Polymer Bulletin 33, 397–404 (1994)

Polymer Bulletin

Polymers containing formamidine groups

2. Synthesis of polyformamidines derived from triethyl orthoformate and aromatic diamines

Maik Rillich, Liane Häussler, Hartmut Komber, Frank Wittig, and Frank Böhme*

Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, D-01069 Dresden, Germany

Summary

Aromatic polyformamidines were synthesized by high temperature solution polycondensation of aromatic diamines with triethyl orthoformate. In order to obtain high molecular weight polymers, general investigations on the influence of reaction conditions such as reaction time, temperature and solvent were carried out on the basis of polyformamidine prepared from 4,4'-methylenedianiline. The proposed structures of aromatic polyformamidines were confirmed by elemental analysis, NMR- and IR-spectroscopy. Molecular weights were determined by ^{1}H NMR end group analysis. Polyformamidines having inherent viscosities of 0.25 - 0.36 dl/g show excellent solubility in polar solvents and in strong acids. Thermal analysis indicated that these polymers are stable up to 300°C, and a 10% weight loss were recorded on the TG curves in the temperature range of 350 - 366°C in nitrogen.

Introduction

The synthesis of polymers containing formamidine groups in the polymer backbone has been described very scarcely so far. Aliphatic polyformamidines were prepared for the first time from aliphatic diamines and s-triazine (1). In the first part of this series (2) we reported on the synthesis of aliphatic polyformamidines with inherent viscosities up to 0.19 dl/g by solution polycondensation of aliphatic diamines with triethyl orthoformate (TEOF) in the presence of a catalytic amount of acetic acid. Literature on aromatic polyformamidines is restricted to two publications by Mathias and Overberger (3,4). The authors synthesized aromatic polyformamidines with intrinsic viscosities up to 0.24 dl/g by reaction of aromatic diamines and TEOF, but only few information about the properties of these polymers was given.

In the present paper the syntheses of a number of new aromatic polyformamidines prepared by a similar synthetic route have been described. The influence of the reaction conditions during the polycondensation on the molecular weight of polymers was investigated and the properties of polyformamidines like solubility, phase behaviour and thermal stability have been discussed.

Experimental

Materials:
Bis[2-(4-aminophenoxy)ethyl]ether was synthesized by reduction of the appropriate dinitro compound which had been prepared by aromatic nucleophilic substitution reaction of 1-fluoro-4-nitrobenzene and diethylene glycol (5). All other aromatic diamines were purchased from Fluka and purified by recrystallization from ethanol. Triethyl orthoformate (TEOF) and dimethyl sulfoxide (DMSO) were stored over molecular sieves and purified by distillation prior to use.

---

*Corresponding author

Polycondensation:

All polyformamidines were prepared in solution under nitrogen by reaction of the appropriate aromatic diamines (25.0 mmol) with TEOF (27.5 mmol). There is a representative procedure, which was used for the preparation of polyformamidine **1b**: A 10 mol% excess of TEOF (4.08 g, 27.5 mmol) was added to a solution of 4,4'-methylenedianiline (4.95 g, 25.0 mmol) in 25 ml DMSO. The temperature of the reaction mixture was gradually raised to 140°C and maintained here for 4 hr. The reaction temperature was then increased to 180°C and held for further 4 hr. After cooling to room temperature the polymer solution was given into acetone. The precipitated polymer was filtered, extracted for 8 hr in a Soxhlet with acetone and dried in vacuum at 90°C for 8 hr.

