

Characterization of an Insoluble Poly(9,9-diphenyl-2,7-fluorene) by Solvent-Free Sample Preparation for MALDI-TOF Mass Spectrometry

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The application of solvent-free sample preparation for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) allowed the characterization of an insoluble fraction of poly(9,9-diphenylfluorene) that was previously hindered by the lack of suitable characterization methods. The MALDI mass spectrometric analysis gives valuable mechanistic information about the heterogeneous polymerization process of the insoluble high molecular weight fraction of the polymer. The fragmentation appearing even under moderate desorption and ionization conditions of this rigid backbone analyte is identified as a multiple loss of the bulky phenyl side groups and can be avoided by applying the new MALDI matrix 7,7,8,8-tetracyanoquinodimethane. A specialized fragmentation study by postsource decay MALDI-TOF MS reveals a molecular weight dependent change in fragmentation mechanism from an exclusive cleavage of side groups from long polymer chains to an additional cleavage of the polymer backbone of short polymer chains.

The characterization of insoluble samples, while often necessary, presents a major problem. In mass spectrometry (MS), only a few methods are available for measuring insoluble materials with molecular masses above 1000 Da. One of them is laser desorption (LD) MS,^{1–5} which can be used to characterize organic samples. However, there is always an upper limit, which is structure dependent, to the size of analytes that can be desorbed as intact molecules. Samples such as biopolymers,⁶ porphyrins,^{7,8} and kerogen extracts can be measured up to ~1000 Da,⁹ coal-derived fractions up to 1500 Da,¹⁰ and polycyclic aromatic hydrocarbons

(PAHs) up to 2000 Da.¹¹ Due to these molecular weight limitations, the application of matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) which is a much “softer” ionization method than LD MS seems to be more appropriate for the characterization of insoluble high molecular weight substances, but traditionally MALDI sample preparation has only been possible with soluble samples. Previous limited attempts to characterize insoluble samples have used time-consuming chemical modifications which increase solubility or decrease molecular weight, e.g., acidolysis of polyesters¹² and hydrolysis of highly cross-linked polymer networks.¹³ Protected sorbitol with a MW < 500, was characterized via MALDI MS following sample preparation by a thermal vapor deposition method.¹⁴ However, this method is limited to compounds that can be vacuum-sublimed without thermal decomposition. Recently, two preparation methods for MALDI MS were published that avoid the use of solvent during sample preparation and that are anticipated to be of general applicability for the characterization of insoluble samples.^{15,16} A soluble polyamide was characterized by MALDI MS after a mortar and pestle treatment of the analyte/matrix mixture and preparation of a pressed pellet similar to a KBr disk as used for IR measurements.¹⁵ Another approach was the mechanical mixing of sample and matrix with a ball mill and direct measurement of the resulting powder (so-called solvent-free sample preparation). This method allowed the successful characterization of an insoluble giant PAH of >2700 Da.¹⁶ The benefits of this solvent-free MALDI sample preparation in comparison to conventional methods have recently been described in the literature.^{17–20} In

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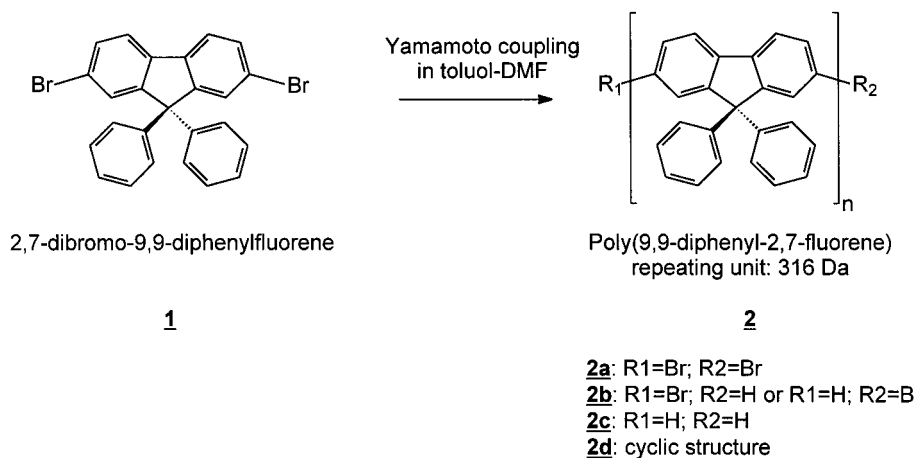


Figure 1. Synthesis and structure of **2** and possible end group functionalities.

this contribution, the application of solvent-free sample preparation was required to characterize the insoluble fraction of a polymer.

