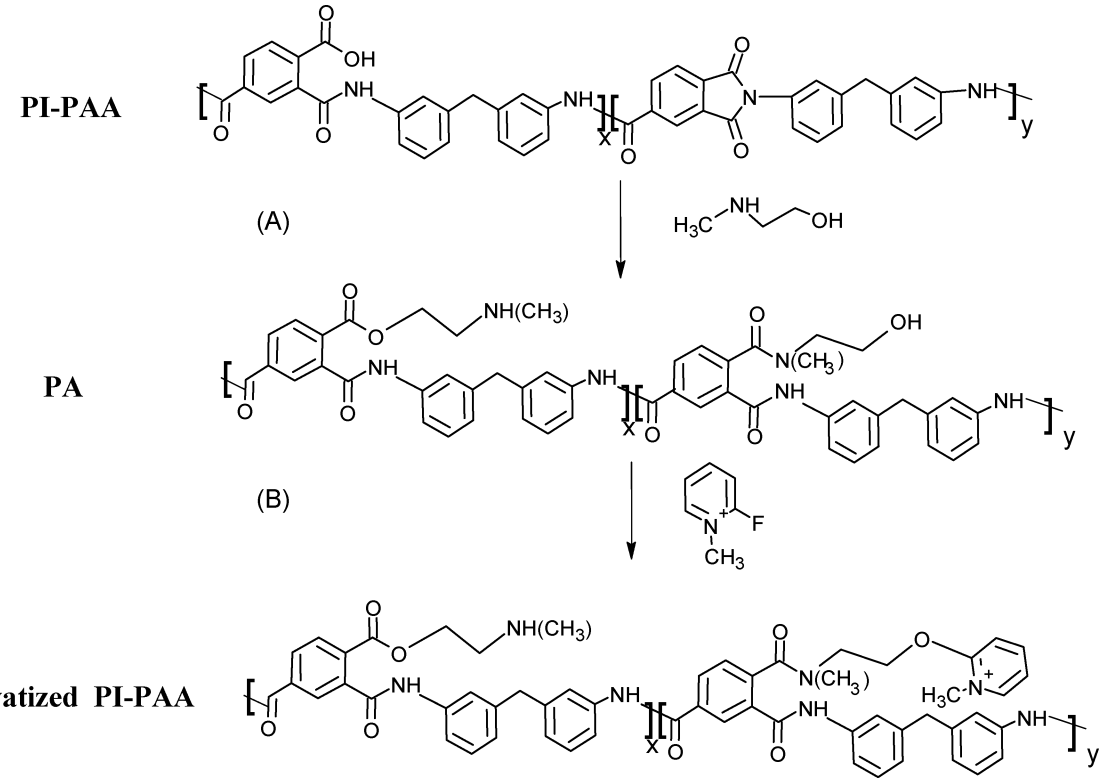
Derivatization Reaction. 0.374 g of the sticky dark brown product (PA) resulting from the ring-opening reaction was suspended in a chloroform/DMF mixture (1:4 v/v) in a three-neck flask. Addition of 0.14 mL of triethylamine (TEA) (Aldrich Chemical Co., Milwaukee, WI) slightly increased the solubility of PA in the chloroform/DMF mixture. 0.112 g of 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FPT) (Aldrich Chemical Co., Milwaukee, WI) dissolved in 1 mL of the chloroform/DMF mixture was then injected into the flask. The reaction proceeded in an inert atmosphere (N_2) at room temperature for 3.5 h. The solvent was removed under vacuum.

Degradation. Hydrazine (Aldrich Chemical Co., Milwaukee, WI) was used to perform chain cleavage of PAA (DuPont), PI (Kapton H film, DuPont) and PI-PAA (Aldrich). 0.9 mg of PAA was suspended in 4 mL of a 0.1 M sodium hydroxide solution in methanol in a three-neck flask. 10 mL of hydrazine were added dropwise with a gastight syringe through a rubber septum into the suspension in an inert atmosphere. Dissolution of solid particles occurred in a few minutes. The reaction was allowed to proceed at 20 °C for 48 h. Removal of the residual solvent under vacuum resulted in an amber sticky product. The same procedure was applied to the polyimide film. Upon hydrazine addition, Kapton H film disintegrated and dissolved rapidly, leaving a yellow solution. Removal of the residual solvent under vacuum resulted in a yellowish precipitate. 10 mL of hydrazine were added dropwise to 1 g of PI-PAA and 200 μL of 14 M ammonium hydroxide in a three-neck flask under an inert atmosphere. PI-PAA dissolved in hydrazine within a few minutes. The degradation proceeded for 24 h at 20 °C. After the reaction was complete, hydrazine was removed under vacuum.

Measurements. a. MALDI MS. MALDI spectra were obtained with a Voyager-DE STR Biospectrometry Workstation (PerSeptive Biosystems, Framingham, MA) reflectron-type TOF mass spectrometer equipped with a nitrogen laser (300 μJ) using a wavelength of 337 nm, a pulse width of 3 ns, and operated at a repetition frequency of 10 Hz. Spectra were acquired in both positive and negative modes using delayed extraction and the reflectron. The acceleration voltage was 20 kV, and 225 single shot mass spectra were summed to give a composite spectrum. All data were processed using the PerSeptive GRAMS/386tm software.

