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Journal of Fluorine Chemistry 113 (2002) 85–91

JOURNAL OF FLUORINE CHEMISTRY

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Molecular structure investigations on fluorine containing polyazomethines by means of the MALDI–TOF–MS technique

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Received 19 June 2001; accepted 7 August 2001

Abstract

Three new aromatic polyazomethines have been synthesized by solution polycondensation reactions of terephthalic dialdehyde with fluorine containing aromatic diamines. The polymers were obtained in high yields. The investigation of these polymers by means of matrix-assisted laser desorption ionization–time-of-flight–mass spectrometry (MALDI–TOF–MS) proved the initial members of the four theoretical possible series of the corresponding oligomers with 2–10 repeating units per molecule. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polyazomethines; Oligomers; MALDI–TOF–MS

1. Introduction

Aromatic polyazomethines or poly(Schiff base)s are an attractive class of high performance polymers due to their high thermal stability, mechanical strength, environmental stability and good optoelectronic properties [1–3]. Several approaches have been undertaken to improve the processability of conjugated polyazomethines by introducing various substituted benzene rings in the main chain [4,5], by using monomers containing certain heterocyclic units such as thiophene [6], oxadiazole, thiadiazole [7–9], pyridine [10], diphenylfluorene [11], and others. Copolymers with phenyl-substituted quinoxaline rings proved to be very beneficial [12,13]. Such copolymers exhibited improved solubility in organic solvents and some applications in microelectronic or in optoelectronic devices have been reported [14]. Recently, vacuum deposited aromatic polyazomethines were described for the preparation of organic light emitting devices (LEDs) [15,16]. Therefore, we considered polyazomethines for their possible use to play an important role for the development of highly ordered thin films for LED applications.

New materials suitable for the process of vacuum deposition polymerization (VDP) of polyazomethines are investigated in the present paper. The synthesis of three polyazomethines by solution polycondensation reaction of terephthalic dialdehyde with fluorine containing aromatic diamines is described. These polyazomethines serve as model compounds for the investigation by means of matrix-assisted laser desorption ionization–time-of-flight–mass spectrometry (MALDI–TOF–MS) to clarify the different molecular structures of the corresponding oligomers.

2. Results and discussion

The polyazomethines II, IV and VI were synthesized by solution polycondensation reactions of equimolar amounts of the aromatic diamines I, III or V with terephthalic dialdehyde, in toluene as a solvent (Scheme 1).

For the reaction products from aromatic diamines with terephthalic dialdehyde four different series of oligomers are possible according to their different end caps (Scheme 2).

The calculated repeating unit in the four series of the polymers is 274.2 g mol^{-1} for polyazomethine II, 426.3 g mol^{-1} for polyazomethine IV and 418.3 g mol^{-1} for polyazomethine VI.

In Figs. 1–3 sectors of the MALDI–TOF–MS of the three polyazomethines are shown. For the three polyazomethines

