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Poly(amidine)s and Poly(guanidine)s – Synthesis and Some Properties

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Synopsis

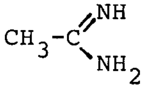
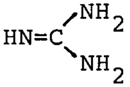
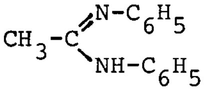
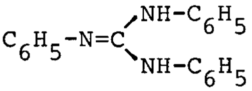
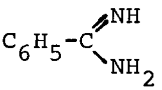
Several poly(amidine) and poly(guanidine) copolymers and their hydrochloride salts were synthesized by introducing the functional groups into suitable polymers. The properties of the resulting copolymers were investigated by base and acid titration.

Introduction

Our laboratory has been successfully using poly-(4-pyridyl ethene) for capturing mineral acids, HCl e. g., from organic reactions and for solvent purification[1]. For a more quantitative removal of mineral acids need arose to have polymers at hand with pendant groups the pK_b of which is markedly lower than for pyridine itself (pK_b = 8.91)[2].

Amidines and guanidines are very strong bases which surmount pyridine appreciably in base strength, a few examples of which are given in Tab.1. Our initial investigations to synthesize the free polymer bases are described in this communication.

Table 1

Amidine Formulae	pK_b	Guanidine Formulae	pK_b
 $CH_3\text{-}C(=NH)\text{-}NH_2$	1.60[3]	 $HN{=}C(NH_2)_2$	.40[4]
 $CH_3\text{-}C(=N\text{-}C_6H_5)\text{-}NH\text{-}C_6H_5$	5.70[3]	 $C_6H_5\text{-}N{=}C(NH\text{-}C_6H_5)_2$	4.90[5]
 $C_6H_5\text{-}C(=NH)\text{-}NH_2$	2.40[3]		

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Preparation of the polymers

Poly(amidine)s

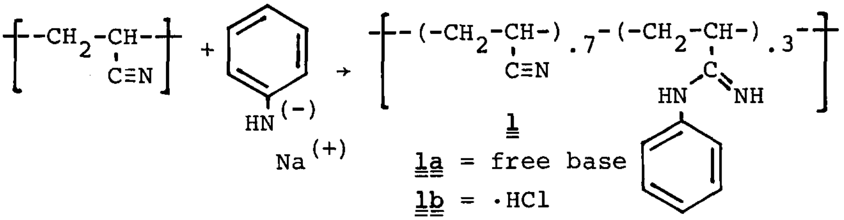
There are two general routes by which amidines can be synthesized:

A) reaction of nitriles with alkaliamide of a primary amine[6],
B) reaction of a nitrile with a primary amine in the presence of $AlCl_3$[7].

We have both the routes applied to the synthesis of poly(amidine)s.

Method A:

5 g Poly(acrylonitrile)[8] in 150 cc aniline was reacted with 2.5 g sodium at 423K for 18 hr. A dark brown material precipitated from the solution and after washing with water the polymer contained 30% of free base amidine groups. At this degree of conversion of nitrile groups to amidine groups the copolymer was insoluble either in acidified or in basic water.



1

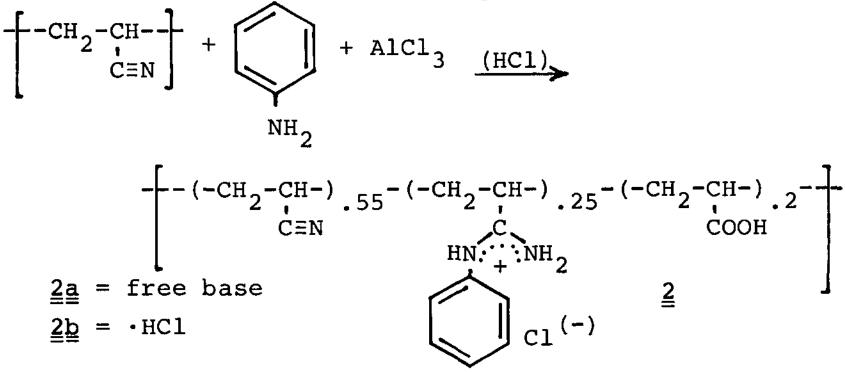
1a = free base

1b = ·HCl

Aliphatic primary amines proved to be less reactive because of their low boiling temperatures (we did not investigate these reactions in an autoclave).