For analysis in the positive mode, PI-PAA derivatized with 2-fluoro-1-methylpyridinium *p*-toluenesulfonate was dissolved in *N*,*N*-dimethylformamide (DMF) at 6 mg/mL. The 2,5-dihydroxybenzoic acid (DHB) (Aldrich Chemical, Co., Milwaukee, WI) matrix solution was prepared by dissolving 20 mg in 1 mL of DMF; matrix and polymer solution were mixed in a 4:1 ratio. Solution droplets (approximately 0.5 μL) of the matrix/sample mixture were deposited on the sample plate target and allowed to dry at room temperature. When using 1,8,9-anthracenetriol (dithranol) (Aldrich) as the matrix, the matrix solution was prepared by dissolving 30 mg of dithranol in 1 mL of DMF. In addition, sodium iodide (NaI) in methanol at a concentration of 2 mg/mL was used as an ionization agent. The MALDI sample targets were prespotted by NaI solution prior to the analyte/matrix deposition.

Scheme 2. Reaction Pathways for (A) Ring-Opening Reaction and (B) Derivatization Reaction of PI-PAA



For analysis in the negative mode, sample concentrations were 10 mg/mL; PAA, ring opened PI-PAA, and degraded PI-PAA were dissolved in 1:1 THF−DMF, while for degraded PAA and PI the solvent was 1:1 acetonitrile−water. The matrix used was 9-aminoacridine (NAA) (Aldrich) in methanol at 18 mg/mL. TEA at a concentration of 50 μL in 1 mL of methanol was added to the matrix solution to enhance ionization. The layer deposition technique gave the best results; the sample was first allowed to evaporate on the sample target. After evaporation, the matrix solution was deposited on top and air-dried.

b. ESI MS. ESI-MS analysis was carried out using a Mariner (PerSeptive Biosystems) mass spectrometer having a TOF mass analyzer. The instrument was operated in the negative-ion mode. The potential on the electrospray needle was ∼−4000 V, and the skimmer potential was ∼11 V. The nozzle potential was set to be ∼110 V. Nebulizing gas and curtain gas were set at ∼0.2 and 2 LPM, respectively. Temperature of the ion source was 140 °C. Samples were infused into the ion source at a flow rate of 2 μL/min. Mass spectra were acquired for ∼100 s over the range 10−4000 Da. The samples were prepared in 1:1 water−acetonitrile at a concentration of 10 μg/mL.

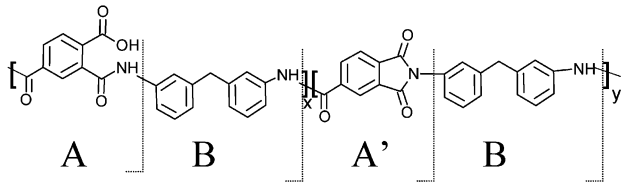
Results and Discussion

Compared to ESI MS, MALDI sample preparation is relatively flexible, and in some cases solid-state sample preparation[22,23] can be as efficient as casting from solution. In many instances, however, the matrix must be soluble in solvents compatible with the analyte so it is able to cocrystallize with the analyte. Moreover, to achieve a highly homogeneous crystal structure of the matrix surrounding the analyte, and thus higher resolution and sensitivity, highly volatile solvents are preferred for MALDI sample preparation.

For ESI MS analysis, a sample must be soluble in ESI-compatible solvents having relatively low surface tension so they are easy to nebulize. Moreover, ESI MS is limited to charged, polar, and basic compounds. Because of these limitations, only a few studies have reported finding ESI MS conditions optimal for synthetic polymer analysis.

To be able to employ MALDI and ESI MS techniques for investigation of the aromatic polyimides at the molecular level, the solubilization reactions described below have been used prior to analysis.

Poly(trimellitic anhydride-*co*-4,4′-methylenedianiline), PI-PAA. a. MALDI Analysis of *N*-Methylethanolamine-Induced Ring Opening of PI-PAA. Poly(trimellitic anhydride-*co*-4,4′-methylenedianiline), PI-PAA, is a thermosetting poly(amide−imide), with approximately 50% amic acid. In the chemical structure **(1)** of this copolymer the acidic part of the monomer unit is marked **A** and its imidized form as **A′**, while **B** denotes the basic part. This notation will be used for the peak assignments in all of the mass spectra.



(1)

Solubility of this low molecular weight (molecular weight estimated on the basis of the acid number is ca. 2000 g/mol) poly(amide−imide) in DMF was enhanced by a ring-opening reaction using *N*-methylethanolamine, NME, as shown in Scheme 2, pathway A. Pathway B in Scheme 2 will be discussed below. Solubilization occurs by partial ring opening that converts the cyclic polyimide to an open amide structure,