The polyfluorenes described here are known to have a high proportion of insoluble material at higher molecular weight that has not been adequately characterized so far. Polyfluorenes are of interest as blue emitters for polymer light-emitting diodes²¹ because of their facile synthesis, high thermal stability, and high quantum efficiencies. Poly(9,9-diphenyl-2,7-fluorene) (**2**); Figure 1) was synthesized²² as the first example of a new class of light-emitting polymers: poly(9,9-diarylfuorene)s. The main part of the polymer is insoluble in organic solvents, but a small soluble fraction can be obtained by extraction with toluene using a Soxhlet apparatus. Hence, conventional solvent-based MALDI MS (MALDI MS utilizing conventional solvent-based sample preparation) can be used to characterize the soluble fraction of **2** whereas solvent-free MALDI MS (MALDI MS utilizing solvent-free sample preparation) allows for the first time the characterization of the insoluble polymer fraction. This investigation also emphasizes the importance of the choice of an appropriate matrix for samples that are sensitive to fragmentation in MALDI MS.

EXPERIMENTAL SECTION

Materials. Poly(9,9-diphenylfluorene) (**2**) was synthesized by Yamamoto Ni(0) coupling in toluene–DMF (72 h) as described elsewhere.²² The polymerization step and the structure of the analyte is depicted in Figure 1. 1,8,9-Trihydroxyanthracene (dithranol), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and metal salts (Li, Na, K, and Ag salts of trifluoroacetate) were purchased from Aldrich (Steinheim, Germany) and used without further purification. The solvent tetrahydrofuran (THF, 99.8%) was obtained from Fluka (Buchs, Switzerland). Toluene was purchased from Riedel-de-Haen (Seelze, Germany).

MALDI-TOF Instrument. LD-TOF, MALDI-TOF, and PSD-MALDI-TOF mass spectra were recorded using a Bruker Reflex

II MALDI-TOF mass spectrometer (Bremen, Germany) equipped with a N₂ laser ($\lambda = 337$ nm) operating at a pulse rate of 3 Hz. For the LD-TOF and MALDI-TOF mass spectra, the ions were accelerated with pulsed ion extraction (PIE design from Bruker) by a voltage of 20 kV. The analyzer was operated in reflection mode unless otherwise stated, and the ions were detected using a microchannel plate detector. A total of 100 shots were accumulated for each mass spectrum.

In the PSD MALDI-TOF fragmentation mode, the ions were accelerated by a voltage of 28.5 kV. Fifteen segments were acquired, accumulating always 200 shots. In each segment, optimization was obtained by adjusting the experimental parameters to increase signal intensity and minimize the noise. With increasing segment number, the optimal individual segment spectra were obtained by increasing the laser power as well as the detection voltage. The 15 optimized segments were pasted together for the final PSD mass spectrum.

Solvent-Free and Conventional Solvent-Based MALDI Sample and Target Preparation. The mixing of analyte and matrix powder was performed using a ball mill MM2000 from F. Kurt Retsch GmbH & Co. KG (Haan, Germany) following our general solvent-free sample preparation protocol.¹⁷ The polymeric analyte and matrix were added initially in a molar ratio of 1/50 without solvents and ground for 10 min. The matrix dilution to 1/500 was carried out by adding matrix to the prepared 1/50 analyte/matrix mixture and was then further milled for 10 min at room temperature.

