STRUCTURAL INFLUENCES ON THE PROPERTIES OF AROMATIC POLYAMIDINES

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Abstract: Polyamidines with both nitrogens in the main chain (-X-NH-CR=N-) were obtained by polycondensation of diamines with different orthoesters. The thermal properties could be tailored by the choice of diamine and orthoester. Quantitative formation of a cyclic trimer could be observed when 2,6-diaminopyridine was converted with triethyl orthoformate. ^{1}H, ^{13}C and ^{15}N NMR spectroscopic investigations in solution and in solid state showed that the configuration of the amidine group was strongly dependent on the residue R. In polyformamidines, strong interactions caused by hydrogen bonds could be evidenced.

INTRODUCTION

Chemistry of low molecular weight amidines has intensively been investigated (Ref. 1). Due to their basic behaviour amidines are able to interact with several substances. Salt formation (Ref. 2) and complexation (Ref. 3) as well as biological (Ref. 4) and catalytical activity (Ref. 5) were described by several authors.

Polymers containing amidine groups are only little known. Amidine groups can be inserted into polymers as laterally bonded functional groups (Refs. 6, 7) or directly with one (Refs. 8-10) or both nitrogens (Refs. 11-15) in the polymer backbone. This paper reports on polyamidines with both nitrogens in the backbone (-X-NH-CR=N-). It is intended to show that the configuration of polyamidines is strongly depended on the structural unit -X- and the substituent R on the amidine group.

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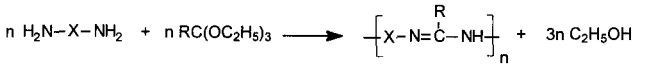
RESULTS AND DISCUSSION

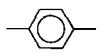
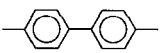
Polyamidines with both nitrogens in the backbone were available via polycondensation of diamines with orthoesters according to *Scheme 1*. Solution polycondensation in DMSO at 140 - 180 °C has proved suitable for the polyformamidines (R: H) **2a** - **2j**. For polymers with larger residues R on the amidine group (**2k** and **2l**), melt polycondensation at 200 - 250 °C in presence of catalytic amounts of trimethylbenzoic acid was performed. Without catalyst reaction did not proceed completely. Intermediate mono- and bisimidoesters of the diamine were formed quantitatively (Ref. 16).

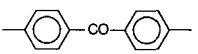
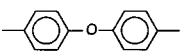
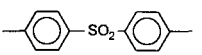
The properties of all polyamidines synthesized are summarized in Table 1.

Scheme 1:



1 **2**

	1a, 2a	**b**	**c**	**d**	**e**	**f**
-X-						
-R-	H	H	H	H	H	H

	1g, 2g	**h**	**i**
-X-			
-R-	H	H	H

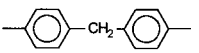
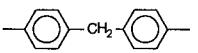
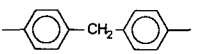
	1j, 2j	**k**	**l**
-X-			
-R-	H	CH_3	

Table 1 Properties of polyamidines

sample	synthesis [a]	η_{inh} [b] in dl/g	T_g [d] in °C	T_m [e] in °C	crystallinity [f]
2a	s	0,22 [c]	-	> 380 (dec.)	0,66
2b	s	0,56	-	> 380 (dec.)	0,46
2c	s	0,18	not det.	255	0,14
2d	s	0,09	-	infusible	0,80
2e	s	not det.	not det.	> 360 (dec.)	amorphous
2f	s	not det.	not det.	> 360 (dec.)	amorphous
2g	s	0,13[c]	-	> 380 (dec.)	0,72
2h	s	0,25	-	350 (dec.)	0,20
2i	s	0,13	163	261 (dec.)	0,27
2j	s	0,30	161	288	0,24
	m	0,12	-	> 350 (dec.)	0,56
2k	m	0,12	142	-	amorphous
	m; g		-	205[d]	0,45
2l	m	0,11	158	-	amorphous

a) s ... synthesized in solution, m ... synthesized in melt, g ... sample obtained after gelation in THF
b) c = 0,5 g/dl in DMAc (3 wt.-% LiCl) at 25 °C
c) c = 0,5 g/dl in conc. sulfuric acid a 25 °C
d) DSC measurements heating rate 10 K/min
e) observed by microscopy
f) detected by WAXS