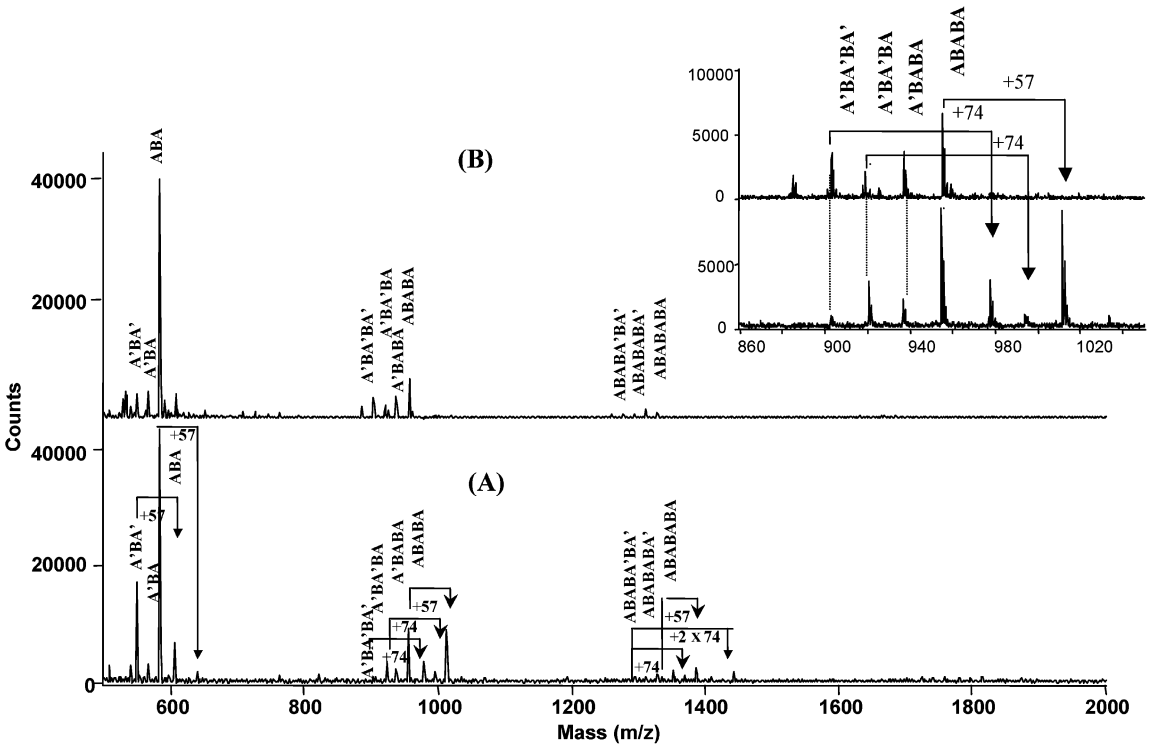


Figure 1. Negative ion MALDI spectra of *N*-methylethanolamine-induced ring-opening reaction of PI-PAA. (A**)** Reaction products, (B**)** the starting material. In (A), peaks with a shift of 74 Da are due to the ring-opening reaction on the polyimide part, and the gain of 57 Da corresponds to esterification of NME at the hydroxyl group of the carboxylic acid on the polyamic acid part of PI-PAA (see Scheme 2). The enlarged detail of the spectra is shown as an inset.

PA. It was anticipated that the secondary amine would not cleave the polymer chain to any significant extent. This does not apply to a primary amine such as hydrazine, as will be discussed below. The negative ion MALDI MS spectrum for the ring-opening reaction products in Figure 1A shows a series of peaks (imidized forms of $A(BA)_n$) with a shift of 74 Da relative to the *m*/*z* values of the peaks in the MALDI MS spectrum of unreacted PI-PAA shown in Figure 1B. These peaks are due to the NME-induced ring-opening reaction on the polyimide part of PI-PAA, as shown in Scheme 2 by pathway A. In addition to the ring-opening reaction, NME is esterified with the hydroxyl group of the carboxylic acid on the polyamic acid part (see Scheme 2, pathway A). This is evidenced by a series of peaks ($A(BA)_n$) in Figure 1A with gain of 57 Da compared to corresponding peaks in the spectrum of unreacted PI-PAA (Figure 1B). In addition to reaction products there also are unreacted PI-PAA oligomer ion species observed in the MALDI spectrum of the ring-opening reaction (Figure 1A). To obtain the maximum conversion, the reaction stoichiometry needs to be optimized, which is not an easy task for a polydisperse sample such as PI-PAA.

b. MALDI Analysis of 2-Fluoro-1-methylpyridinium (FMP) Derivatized PI-PAA. Our experiments on screening a variety of matrices and salts/additives for optimum MALDI sample preparation of PI/PAA revealed that PAA as well as PI-PAA and its NME derivative (PA) in the positive mode seem to promote formation of matrix clusters up to approximately *m*/*z* 2000. This phenomenon is particularly pronounced when using dithranol in the presence of NaI, as shown in Figure 2. A series of ion peaks spaced by 226 Da (Figure 2A), which corresponds to the mass of dithranol, are seen in the spectrum of PI-PAA. These peaks are not detected in the MALDI spectrum of the blank (dithranol with NaI) and can be assigned to sodiated dithranol clusters, $[nM + Na]^+$ (*n* denotes the number of associated matrix molecules) (Figure 2B).

To aid in MALDI MS analysis of both polyimides and their precursors in the positive mode, 2-fluoro-1-methylpyridinium *p*-toluenesulfonate was used to introduce a cationic site covalently bonded to the NME-induced ring-opening reaction product of PI-PAA. On the basis of previous studies of derivatized biomolecules for analysis by fast atom bombardment mass spectrometry,[24] it was anticipated that 2-fluoro-1-methylpyridinium *p*-toluenesulfonate would react with hydroxyl groups of NME attached to the carbonyl groups of the polymeric carrier. The derivatization reaction is shown in Scheme 2, pathway B. In contrast to the underivatized sample, which tends to promote matrix clustering (see Figure 2A), derivatization provided intense spectra in the positive ion MALDI mode without the need to add cations to the solvent, as shown in Figure 3A. Two series of peaks observed in the positive ion spectrum in Figure 3A can be assigned to the structure of PA with FMP attached to the carboxyl acid group (series I, peaks $A(BA)_n + 93$, $A(BA)_n + 57 + 93$, and $AB + 57 + 93$) and PA with FMP attached to the hydroxyl group of NME (series II, peaks $A(BA)_n + 75 + 93$ and $(AB)_n + 75 + 93$). In each case, the attachment of FMP results in a mass gain of 93 Da for derivatized ions compared to the underivatized ones (Scheme 2). The mass shifts of 75 and 57 Da are due to the ring-opening reaction as discussed above. Only a few low-intensity ion peaks, which belong to unreacted starting material, are observed in the negative ion MALDI spectrum of PA derivatized with FMP (Figure 3B). The experimental

