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Polymers containing formamidine groups

3. Synthesis and properties of aromatic polyformamidines

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Summary

New aromatic polymers containing formamidine groups were prepared by high temperature solution polycondensation of triethyl orthoformate with various aromatic diamines. The resulting polyformamidines were characterized by elemental analysis, IR and ^{1}H NMR spectroscopy, viscosity measurements, thermogravimetry, DSC- and WAXS measurements. With few exceptions aromatic polyformamidines show excellent solubility in polar solvents and strong acids, but they were gradually decomposed in extended contact with moisture. Polyformamidines containing rigid para structures are well crystallizing materials, which was proved by WAXS investigations. Glass transition temperatures in the range of 62 - 163 °C were observed for semicrystalline or amorphous polymers. All aromatic polyformamidines are thermally stable in nitrogen up to 300°C.

Introduction

Up to now polymers containing formamidine groups have only rarely been synthesized and investigated. Only few information about the properties of aliphatic polyformamidines obtained from aliphatic diamines and s-triazine as well as aromatic polyformamidines prepared from aromatic diamines and triethyl orthoformate (TEOF) have been given in the known literature (1-3).

Recently we found that the synthesis of aliphatic polyformamidines by solution polycondensation of aliphatic diamines and TEOF is only successful in the presence of catalytic amount of acid (4). The resulting polymers having inherent viscosities up to 0.19 dl/g are readily soluble in common organic solvents and strong acids, but they are gradually decomposed in the extended contact with moisture. In our previous paper (5) we reported on the preparation and characterization of the polyformamidine derived from 4,4'-methylenedianiline and TEOF. The influence of reaction conditions on the molecular weight of this polyformamidine was investigated in detail.

The present paper deals with the synthesis and properties of new aromatic polyformamidines prepared by high temperature solution polycondensation of TEOF and various aromatic diamines. Solubility, hydrolytic stability, thermal properties and the results of X-ray investigations of these polymers have also been discussed.

Experimental

Materials:

1,4-bis(4-aminobenzoyloxy)butane **1l** and bis[2-(4-aminobenzoyloxy)ethyl]-ether **1m** were prepared from 4-nitrobenzoyl chloride and the appropriate aliphatic diol (6) followed by

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reduction of the dinitro compounds with hydrazine/ Raney-Ni. Bis[2-(4-aminophenoxy)ethyl]ether **1k** was synthesized by reduction of the appropriate dinitro compound which had been prepared by an aromatic nucleophilic substitution of 1-fluoro-4-nitrobenzene and diethylene glycol (7). All other diamines were used without further purification if they were received from the manufactures with a high purity. Otherwise they were purified by recrystallization from ethanol. Triethyl orthoformate (TEOF) and dimethyl sulfoxide (DMSO) were stored over molecular sieves and purified by distillation prior to use.

Polycondensation:

The preparation of polyformamidines was carried out as described previously (5). Polyformamidines obtained were characterized by elemental analysis, IR and ^1H NMR spectroscopy. The results are summarized in Tab. 2.

Measurements:

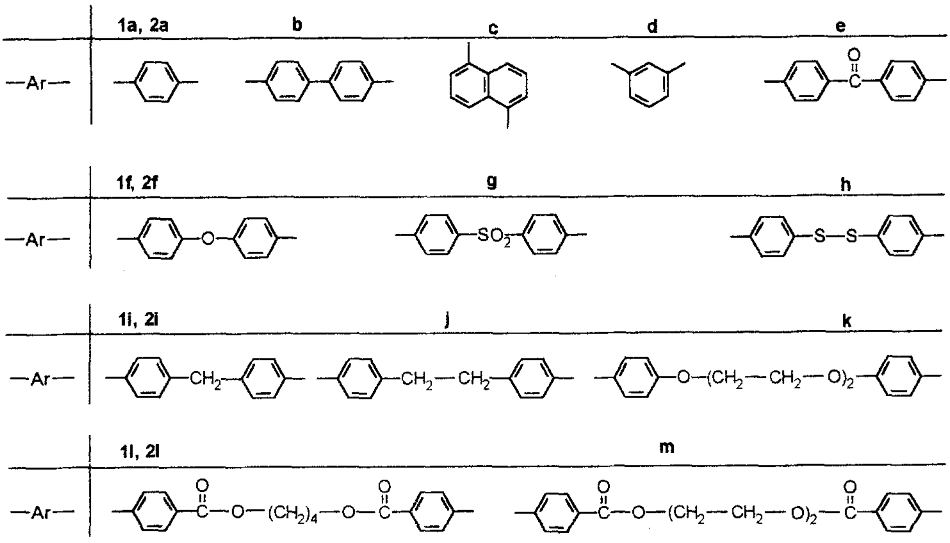
Infrared spectra were recorded on a Perkin-Elmer 1760X spectrometer using KBr discs. ^1H NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.13 MHz. The samples were measured at ambient temperature using DMSO-d_6/LiCl (3 wt.-%) as solvent and internal standard (2.50 ppm). The inherent viscosities were measured at 25°C in DMAc (3 wt.-% LiCl) or in conc. sulphuric acid with a Schott automatic Ubbelohde viscosimeter. The concentration was 0.5 g/dl in all cases.