Polyformamidines based on *para*-substituted diamines (**1a**, **1b**) exhibited the highest crystallinity. They did not melt until decomposition and were only soluble in strong acidic solvents such as sulfuric acid and trifluoroacetic acid. Crystallinity could be suppressed completely by copolymerization of **1a** and **1b**. The resulting copolyformamidines showed liquid crystalline behaviour (Ref. 17). Other possibilities to reduce melting points and to improve solubility of polyformamidines are incorporation of *meta*-substituted aromatic units (**2c** - **2f**) or incorporation of flexible monomers into the polymer chain (**2g** - **2j**). Properties of these polymers has already been reported (Ref. 18, 19). As can be seen from Table 1, polyformamidines possess

high glass transition and melting temperatures. They are thermally stable until 300 °C, but they decompose relatively easy in presence of water (Ref. 18).

An unusual reaction course was observed when *meta*-substituted aromatic diamines where converted with triethyl orthoformate (**2c** - **2f**). In case of 1,3-phenylenediamine, an oligomer (**2c**) with a degree of polymerization of approx. 13 was obtained, whereas the reaction of the structurally similar 2,6-diaminopyridine resulted almost quantitatively in a cyclic trimer. This could be evidenced by NMR and MALDI-TOF spectroscopy (Ref. 19). MALDI-TOF spectra of **2c** and **2d** are shown in Figures 1 and 2. The MALDI-TOF spectra of **2c** shows the typical distribution of an oligomeric polycondensate (M_n = 1580 and M_w/M_n = 1.26). Splitting of the single peaks is caused by different terminal groups and associates with the matrix. In contrast with this, the spectra of **2d** shows only one molecule ion peak at 358.5 (Fig. 2) which corresponds nearly exactly with the molecular weight of the protonated cyclic trimer. For **2e** and **2f** cyclization could also be detected, however, polymerization took place simultaneously. The content of the cyclic trimer was about 50 mol% for **2e** and 10 mol% for **2f**.

Ring formation can be attributed to steric reasons. As know from Anulewicz at al. (Ref. 20) and others, the amidine group in diphenylformamidine is preferably in *E-syn* configuration. Due to steric repulsion between the two protons of the phenyl groups in *ortho*-position to the amidine group and the CH proton of the formamidine group, the phenyl groups are twisted out of the plane of the amidine group. Similar interactions have to be assumed in polymer **2c**, as a result of which ring formation is unlikely. In **2d**, where the phenyl groups are replaced by

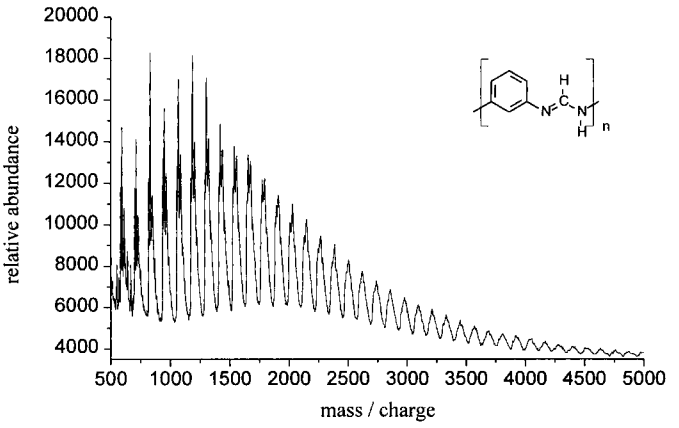


Figure 1 MALDI-TOF spectrum of sample **2c**

pyridyl groups having the nitrogen in *ortho*-position to the amidine group, steric repulsions are confined only to one *ortho*-proton. This constrains the molecule in a structure in which steric hindrance is minimized and ring formation is favoured. Due to the lack of *ortho*-protons in the pyrimidine and triazine rings, steric interactions are less significant for **2e** and **2f**. Consequently, there is no structural preference and ring formation only takes place accidentally.