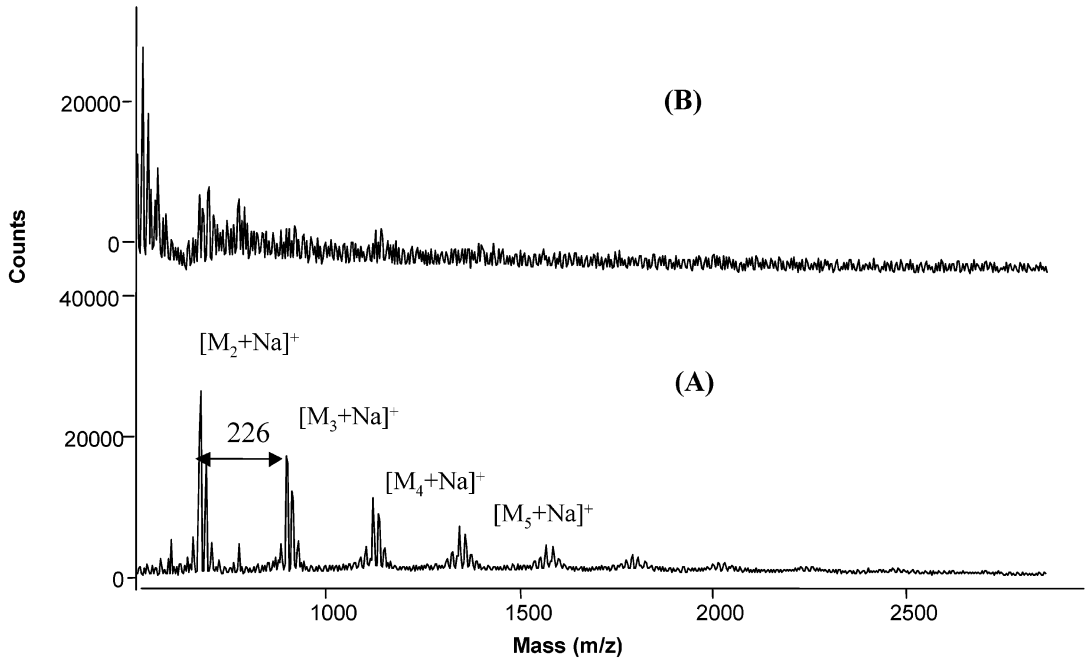


Figure 2. Positive ion MALDI spectra of (A**)** dithranol with NaI in the presence of PI-PAA and (B**)** dithranol with NaI. The spacing between ions in (A**)** corresponds to the mass of the matrix (226 Da).