The bulk product **2** was extracted with toluene for 5 days using a Soxhlet apparatus. The insoluble fraction was dried, and the soluble part was concentrated to an oil. For the solvent-based (toluene) and solvent-free sample preparation, matrixes such as dithranol and TCNQ were applied using a molar ratio of analyte/matrix of 1/500. The solvent-free prepared analyte/matrix powder mixture of the insoluble fraction was then spread on the target. When a metal salt was added in solvent-free sample preparation, the molar ratio of analyte/matrix/salt was 1/500/50. LD mass spectra were obtained by measuring the extracted insoluble fraction spread on the target. The soluble fraction was prepared by dissolving the analyte and the matrix in toluene. When a metal salt was added in solvent-based sample preparation, the molar ratio of analyte/matrix/salt was 1/500/10.

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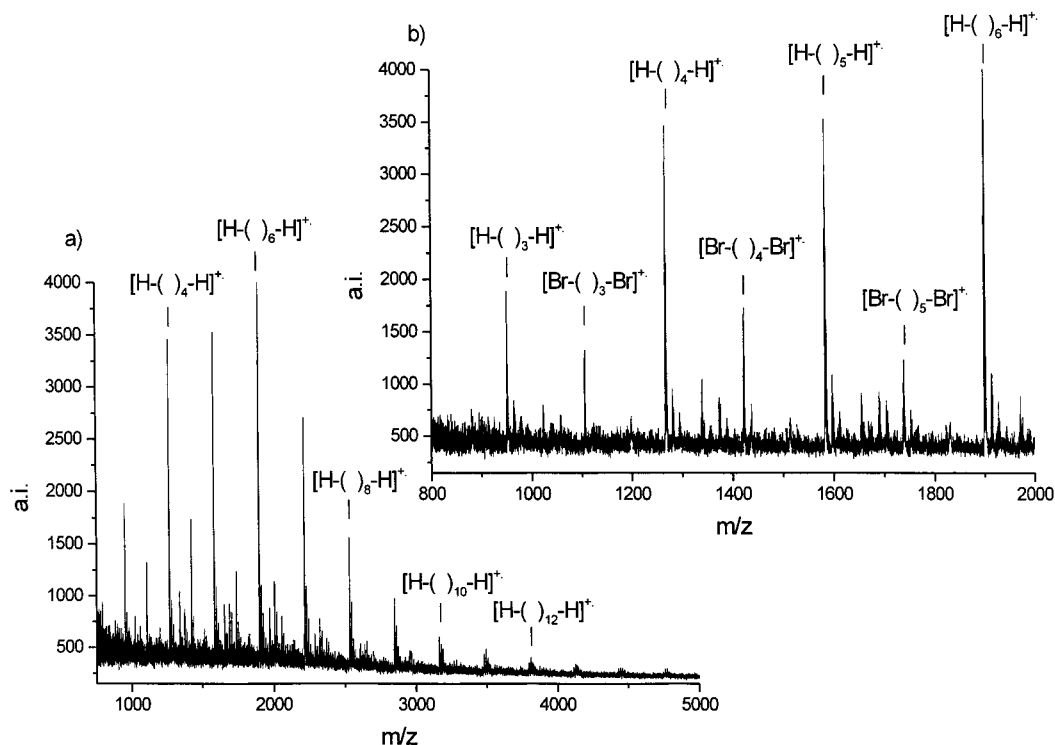


Figure 2. MALDI mass spectra of the soluble fraction of **2** utilizing conventional solvent-based sample preparation (dithranol/toluol): (a) full mass spectrum; (b) expanded mass region of the four major signals.

Calibration. Calibration was carried out before each measurement using PS 2 kDa from PSS (Mainz, Germany) dissolved in THF together with dithranol and silver salt in a mixing ratio of 1/500/10. A multipoint calibration was carried out using the lowest isotopes of different resolved PS oligomers.