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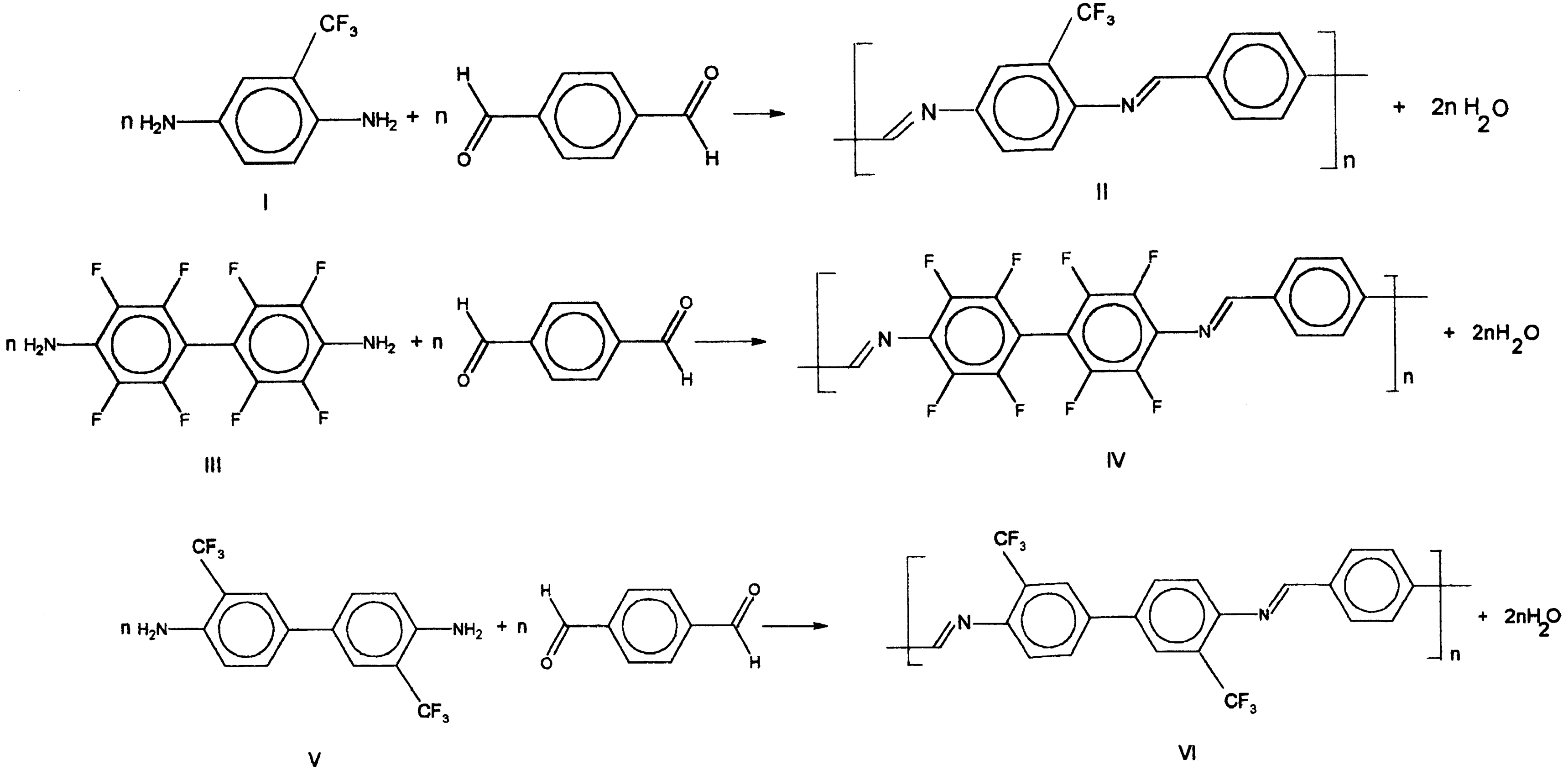