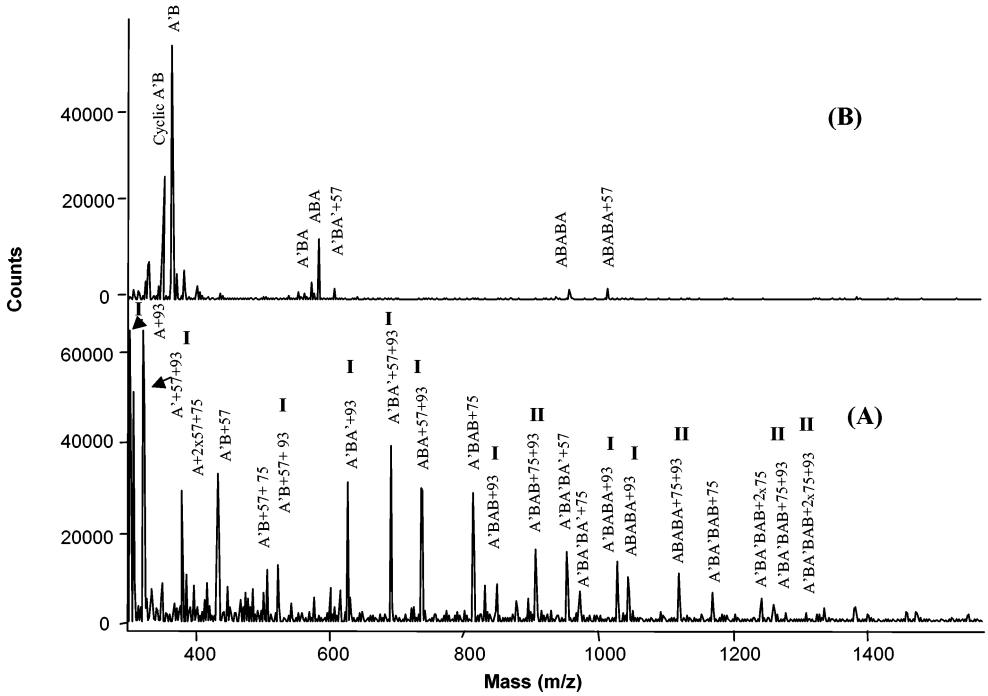
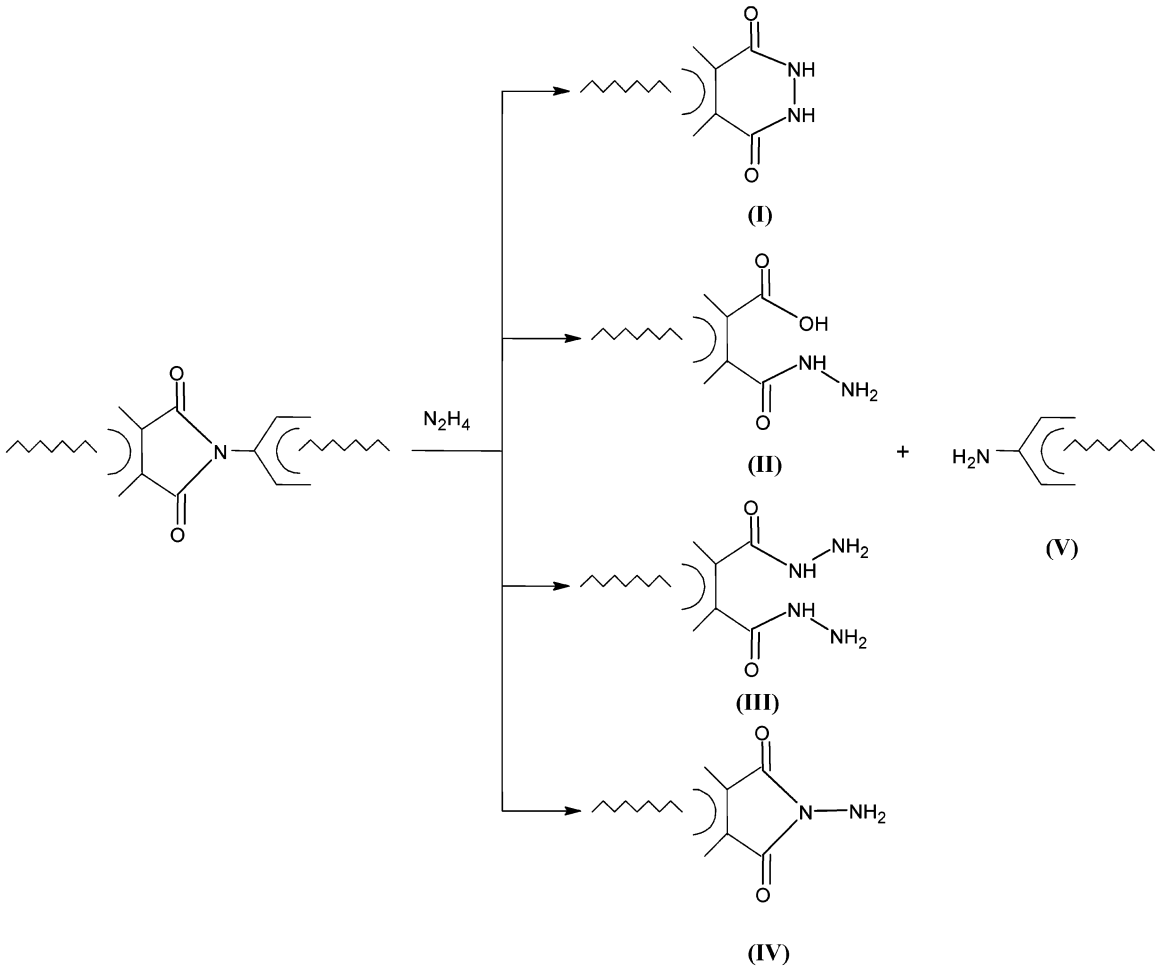


Figure 3. MALDI spectra for PA derivatized with FMP in (A**)** positive mode and (B**)** negative mode. For peak assignment, see text. Series **I** corresponds to the FMP attachment to the carboxyl acid group, and in series **II** FMP is attached to the hydroxyl group of NME. The mass shifts of 75 and 57 Da are due to the ring-opening reaction (see Scheme 2).

results indicate that FMP *p*-toluenesulfonate can be used to derivatize PI/PAA as the reaction satisfies several requirements for successful derivatization: the derivatization reaction is relatively simple; it occurs readily at room temperature and generates molecular ions that are observed in the positive ion MALDI mode. The derivative does not require purification prior to the analysis.

c. MALDI Analysis of PI-PAA Degraded with Hydrazine. Polyimides readily undergo hydrolytic degradation when exposed to hydrazine, and the yellow powder formed is characteristic of this reaction. Anticipated degradation products for this type of reaction are hydrazide derivatives **(I**, **II**, **III**, **IV)** and a diamine **(V),** as seen in Scheme 3. Our experiments showed that degradation products are soluble in dilute basic solutions, whereas precipitation occurs from acidic solutions. This observation is in good agreement with the solubility data reported for hydrazide derivatives in the literature.[24] Therefore, to avoid precipitation of the analyte in the presence of acidic matrices, 9-aminoacridine with TEA as an additive was used for MALDI analysis of

Scheme 3. Reaction of Hydrazine with Polyimides[a]



[a] Products **I**, **II**, **III**, and **IV** vary with reaction conditions.

