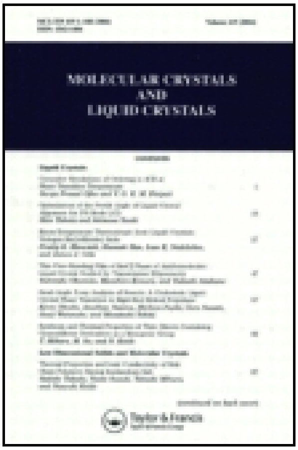

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ELECTRICAL CONDUCTIVE AsF_5-COMPLEXES OF POLY (2,5-THIOPHENEDIYL)

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Poly(2,5-thiophenediyl) (2) reacts with AsF_5 in a gas phase reaction yielding poly(2,5-thiophenediyl) complexes with cationic centers and $AsF_6^{\ominus}$ counterions (1). Polymeric complexes of the same structure are formed by gas phase reactions of AsF_5 with thiophene (3) and 2,2-bithienyl (4) via an oxidative polycondenzation reaction. Treatment of the polymeric complexes 1 with aqueous ammonia yields 2. These complexes are stable materials due to the strong electron donating property of the thiophene system. They may be handled without any special precaution. They have electrical conductivities as high as 0.02 $\Omega^{-1}cm^{-1}$ (activation energy: E = 0.04eV). A possible mechanism for the formation of the polymeric complexes 1 is proposed according to the KOVACIC polycondenzation reaction of aromatic hydrocarbons.

PREPARATION OF THE AsF_5-COMPLEXES OF POLY(2,5-THIOPHENEDIYL)

Poly(2,5-thiophenediyl) (2) was prepared by the method of T. YAMAMOTO et al. (1) from 2,5-dibromothiophene and magnesium in the presence of $NiCl_2$ in waterfree tetrahydrofurane and exhaustively extracted with methanol, chloroform and acetone. The brown polymer 2 was brought into vacuum and afterwards treated with gaseous AsF_5(from MATHESON, B 2431 Oevel, Belgium; purity: 99.5%) at room temperature and pressures ranging from 40 to 700 torr.

The formed AsF_5-complexes of poly(2,5-thiophenediyl) (1) are stable in dry air for several months (see tab. 1).

Treatment with aqueous ammonia reverts these polymeric complexes 1 to polymers which are identical with the starting polymer 2 shown by their ir-spectra and their values of the electrical conductivity.

Even black, insoluble, and infusible polymeric AsF_5-complexes 1 were obtained by the reaction of thiophene (3) respectively 2,2-bithienyl (4) with AsF_5 as described above. In these reactions, no low-molecular donor acceptor complexes are formed. AsF_5 acts as an oxidative polycondenzation reagent.

These polymeric complexes 1 can be converted to brown polymers identical with polymer 2 by the action of aqueous ammonia. The structures of these polymers 2 are confirmed by their ir-spectra and their values of the electrical conductivity (see tab. 1-3).

During the gas phase reaction of 3 and 4 with AsF_5 also thin black films (thickness: 0.04 mm) were formed on the wall of the reaction vessel. Treatment with aqueous ammonia yields insoluble and infusible films of a silver-like appearance having the structure of polymer 2.

Under these conditions, benzene does not form any polymeric complex with AsF_5. Biphenyl and p-terphenyl form black, insoluble and infusible polymeric AsF_5-complexes during reactions with gaseous AsF_5 as reported by H. BAUGHMAN et al. (2).

STRUCTURE OF THE POLYMERIC COMPLEXES

The same polymeric complexes 1 are formed by the action of gaseous AsF_5 on 2, 3 or 4, having the structure of poly(2,5-thiophenediyl) with cationic centers and $AsF_6^{\ominus}$ counterions.

The ir-spectra of the polymeric complexes are identical and in very close relationship to the ir-spectrum of 2. The ir-spectra have the typical absorptions of the thiophene system (1500, 1400, 1230, 1200, 1080 and 1050 cm^{-1}) the characteristic absorption of the 2,5 disubstituted thiophene system at 800cm^{-1}. The absorption at 850cm^{-1} (characteristic for the 2-thienyl system) decreases, if 4 is reacted with AsF_5. The very strong absorptions at 700 and $400 cm^{-1}$ clearly show the presence of $AsF_6^{\ominus}$ ions (3,4).