RESULTS AND DISCUSSION

Characterization of Poly(9,9-diphenyl-2,7-fluorene). Poly(9,9-diphenyl-2,7-fluorene) (**2**; Figure 1) was recently synthesized by Yamamoto coupling and represents the first example of a new class of light-emitting poly(9,9-diarylfuorene)s.²² The bulk of the polymer is insoluble in common organic solvents. A small soluble fraction could be obtained by Soxhlet extraction of the bulk product **2** with toluene for 5 days. The amount of the soluble fraction was less than 10% of the total polymer yield. The separated soluble and insoluble fractions were characterized with MALDI MS independently applying two in principle different sample preparation methods with dithranol as matrix in both cases. Thus, conventional solvent-based MALDI MS is applied to characterize the soluble fraction (Figure 2) whereas solvent-free MALDI MS allows the characterization of the insoluble fraction of **2** (Figure 3). It should be emphasized that the mass spectrum of the insoluble fraction could only be obtained with solvent-free MALDI MS whereas a MALDI test measurement applying conventional sample preparation failed completely. The mass spectrum of the soluble fraction (Figure 2) shows a molecular mass distribution ranging from 800 ($n = 3$) to <5000 Da ($n = 15$), and the most intense signal indicates an oligomerization degree of $n = 6$. The insoluble fraction (Figure 3) shows a molecular mass distribution ranging from 1500 ($n = 5$) to ~ 8000 Da ($n = 25$), whereas the major signal intensity indicates an oligomerization degree of $n = 8$. It is obvious that the polymer distribution is slightly shifted to

higher molecular weights but it contains polymers with chain lengths that are also present in the soluble fraction.

It seems that simple Soxhlet extraction cannot rigorously separate the soluble from the insoluble fraction. Thus, the two fractions are enriched with the respective components but still "contaminated" by polymers of the other fraction. Since the most intense signals of the insoluble fraction belong to the same homologous series of polymers as the signals of the soluble fraction of **2**, we can conclude that the polymer chain continued to grow during its synthesis even after the material has passed the maximum length for solubility in the reaction mixture. This indicates that the reaction may also proceed at the surface of the precipitated polymer as has been previously suggested by Yamamoto.²³ The maximum degree of polymerization of **2** determined by mass spectrometry is approximately $n = 25$ and suggests that at least 10 cycles of polymerization can take place at the surface of the precipitated polymer ($n(\text{max})_{\text{insoluble fraction}} = 25$, $n(\text{max})_{\text{soluble fraction}} = 15$ when dithranol is used as matrix). It should be mentioned that this result is only qualitative because the individual signal intensities and hence the shape of the polymer distributions highly dependent on the applied experimental conditions. For this reason, we applied the same experimental conditions (e.g., laser power, instrumental settings, matrix, etc.) for both fractions to ensure a reliable comparison. These MS results do not claim to reflect the maximum degree of polymerization of any of the investigated fractions but to give reliable information on the different fractions.

End Group Analysis of the Reaction Mixture. For an unequivocal structural assignment, it is indispensable to investi-

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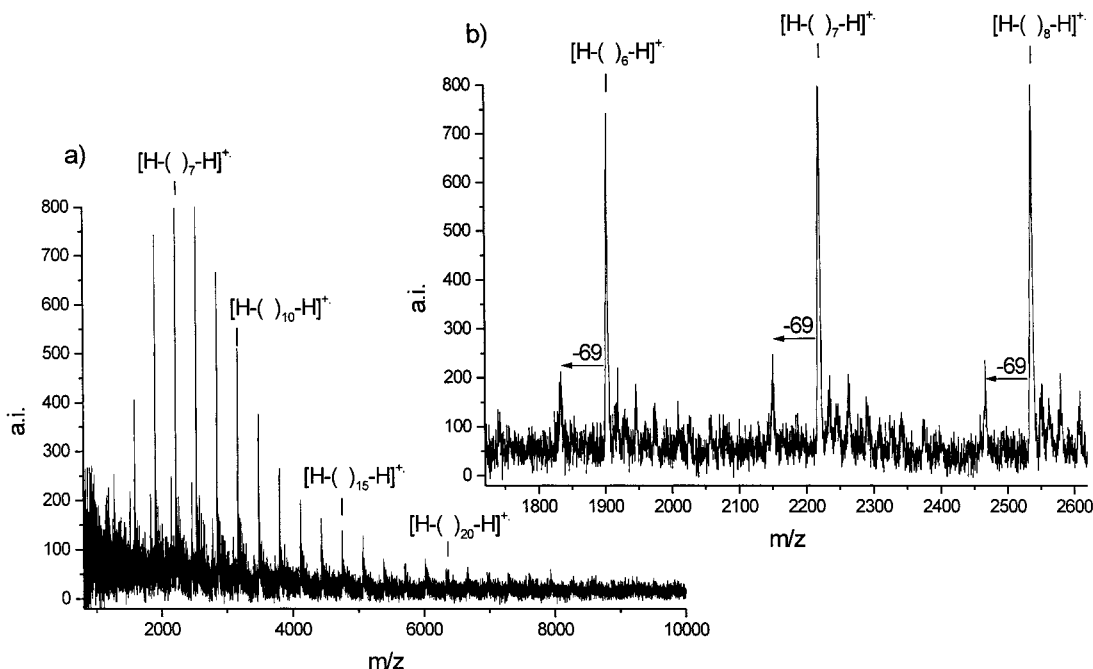