Method B:

Reaction of 5 g poly(acrylonitrile) with equimolar amounts of aniline and $AlCl_3$ in boiling toluene



2a = free base

2b = ·HCl

2

suspension yielded a copolymer which, after treatment with dilute HCl, was soluble in water with an intensive green color. From IR and elemental analysis data a minor fraction of nitrile groups was converted to carboxilic acid groups.

Both these reactions were also applied to cross linked poly(acrylonitrile) and the corresponding cross linked amidines were thus obtained.

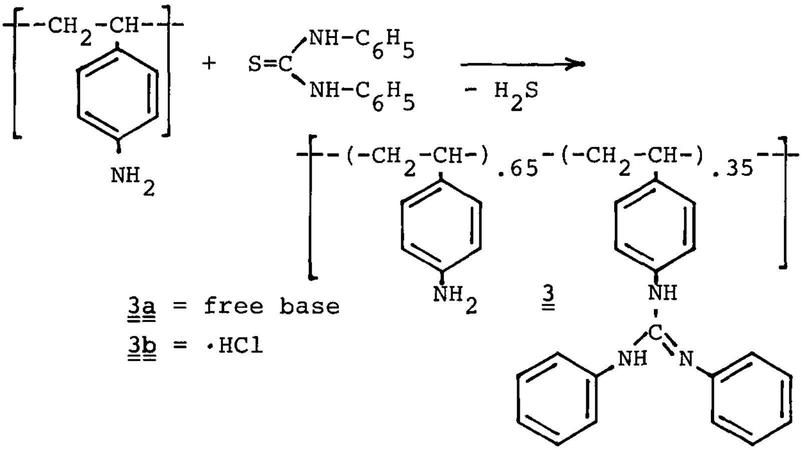
Poly(guanidine)s

Again, for the guanidine synthesis there are two general routes known in the literature:

A) reaction of aniline with N,N'-diphenyl thiourea under the evolution of H_2S to form N,N',N''-triphenyl guanidine[9],
B) reaction of aniline with methylisothiuronium sulfate under the evolution of methylmercaptane to form N-phenyl guanidine[10].

We have both these routes applied to poly(p-amino styrene) for the synthesis of poly(guanidine)s.

Method A:



3a = free base

3b = ·HCl

3

To a solution of 500 mg poly(4-aminostyrene)a)[11] in 70 cc DMF, 1.14 g N,N'-diphenyl thiourea was added, the solution was refluxed for 3 hr, whereby a large quantity of H_2S escaped through the reflux condenser. After a while a solid material precipitated. The polymer was filtered, washed thoroughly with water, and dried in vacuo at 323K. 750 mg polymer was recovered. IR: 670, 715, 775, 840, 1110, 1275, 1540, 1685 cm^{-1}.

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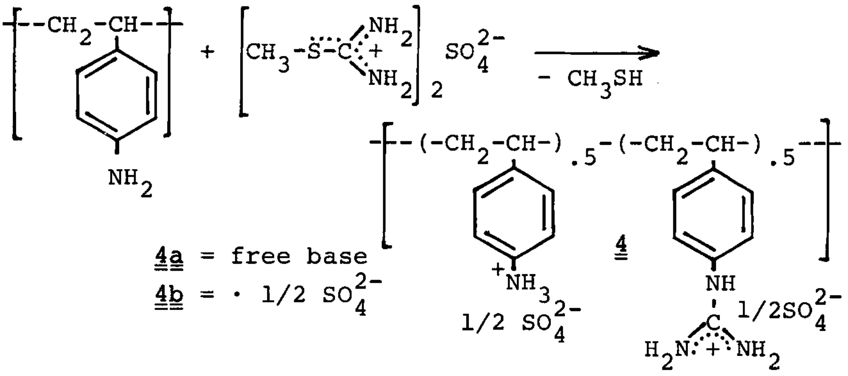
a) This polymer was prepared from poly(4-nitrostyrene) by reduction with phenylhydrazin; it contained, after all, a small fraction of unreacted 4-nitrostyrene units.

