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CONDUCTING SN POLYMERS WITH INTEGRATED ORGANIC GROUPS

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Résumé: Des polymères composés d'une part d'unités soufre-azote, d'autre part de groupes bifonctionnels hétérocycliques, sont synthétisés par décomposition de la liaison Si-N. On obtient tous les composés avec un bon rendement dans la plupart des cas comme une substance fortement colorée ou noire qui est insoluble dans des solvants organiques usuels. Les polymères non traités montrent une conductibilité électrique entre 5.10^{-16} et 5.10^{-5} Ohm^{-1} cm^{-1}. Généralement la conductibilité des polymères peut être augmentée par oxydation du matériau au moyen d'accepteurs comme par exemple l'iode.

Abstract: Polymers consisting of alternating sulfur nitrogen moieties and bifunctional heterocyclic groups are prepared via Si-N bond cleavage. All compounds are obtained in good yields as highly coloured or black materials which are insoluble in common organic solvents. The pristine materials show conductivities of approximately $5\cdot10^{-16}$ - $5\cdot10^{-5}$ Ohm^{-1} cm^{-1}. In most cases higher conductivities can be achieved by doping the samples with acceptors, e.g. iodine.

Introduction

In contrast to the great number of well established organic conducting polymers the inorganic counterpart $(SN)_x$ is considered to be unique. Thus only few modifications - most of them dealing with doping - are known /1/. Our aim is to increase the variability of S-N-polymers by introducing suitable organic groups into the SN chain and to study the electrical properties depending on the resulting chemical structure (e.g. type of organic groups, length of SN moieties). We have recently shown, that a wide variety of such polymers with alternating sulfur-nitrogen and p-phenylene groups can be prepared by a simple and versatile route /2/. Similar S-N-polymers with bifuncitonal heterocyclic groups are presented in this paper.

Synthesis and Properties

Compounds 1 to 6 are prepared via Si-N bond cleavage in solution. As starting materials sulfur chlorine and silylated nitrogen compounds are used.

$$>N-Si(CH_3)_3 + Cl-S- \longrightarrow >N-S- + Cl\,Si(CH_3)_3$$

Details are given in the reaction scheme below.

All reactions are carried out in dry nitrogen atmosphere. The solvent (CH_2Cl_2) is purified and dried carefully before use. The sulfur chlorine compound (educt I, A-C), dissolved in CH_2Cl_2, is added at ambient temperature to a solution of the silylated nitrogen compound (educt II, D-F). Equimolar amounts of both components are used. Formation of $Cl\,Si(CH_3)_3$ is readily established by following the reac-

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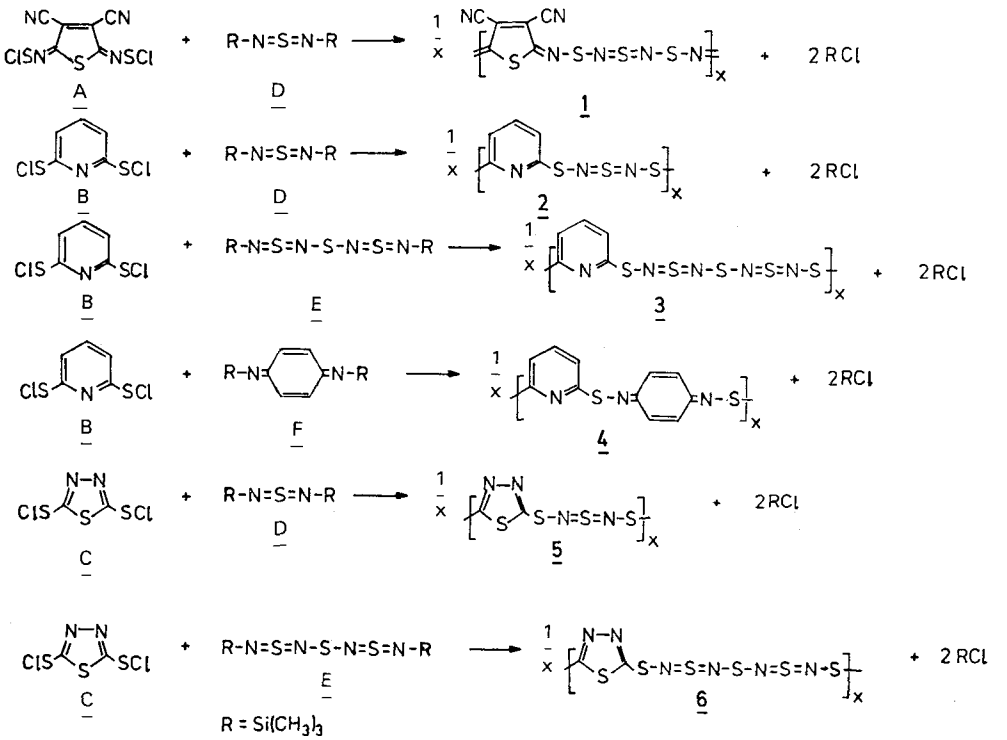

tion ^{1}H-NMR spectroscopically. The polymers precipitate as highly coloured or black powders. After treating the substances with solvent until the washings are colourless, they are dried in vacuo for several hours.