Figure 3. MALDI mass spectra of the insoluble fraction of **2** utilizing solvent-free sample preparation (dithranol): (a) full mass spectrum; (b) expanded mass region of the three major signals.

gate the ionization mechanism of **2**. It turns out that cationization by Li, Na, or K does not occur, whereas cationization by silver is successful, but the resulting mass spectra are of poor quality. The preferential ionization mechanism of structure **2**, however, is the formation of a radical cation as has been described previously for rigid rod-type polymers with a poly(*p*-phenylene) structure.^{24,25} Radical cation formation is an unusual process in MALDI mass spectrometry, but we commonly observe it with analytes that have a significant UV absorption at 337 nm (the wavelength of the nitrogen laser used for MALDI). In such cases, the analytes are ionized by photoionization and generally show a high fragmentation tendency. Analytes with direct laser-light absorption have an increased internal energy, and thus, partial fragmentation can sometimes not be avoided completely even at threshold laser irradiance.

Thus, the measurements were carried out with minimum laser power, and solvent-free MALDI MS of the insoluble fraction and solvent-based MALDI MS of the soluble fraction reveal that the polymer chains of the main series in both cases (Figures 2b and 3b) are detected as radical cations bearing hydrogen end groups (structure **2c**). A more detailed spectra interpretation of the soluble fraction of **2** shows additional intense signals which can be attributed to radical cations of structure **2a** bearing two terminal bromine atoms. This structural assignment is also in accordance with simulations of the isotopic distributions of **2a** and **2c**. Even though it is known that halide substituents have a high fragmentation tendency in MALDI measurements, we know from previous investigations of similar polymers with a poly(phenylene) backbone and terminal bromines that they can be detected as intact molecules without appearance of debrominated fragments under appropriate MALDI conditions.²⁵

Hence, it can be concluded, that the polymer growth of this species was terminated by a side reaction that leads to a substitution of the reactive bromine atoms by hydrogen during the synthesis (Figure 1) rather than during MALDI analysis.

Thus, we can assume that the traces of the reactive structure **2a** occur in the final polymer due to the precipitating polymer forming an insoluble wrapping around **2a** so that the included molecules were not accessible for a further polymerization or debromination reaction. Even though a cyclic structure **2d** could theoretically be obtained, the MALDI mass spectra of both fractions do not support its presence.

The mass spectrum of the insoluble fraction (Figure 3b), however, shows a subseries with a repeating unit of **2** (316 Da) and a mass difference of -69 Da relative to the main series of the hydrogen-terminated polymer **2c** that could not be assigned to the assumed end groups such as hydrogens or bromines (structures **2a**, **2b**, and **2c**) or to a pseudomolecular ion formation of **2** with any common metal ion or to side reactions during the synthesis. It can be observed that a similar series appears also in the mass spectrum of the soluble polymer fraction when the laser power is increased for the measurement. The signal intensity of this particular subseries increases with increasing laser power to a higher extent than the other subseries. Hence, this unidentified signal series seems to be explicable only by fragmentation of structure **2c**. Since the measurements were carried out in the reflection mode of the time-of-flight mass spectrometer, signals from those fragments, which are produced due to a postsource decay (PSD), do not appear at positions corresponding to their correct masses and have to be identified using a PSD calibration, which is described in the next section. The PSD nature of these fragments can also be verified by measurements in the linear mode of the TOF instrument where the PSD fragments are not present. The appearance of fragments in the reflection spectrum can be avoided completely when the laser power is adjusted only