Polyformamidine 1b:

^{1}H NMR: (see Fig. 1):

δ [ppm] = 10.10 (s; NH-CHO); 9.63 (broad; NH-CH=N); 8,70 (d; J = 11.2 Hz, NH-CHO, *trans*); 8.22 (d; J = 2.2 Hz, NH-CHO, *cis*); 8.10 (s; NH-CH=N); 7.48 (d; CH arom.); 7.17 (m; CH arom.); 6.84 (d; CH arom.); 6.47 (d; CH arom.); 4.80 (broad; NH_2); 3.81 (s; CH_2); 3.67 (s; CH_2)

^{13}C NMR: (see Fig. 2):

δ [ppm] = 162.4 (NH-CHO, *trans*), 159.3 (NH-CHO, *cis*); 147.6 (NH-CH=N); 146.5 (C arom.); 143.9 (C arom.); 136.6 - 136.2 (C arom.); 135.4 (C arom.); 129.1 (C and CH arom.); 119.2 and 117.8 (CH arom., *cis* and *trans*); 118.8 (CH arom.); 113.9 (CH arom.); 36.7 (CH_2, not shown in Fig. 2 due to overlapping with solvent signals)

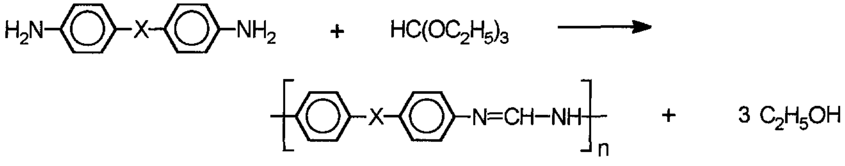
Measurements:

IR spectra were recorded on a Perkin-Elmer 1760X spectrometer using KBr discs. NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.13 MHz for ^{1}H and at 75.47 MHz for ^{13}C. The samples were measured at ambient temperature using DMSO-d_6 as solvent and internal standard (2.50 ppm and 39.56 ppm, resp.). The inherent viscosities were measured at 25°C in N,N-dimethylacetamide (DMAc) (3 wt.-% LiCl) with a Schott automatic Ubbelohde viscosimeter. The concentration was 0.5 g/dl. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC-7 at a heating and cooling rate of 10 K/min. Thermogravimetric analysis was conducted with a Perkin Elmer TGS-2 at a heating rate of 10 K/min. WAXS curves were obtained with HZG 4A-2 (Seifert - FPM, FRG) using Ni-filtered Cu-Kα-radiation.

Results and discussion

Based on the procedure described by Overberger et al. (4), a series of new polyformamidines were synthesized according to Scheme 1. In order to obtain higher molecular weights the reaction conditions were changed and optimized. In the following, different influences on the molecular weight of polyformamidine **1b** will be described.

Scheme 1



1

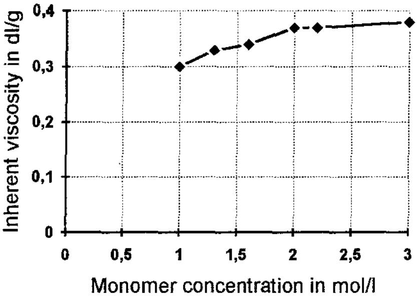
1a: X = O **1b**: X = CH_2 **1c**: X = CH_2-CH_2 **1d**: X = O-(CH_2-CH_2-O)$_2$

In accordance with the results of Overberger (4) an excess of TEOF was found to be necessary to obtain high molecular weight polymers. A part of TEOF is removed from the reaction mixture as a result of nitrogen flow and distillation of ethanol formed during the reaction. Consequently, the exact equivalency of reactants is disturbed resulting in relatively low molecular weights. The best polycondensation results were achieved with an excess of 10 mol% TEOF.

Table 1 shows the effect of monomer concentration (amount of aromatic diamine per volume solvent) on the inherent viscosity of polyformamidine **1b** prepared in DMSO. Up to a monomer concentration of 2.0 mol/l the polycondensation took place in homogeneous solution, from which polyformamidines **1b** were obtained with inherent viscosities up to 0.37 dl/g. At higher monomer concentrations the polymers precipitated from the solution.