The substances 1 - 6 are presumably microcrystalline and insoluble in common organic solvents. The composition and constitution of the polymers is deduced from the synthesis principle. Due to the mild reaction conditions we believe that no major side reactions take place. Small cyclic compounds are expected to be at least slightly soluble in organic solvents whereas formation of large rings is thermodynamically unreasonable. Evidence for average polymerization degrees greater 10 is given by least-square calculations based on elemental analysis (assuming that no side products result and the chains are terminated by $Si(CH_3)_3$- and Cl-groups).

The pristine substances 1 to 5 are satisfactory stable to air, while 6 must be stored in dry nitrogen atmosphere. No melting was observed by DSC in the temperature range between 295 K and decomposition temperature.

Results of elemental analysis as well as other experimental data are given in tab.1.

Electric Conductivity of the undoped Polymers

In tab. 2 the conductivities at 298 K, activation energies and pre-exponential factors (measured by compressing milligram quantities of polymer to a thin wafer between conducting steel electrodes - pressure 3000 kp/cm^2) of the undoped materials are given. The pristine substances 2 - 6 are insulators, whereas 1 shows a comparatively high conductivity, possibly due to its electronegative cyano-groups as structural elements.

Tab. 1

Experimental Data and Elemental Analysis of Compounds 1 - 6

Compound	Educt I (mmol)/solvent (ml)	Educt II (mmol)/solvent(ml)	Yield (precipitate) %	Elemental Analysis (%) calc./found C	H	N	Colour	Decomposition Temperature*) (K)
1	A /3/ 3.6/300	D /4/ 3.6/300	59	25,3 24.9	0 0.47	29.5 28.7	black	451
2	B**) 1.9/30	D 1.9/30	90	29.8 29.3	1.50 1.60	20.9 19.5	red	398
3	B 2.35/30	E /5/ 2.35/30	87	20.5 20.2	1.03 1.45	23.9 22.7	blue-black	400
4	B 2.0/30	F /6/ 2.0/30	80	53.8 46.3	2.88 3.22	17.1 14.6	green-black	474
5	C**) 3.2/30	D 3.2/30	60	11.5 11.8	0 0.80	26.9 24.5	red	395
6	C 2.5/30	E 2.5/30	95	8.0 8.6	0 0.53	27.9 26.8	black	not measured

*) as evaluated by Differential Scanning Calorimetry (Perkin Elmer DSC 2, Temperature of beginning decomposition)

**) Substances B and C are prepared by adding excess SO_2Cl_2 to the corresponding S-H-compounds and heating to ca. 40 - 50 °C. After pumping they are recrystallized from pentane (c.f. /7/)

Tab. 2

Electric conductivity of the undoped polymers

Compound	$\sigma_{298\ K}$ ($Ohm^{-1}cm^{-1}$)	σ_{∞} ($Ohm^{-1}cm^{-}$)	E_a (eV)	remarks
1	$1.03 \cdot 10^{-5}$	0.082	0.23	1.Measurem.*
	$6.0 \cdot 10^{-5}$	0.260	0.212	2.Measurem.*
2	$4.4 \cdot 10^{-16}$	0.055	0.83	1.Measurem.*
	$1.0 \cdot 10^{-15}$	0.914	0.89	2.Measurem.*
3	$2.2 \cdot 10^{-11}$	$7.8 \cdot 10^{-3}$	0.504	-
4	$2.55 \cdot 10^{-12}$	$9.56 \cdot 10^{-4}$	0.57	-
5	$2.0 \cdot 10^{-14}$	$5.1 \cdot 10^{-3}$	0.675	-
6	$9.57 \cdot 10^{-10}$	$2.32 \cdot 10^{11}$	1.21	-

*Different samples

Doping

Doping is achieved by heating the samples together with some crystals of iodine in evacuated sealed glass tubes. Excess dopant is removed by pumping for some hours. Conductivity is measured immediately after doping.

Tab. 3 shows the results of iodine doping experiments with samples 1, 2 and 5.

Tab. 3

Doping Conditions and Electrical Conductivity of doped Polymers

Compound	$\sigma_{298\ K}$ ($Ohm^{-1}cm^{-1}$)	$\sigma_{dop.}/\sigma_{pristine}$	Doping Temp. (°C)	Doping Time (h)
1	$1.4 \cdot 10^{-6}$	0.14	50	20
2	$2.1 \cdot 10^{-6}$	$2 \cdot 10^{-9}$	50	23
5	$1.3 \cdot 10^{-7}$	$6.5 \cdot 10^{-6}$	50	20

The conductivity of 1 cannot be increased by doping with iodine, whereas the conductivities of 2 and 5 can be enhanced by several orders of magnitude. Doping of 2 and 5 gives rise to a colour change from red to black.

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