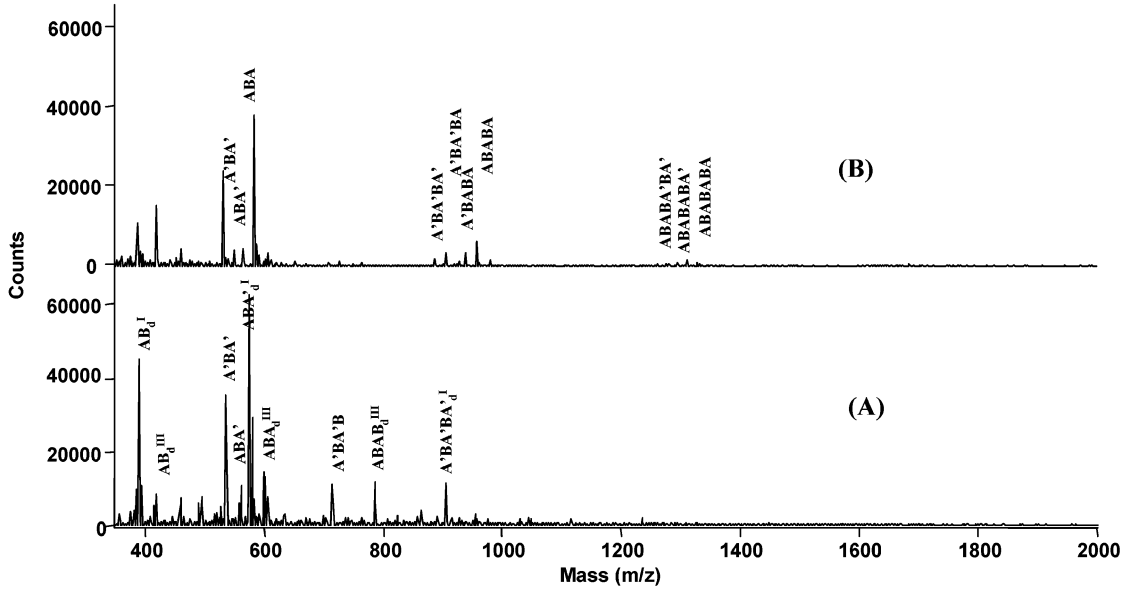


Figure 4. Negative ion MALDI spectra of PI-PAA (A**)** degraded with hydrazine and (B**)** undegraded. For peak assignments, see text.

reaction products from hydrazinolysis. The MALDI spectrum of reaction products (Figure 4A) shows the presence of characteristic molecular ion peaks of degradation products **I** ($(AB)_{nd}^{I}$, $A(BA')_{nd}^{I}$) and **III** ($(AB)_{nd}^{III}$, $A(BA)_{nd}^{III}$) shown in Scheme 3. Occurrence of product **IV** is also possible, however, because it cannot be easily distinguished from product **I** as it has an identical *m*/*z* ratio. The negative ion MALDI spectrum of undegraded

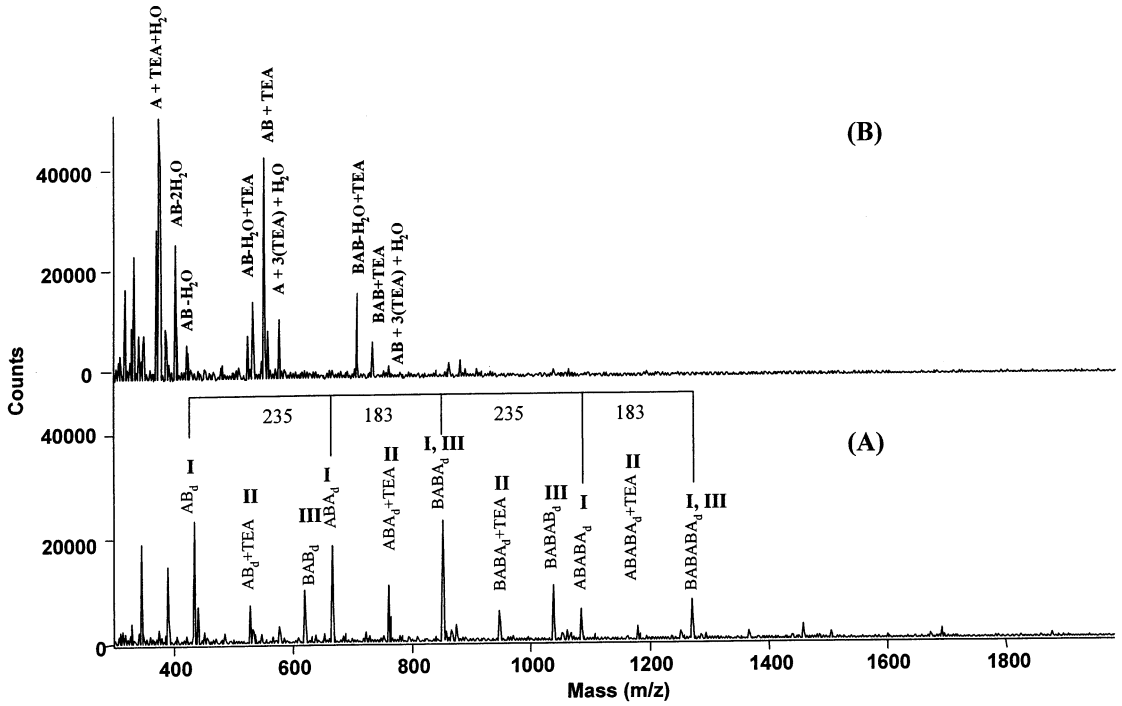
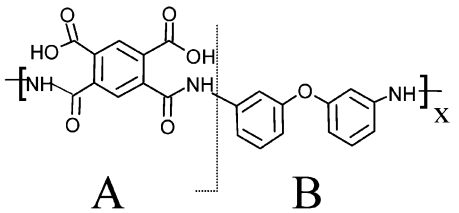


Figure 5. Negative ion MALDI spectra of PAA (A**)** degraded with hydrazine and **(**B**)** undegraded. For peak assignments, see text.