Tab. 1 Influence of monomer concentration on the inherent viscosity of polyformamidine **1b** [a]

Monomer concentration in mol/l	Polymer	
	Yield in %	η_{inh} [b] in dl/g
1.0	92	0.30
1.3	89	0.33
1.6	90	0.34
2.0	94	0.37
2.2	94 [c]	0.37
3.0	97 [c]	0.38



[a] Reaction conditions: 10 mol % excess of TEOF, DMSO, reaction time 4 h at 140°C and further 4h at 180°C

[b] Measured in DMAc (3 wt.-% LiCl) with c = 0.5 g/dl at 25°C

[c] Polymers precipitate during the reaction

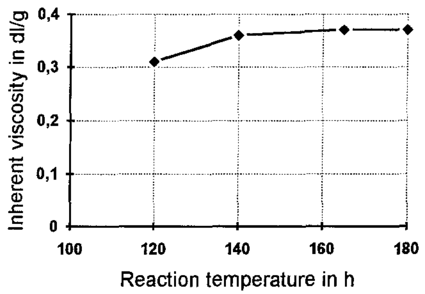
The effect of reaction temperature on the inherent viscosity of polyformamidine **1b** was examined in DMSO at a monomer concentration of 2.0 mol/l. As can be seen from Tab. 2 the inherent viscosity increases if the temperature is raised to 140°C. Further increase in temperature does not significantly influence the molecular weight. An important point to note is that the reaction temperature was only allowed to increase gradually up to the boiling point of TEOF at 146°C. Otherwise TEOF distills off without taking part in the polycondensation reaction.

Polyformamidine **1b** with the highest inherent viscosity was obtained after a reaction time of 8 h (Tab. 3). Obviously, the polycondensation is nearly complete within 8 h. A distinct prolongation of the reaction time causes a decrease of molecular weight, probably by decomposition. This is indicated by increasing coloration of polymers.

The influence of solvents on the inherent viscosity of polyformamidine **1b** is shown in Tab. 4. The synthesis of polyformamidines has been found to be possible also in NMP and DMAc. The inherent viscosities of all polymers synthesized in various solvents are approximately the same. For its carcinogenic properties we renounced the application of HMPT which had been used as polycondensation solvent by Overberger (4).

Tab. 2 Influence of reaction temperature on the inherent viscosity of polyformamidine **1b** [a)]

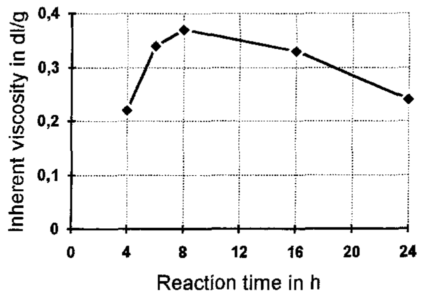
Temperature	Time	Polymer	
		Yield	η_{inh} [d)]
in °C	in h	in %	in dl/g
120	8	89	0.31
140	8	90	0.36
140/165 [b)]	8	92	0.37
140/180 [c)]	8	94	0.37



[a)] Reaction conditions: 10 mol % excess of TEOF, DMSO, monomer concentration: 2.0 mol/l
[b)] Synthesis was carried out 4 h at 140°C and further 4 h at 165°C
[c)] Synthesis was carried out 4 h at 140°C and further 4 h at 180°C
[d)] Measured in DMAc (3 wt.-% LiCl) with c = 0.5 g/dl at 25°C

Tab. 3 Influence of reaction time on the inherent viscosity of polyformamidine **1b** [a)]

Time	Temperature	Polymer	
		Yield	η_{inh} [c)]
in h	in °C	in %	in dl/g
4	140	87	0.22
6 [b)]	140/180	92	0.34
8 [b)]	140/180	94	0.37
16 [b)]	140/180	90	0.33
24 [b)]	140/180	75	0.24



[a)] Reaction conditions: 10 mol % excess TEOF, DMSO, monomer concentration 2.0 mol/l
[b)] Synthesis was carried out at 140°C during the first 4 h; the following hours at 180°C
[c)] Measured in DMAc (3 wt.-% LiCl) with c = 0.5 g/dl at 25°C

Tab. 4 Influence of solvent on the inherent viscosity of the polyformamidine **1b** [a)]

Solvent	Polymer	
	Yield	η_{inh} [b)]
	in %	in dl/g
DMSO	92	0.30
NMP	90	0.28
DMAc [c)]	86	0.26