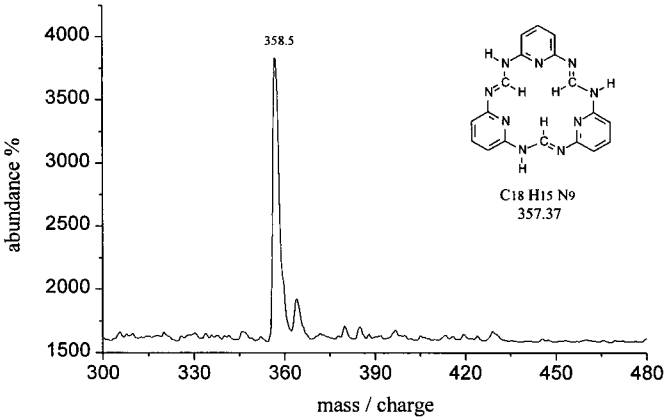


Figure 2 MALDI-TOF spectrum of sample **2d**

Another possibility to influence the properties of polyamidines is the change of substituent R. It could be shown earlier that aliphatic or aromatic residues on the amidine group improved the hydrolytic stability (Ref.16). From low molecular weight compounds, it is known that R strongly influences the configuration of the amidine group. We investigated the configuration of different polyamidines based on 4,4'-diaminodiphenyl methane by means of NMR spectroscopy (Ref. 21, 22). Figure 3 and 4 show the ^{1}H and ^{13}C NMR spectra of **2i** and **2k** in DMSO-d_6. Beside the signals of the main chain also end group signals could be detected. Their assignment has been shown in Ref. 16.

For polyacetamidine **2k** different ^{13}C NMR signals could be detected for the carbon atoms in 4 and 4' as well as in 3 and 3' position. The ^{1}H NMR spectrum exhibit also different signals for the protons in 3 and 3' position. That means that both phenyl rings are non-equivalent. The imino and the amino moiety of the amidine group influence the chemical shift of the adjacent phenyl groups differently. For polybenzamidine **2l** a similar signal splitting could be observed.