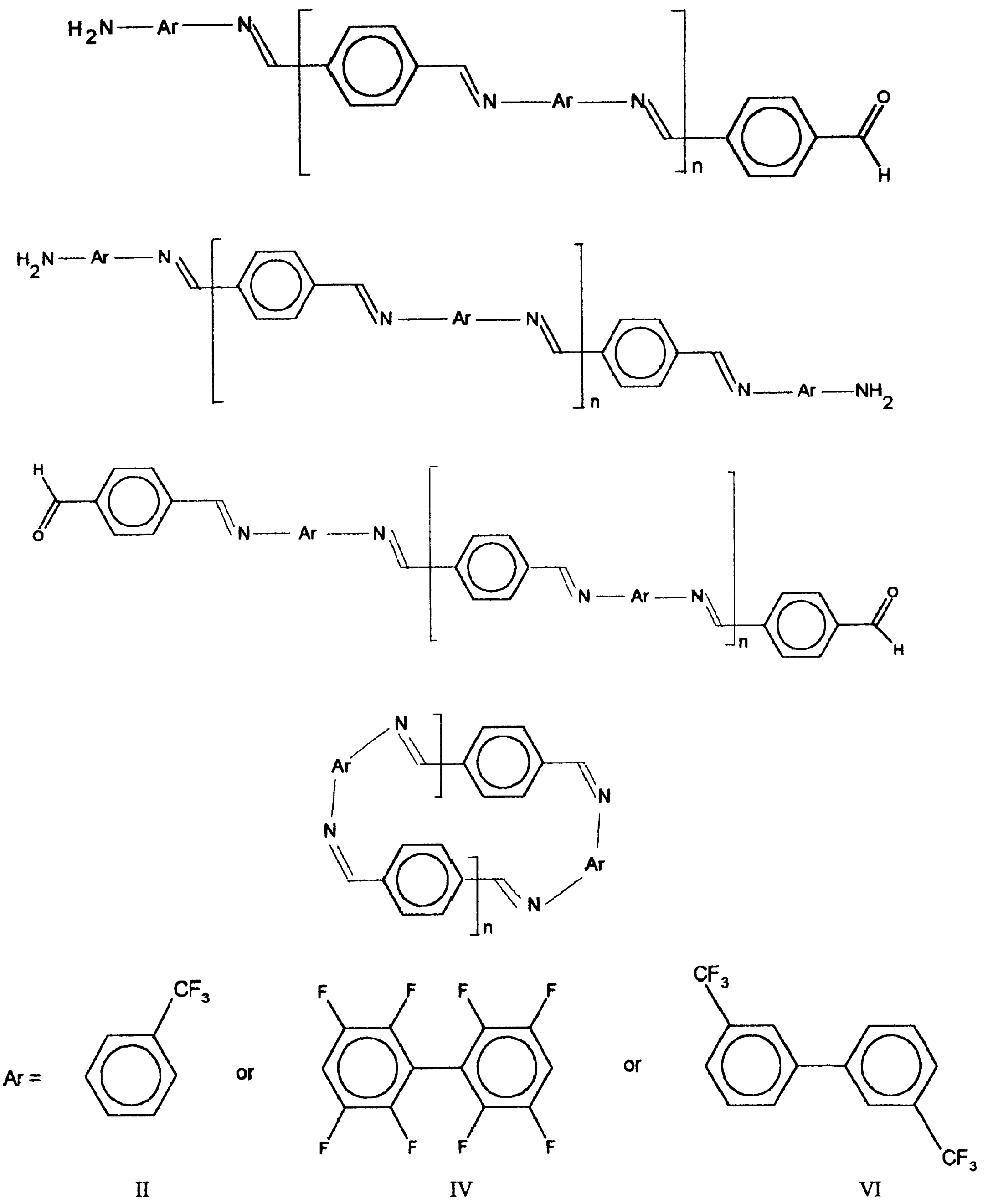
PII: S0022-1139(01)00498-5