PI-PAA is shown in Figure 4B.



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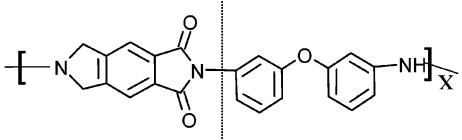

(3)

Poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline), PAA, and PI. a. MALDI Analysis of Poly(pyromellitic dianhydrade-*co*-4,4′-oxydianiline), Amic Acid, Degraded with Hydrazine. MALDI analysis of the poly(amic acid) precursor (PAA) **(2)** of Kapton H film (PI) **(3)** was also carried out in order to examine the structural change of PAA caused by degradation with hydrazine. Figure 5 shows a comparison between the negative ion MALDI spectra of degraded **(**A**)** and undegraded PAA **(**B**)**. The peaks in the spectrum of undegraded PAA, which are hard to rationalize, are presumably due to ionization of the amic acid via acylammonium ion formation in the presence of TEA. It is also observed that, despite its relatively high basicity, TEA does not promote imidization to any significant extent. A similar observation was reported by Kailani et al.[25] for TEA-catalyzed imidization of a polyamic acid in *N*-methylpyrollidone solution. In contrast to the undegraded PAA (Figure 5B), the MALDI spectrum for degraded PAA (Figure 5A) clearly proves the identity of the poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline) amic acid. Three series consisting of $(AB)_{nd}$ and $A(BA)_{nd}$ (series I), $(AB)_{nd}$ + TEA and $A(BA)_{nd}$ + TEA (series II), and $B(AB)_n$ (series III) can be observed in the spectra of PAA degradant. The peaks in the individual series are separated by 235 and 183 mass units following one after the other in order. This corresponds to the alternating sequence of PMDA (235 Da) and ODA (183 Da) along the chain. The fragments observed in the spectrum are products of CO−NH bond cleavages since amide formation is not possible. This fragment uniformity makes PAA identification easier compared to PAA-PI, where determination of the repeat unit is more difficult due to the end-group distribution of reaction products (see Figure 4). On the basis of its solubility in polar protic solvents such as water, methanol and acetonitrile, it is assumed that the PAA degradants are present as their sodium salts, originating from the presence of NaOH in the reaction mixture. As a result, solubility of the degradants in the acetonitrile/water mixture significantly improves the MALDI sample preparation procedure, which subsequently leads to increased ionization efficiency and intensity in the negative ion MALDI spectra.

b. ESI Analysis of Poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline), Amic Acid Form, Degraded with Hydrazine. Although degraded PAA is soluble in ESI friendly solvents such as 50:50 (v/v %) water mixed with either acetonitrile or methanol, ESI MS did not provide satisfactory results for this sample. As a result of multiple charging and broad polydispersity, the degraded PAA gives very complex ESI mass spectra such as that shown in Figure 6. The maximum of the charge distribution in the PAA spectrum is

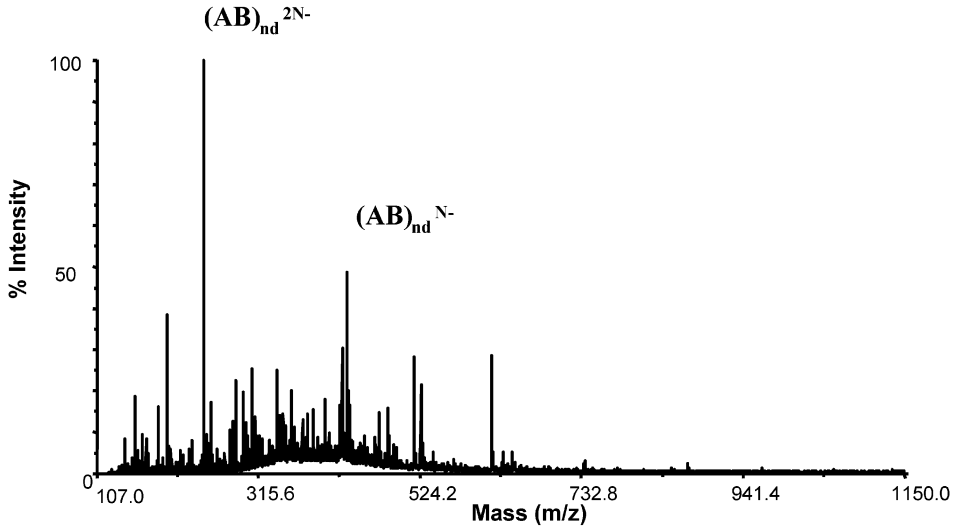

Figure 6. Negative ion ESI spectra of PAA degraded with hydrazine. $(AB)_{nd}^{N-}$ denotes an oligomer ion with the number of charges N equal to the number of monomer units n in the chain; $(AB)_{nd}^{2N-}$ represents an oligomer having two charges on each monomer unit.