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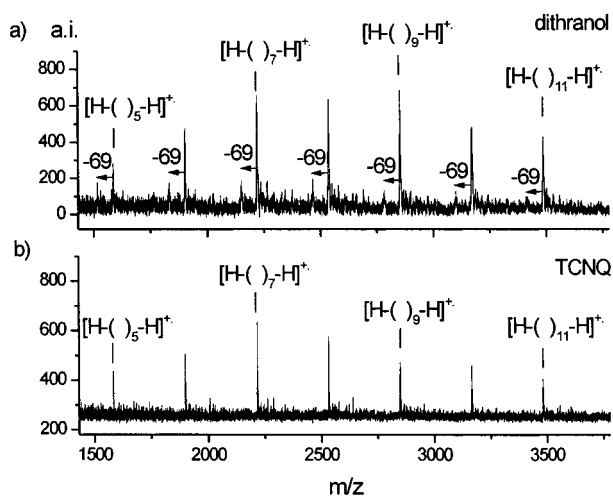


Figure 4. MALDI mass spectra of the expanded mass region of the insoluble fraction of **2** utilizing solvent-free sample preparation and threshold irradiance of different matrixes: (a) dithranol (baseline corrected); (b) TCNQ.

slightly above the desorption/ionization threshold for the signals of **2c** as long as the soluble fraction is measured; however, it is not possible to avoid fragmentation in the insoluble fraction even at threshold irradiance (Figure 4a). Therefore, we tested the new matrix TCNQ, which was successfully applied in an earlier investigation of an insoluble giant PAH.¹⁶ Indeed, TCNQ allows an improved measurement of the insoluble fraction with a complete suppression of fragmentation at threshold irradiance (Figure 4b). We attribute this to the very low desorption threshold of TCNQ and its stabilizing effect for radical cations. It should be stressed that even though TCNQ shows a low solubility in most of the common solvents (e.g., tetrahydrofuran, dichloromethane, and toluene), this compound can be applied conveniently as a matrix since MALDI MS is not dependent on solubility of either analyte or matrix when solvent-free sample preparation is used.

Besides the suppression of fragmentation, the measurements with TCNQ indicate an improved signal-to-noise ratio for both fractions and, in particular, a higher oligomerization degree for the insoluble fraction ($n = 30$) in comparison to the application of dithranol as matrix ($n = 25$). It should be mentioned that MALDI most probably does not show the real upper molecular weight limit of this polymer, and we assume that polymers with higher masses are also present, which are beyond the mass spectrometric detection limit.

Investigation of Fragmentation by PSD MALDI-TOF MS.

To elucidate the origin of the fragmentation, the measurements were carried out with deliberately high laser power. The resulting mass spectrum (Figure 5) shows a cascade of equal mass differences of up to three times -69 and -77 Da relative to the main signal series of the insoluble sample, which was prepared with TCNQ as matrix. Whereas the mass difference of -77 Da can be attributed directly to the loss of a phenyl substituent, which additionally takes place by in-source decay (ISD) under high laser irradiation, the mass difference of -69 Da that originates from a postsource decay does not show the correct masses and must be measured with a PSD calibration to identify the real mass values.

Therefore, the fragmentation behavior was investigated by PSD MALDI MS. From a sample of the solvent-free prepared insoluble fraction of the polymer, the most intense signal in Figure 5 with a mass of 2214 Da ($n = 7$) was selected for the fragmentation study. The corresponding PSD fragment ion spectrum (Figure 6a) shows a cascade of three intense signals with equal mass differences of -77 Da originating from the selected parent ion of structure **2c**. This proves unequivocally the metastable loss of up to three phenyl substituents of the parent ion (-77 , -154 , -231 Da). The fragmentation of the backbone of structure **2c** is negligible under the conditions applied. The strong signals for the loss of phenyl side groups as well as the lack of backbone cleavage underline the high and preferential fragmentation