Very valuable information on the structure of the polymeric complexes 1 is obtained from the mass spectra (7).

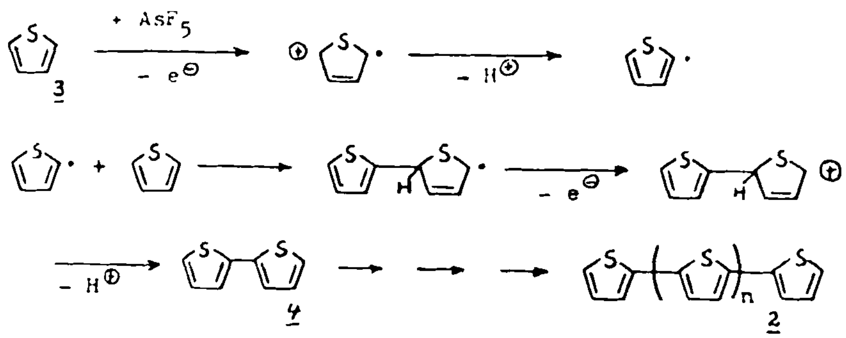
Polymer 2 has the structure of pure poly (2,5-thiophenediyl). It contains oligomers up to the undecathiophenediyl. Working with an ion source temperature up to 450°C, no bromine containing products are detectable.

The polymeric complexes 1, prepared from 3 and AsF_5, contain oligomers up to the nonathiophenediyl. Moreover, the characteristic masses of As_4O_6 (m/z 396) and of As_3O_4 (m/z 289) as typical products of partial decomposition can be seen.

The polymeric complexes 1, prepared from 4 and AsF_5, contain oligomers as high as decathiophenediyl. The mass spectra also have the typical fragments of $(T)_n$-S, $(T)_n$-CH_2, $(T)_n$-CH_2, -S with $n \leqslant 6$ (T means thiophene systems), and the characteristic masses of As_4O_6 and As_3O_4.

The formation of the polymeric complexes 1 from 3 and 4 by the LEWIS acid AsF_5 via a polycondenzation process may be explained by the following mechanism comparable with the oxidative polycondenzation reaction of aromatic hydrocarbons like benzene studied by KOVACIC et al., who have investigated the oxidative polycondenzation reaction of thiophene with $AlCl_3$(5) and trifluoroacetic acid (6), too.

The mechanism may involve the following steps:



The oxidation may be connected with the reduction of $\mathrm{AsF_5}$

$$\mathrm{AsF_5 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow AsF_3 + 2HF}$$

and the formation of $\mathrm{AsF_6^{\ominus}}$

$$\mathrm{AsF_5 + HF \longrightarrow H^{\oplus}\,AsF_6^{\ominus}}$$

ELECTRICAL CONDUCTIVITY OF THE POLYMERIC COMPLEXES

As shown in table 1, the electrical conductivities of polymer 2 increase with the degree of complex formation at higher pressures of $\mathrm{AsF_5}$ up to 450 torr. At higher pressures (700 torr) and longer reaction times (140 h), the electrical conductivity decreases. After treatment of the polymeric complex 1 (prepared from 2 with 450 torr $\mathrm{AsF_5}$ in 24 h) with aqueous ammonia, the polymer 2 is formed again.

Table 1 Reaction of 2 with $\mathrm{AsF_5}$ and the Electrical Conductivities of the Polymeric $\mathrm{AsF_5}$-Complexes

Reaction conditions	σ_{298K} ($\Omega^{-1}\mathrm{cm}^{-1}$)	σ_0 ($\Omega^{-1}\mathrm{cm}^{-1}$)	E (eV)
	$5.7\cdot10^{-11}$	$2.4\cdot10^{-5}$	0.66
40 torr - 24 h	$5.9\cdot10^{-8}$	$2.7\cdot10^{+1}$	1.02
200 torr - 24 h	$5.4\cdot10^{-4}$	$6.4\cdot10^{-1}$	0.36
450 torr - 24 h	$3.1\cdot10^{-3}$	$1.4\cdot10^{-7}$	0.20
.... + $\mathrm{NH_3/H_2O}$	$4.5.10^{-10}$	$2.2\cdot10^{-7}$	0.32
700 torr - 140 h	$7.3\cdot10^{-5}$	$2.6\cdot10^{-3}$	0.18