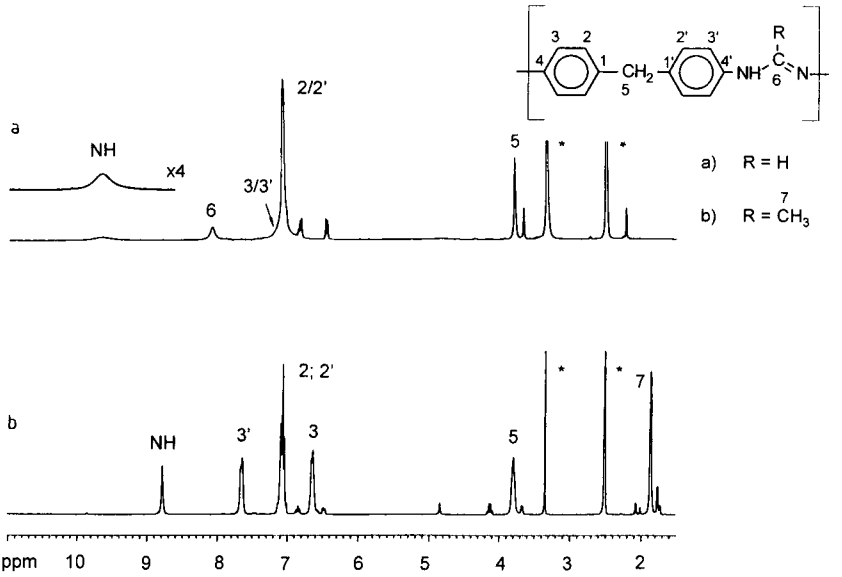


Figure 3 ^{1}H NMR spectra of **2j** (a) and **2k** (b) in DMSO-d_6

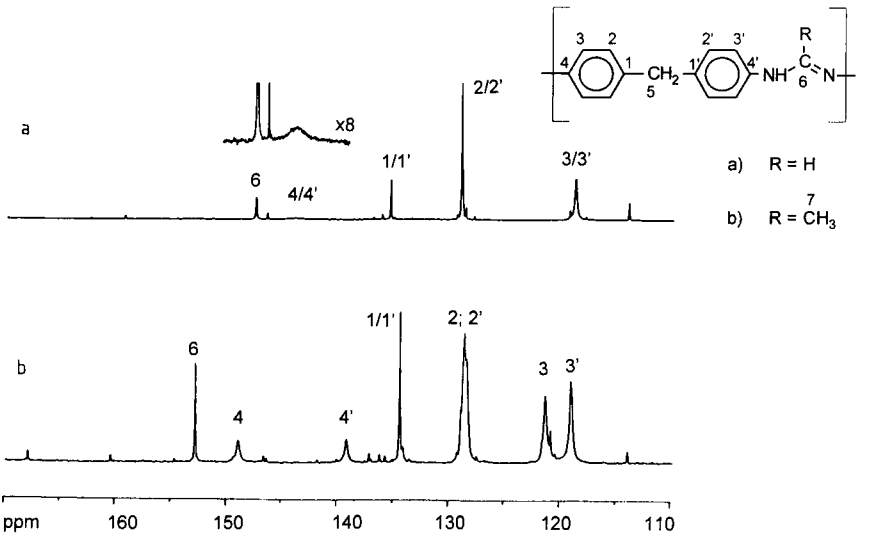


Figure 4 ^{13}C NMR spectra of **2j** (a) and **2k** (b) in DMSO-d_6

In contrast with this, the signals of both phenyl rings of polyformamidine **2j** are indistinguishable. These findings can be explained by prototropic tautomerism of the amidine group: ($R^2HN-CR^1=NR^3 \longleftrightarrow R^2N=CR^1-NHR^3$) which is fast on the NMR time scale for the polyformamidine and slow for the polyacetamidine and the polybenzamidine. An additional proof for prototropic tautomerism provided the ^{15}N NMR solution spectra. Whereas two different signals for the amino and the imino nitrogen appeared in the spectra of **2k** and **2l**, no signal could be detected for **2j** due to strong exchange broadening (Ref. 21).

^{15}N CPMAS spectroscopic investigations evidenced similar relations in the solid phase. In Figure 5 the ^{15}N CPMAS spectra of **2j** and two differently prepared samples of **2k** are depicted. One sample of **2k** was the as-synthesized product, the other one was obtained after gelation from THF solution and subsequent evaporation of the solvent. The latter one proved highly crystalline, whereas the as-prepared sample was amorphous. **2j** showed only one strongly broadened signal. In the spectra of both samples of **2k**, well separated signals of the imino and the amino nitrogen could be found. The ^{15}N chemical shift changes and signal narrowing observed for the crystalline sample indicate stronger interactions over hydrogen bonds as can be concluded from investigations on model compounds (Ref. 22) .

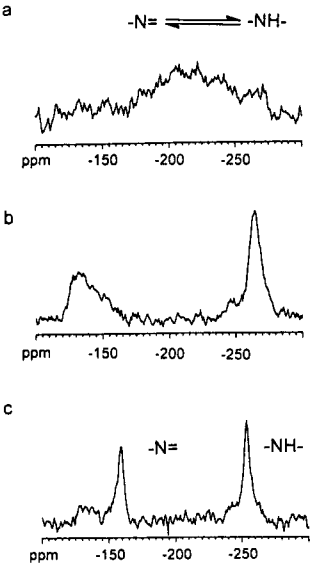


Figure 5 ^{15}N CPMAS spectra of **2j** (a), amorphous **2k** (b) and crystalline **2k** (c)

From low molecular weight compounds it is known that the configuration of the amidine group is dependent from the residue R on the amidine group. As shown in Figure 6, formamidine groups adopt the *E-syn* configuration preferably, resulting in the formation of cyclic dimers. These cyclic dimers promote fast proton exchange which could also be evidenced in polyformamidine **2j**. Due to the strong interactions polyformamidines are highly crystalline.

