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Polymers containing formamidine groups

1. Synthesis and characterization of aliphatic polyformamidines

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Summary

Aliphatic polyformamidines have been synthesized by reaction of aliphatic diamines with triethyl orthoformate in presence of catalytic amounts of acetic acid. The reaction has been carried out in DMSO at 180°C. The polymer structure has been confirmed by IR and NMR spectroscopy. For determination of molecular weights ^{1}H NMR end group signals have been used.

Introduction

Only few examples of polyformamidines are known from the literature. Mathias et al. (1) reported on the synthesis of aromatic polyformamidines by solution polycondensation of aromatic diamines with triethyl orthoformate (TEOF). Aliphatic polyformamidines were synthesized for the first time by Grundmann et al. (2). The authors described a two step condensation procedure of aliphatic diamines with s-triazine. In a first step, oligoamidines were prepared with an index of repeating units n = 2 or 5 and in a second step, oligoamidines were thermally converted in vacuo to polyformamidines with molecular weights in the range of 5000 - 6000 daltons. In the present paper we report on the synthesis of aliphatic polyformamidines by reaction of aliphatic diamines with triethyl orthoformate in the presence of a small amount of acetic acid. The solubility as well as the IR and NMR spectra of these polymers have been discussed.

Experimental

Materials:
All aliphatic diamines were purchased from Fluka and used without purification. Triethyl orthoformate (TEOF) and dimethyl sulfoxide (DMSO) were stored over molecular sieves and purified by distillation prior to use.

Polycondensations:
All polycondensations were carried out under nitrogen atmosphere. A 10 mol% excess of TEOF and three drops of acetic acid were added to aliphatic diamine (0.05 mol) in 33 ml DMSO. The temperature of the reaction mixture was gradually raised to 140°C and maintained there for 4 hr. The reaction temperature was then brought to 180°C and held for another 4 hr. After cooling, the precipitated polymer was filtered, extracted for 5 hr in a Soxhlet with acetone and dried in vacuo at 70°C for 3 hr. It is

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important to note that both synthesis and processing of the polyformamidines were carried out under exclusion of moisture.

Measurements:
IR spectra were recorded on a Perkin-Elmer 1760X spectrometer using KBr discs. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C. The samples were measured at ambient temperature using $CDCl_3$ as solvent and as internal standard (7.26 ppm and 77.0 ppm, resp.). The inherent viscosities were measured by an automated Ubbelohde viscosimeter thermostated at 25°C. Solutions of 100 mg polymer in 20 ml chloroform were used in all cases.

Results and discussion

Taylor et al. (3) synthesized a number of symmetrical N,N'-dialkyl-formamidines by reaction of aliphatic amines with TEOF in presence of acetic acid. The authors mentioned that the amount of acetic acid strongly influenced the yield of reaction. The highest yields were found for equimolar amounts of acetic acid. This should be caused by formation of formamidinium acetate salts separating from the reaction mixture during the reaction. We tried to use this procedure for synthesis of aliphatic polyformamidines starting from aliphatic diamines according to the following reaction scheme.

$$H_2N\text{-}R\text{-}NH_2 \;+\; HC(OC_2H_5)_3 \;\longrightarrow\; \underset{\mathbf{1}}{\left[R\text{-}N{=}CH\text{-}NH\right]_n} \;+\; 3\,C_2H_5OH$$

Under the same reaction conditions as used by Taylor et al. (3) the polymer synthesis failed. We assume that only oligomers can be formed because of formamidinum salt formation separating from the reaction mixture . Therefore the reaction procedure was modified.
We carried out this polycondensation reaction in DMSO as solvent at 180°C in presence of catalytic amounts of acetic acid. Under these reaction conditions a series of aliphatic polyformamidines **1** could be obtained with reasonable molecular weights. Attempts to prepare polyformamidine in absence of acetic acid failed. The results are summarized in Table 1.