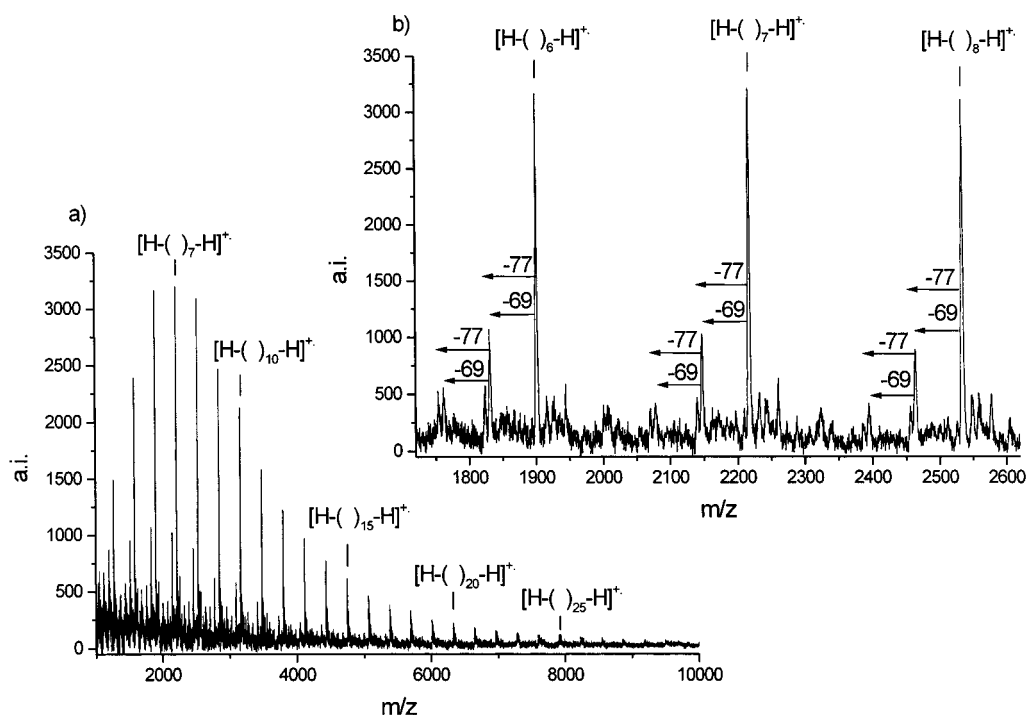


Figure 5. MALDI mass spectra (baseline corrected) of the insoluble fraction of **2** utilizing solvent-free sample preparation (TCNQ) using high laser power: (a) full mass spectrum; (b) expanded mass region of the three major signals.

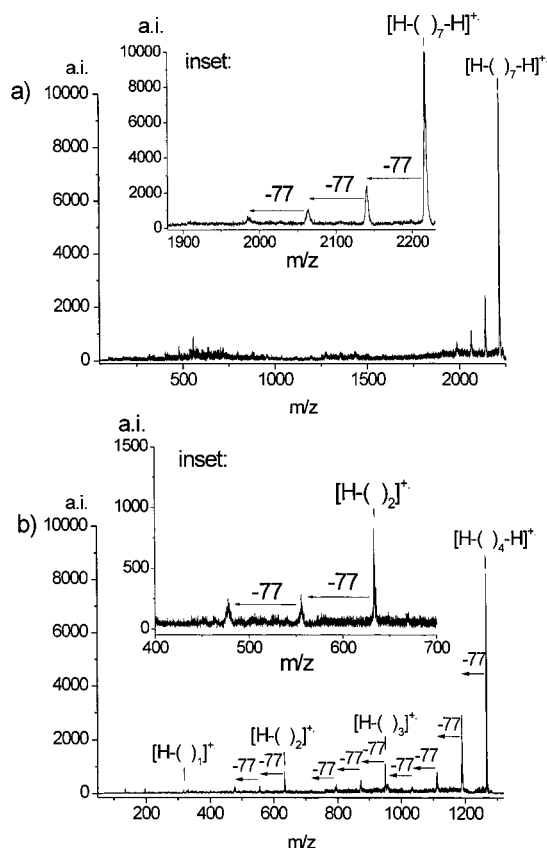


Figure 6. PSD MALDI mass spectrum of the insoluble fraction ($n = 7$ of structure **2c**) utilizing solvent-free sample preparation (TCNQ): (a) full mass spectrum (inset: expanded mass region of the parent ion); PSD MALDI mass spectrum of the soluble fraction ($n = 4$ of structure **2c**) utilizing solvent-based sample preparation (TCNQ): (b) full mass spectrum (inset: expanded mass region of the fragments).

