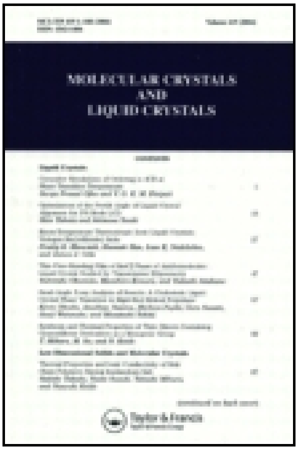


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis and Conductivity of Thianthrene-Type Polymers

Paolo Costa Bizzarri [a] & Carlo Delia Casa [a]
[a] Istituto di Chimica degli Intermedi, Unlversità, 40136, Bologna, Italy

Version of record first published: 17 Oct 2011.

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 245-248
0026-8941/85/1184-0245/$10.00/0

SYNTHESIS AND CONDUCTIVITY OF THIANTHRENE-TYPE POLYMERS

PAOLO COSTA BIZZARRI and CARLO DELLA CASA
Istituto di Chimica degli Intermedi, Università,
40136 Bologna, ITALY

Abstract Different methods to obtain oligomeric sulfur derivatives of thianthrene-type with cyclic chain structure are described. The pristine compounds are insulators. Values in the semiconductors range can be achived by doping the samples with $SbCl_5$. The conductivity increases up to about 10^{-5} S/cm.

INTRODUCTION

Over the past few years extensive research has been carried out on the synthesis and conductivity of sulfur-containing conjugated polymers. The most representative among these are PPS and poly(2,5-thienylene). The sulfur atoms of PPS interact with the aromatic system and account for the conduction along the polymer chain.[1] Poly(2, 5-thienylene) has a π-conjugation system similar to that of polyacetylene, but with a chain structure stabilized by sulfur.[2] In this paper, we summarize the synthesis and conductivity of oligomeric sulfur derivatives, in which sulfur bridges give rise to a partially rigid backbone.

SYNTHESIS OF THE POLYMERS

It is known that the reaction of diphenylsulfide, DPS, with $AlCl_3$ at high temperature (225°C) results in an oligomeric ladder polymer with a structure consisting of intramolecular cyclic sulfide groups of thianthrene-type.[3] We obtain similar polymer by the following methods: a)backbone modification of poly(m-phenylene disulfide),[4] PMPDS, and PPS, by way of a likely molecular rearrangement;[5] b)Friedel-Crafts polymerization of thianthrene.

The reactions were carried out in mild conditions. In a typical experiment PMPDS together with sulfur and $AlCl_3$ was heated at 80°C in n-heptane for 3.5 hr. After decomposition of the reaction mixture, the residue was fractionated by acetone and $CHCl_3$ extractions. Results are given in Table I.

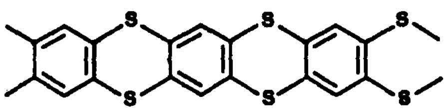
TABLE I Preparation of thianthrene-type polymers.

Polymer	Starting material	Yield(°/o)[a]	$CHCl_3$-soluble / $CHCl_3$-insoluble
1	PMPDS	27	52/48
2	PPS	14	77/23
3	THIANTHRENE	25[b]	16/84
4	DPS	34[c]	4/96

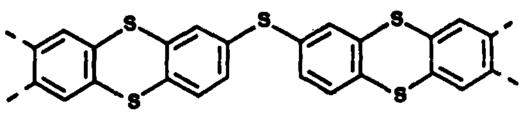
(a)Insoluble in acetone.
(b)Reaction time 48 hr.
(c)Reaction carried out in a way similar to Ref.3.

From elemental analysis, IR spectra, and comparison with polymer 4, synthesized in a way similar to the literature, we conclude that the structures of our polymers are best represented by a mixture of the following fragments

I



II



A qualitative measure of the cyclization can be obtained from the intensity ratio between the peaks at 875 and 805 cm^{-1}, assigned to to the out of plane bending of isolated and adjacent hydrogens, respectively. As the cyclization increases, this ratio becomes larger.

C/H atomic ratios from elemental analysis as well as the presence of chain terminations constituted by thianthrene units are in agreement with the experimental low molecular weight of the polymers. These are partially crystalline as determined by X-ray diffraction.[6]

DOPING AND ELECTRICAL CONDUCTIVITY

Doping was achieved by treating the polymer powder with solutions of $SbCl_5$ in $CHCl_3$. The dopant concentration was estimated from the weight uptake of the powder, after prolonged evacuation. On doping, the black polymers show an IR new broad band at 335 cm^{-1} due to Sb-Cl stretching mode, suggesting hexachloroantimonate(V) ion.

The conductivity was measured at room temperature on pressed pellets (6000 kg/cm^2), using electrodag contacts. The pristine substances 1-4 are insulators with conductivities ranging from 10^{-14} to 10^{-16} S/cm. σ values of doped samples are given in Table II.

TABLE II Room temperature conductivities (S/cm) of doped $CHCl_3$-insoluble polymers.

Polymer	σ_{doped}	$\sigma_{doped}/\sigma_{pristine}$	$SbCl_5$/polymer (wt°/o)
1	5.5×10^{-6}	3.4×10^{9}	76
2	1.2×10^{-5}	2.5×10^{8}	50
3	4.4×10^{-5}	6.5×10^{9}	50
4	3.8×10^{-6}	1.4×10^{9}	54

A study of the conductivity of the most cyclized polymer 4 has been carried out as a function of dopant concentration. The electrical conductivity increases sharply over many orders of magnitude at low concentration, then saturates at higher dopant levels, above approximately 25-30 wt°/o, suggesting a change in transport behaviour. Above this critical concentration, a limiting value of about 10^{-5} S/cm is attained.

For comparison, the conductivity of $SbCl_5$-heavily doped samples of the starting materials PPS and thianthrene[7] is 4.7×10^{-7} and 3.3×10^{-10} S/cm, respectively.

ACKNOWLEDGEMENTS

This work has been supported by C.N.R. "Progetto Finalizzato Chimica Fine e Secondaria".

REFERENCES

1. R. L. Elsenbaumer, L. W. Shacklette, J. W. Sowa, and R. H. Baughman, Mol. Cryst. Liq. Cryst., 83, 229 (1982).
2. M. Kobayashi, J. Chen, T.-C. Chung, F. Moraes, A. J. Heeger, and F. Wudl, Synth. Met., 9, 77 (1984).
3. V. A. Sergeev, V. I. Nedel'kin, and V. Ya. Lepilin, Vysokomol. Soedin., Ser. B, 21, 252 (1979); Chem. Abstr., 91, 21225w (1979).
4. Preparative details as well as polymer properties will be published elsewhere.
5. T. Fujisawa, N. Ohtsuka, and G.-I. Tsuchihashi, Bull. Chem. Soc. Japan, 43, 1189 (1970); J. Giordan and H. Bock, Chem. Ber., 115, 2548 (1982).
6. W. Porzio, preliminary results.
7. V. G. Koshechko, V. A. Krylov, and V. D. Pokhodenko, Elektrokhimiya, 16, 1812 (1980).