Polyformamidines obtained in excellent yields are white or slightly yellow crystalline solids, which gradually decompose in extended contact with moisture. All polymers are readily soluble in ethanol, chloroform and strong acids, such as trifloroacetic acid and conc. sulphuric acid, but insoluble in acetone and DMSO. The polyformamidines show inherent viscosities in the range of 0.14 to 0.19 dl/g. The structure of the polymers synthesized has been confirmed by IR and NMR spectroscopy and elemental analysis (Tab.1).

The IR spectrum of the polyformamidine **1b** is presented in Figure 1 to illustrate the characteristic bands of those polymers. The characteristic -N=C- absorption of formamidine group occurs between 1664 and 1642 cm^{-1}. The IR spectra of all polyformamidines show absorption bands due to NH stretching vibration (3222 - 3202 cm^{-1}), CH stretching vibration (3029 - 3012 cm^{-1}) and NH deformation vibration

Table 1. Yields and properties of aliphatic polyformamidines **1**, prepared from triethyl orthoformate and various aliphatic diamines

Polymer	R	Yield in %	η inh [a] in dl/g	DP_n [b]	Elem.formula (Form. weight)	Elemental analysis				T_m in °C
							C	H	N	
1a	$(CH_2)_4$	85	0,16	-	$(C_5H_{10}N_2)_n$	Calc.	61.19	10.27	28.54	105 - 108
					$(98.1)_n$	Found	61.03	10.11	28.37	
1b	$(CH_2)_6$	86	0,16	17	$(C_7H_{14}N_2)_n$	Calc.	66.61	11.19	22.20	108 - 112
					$(126.1)_n$	Found	66.65	11.21	22.00	
1c	$(CH_2)_7$	88	0,14	17	$(C_8H_{16}N_2)_n$	Calc.	68.51	11.51	19.98	95 - 97
					$(140.1)_n$	Found	68.27	11.62	19.76	
1d	$(CH_2)_8$	92	0,19	16	$(C_9H_{18}N_2)_n$	Calc.	70.06	11.77	18.17	102 - 105
					$(154.1)_n$	Found	69.91	12.03	18.06	
1e	$(CH_2)_9$	87	0,15	14	$(C_{10}H_{20}N_2)_n$	Calc.	71.36	11.99	16.64	104 - 107
					$(168.2)_n$	Found	70.82	12.56	16.39	
1f	$(CH_2)_{10}$	91	0,17	18	$(C_{11}H_{22}N_2)_n$	Calc.	72.46	12.17	15.37	104 - 106
					$(182.2)_n$	Found	72.17	12.59	15.15	
1g	$(CH_2)_{12}$	94	0,14	12	$(C_{13}H_{26}N_2)_n$	Calc.	74.21	12.47	13.32	105 - 107
					$(210.2)_n$	Found	73.98	12.62	13.22	

[a] Inherent viscosity measured at 25°C with c = 0.5 g/dl in $CHCl_3$

[b] Number - average degree of polycondensation determined by ^1H NMR using the intensities of the end group signals (a) and (c) and the CH-proton (A) intensity of formamidine groups in Fig.2