[a)] Reaction conditions: 10 mol% excess TEOF, reaction time: 4 h at 140°C and further 4 h at 180°C, monomer concentration 1.0 mol/l
[b)] Measured in DMAc (3 wt.-% LiCl) with c = 0.5 g/dl at 25°C
[c)] Reaction temperature after 4 h at 163°C

Under the optimum reaction conditions determined, i.e. 10 mol% excess TEOF, 4 h at 140°C and 4 h at 180°C, 25.0 mmol aromatic diamine in 25 ml DMSO, four aromatic polyformamidines 1 were prepared with reasonable molecular weights. The results are summarized in Table 5.

Tab. 5 Yields and properties of aromatic polyformamidines **1**

Polymer	Yield in %	η_{inh} [a] in dl/g	Solubility [b]		
			DMAc	DMSO	DMAc/LiCl [c]
1a	96	0.25	-	o	+
1b	92	0.30	-	+	+
1c	95	0.30	-	+	+
1d	90	0.36	o	+	+

[a] Measured in DMAc (3 wt.-% LiCl) with c = 0.5 g/dl at 25°C
[b] - insoluble, o only low molecular part of polymers is soluble, + soluble
[c] DMAc with 3 wt.-% LiCl

Polyformamidines obtained in excellent yields are white powders with inherent viscosities in the range of 0.25 to 0.36 dl/g. Aromatic polyformamidines show a similar solubility behavior like aromatic polyamide. All polymers are readily soluble in strong acid, such as trifluoroacetic acid and conc. sulphuric acid and in aprotic dipolar solvents, such as DMAc (3 wt.-% LiCl) (Tab. 5). The extension of the flexible unit X in the polymer backbone causes improved solubilities of polyformamidines in aprotic dipolar solvents.

The structure of the synthesized polymers has been confirmed by IR and NMR spectroscopy and elemental analysis (Tab. 6).
The ^1H NMR spectrum of a low molecular weight polyformamidine **1b** in DMSO-d_6 and the assignment of the signals are presented in Fig. 1. The characteristic signal of the formamidine CH proton appears at 8.10 ppm as singlet. The formamidine NH signal has been observed at 9.63 ppm as broad singlet. By contrast Overberger indicated the chemical shift of this NH proton at 3.2 - 3.6 ppm (4). The amino and formamide end group signals have been clearly identified using the spectra of 4,4'-methylenedianiline and its appropriate bisformamide. Because of hindered rotation of the CN partial double bond of the formamide end group some signals appear twice (g, 8, 10 in Fig. 1 and Fig. 2) The intensities of the end group signals and the CH proton intensity of formamidine group allowed to determine the number-average molecular weights of polyformamidine **1b**.

Fig. 3 shows the lg $[\eta] = f(\lg \overline{M}_n)$ plot of polyformamidine **1b**. In a first approximation inherent viscosities η_{inh} have been used instead of $[\eta]$. From the plot the Kuhn-Mark-Houwing exponent of 0.72 could be determined, which points out a coiled chain conformation in the solvent used.

In addition, the structure of a low molecular weight polyformamidine **1b** was confirmed by ^{13}C NMR spectroscopy (Fig. 2). All signals could be assigned by increment calculations and comparison with the spectra of 4,4'-methylenedianiline and its appropriate bisformamide. The signal of the methylene group is overlapped by solvent signals.
Due to the limited solubility of some polyformamidines in DMSO, all ^1H NMR spectra were recorded in DMSO-d_6 with 3 wt.-% LiCl, in which all polymers are completely soluble. The chemical shifts of the typical N=CH-N signals are summarized in Table 6.

