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An ionene with spirane structure (spiroionene)

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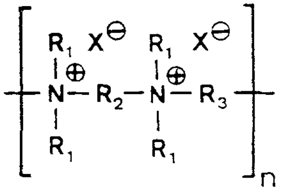
Abstract

The secondary diamine 1,3,5,7-tetrahydro[1,2c:4,5c']benzodipyrrole (**3**) and 1,2,4,5-tetrabromomethylbenzene (**1**) form a polymeric ionene with spirane structure through a repetitive alkylation reaction. The structure of the product could be proven by ^{13}C-NMR spectroscopy by comparison with suitable reference compounds. Solutions in aqueous methanol exhibit a typical polyelectrolyte effect. Variation of the counterions produces sufficient solubility in organic solvents. From the crystal structure of a similar model compound one can conclude that the synthesized polymer has a rod-like shape.

Introduction

Polymeric ammonium salts of general structure **A** are termed ionenes (1).



$$\left[-\overset{\overset{R_1\ X^\ominus}{|\oplus}}{\underset{\underset{R_1}{|}}{N}}-R_2-\overset{\overset{R_1\ X^\ominus}{|\oplus}}{\underset{\underset{R_1}{|}}{N}}-R_3- \right]_n$$

A

Scheme 1

In most cases R_2 and R_3 are oligomethylene chains having identical or different lengths. However, cycloaliphatic, aromatic, and heteroaromatic linkages can also be introduced. The most common method of synthesis is the repetitive Menschutkin-reaction of N,N,N',N'-tetraalkyldiamines and 1,n-bromoalkanes or related bifunctional electrophiles. The products are soluble in water or polar solvents as methanol, dimethylformamide or dimethylsulfoxide, and exhibit behavior typical for polyelectrolytes (2). The molecular weights are generally in the range of 10,000 to 50,000 g/mol. The bromide counterions formed upon the nucleophilic substitution reaction

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can be replaced by a variety of inorganic and organic anions. Charge-transfer salts of ionenes with acceptors such as tetracyanoquinodimethane exhibit electrical conductivity (1). In recent investigations, Wegner and co-workers determined the crystal structure of ionenes (3). Here, we report the synthesis of a novel polymeric ionene **6** and a related model compound **5** in which two spiro-conjugated five-membered rings have a central quaternary nitrogen in common.

Experimental part

Synthesis of (**5**) : N,N'-Dispiro-bis-N,N,N',N'(α,α',α'',α'''-o-xylyl)-1,3,5,7-tetrahydrobenzo[2,3 c:5,6 c']dipyrrolium-dibromide.

A solution of 1,2-dibromomethylbenzene (**4**) (4 g, 15.2 mmol) in 30 ml of benzene, 25 ml of aqueous NaOH (20 %) and 2 ml of tetra-n-butyl ammonium bromide in tetrahydrofuran (0.5 m/l) were placed in a 100 ml two-necked flask and heated to reflux with stirring. A solution of amine **3** (as dihydrobromide) (1 g, 3.1 mmol) in 15 ml of water was added dropwise over a period of 15 minutes and the mixture was refluxed (5 h) under vigorous stirring. After cooling to room temperature the resulting precipitate was separated by filtration. A solution of the latter in 40 ml of aqueous hydrobromic acid (2N) gave 1.13 g of the solid product **5** (69.5 %) upon cooling. ^{1}H-NMR (200 MHz, D_2O): δ = 4.94, 4.96 (2s, 16H), 7.34 (m, 10H) ppm. The strongly hygroscopic character of bromide **5** did not permit an elemental analysis. However, dropwise addition of an aqueous solution of **5** to a concentrated aqueous solution of picric acid provided the corresponding dipicrate as a yellow precipitate which could be subjected to combustion. Elemental analysis : $C_{38} H_{30} N_8 O_{14}$ (M = 822.71), calc.: 55.5 % C, 3.6 % H, 13.5 % N; found: 55.3 % C, 3.4 % H, 13.7 % N.

X-ray structural analysis: Monoclinic, a = 12.194(2), 7.201(1), 21.231(4) Å, ß = 101.74(2)°, V = 1825.21 Å^3 (by least-squares technique involving diffractometer 2Θ angles for 25 automatically centered reflections, λ = 0.71069 Å), space group $P2_1/n$, Z = 2, D_{calc} = 1.497 g/cm^3. Data for the structural studies were collected utilizing an Enraf-Nonius CAD-4 diffractometer. A total of 3962 reflections were measured at room temperature with graphite-monochromated MoK$_\alpha$ radiation up to Θ = 27°, using an ω-2Θ scan mode. After data reduction, 2496 reflections with $I \geq 2\sigma(I)$ were taken as observed. The structure was solved by direct methods, hydrogen atoms were obtained from a difference Fourier map. The following full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms led to R = 0.043 and R_w = 0.051 for

331 variables. The final difference Fourier map showed no significant features.