Scheme 1. Synthesis of azomethine polymers.



Scheme 2. Series of azomethine oligomers II, IV, VI (n = number of repeating units). Series 1: reaction products from dialdehyde ($n+1$) and diamine ($n+1$). Series 2: reaction products from dialdehyde ($n+1$) and diamine ($n+2$). Series 3: reaction products from dialdehyde ($n+2$) and diamine ($n+1$). Series 4: cyclic reaction products from dialdehyde ($n+1$) and diamine ($n+1$).

II, IV and VI we found the four theoretical possible series.

We calculated the theoretical values of the different series of the oligomers and compared them with the experimental data. For polyazomethine II the peaks with the highest intensities correspond to series 1 and 2, respectively. These results are given in Table 1.

For polyazomethine IV we found similar results. The peaks with the highest intensities correspond to series 1 and 2, respectively, but for VI the peaks with the highest intensities correspond to series 4, the cyclic reaction products.

In addition, the spectra show that obviously these oligomers under the chosen measurement conditions the species exist predominantly with an attached proton. Further we found, for II the peaks with lower intensities of another six series with a monomer mass difference of about 274.2 g mol^{-1}. These series correspond to species which either exist

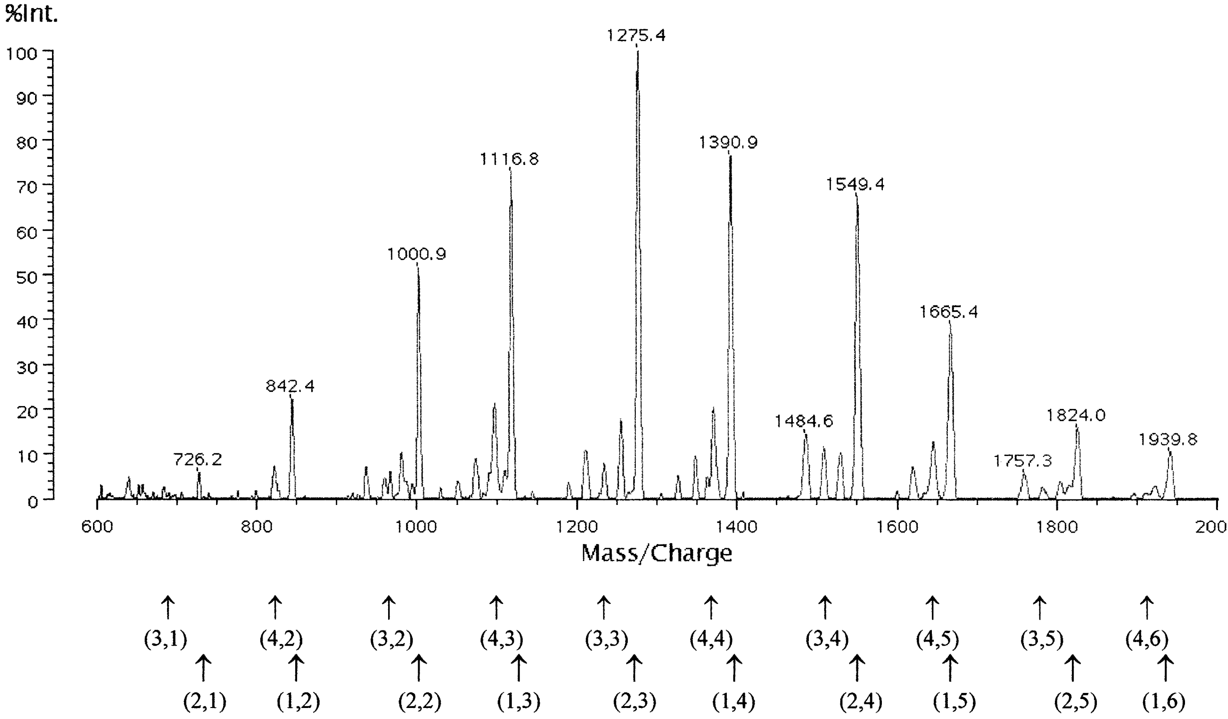


Fig. 1. MALDI–TOF–MS of II (sector): (x, y), species which exist with an attached proton; x = number of the series, $y = n$ = number of repeating units.

with an attached sodium ion or species with a missing CF_3-group. No other peaks were found. These results are shown in Fig. 4.

For the polyazomethines IV and VI similar results were obtained. Besides the species of series 1–4 which exist with an attached proton we found for IV another five series with a monomer mass difference of about 426.3 g mol^{-1} and for VI another seven series with a monomer mass difference of about 418.3 g mol^{-1}. These series possess peaks of lower intensity and correspond to species which either exist with an attached sodium ion or species with a missing F-atom (IV) or a missing CF_3-group (VI), respectively.