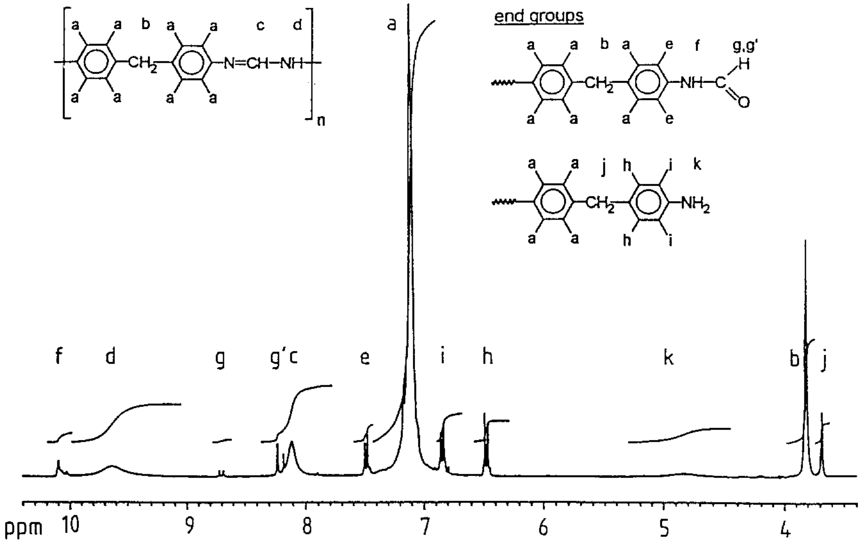


Fig. 1 ^{1}H NMR spectrum of low molecular weight polyformamidine **1b** (η_{inh}= 0.15 dl/g) in DMSO-d_6

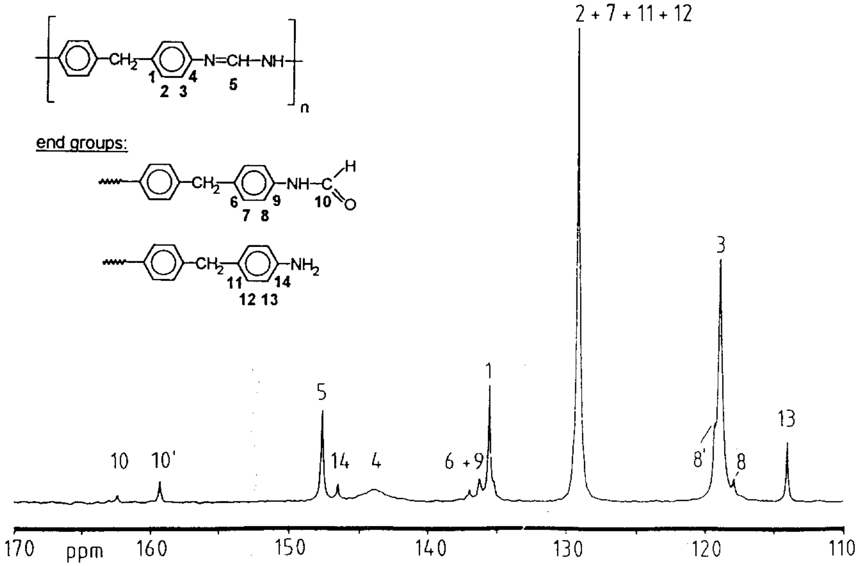


Fig. 2 ^{13}C NMR spectrum of low molecular weight polyformamidine **1b** (η_{inh} = 0.15 dl/g) in DMSO-d_6

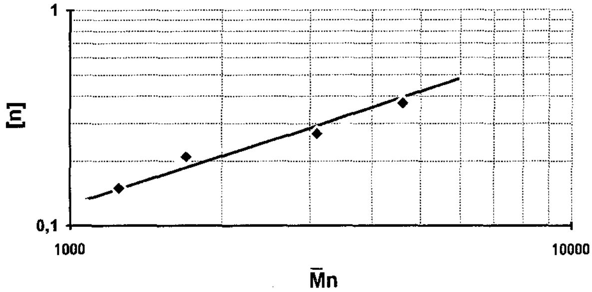


Fig. 3 lg [η] = f (lg $\overline{M}_n$) of polyformamidine **1b**

Tab. 6 IR and ^{1}H NMR spectral data and elemental analysis of polyformamidines **1**