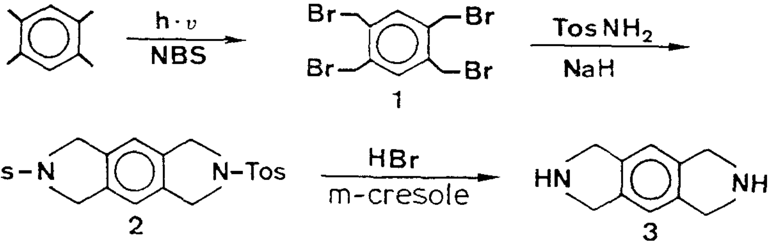
Synthesis of polymer **6**

Tetrabromide **1** (6.98 g, 15.5 mmol), N-ethyl-N,N-diisopropylamine (10 g, 77 mmol) and 1.000 ml of DMF were placed in a 4 l round-bottomed flask, and amine **3** (as dihydrobromide) (5.0 g 15.5 mmol) in 100 ml of water was rapidly added. Stirring of the mixture for 1 minute produced a strong turbidity which disappeared upon the addition of 750 ml of water. The solution was stirred at 60°C for 2 h. The water and a small amount of DMF were evaporated under reduced pressure until the solution became turbid again. The solution was poured into 2 l of dioxane, producing a precipitate which was centrifuged, dried under high vacuum, washed with acetone, and dried again. Yield 5.95 g (85.5 %). ^{1}H-NMR (200 MHz, D_2O): δ = 5.1 (s, 8H), 7.5 (s, 2H) ppm. The elemental analysis was performed as described for model compound **5**: C_{16} H_{12} N_4 O_7, calc. 51.6 % C, 3.2 % H, 15.1% N; found: 50.96 % C, 3.4 % H, 15.0 % N.

Results and discussion

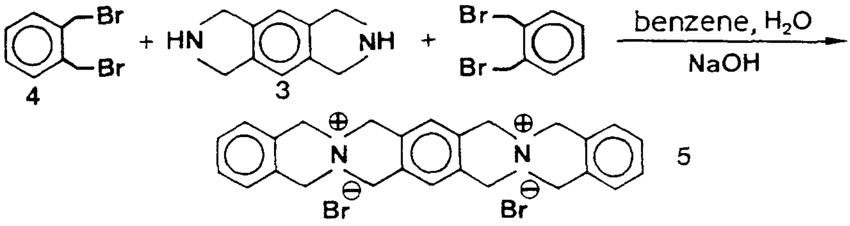
The synthesis of polymeric ionenes with spirane structure should be feasible from tetrabromide **1** and diamine **3** via a repetitive alkylation reaction.

1 was readily synthesized by photobromination of durene (4), **3** could be prepared from ditosylamide **2** by reductive cleavage with hydrobromic acid in m-cresol (4) according to Scheme 2.



Scheme 2

In order to test whether **3** can transform into a spiro-conjugated ammonium salt, the ring formation was first performed for the reaction of 1,2-dibromomethylbenzene (**4**) and **3** which, indeed, produced dication **5**.



Scheme 3

The structure of **5** could be derived from its ^{1}H- and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum (D_2O, 200 MHz) shows two singlets (δ = 4.94, 4.96 ppm) from the methylene hydrogens which are shifted towards lower field compared to **1** (δ = 4.58 ppm, $CDCl_3$) and **3** (as dihydrobromide) (δ = 4.50 ppm, D_2O); this effect is due to the neighboring quaternary nitrogen nuclei. The aromatic hydrogens appear as a broad singlet centered at δ = 7.34 ppm. The ^{13}C-NMR spectrum exhibits signals of 5 aromatic and 2 methylene carbons. A DEPT-135° spectrum shows that 2 of the 5 aromatic carbons are quaternary, which fully agrees with the presumed structure of **5**.