DSC measurements were performed on a Perkin Elmer DSC-7 at a heating and cooling rate of 10 K/min. For the thermogravimetric investigations a Perkin Elmer TGS-2 (heating rate of 10 K/min) was used. WAXS curves were obtained with HZG 4A-2 (Seifert - FPM, FRG) using Cu-K_α-radiation.

Results and discussion

A series of novel polyformamidines **2** were synthesized from various aromatic diamines **1** and triethyl orthoformate by high temperature polycondensation in DMSO.

$$\underset{\mathbf{1}}{H_2N{-}Ar{-}NH_2} \;+\; HC(C_2H_5O)_3 \;\longrightarrow\; \underset{\mathbf{2}}{\left[Ar{-}N{=}CH{-}NH \right]_n} \;+\; 3\,C_2H_5OH$$



Most of the reactions proceeded readily in homogeneous solutions by using the conditions described in Tab. 1. In some cases, **1a**, **1b**, **1c** and **1e**, the resulting polymers precipitated during the polycondensation. The results of polycondensations are given in Tab. 1. The white to deep yellow polymers were isolated in good yields with inherent viscosities of 0.13 - 0.56 dl/g.

Tab. 1 Preparation of polyformamidines **2** from triethyl orthoformate and various aromatic diamines **1** [a)]

Polymer	Appearence [b)]	Yield in %	η_{inh} [c)] in dl/g	Colour
2a	P	95	0.22 [d)]	Yellow
2b	P	96	0.56	Yellow
2c	P	88	0.18	Light brown
2d	S	92	0.18	White
2e	P	93	0.13 [d)]	Yellow
2f	S	96	0.25	White
2g	S	87	0.13	Light brown
2h	S	87	0.10	Yellow
2i	S	92	0.30	White
2j	S	95	0.30	White
2k	S	90	0.36	White
2l	S	90	0.13	White
2m	S	87	0.13	White

[a)] Polycondensations were carried out using 25.0 mmol aromatic diamine and 27.5 mmol TEOF in 25 ml DMSO at 140°C for 4h and another 4h at 180°C.
[b)] P = polymer precipitates; S = homogeneous solution
[c)] Inherent viscosities were measured with c = 0.5 dl/g in DMAc (3 wt.-% LiCl) at 25°C
[d)] Measured with c = 0.5 dl/g in conc. sulfuric acid at 25°C

The ^{1}H NMR and IR spectra of all polyformamidines as well as the results of elemental analysis are in agreement with the supposed structures. The chemical shift of the typical N=CH-N signals and the characteristic C=N stretching vibration bands of the formamidine group are summarized in Tab. 2.

All polyformamidines prepared were insoluble in common organic solvents like benzene and chloroform. Polymer **2d** containing m-phenylene units and polymers with large flexible groups in the polymer backbone, for example **2l** and **2m**, showed excellent solubility even in DMAc (Tab. 3). Some polymers with rigid para structures, such as **2a**, **2b**, **2c** and **2e**, are insoluble in polar solvents like DMAc and DMSO. This may be caused by the high crystallinity of these polymers, which was evidenced by WAXS measurements (Tab. 3). All polymers except **2a** and **2e** were completely soluble in DMAc with 3 wt.-% LiCl. Furthermore they possess with few exceptions an excellent solubility in very strong acids listed in Tab. 3, which is probably caused by the formation of polyformamidinium salts.