tendency in this rigid backbone analyte under moderate fragmentation conditions. A similar behavior was also observed for other rigid backbone polymers with side-chain substituents.²⁴

However, the fragmentation behavior changes when a polymer chain of **2c** with lower molecular weight ($n = 4$) was investigated (Figure 6b). In contrast to the polymer with $n = 7$, the smaller polymer chain now also shows a fragmentation of the main chain with intense signals at 949 and 633 Da that correspond to the loss of one or two complete repeating units, respectively. The signals below the trimeric and dimeric main-chain fragments show also mass differences of -77 Da and can be attributed to additional side group cleavages of phenyl rings. Thus, in the case of the smaller oligomer ($n = 4$ of structure **2c**), the fragmentation of the substituents is less dominant than for the higher oligomer ($n = 7$ of structure **2c**) and competes with fragmentation by backbone cleavages.

With the knowledge about the fragmentation behavior gained by the PSD measurements and our experience from previous investigations, that poly(*p*-phenylene) structures with bromine end groups can be analyzed by MALDI mass spectrometry without the loss of bromine,²⁵ we are now able to state that the polymerization reaction of **1** mainly leads to the desired structure **2c** since the detected low-intensity subseries of the insoluble polymer

fraction can be assigned to mass spectrometric fragments and are thus not due to side products from synthesis.

CONCLUSION

One important advantage of solvent-free sample preparation is the ability to characterize insoluble samples by MALDI MS and to provide detailed information where other methods, such as NMR spectroscopy or gel permeation chromatography, fail completely. The characterization of the mostly insoluble poly(9,9-diphenyl-2,7-fluorene) (**2**) reveals that there is no structural difference between the soluble and insoluble polymer chains in principle, but there is a difference in the end group composition: Whereas the soluble fraction shows polymers with either two bromine or two hydrogen end groups, the insoluble fraction shows only hydrogen-terminated polymers. An additional signal series with a mass difference of -69 Da in comparison to signals of **2c** can be explained by a fragmentation reaction that takes place during the flight time of the ions in the mass spectrometer and originates from the cleavage of phenyl side groups from the rigid polymer backbone. This indicates a certain lability of such structure types under MALDI conditions. A similar fragmentation tendency was previously observed for other conjugated rigid backbone polymers²⁴ and can be attributed to an electronic absorption of these structures at 337 nm, which is the excitation wavelength of the employed nitrogen laser. Laser light-absorbing analytes experience a direct laser excitation and have an increased internal energy in contrast to nonabsorbing analytes. However, they can be analyzed successfully by MALDI, when matrixes with very low desorption thresholds are used. For this reason, the appearance of fragments from the insoluble fraction of polymer **2c** could be suppressed by applying TCNQ as a matrix instead of dithranol, which demonstrated the importance of choosing the appropriate experimental conditions for laser light-absorbing analytes. For future applications, the solvent-free MALDI MS reveals very useful aspects: (i) new classes of analytes can be characterized regardless of solubility, (ii) new compounds with low solubility (e.g., TCNQ) can be used as matrixes, and (iii) any combination of analyte and matrix is now possible without the restriction of a common solvent.

Characterization of insoluble samples by MALDI MS is still challenging, since most of the traditional analytical methods depend on good solubility of the analytes being investigated, and therefore, there is a lack of additional or complementary methods. Thus, supporting evidence for the mass spectrometric results from other analytical techniques cannot be expected. This contribution is a step toward the elucidation of the chemistry of insoluble samples since it eliminates a long-lasting misjudgment, that MALDI can only be applied to soluble samples.

ACKNOWLEDGMENT

The authors acknowledge A. Rouhanipour for excellent experimental support, MPI for Polymer Research (Mainz, Germany), and Dr. T. P. Knepper, ESWE Institute (Wiesbaden, Germany) for critical discussions.

Received for review November 15, 2001. Accepted May 2, 2002.

AC0111863