Polymer	IR υ (C=N) in cm^{-1}	^{1}H NMR [a] δ (N=CH-N) in ppm	Elem. formula (Form. weight)	Elemental analysis	C	H	N
1a	1646	8.10	$(C_{13}H_{10}N_2O)_n$ $(210.23)_n$	Calc. Found	74.27 72.84	4.79 4.84	13.33 13.12
1b	1646	7.93	$(C_{14}H_{12}N_2)_n$ $(208.26)_n$	Calc. Found	80.75 78.50	5.81 5.83	13.45 13.03
1c	1648	7.93	$(C_{15}H_{14}N_2)_n$ $(222.29)_n$	Calc. Found	81.04 78.81	6.35 6.34	12.61 12.26
1d	1641	7.83	$(C_{17}H_{17}N_2O_3)_n$ $(297.33)_n$	Calc. Found	68.67 67.14	5.76 5.87	9.42 9.23

[a] DMSO-d_6 (3 wt.-% LiCl)

The IR spectra of all polyformamidines show characteristic absorption bands due to NH stretching vibration (near 3390 cm^{-1}), C=N stretching vibration (near 1645 cm^{-1}) and CN stretching vibration (near 1310 cm^{-1} and 1210 cm^{-1}) of the formamidine group. Furthermore, the absence of the characteristic absorption bands of amino groups at 3440 - 3340 cm^{-1} (υ(NH_2)) and 1630 cm^{-1} (δ(NH_2)) is an indication of the polymer formation.

WAXS investigations proved that aromatic polyformamidines with flexible groups in the polymer backbone are semicrystalline with a low degree of crystallinity, e.g. ; **1b**: α = 0.24. In correlation with the decreasing tendency of crystallisation the solubility is improved and the transition temperatures are distinctly lowered.

Glass transition temperatures in the range of 62°C - 161°C and melting points at 255°C - 286°C were observed by DSC (Tab. 7). Polyformamidine **1a** decomposes thermally below its melting temperature of 350°C. The thermal behavior of polyformamidines was studied by thermogravimetric analysis in air and nitrogen.

Tab. 7 Thermal properties of aromatic polyformamidines **1**

Polymer	T_g [a] in °C	T_m [a] in °C	Loss of weight at the following temperatures in °C [b]			T_{DTG} [c]
			5%	10%	30%	
1a	-	350 [d]	310	362	401	419
1b	161	286	331	357	388	410
1c	125	255	332	350	390	409
1d	62	-	342	366	385	417

[a] DSC measurements at heating and cooling rate of 10 K/min, 2nd heat after removal of solvents and cooling from the melt

[b] Termogravimetric analysis with a heating rate of 10 K/min in nitrogen

[c] Maximum temperature of the DTG -curve

[d] Due to the decomposition T_g or T_m could not be observed by DSC. The value was detected by microscopy

All polyformamidines start to decompose around 300°C in both air and nitrogen atmosphere. In all cases a 10% weight loss was observed in the temperature range of 350 - 366°C in nitrogen (Tab. 7). The thermal stability of polyformamidine **1b** is distinctly higher than that of the corresponding polyurea which is probably caused by the presence of conjugation through the formamidine groups.

Acknowledgements

We are gratefully indebted to the Bundesminister für Forschung und Technologie (project 03 M 40567) for financial support. The authors wish to thank Dr. D. Jehnichen for WAXS investigations and Mrs. Adam for recording the IR spectra.

References

1. C. Grundmann, A. Kreutzberger, *J. Polym. Sci.* **38**, 425 (1959)
2. M. Rillich, H. Komber, F. Böhme, *Polym. Bull.* **31**, 381 (1993)
3. L. J. Mathias, C. G. Overberger, *Polym. Prepr.* **19**, 63 (1978)
4. L. J. Mathias, C. G. Overberger, *J. Polym. Sci., Part A: Polym. Chem.* **17**, 1287 (1979)
5. W. A. Feld, B. Ramalingam, F. W. Harris, *J. Polym. Sci., Polym. Chem. Ed.* **21**, 319 (1983)

Received: 25 April 1994/Revised version: 23 June 1994/
Accepted: 27 June 1994