The electrical conductivities of the polymeric complexes 1 prepared from 3 and $\mathrm{AsF_5}$ increase up to a pressure of 450 torr. Reaction at 650 torr yields a polymer of lower electrical conductivity, but in this case a film was formed on the wall of the reaction vessel. Reaction of the polymeric complex 1 (prepared from 3 and 450 torr $\mathrm{AsF_5}$) with aqueous ammonia yields polymer 2.

Table 2 Reaction of 3 with AsF$_5$ and the Electrical Conductivities of the Polymeric AsF$_5$-Complexes

Reaction conditions	σ_{298K} ($\Omega^{-1}cm^{-1}$)	σ_0 ($\Omega^{-1}cm^{-1}$)	E (eV)
200 torr - 24 h	$6.9.10^{-8}$	$1.9\cdot10^{0}$	0.88
300 torr - 24 h	$6.5\cdot10^{-7}$	$1.7\cdot10^{-2}$	0.52
450 torr - 60 h	$2.1\cdot10^{-2}$	$4.8.10^{-2}$	0.04
.... + NH_3/H_2O	$1.3\cdot10^{-12}$	$9.8.10^{-8}$	0.58
650 torr - 48 h	$7.4\cdot10^{-4}$	$2.2\cdot10^{-2}$	0.17
film (d: 0.04 mm)	$1.1\cdot10^{-3}$	$2.2\cdot10^{-3}$	0.04

Tab. 3 contains the electrical conductivities of polymeric complexes prepared from 4 and AsF$_5$. Also a film was formed at a pressure of 450 torr AsF$_5$. Treatment of a polymeric complex yields polymer 2. Reaction with AsF$_5$ for a second time forms a polymeric complex 1 with a higher electrical conductivity than the complex which was formed for the first time. Repeated treatment with aqueous ammonia and AsF$_5$ does not result in polymeric complexes 1 with higher electrical conductivities.

Table 3 Reaction of 4 with AsF$_5$ and the Electrical Conductivities of the Polymeric AsF$_5$-Complexes

Reaction conditions	σ_{298K} ($\Omega^{-1}.cm^{-1}$)	σ_0 ($\Omega^{-1}.cm^{-1}$)	E (eV)
400 torr - 60 h	$7.1\cdot10^{-4}$	$2.9\cdot10^{-2}$	0.19
film (d: 0.05 mm)	$1.5\cdot10^{-5}$	$5.2\cdot10^{-5}$	0.42
.... + NH_3/H_2O	$4.5\cdot10^{-11}$	$2.9\cdot10^{-6}$	0.57
650 torr - 24 h	$5.5\cdot10^{-4}$	$5.0\cdot10^{-3}$	0.11
.... + NH_3/H_2O	$1.3.10^{-11}$	$2.1\cdot10^{-4}$	0.86
.... + AsF_5(650 torr-24h)	$1.7\cdot10^{-3}$	$2.5\cdot10^{-2}$	0.14

Tab. 4 contains the electrical conductivities of the polymeric complexes having been prepared from biphenyl (5), or p-terphenyl (6) respectively and AsF$_5$ and also the polymers after treatment with aqueous ammonia having the structure of poly (p-phenylene).

Table 4 Reaction of 5 respectively 6 with AsF_5 and the Electrical Conductivities of the Polymeric AsF_5-Complexes

Starting material	Reaction conditions	σ_{298K} ($\Omega^{-1}.cm^{-1}$)	σ_0 ($\Omega^{-1}.cm^{-1}$)	E (eV)
5	450 torr - 60 h	$2.6 \cdot 10^{-7}$	$2.6 \cdot 10^{-4}$	0.36
	....+ NH_3/H_2O	insulator		
6	450 torr - 60 h	$5.0 \cdot 10^{-3}$	$5.6 \cdot 10^{-1}$	0.24
	... + NH_3/H_2O	insulator		

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