Method B:



4a = free base
4b = · 1/2 SO_4^{2-}

A mixture of 500 mg poly(4-aminostyrene), 700 mg methylisothiuronium sulfate[12] was stirred at 393K for several hr. From time to time methylmercaptane was removed in vacuo. The polymer precipitated from the solution, it was filtered with suction, washed successively with water, ethanol, and ether, and was dried in vacuo at 323K. 700 mg of polymer was recovered.
IR: 845, 1120, 1435, 1540, 1700 cm^{-1}.

Both these reactions were also applied to cross linked poly(4-aminostyrene) and the corresponding cross linked guanidines were thus obtained.

Titration experiments

The polymers were titrated in water solution and suspension, respectively. For pH measurements an INGOLD HA 405-60 electrode was used attached to a digital pH meter type 643 of Fa. KNICK, FRG.

Poly(amidine)s

Fig.1 presents titration curves of polymer 1, in which A is the titration curve of 1b as the hydrochloride salt, and 1a the free base. The vertical lines in the diagrams indicate the neutral points as they were calculated from copolymer composition. In this heterophase titration -the polymer is and remains insoluble throughout the titration experiment- we have observed that after the addition of a few drops of base or acid, respectively, it acquires several minutes before a constant pH is reached. This phenomenon derives from heterophase protonation and deprotonation reaction. As the experiments are carried out with the cross linked copolymers, this effect is even more evident.

The titration curves of the water soluble linear copolymer 2 exhibit two equivalent plateaus which belong to the two different functional groups in the copolymer sensitive to base or acid addition which immediately react.

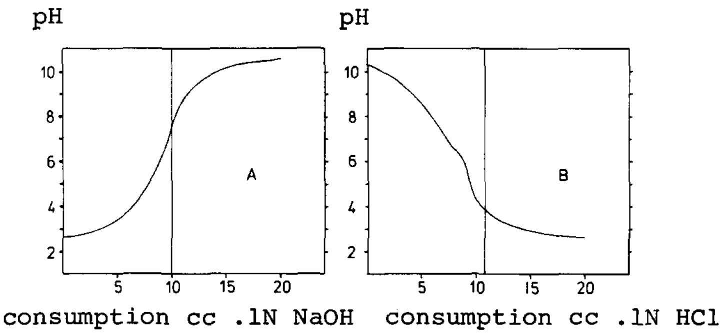


Fig.1 Titration curves of copolymer **1**
A: 500 mg **1b** in 100 cc H_2O at 318K with .1N NaOH
B: 500 mg **1a** in 100 cc H_2O at 318K with .1N HCl

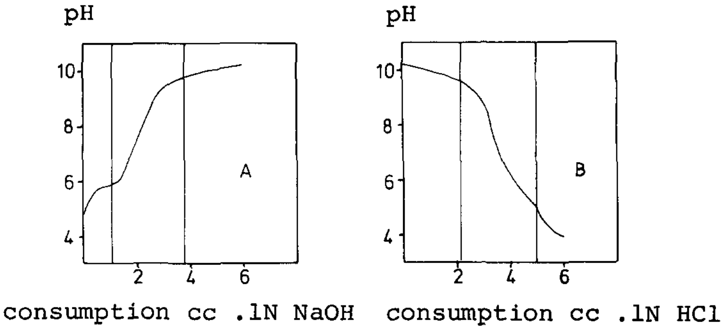


Fig.2 Titration curves of copolymer **2**
A: 100 mg **2b** in 100 cc H_2O at 318K with .1N NaOH
B: 100 mg **2a** in 100 cc H_2O at 318K with .1N HCl