In amidines with larger residues R the *E-anti* configuration is predominant. Proton exchange in *E-anti* configuration is retarded. For low molecular weight compounds formation of infinite molecule chains connected by single hydrogen bonds has been described. From the NMR spectroscopic investigations of polyacetamidine **2k** one can conclude that the amidine groups adopt *E-anti* configuration. The lack of crystallinity, however, indicates low interactions between the polymer chains in the solid state. Due to higher mobility of the polymer chains in solution stronger interactions are possible resulting in gelation of the sample in THF. For the highly crystalline sample obtained after evaporation of THF, interactions over single hydrogen bonds as observed for low molecular weight compounds are assumed. It is worth mentioning that only the polyacetamidine gelled in solution. Polyamidines with larger aliphatic or aromatic residues did not show gelation.

From our results one can conclude that the residue R and the configuration of the amidine group strongly influence the solid phase structure of polyamidines. Due to strong hydrogen bonds polyformamidines tend to crystallize, whereas higher homologues form amorphous solids.

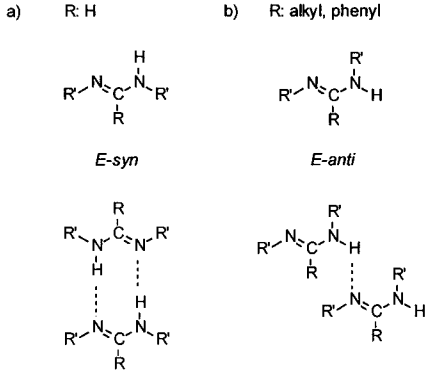


Figure 6 Configuration of amidine groups: (a) *E-syn* configuration forming a cyclic dimer (b) *E-anti* configuration forming a linear dimer

EXPERIMENTAL

Polycondensation:

Polyamidines **2a** - **2i** were synthesized by solution polycondensation of diamines with triethyl orthoformate as described in Ref. 18.

Polyamidines **2j** - **2l** were synthesized by melt polycondensation. Two mol of 4,4'-diaminodiphenyl methane (DAPM) were mixed with a slight excess of the respective orthoester **1**. Additionally, 1 - 10 mol % 2,4,6-trimethylbenzoic (based on DAPM) was added as catalyst. The mixture was heated under nitrogen to 80 - 120 °C with stirring and continuous removing of the resulting alcohol by distillation. After 10 - 45 min the temperature was raised to 200 - 250 °C and the pressure was reduced to 0.1 - 10 mbar for 1 - 3 h. The reaction vessel was flushed with nitrogen and cooled to ambient temperature. Polyformamidine **2j** was isolated as a white powder, whereas polyamidines **2k** - **2l** formed light coloured, glassy solids.

NMR measurements

The NMR measurements (Ref. 21) were carried out on a Bruker AMX 300 NMR spectrometer operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C and 30.41 MHz for ^{15}N. The deuterated solvents (DMSO-d_6) were used as lock. The ^{1}H and ^{13}C spectra were referenced on solvent signals. The ^{15}N spectra were referenced on external nitromethane ($\delta(^{15}N) = 0$ ppm). For ^{15}N CPMAS measurements (Ref. 22) the samples were spun at 4 kHz in a 5 mm CPMAS probe head from Bruker. Chemical shifts were referenced to external glycine. These values were converted in the nitromethane scale (glycine = -347 ppm on the nitromethane scale).

MALDI-TOF measurements

MALDI-TOF (matrix assisted laser desorption/ionization mass spectroscopy) experiments were performed on a HP G2030A MALDI-TOF-MS system (Hewlett Packard). Desorption and ionisation was induced by a pulsed N_2-laser. The mass spectra were obtained at 28 kV acceleration voltage. The matrix was 2,5-dihydroxybenzoic acid. For **2f** dihydroxyacetophenone was used as matrix. Sample and matrix were dissolved in DMSO and THF, respectively. The solutions were subsequently mixed, given on a sample holder and dried by vacuum. The measurements were carried out in linear mode and positive polarity.

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