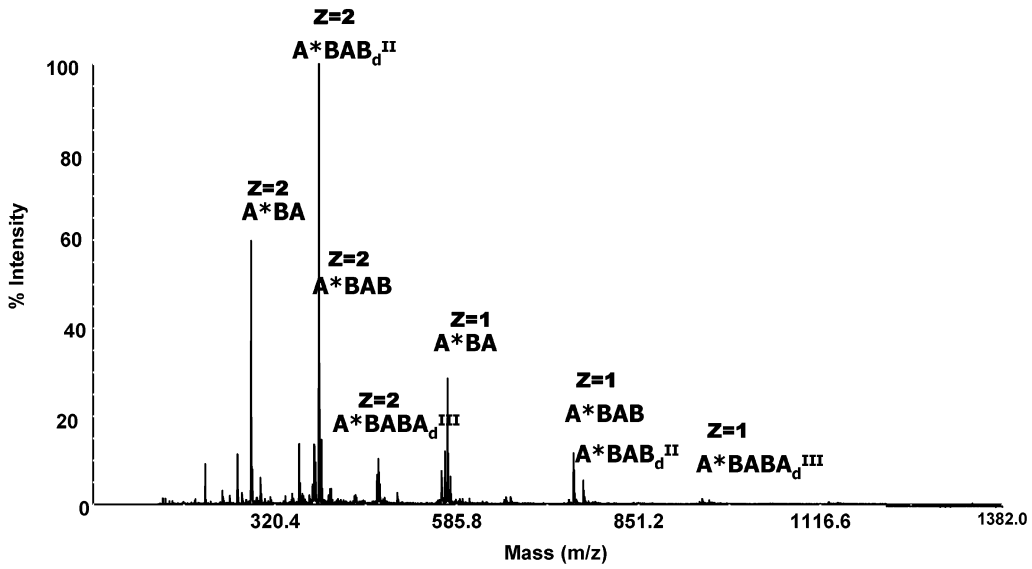

Figure 7. Negative ion ESI spectrum of PI degraded with hydrazine: $Z = 1$, singly charged species; $Z = 2$, doubly charged species. A* denotes an end group with a mass of 190 Da.

approximately at the mass of the monomer unit. This means that, on the average, each monomer unit in the PAA chain carries one negative charge. Thus, in Figure 6 the PAA chain with number of monomer units n equal to the number of charges N is denoted $(AB)_{nd}^{N-}$. Moreover, the highest signal intensity in the spectrum can be assigned to the PAA chain carrying two negative charges on each monomer unit, $(AB)_{nd}^{Nn-}$. For such complex spectra even combining deconvolution and high mass resolution ESI/FTMS, which allows to determination of the charge states from the spacing between the isotope peaks, and subsequent transformation to the singly charged representation, will be very difficult. Another approach, which we intend to investigate in the near future, is to reduce the number of components entering the ESI source by coupling ESI-MS with a separation technique.

c. ESI Analysis of Poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline), Imide Form, Degraded with Hydrazine. The solubility of chemically degraded Kapton H film (PI) **(3)** in water−acetonitrile is approximately 10 times lower than for its degraded polyamic acid precursor. Therefore, ESI MS was chosen for analysis of the postreaction products of Kapton H film hydrolysates. An ESI spectrum of Kapton film degraded with hydrazine (Figure 7) shows a series of doubly ($z = 2$) and singly ($z = 1$) charged degraded $(AB)_{nd}$ and $A(BA)_{nd}$ oligomer ions. Similarly to the PI-PAA hydrolysate (Figure 4), products **II** and **III** (Scheme 3) were found in the ESI spectrum of PI degraded with hydrazine. Interestingly, all oligomer ions shown in the ESI spectrum were found to carry an end group marked as A* with a molar mass of 190 Da. Although a precise identification of this end group is not yet possible, a reasonable possibility is the presence of trimellitic anhydride, which can be used as a chain stopper in polyimide preparation.

The spectrum of the Kapton degradant is not nearly as complex as that observed for its degraded precursor (Figure 6), presumably due to a smaller extent of multiple charging as well as lower masses. Therefore, it can be anticipated that in the case of Kapton film the degradation reaction proceeded more extensively than degradation of its poly(amic acid) precursor.

These preliminary studies show that proper chemical pretreatment can facilitate analysis of intractable and insoluble polymers such as polyimides with MALDI and ESI mass spectrometry. Further, to determine molecular weight and polydispersity for commercial polyimides, a systematic study on the reaction/degradation process must be followed as a function of the exposure time using the combination of both mass spectrometry and a separation method. Such studies are currently under investigation in our laboratory.

Conclusions

Structure characterization of polyimides and their precursor polyamic acids has been demonstrated using MALDI and ESI MS for the first time. Ring-opening and degradation reactions were used to solubilize the sample prior to analysis. The following are conclusions based on our studies.

N-Methylethanolamine effectively induces ring opening of the poly(amide−imide), thus increasing its solubility in DMF. The reaction product is amenable to MALDI analysis preferably in the negative ion mode.

The positive ion MALDI spectrum for the product of the ring-opening reaction derivatized with 2-fluoro-1-methylpyridinium *p*-toluenesulfonate shows significant improvement in detection level over that afforded by the underivatized sample. Preformed charges are due to the attachment of FMP to both the carboxylic acid group and the hydroxyl group of NME.

Polyimides can be readily hydrolyzed with hydrazine. The solubility of the hydrolyzate is dramatically increased when sodium hydroxide is used as a catalyst, most likely due to sodium salt formation. Hydrazinolysis facilitates interpretation of MALDI mass spectra of the polyamic acid precursor and makes polyimides amenable to MALDI and ESI MS analysis.

Acknowledgment. We thank Dr. Jack Kreuz for valuable scientific discussions. This work was supported by the National Science Foundation, Grant CHE-9985864, and E. I. du Pont de Nemours.

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MA030555P