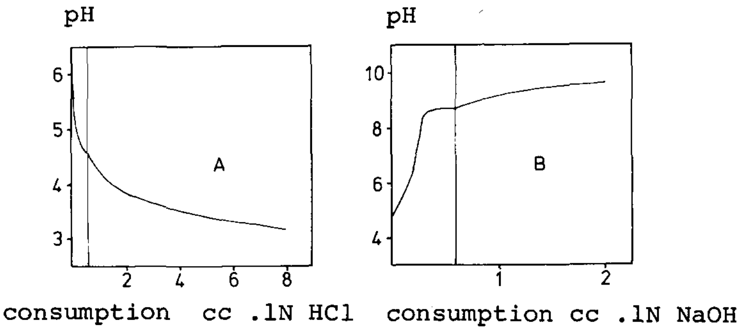
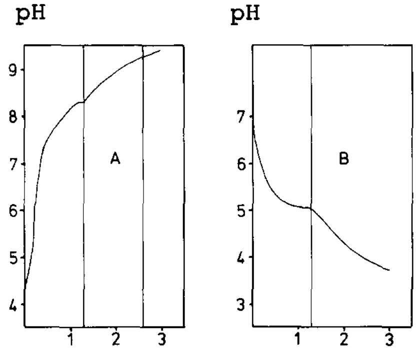


Fig.3 Titration curves of copolymer **3**
A: 100 mg **3a** in 100 cc H_2O at 318K with .1N HCl
B: 100 mg **3b** in 100 cc H_2O at 318K with .1N NaOH

Poly(guanidine)s

Both the copolymers **3** and **4** were insoluble during the titration experiments. We therefore again observed



consumption cc .1N NaOH consumption cc .1N HCl

Fig.4 Titration curves of copolymer 4

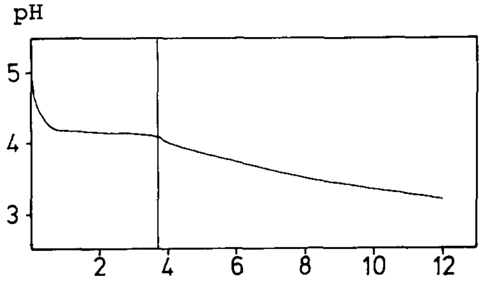
A: 100 mg 4a in 100 cc H_2O at 318K with .1N NaOH

B: 100 mg 4b in 100 cc H_2O at 318K with .1N HCl

a slow reaction with acid or base, respectively, at the beginning which is very fast near the equivalent point.

After acid titration of 3, Fig.3, the polymer was isolated, identified by elemental analysis which proved the polymer to be the corresponding hydrochloride, and then titrated with base to give the same equivalent point. This indicates that the amino groups in the polymer resulting from the incomplete conversion to guanidine residues are by far weaker bases.

Fig.4 presents the same experiments for copolymer 4.



consumption cc .1N HCl

Fig.5 Titration curve of 100 mg poly(4-pyridyl ethene)

In poly(4-pyridyl ethene) titration, Fig.5, at a consumption of 3.7 cc .1N HCl, the equilibrium of proton takeup by the polymer is attained and further acid addition only induces a slow decrease of solution pH.

Table 2

Proton Acceptor Capacity of Different Polymers

Polymer	%f.g.	mmole f.g. /100 mg	V(cc)	V'=V/mmole f.g.	V'/ %f.g.
P4PE	100	.95	3.7	3.89	.039
1a	30	.370	3.3	8.92	.297
2a	25	.324	2.8	8.64	.346
3a	35	.188	2.1	11.17	.319
4a	50	.357	3.0	8.4	.168

f.g. = functional groups monomer in copolymer
V = acid consumption/100 mg copolymer

From Tab.2 it becomes obvious that the amidine and guanidine copolymers the synthesis of which has been described in this contribution, are by one order of magnitude better proton acceptors compared to poly-(4-pyridyl ethene) which we have hitherto been using.

Acknowledgement

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