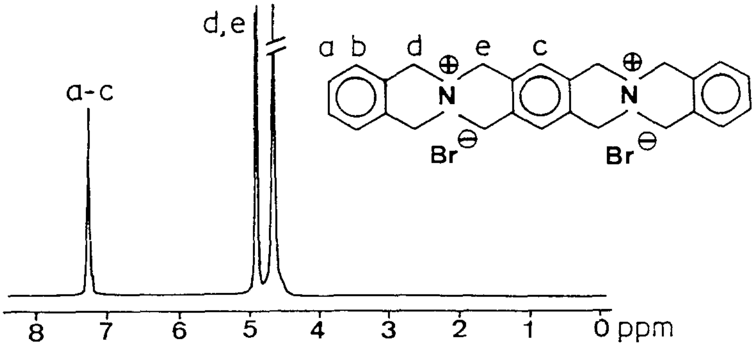


Figure 1 : ^{1}H-NMR spectrum (200 MHz, D_2O) of **5**

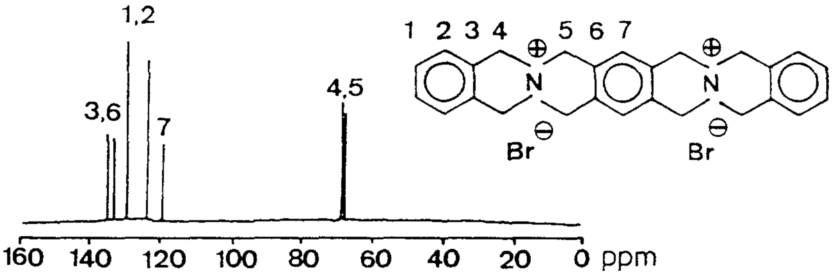
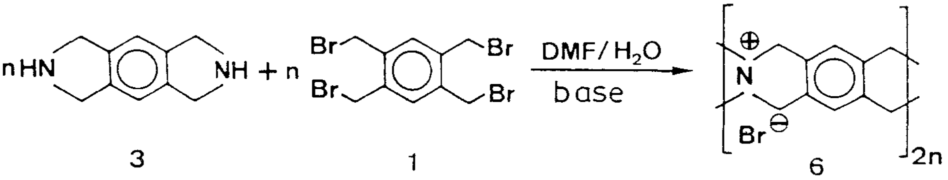


Figure 2 : ^{13}C-NMR spectrum (100.6 MHz, D_2O) of **5**

Conductometric titration of the bromide ions versus silver nitrate confirms the formation of two quaternary nitrogens per molecule of **5**. Compound **5** is soluble in water, and mixtures of water with either methanol, DMF or DMSO. It does not give a sharp melting point, instead, decomposition is observed upon heating to temperatures above 380°C.
The related reaction of **1** and **3** is depicted in Scheme 4.



Scheme 4

The polyalkylation procedure was performed in the presence of N-ethyl-N,N-diisopropylamine in a mixture of DMF and water. The structure of the resulting polymer **6** can be proven by its ^{13}C-NMR spectra (Figure 3) and, in particular, by a comparison with model compound **5** (see Figure 2).
According to formula **6** only 3 signals in the ^{13}C-NMR spectrum can be expected which is in full agreement with Figure 3. The chemical shift differences taken with respect to the aromatic and benzylic carbons of the inner tetrahydrobenzodipyrrolium system of **5** are less than 1 ppm.

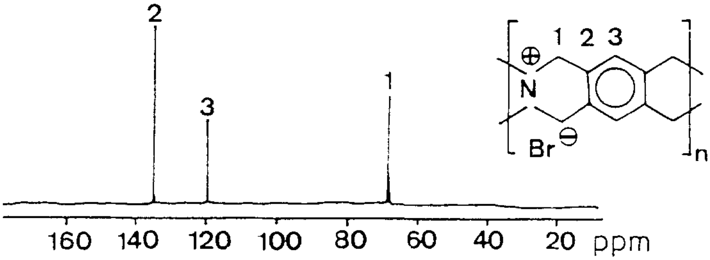


Figure 3 : ^{13}C-NMR spectrum (50.3 MHz, D$_2$O) of **6**

The ^{13}C-NMR spectrum of polymer **6** fails to exhibit signals corresponding to end groups. Also, there is no indication of structural inhomogeneities. The conductometric titration of bromide ions versus silver nitrate gave 96 % of the bromide content calculated according to formula **6**. Similar to model compound **5**, polymer **6** is soluble in water and mixtures of water with methanol, DMF, and DMSO. The highest solubility (25 g/l) was observed for H$_2$O/DMF 3:1. If the bromide counterions were replaced by camphor sulfonate or picrate anions, the polymer became soluble in organic solvents (methanol, DMF, DMSO). Camphor sulfonate could be introduced by treating a solution of polymer **6** in aqueous methanol with silver camphor sulfonate (in aqueous methanol), filtration of silver bromide and evaporation of the solvent. The analogous picrate was obtained as described for dication **5**. Polymer **6** decomposes above 310°C without melting. Viscosimetric measurements of polymer **6** (bromide, H_2O or H_2O/methanol) reveal a polyelectrolyte effect. The Fuoss-Plot (Figure 4) provides a limiting viscosity number of 129 ml/g (25°C, H_2O/methanol 4:1).