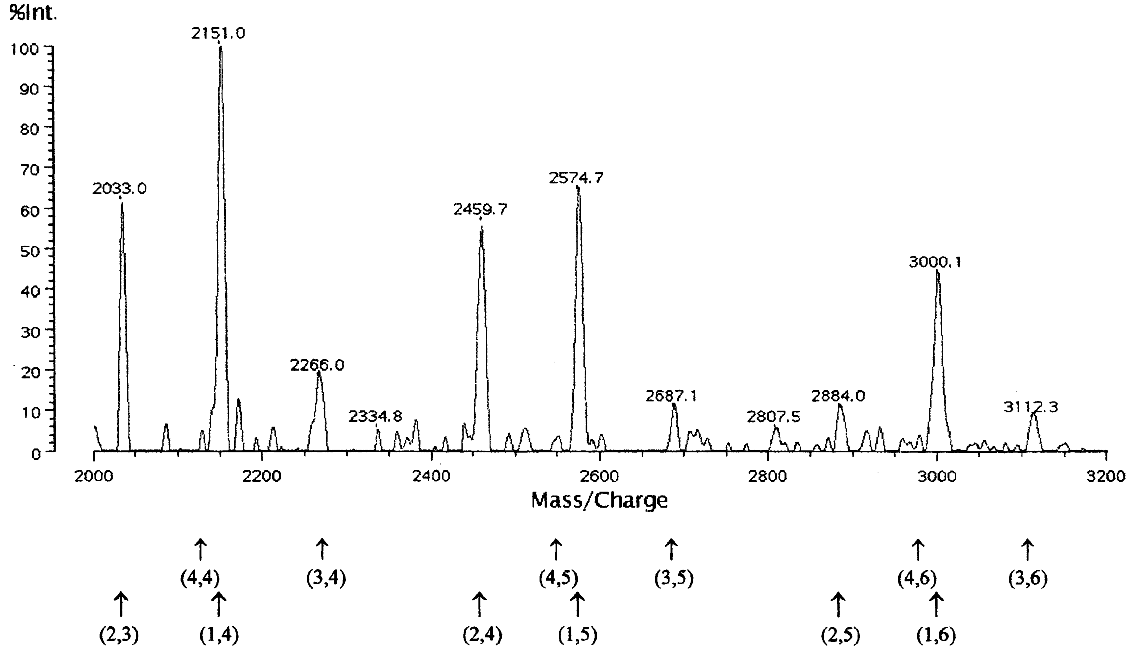


Fig. 2. MALDI–TOF–MS of IV (sector): (x, y), species which exist with an attached proton; x = number of the series, $y = n$ = number of repeating units.