The thermal behaviour of the polymers was evaluated by means of differential scanning calorimetry (DSC) and thermogravimetry (TG) (Tab. 4). Polymers with rigid para structures, like **2a**, **2b**, **2c** and **2e**, decompose below their melting temperatures (T_m). For these polymers glass transition temperatures (T_g) could not be detected by DSC. WAXS investigations showed that such polyformamidines having a small solubility in organic solvents are materials with a considerable degree of crystallinity.

Tab. 2 IR and ^{1}H NMR data and elemental analysis of polyformamidines **2**

Polymer	IR ν (C=N) in cm-1	^{1}H NMR [a] δ (N=CH-N) in ppm	Formula (Mol. weight)	Elemental analysis			
					C	H	N
2a	1631	- [b]	$(C_7H_6N_2)_n$	Calc.	71.17	5.12	23.71
			$(118.14)_n$	Found	68.42	5.16	22.50
2b	1642	8.10	$(C_{13}H_{10}N_2)_n$	Calc.	80.39	5.19	14.42
			$(194.24)_n$	Found	77.33	5.48	13.46
2c	1638	- [b]	$(C_{11}H_8N_2)_n$	Calc.	78.55	4.79	16.66
			$(168.20)_n$	Found	75.76	4.97	15.71
2d	1650	8.07	$(C_7H_6N_2)_n$	Calc.	71.17	5.12	23.71
			$(118.14)_n$	Found	68.48	5.22	22.43
2e	1646	- [b]	$(C_{14}H_{10}N_2O)_n$	Calc.	75.66	4.54	12.60
			$(222.25)_n$	Found	73.56	4.72	12.03
2f	1646	8.10	$(C_{13}H_{10}N_2O)_n$	Calc.	74.27	4.79	13.33
			$(210.23)_n$	Found	72.84	4.84	13.12
2g	1648	8.23	$(C_{13}H_{10}N_2O_2S)_n$	Calc.	60.45	3.90	10.85
			$(258.29)_n$	Found	58.02	4.15	10.12
2h	1644	8.03	$(C_{13}H_{10}N_2S_2)_n$	Calc.	60.44	3.90	10.84
			$(258.33)_n$	Found	59.37	4.03	10.46
2i	1646	7.93	$(C_{14}H_{12}N_2)_n$	Calc.	80.75	5.81	13.45
			$(208.26)_n$	Found	78.50	5.83	13.03
2j	1648	7.93	$(C_{15}H_{14}N_2)_n$	Calc.	81.04	6.35	12.61
			$(222.29)_n$	Found	78.81	6.34	12.26
2k	1641	7.83	$(C_{17}H_{17}N_2O_3)_n$	Calc.	68.67	5.76	9.42
			$(297.33)_n$	Found	67.14	6.07	9.23
2l	1648	8.19	$(C_{19}H_{18}N_2O_4)_n$	Calc.	67.45	5.36	8.28
			$(338.33)_n$	Found	66.07	5.34	8.41
2m	1649	8.15	$(C_{19}H_{18}N_2O_5)_n$	Calc.	64.40	5.12	7.90
			$(354.33)_n$	Found	62.64	5.20	8.29

[a] Measured in DMSO-d_6 (3 wt.% LiCl) at 300 MHz

[b] not detected

So the general rule that the solubility decreases with increasing crystallinity has been confirmed. In order to increase the solubility and to reduce T_m below the temperature of decomposition, the para substituted aromatic units were replaced by kinked and flexible units, respectively. Depending on the monomer structure used the thermal properties of polyformamidines could be varied within a wide range.

Polyformamidines with flexible groups in the polymer backbone are semicrystalline with a low degree of crystallinity or almost amorphous (Tab. 3). For these polymers glass transition temperatures could be detected by DSC in the range from 62°C - 163°C. With increasing length of flexible units in the polymer backbone both T_g and T_m of these polyformamidines are distinctly lowered.
Thermogravimetric analysis indicates that all polyformamidines are thermally stable without significant weight loss up to temperatures of 300°C in nitrogen atmosphere (Tab. 4). A 10% weight loss was recorded in the range of 327 - 422°C in nitrogen depending on the structure. The maximum of decomposition rate was observed in the temperature range of 385 - 457°C.