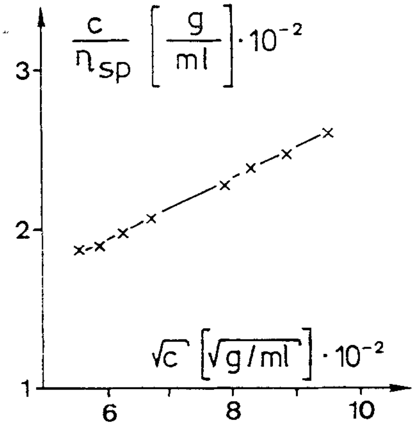


Figure 4 : Fuoss-Plot of **6** (water/methanol 4:1, 25°C)

This finding provides supporting evidence for the polymeric nature of **6**. It is not possible to determine Mark-Houwink parameters for this polymer from our present data, thus molecular weight determinations by viscosimetric measurements must await further investigations.

A GPC-analysis, clearly, reveals different elution volumes for polymer **6** and the corresponding bis-ammonium salt **5**. Comparison of elution volumes for **5** and other molecules of similar size reveal specific interactions of **5** with the column material.

In order to gain information on the shape of polymer **6** we determined the crystal structure of **5** (dipicrate, Figure 5). The latter is determined by the bonding of the nitrogen nuclei and the conformation of the five-membered rings. The orthogonal arrangement of the spiro-conjugated pyrrolidine rings (measured 88.8°) implies that the terminal benzene rings are parallel and nearly orthogonal with respect to the inner one. However, the linear structure of the centrosymmetric molecule **5** is prevented by the envelope-conformation of the five-membered rings which causes a deviation from the plane of the neighboring benzene unit by 30° and 31.8°, respectively, depending on the location of the ring in the molecule.

The picrate anions are nearly parallel to the terminal benzene rings of the dication with a face-to-face distance of 3.1 - 3.4 Å. The equivalence of the geminal benzylic protons in the ^{1}H-NMR spectrum of **5** indicates that the ring inversion of the five-membered rings is rapid on the time-scale of the experiment.

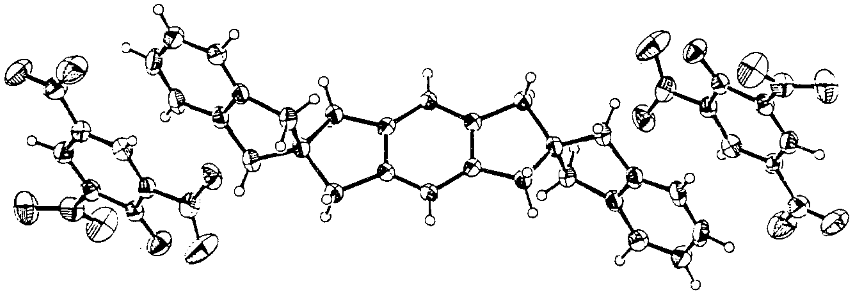


Figure 5 : Crystal structure of **5** (dipicrate)

References

1. A. Rembaum, W.Baumgartner,A.Eisenberg,J.Polym.Sci.,Polym. Lett. 6, 159 (1968); A. Rembaum, J . Macromol. Sci., Chem. A3, 87 (1969); A. Rembaum, S.P.S. Yen, R.F. Landel, M. Shen, J. Macromol. Sci., Chem. A4 715 (1970).
2. D. Casson, A. Rembaum, Macromolecules 5, 75 (1972).
3. L. Dominguez, W.H.Meyer, G. Wegner, Makromol. Chem.,Rapid Commun. 8, 151 (1987); L. Dominguez, V. Enkelmann, W.H.Meyer, G. Wegner, Polymer 30, 2023 (1989).
4. J.T. Stapler, J. Bornstein, J. Heterocycl. Chem. 10, 983 (1973)

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