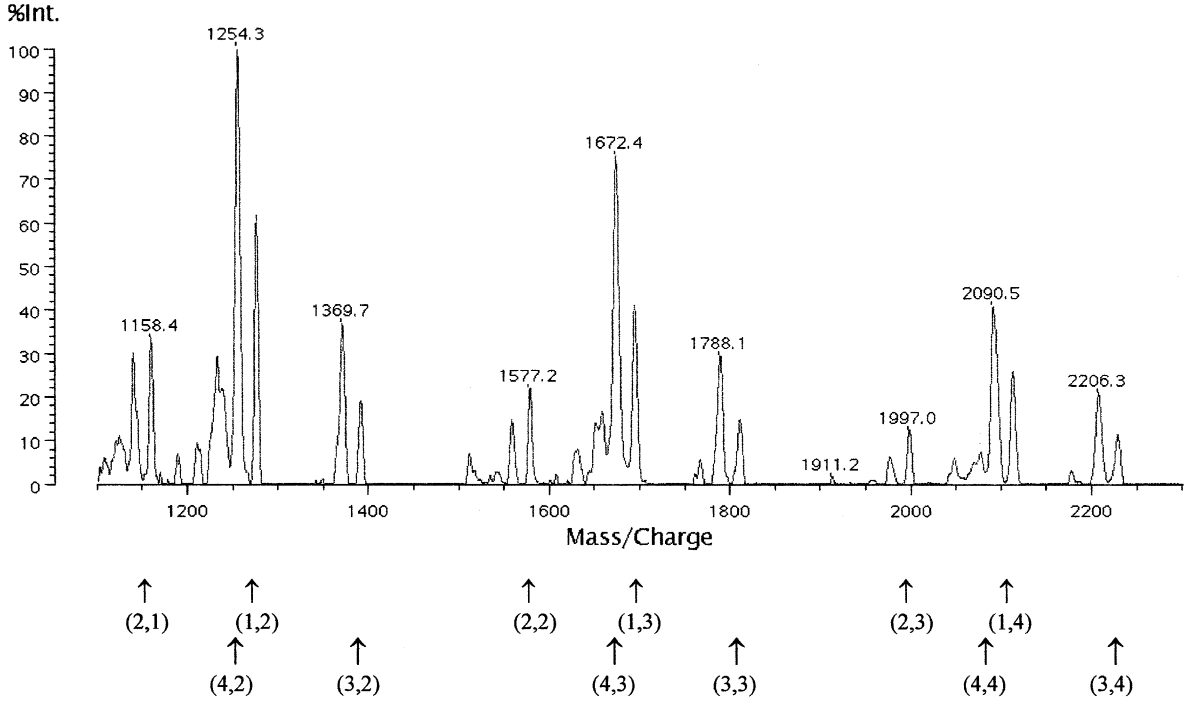


Fig. 3. MALDI–TOF–MS of VI (sector): (x, y), species which exist with an attached proton; x = number of the series, $y = n$ = number of repeating units.

Table 1
Calculated mass of II and experimental results of MALDI–TOF–MS for peaks with the highest intensities[a]

n	Series 1			Series 2		
	M + H (calculated)	M^* (found)	Δ	M + H (calculated)	M^* (found)	Δ
0	293.4	–		451.4	452.2	
1	567.5	567.9		725.6	726.2	274.0
2	841.7	842.4	274.5	999.9	1000.9	274.7
3	1116.0	1116.8	274.4	1274.1	1275.4	274.5
4	1390.2	1390.9	274.1	1548.3	1549.4	274.0
5	1664.5	1665.4	274.5	1822.6	1824.0	274.6
6	1938.7	1939.8	274.4	2096.8	2097.5	273.5
7	2212.9	2213.4	273.6	2371.1	–	
Average			274.2			274.2

[a] M = molecular mass (g mol^{-1}), Δ = found mass difference between the oligomers (g mol^{-1}), M^* = found mass by MALDI–TOF–MS (g mol^{-1}), n = number of repeating units. Calculated monomer mass is 274.2 g mol^{-1}.

It is a remarkable and unusual fact for MALDI–TOF–MS investigations of synthetic polymers that the species predominantly exist with an attached proton. Also after doping the polymers with LiCl no lithium adducts were observed. We got the same values, no changes in the spectra were detected.

3. Experimental details

3.1. Synthesis of the polymers

The following example of polyazomethine II illustrates the general procedure (all diamines were obtained from ABCR, Karlsruhe):

Polyazomethine II: Diamine I 2.5 g (14.2 mmol), terephthalic dialdehyde 1.9 g (14.2 mmol) (Aldrich, Steinheim), 50 ml toluene and 50 mg p-toluenesulfonic acid as a catalyst were placed in a 100 ml three-necked flask equipped with a mechanical stirrer and a reflux condenser. The mixture was heated to reflux under stirring for 4 h. The precipitated polymer was collected by suction filtration, washed with 100 ml of methanol in four portions and extracted twice with 50 ml boiling methanol. The remaining solid was dried for 2 h at 60 °C. After drying 3.35 g of the bright yellow polymer II were obtained (81% yield). This polymer shows a poor solubility in pyridine, hexamethylphosphoric triamide and 1-methyl-2-pyrrolidinone.