Tab. 3. Solubility and crystallinity of polyformamidines **2** a)

Polymer	Solubility b)						Crystallinity c)
	DMAc	DMSO	DMAc +3 wt.-% LiCl	conc. H_2SO_4	TFA	HFIP	
2a	-	-	+-	+	+	+	0.66
2b	-	-	+	-	-	+-	0.46
2c	-	-	+	+	+	-	- d)
2d	+	+	+	+	+	+	0.14
2e	-	-	+-	+	-	-	0.72
2f	-	+-	+	+	+	+	0.20
2g	+	+	+	+	+	+-	0.27
2h	+	+	+	+	+	+	0.23
2i	-	+	+	+	+	+	0.24
2j	-	+	+	+	+	+	0.16
2k	+-	+	+	+	+	+	- d)
2l	+	+	+	+	+	+	- d)
2m	+	+	+	+	+	+	- d)

a) +: Soluble at room temperature; +-: partially soluble; -: insoluble.

b) DMAc: N,N-dimethylacetamide; DMSO: dimethyl sulfoxide; TFA: trifluoroacetic acid; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol.

c) Detected by WAXS investigations

d) not detected

Tab. 4. Thermal properties of polyformamidines **2**

Polymer	T_g a) in °C	T_m b) in °C	Loss of weight at the following temperatures in °C c)		T_{DTG} d) in °C	Char yield e) in %
			5%	10%		
2a	-	> 380 (dec.)	398	422	457	20
2b	-	> 380 (dec.)	317	350	385	35
2c	-	> 380 (dec.)	322	361	395	67
2d	not det.	255	294	334	393	31
2e	-	> 380 (dec.)	319	365	431	29
2f	-	350 (dec.)	310	362	419	18
2g	163	261	337	370	414	23
2h	98	238	295	327	335	24
2i	161	285	331	357	410	21
2j	125	265	332	350	409	16
2k	62	145	342	366	417	28
2l	91	228	332	357	422	15
2m	77	165	345	372	409	18

a) Glass transition temperature from DSC measurements at a heating and cooling rate of 10 K/min, second heat after removal of solvents

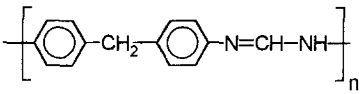
b) Observed by microscopy

c) Thermogravimetry at a heating rate of 10 K/min in nitrogen

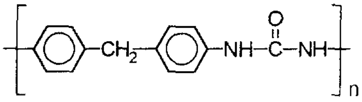
d) Maximum temperature of the DTG -curve

e) Residual weight-% at 600°C in nitrogen

Comparative investigations showed that the polyformamidine group is thermally more stable than the urea group. The TG curves of the following types of polymers



2i



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are shown in Fig. 1. The differences in thermal behaviour may be caused by conjugation effects through the respective bridging group. So polyurea **3** with a similar structure like polyformamidine **2i** has a lower thermal stability in both nitrogen and air atmosphere.

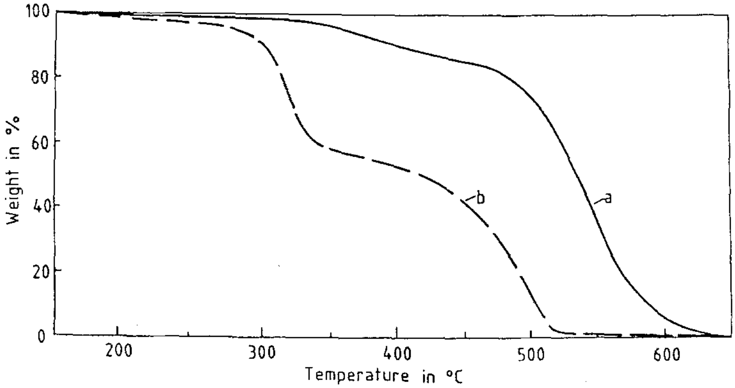

Fig.1 TG curves of polyformamidine **2i** (a) and polyurea **3** (b) in air

One essential disadvantage of polyformamidines is their insufficient hydrolytic stability. Polyformamidines easily decompose in water or organic solvents containing water. Especially in the presence of acids polyformamidines hydrolyze to the corresponding diamines and formamides, which then hydrolyze, but more slowly, to formic acid and aromatic diamine.

Summarizing, it can be stated that aromatic polyformamidines are characterized by reasonable thermal stability. Furthermore they are soluble in aprotic dipolar solvents and strong acids. However, insufficient hydrolytic stability causes a restricted applicability of this type of polymers.

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