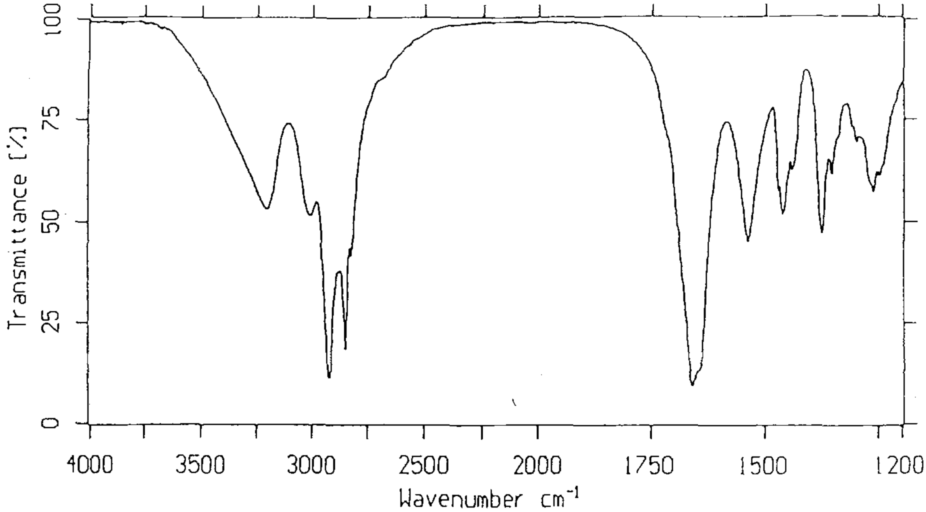

Fig. 1. IR spectrum of polyformamidine **1b**

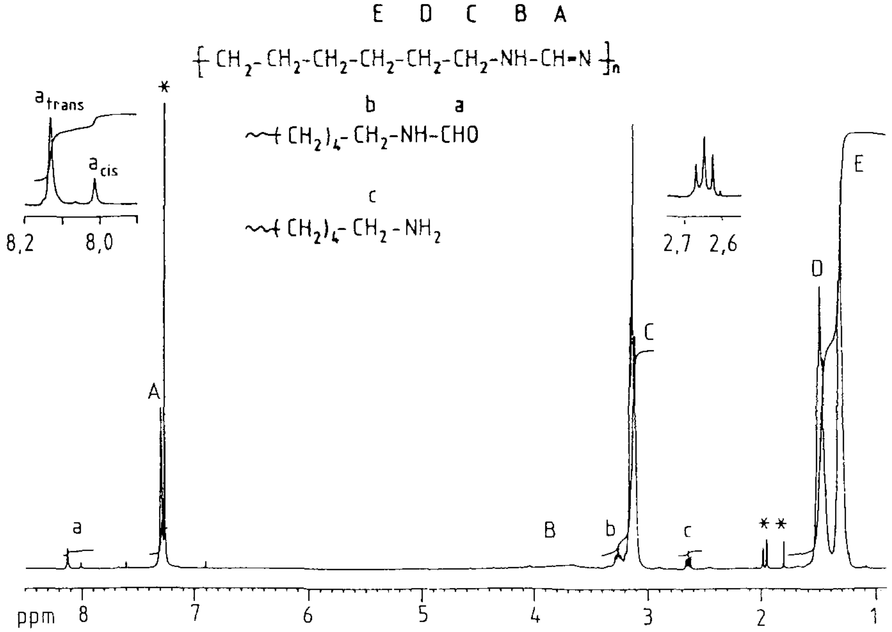

Fig. 2. 300 MHz ^1H NMR spectrum of polyformamidine **1b** in $CDCl_3$ (* $CHCl_3$ and impurities

(1556 -1533 cm^{-1}) of the formamidine group. This result agrees with the IR absorption regions of N,N'- disubstituted amidines (4,5). Furthermore, the absence of the characteristic absorption bands of amino groups at 3330 - 3168 cm^{-1} ($\upsilon(NH_2)$) and 1606 cm^{-1} (δ (NH_2)) is indicative of polymer formation.

The ^1H NMR spectrum of **1b** (Fig.2) is typical of all polyformamidines synthesized. The characteristic signal of the formamidine CH proton appears at 7.29 ppm as singlet. The methylene group signals have been observed at 3.13 ppm (α-position to formamidine group), 1.49 ppm (β-position) and 1.30 ppm (γ- and higher position). The NH proton of the formamidine group is exchanged between both nitrogens and give a broad signal at about 3.7 ppm.
These assignments for polyformamidine agree well with those for N,N'-dialkylformamidines in $CDCl_3$ (6).·The amino and formamide end group signals have been identified using diaminohexane and N,N'-bisformyl-diaminohexane as model compounds. Two signals have been observed for the N-CHO proton due to its position relative to the alkyl chain. The *trans* - arrangement predominates (7).

The ^{13}C NMR signals of the polymer chain of **1b** appear at 151.9 ppm (N=CH-NH), 48.8 ppm (α-CH_2), 31.2 ppm (β-CH_2) and 26.8 ppm (γ-CH_2) and confirm the structure. The signal of the α-carbon is broadened due to the exchange of the NH-proton. The carbonyl signals of both formamide end group conformations appear at 161.0 ppm (*trans*) and 164.6 ppm (*cis*).

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