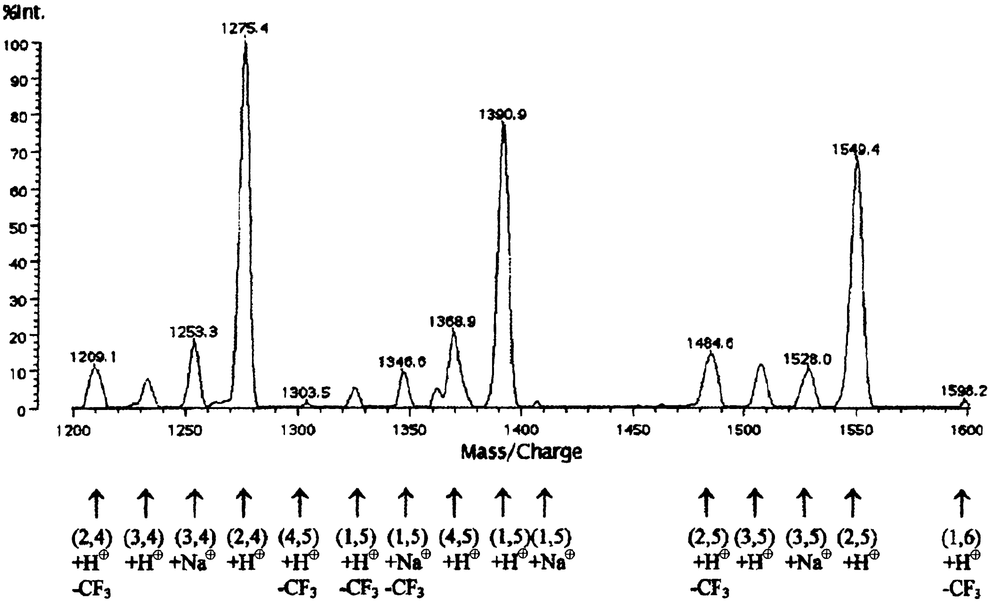


Fig. 4. MALDI–TOF–MS of II (sector): (x, y), species which exist with an attached proton; x = number of the series, $y = n$ = number of repeating units; $+\mathrm{H}^{\oplus}$, species which exist with an attached proton; $+\mathrm{Na}^{\oplus}$, species which exist with an attached sodium ion; $-\mathrm{CF_3}$, a $\mathrm{CF_3}$-group is substituted by a H-atom.

Analysis calculated for $n \to \infty$:[1] *F*, 20.78%, found: *F*, 20.38%; IR (KBr): 1046, 1132, 1190 (C–F); 1318 ($-\mathrm{C_6H_3(CF_3)}-$); 1485, 1584 $(\mathrm{C{-}H})_{\mathrm{arom}}$; 1622 $\mathrm{cm^{-1}}$ (C=N).

Polyazomethine IV: Yield: 75%; pale yellow powder; insoluble in organic solvents.

Analysis calculated for $n \to \infty$ (see footnote 1): *F*, 35.66%, found: *F*, 33.36%; IR (KBr): 970, 1002, 1042, 1051 (C–F); 1478 (CF in $-\mathrm{C_6F_4}-$); 1560 $(\mathrm{C{-}H})_{\mathrm{arom}}$; 1624 $\mathrm{cm^{-1}}$ (C=N).

Polyazomethine VI: Yield: 92%; bright yellow powder; poor solubility in 1-methyl-2-pyrrolidinone.

Analysis calculated for $n \to \infty$ (see footnote 1): *F*, 27.25%; found: *F*, 25.15%; IR (KBr): 1047, 1054, 1137, 1199 (C–F); 1340 ($-\mathrm{C_6H_2(CF_3)_2}-$); 1483, 1560 $(\mathrm{C{-}H})_{\mathrm{arom}}$; 1628 $\mathrm{cm^{-1}}$ (C=N).

Because of the poor solubility of the polymers no NMR-investigations were possible.

3.2. Measurements

MALDI–TOF–MS were recorded with a Kratos Kompact MALDI III (Shimadzu Europa GmbH, Duisburg, Germany) using a nitrogen laser source ($\lambda = 337$ nm), a positive polarity and 20 kV acceleration voltage. The samples were suspended in THF (1 mg $\mathrm{ml^{-1}}$) and mixed with the matrix of 2,4,6-trihydroxyacetophenone (25 mg $\mathrm{ml^{-1}}$ THF) before drying. The solid mixture was impressed on the slide with a spatula. The equipment was calibrated with bovine insulin.

4. Conclusions

New aromatic polyazomethine model compounds have been prepared by solution polycondensation of terephthalic dialdehyde with fluorine containing aromatic diamines in high yields. According to the possible different end caps four series with different molecular structures are possible. A proof of all these theoretical possible series was furnished by means of the MALDI–TOF–MS technique. The initial members of the corresponding oligomers with 2–10 repeating units per molecule were found. Further investigations on vacuum deposited polyazomethines are provided.

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