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Gotthelf Wolmershäuser [a], JÜRgen Fuhrmann [a], Raimund Jotter [a], Thomas Wilhelm [a] & Otto J. Scherer [a]

[a] Fachbereich Chemie der Universität Kaiserslautern, Postfach 3049, D-6750, Kaiserslautern, Federal Republic of Germany

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SULFUR NITROGEN POLYMERS WITH INTEGRATED ORGANIC GROUPS: A SUMMARY*

GOTTHELF WOLMERSHÄUSER, JÜRGEN FUHRMANN, RAIMUND JOTTER, THOMAS WILHELM AND OTTO J. SCHERER
Fachbereich Chemie der Universität Kaiserslautern, Postfach 3049, D-6750 Kaiserslautern, Federal Republic of Germany

Abstract An overview is presented concerning chemically modified sulfur nitrogen polymers which are composed of organic and SN moieties. Properties, particularly conductivity, of these polymers are discussed in terms of chemical and physical structure.

INTRODUCTION

Several attempts to modify chemical, electrical and mechanical properties of $(SN)_x$ have been made in the past[1,2]. Our approach is to insert organic moieties into the SN chain, or - from a different point of view - to insert sulfur nitrogen moieties into a polyaromatic or polyheterocyclic chain. The resulting polymers of the type $(-Org-S_nN_m-)_x$ where "Org" is an iso- or heterocyclic ring can be considered as links between the well established "boundaries" $(SN)_x$ and polyaromatic or polyheterocyclic chains. We have shown recently[3-5] that a wide variety of such polymers are accessible by a very simple and versatile synthetic route.

SYNTHESIS

The synthetic pathway into this novel class of conducting polymers is based on a polycondensation reaction:

$$\geq N\text{-}Si(CH_3)_3 + Cl\text{-}S\text{-} \longrightarrow \geq N\text{-}S\text{-} + Cl\text{-}Si(CH_3)_3$$

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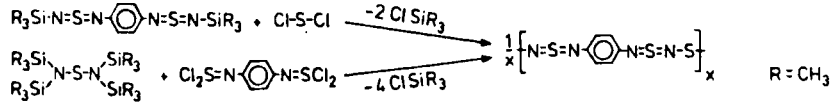
Typical example:



The major advantages are moderate and simple experimental conditions (ambient temperatures; no sophisticated apparatus necessary) and the ability to vary both the organic and sulfur nitrogen moiety.

CONDUCTIVITY OF UNDOPED MATERIALS

The conductivities of a representative set of undoped polymers (milligram quantities compressed to a thin wafer and measured between conducting steel electrodes at a pressure of approximately 3000 kp/cm^2) are shown in Figure 1. Room temperature conductivities range from 10^{-16} to $5 \cdot 10^{-5}$ Ω^{-1} cm^{-1}, activation energies (calculated from $\sigma = \sigma_0 \cdot e^{-E_a/kT}$) from 0.21 to 1.21 eV.

DISCUSSION

Conductivity of polymers depends on several parameters such as morphology, polymerization degree, constituion, conformation and doping.

Very little is known concerning the morphology of the synthesized polymers. The materials are presumably microcrystalline or amorphous and insoluble in common organic solvents. The composition and constitution is deduced from the synthesis principle. Classical methods for the determination of molecular weights (e.g. GPC) are not applicable due to insolubility of the polymers. Evidence for average polymerization degrees from 3 to 40 is given by least-squares calculations based on elemental analysis (assuming that no side products result and the chains are terminated by $Si(CH_3)_3$- and Cl-groups).

From the data given in Figure 1 it is evident that the conductivity is higher when nitrogen is the link between organic group

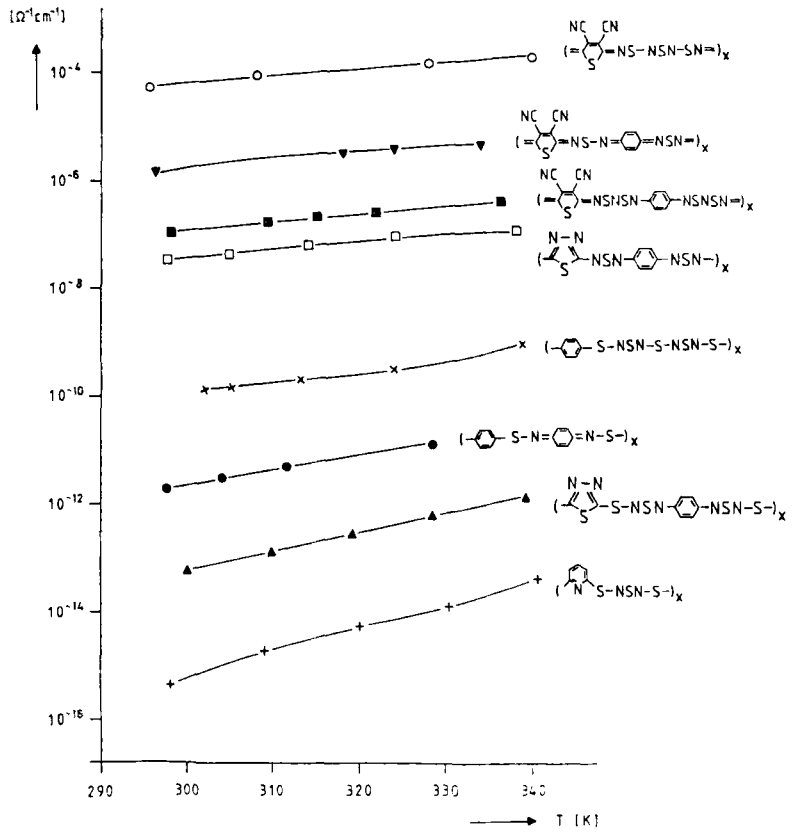


FIGURE 1 Conductivities of a representative set of sulfur nitrogen polymers with integrated organic groups

and sulfur nitrogen chain, whereas sulfur links lead to polymers of lower conductivities. The highest values are shown by polymers containing  as organic group.

This may be ascribed to intrinsic doping, i.e. the highly electronegative cyano-groups reduce the electron densitiy of the conjugated chain, acting as an intramolecular dopant. The conductivity of polymers containing such a "thiophene" unit cannot be increased by extrinsic doping with electron accepting iodine. In contrast,

the conductivity of polymers containing other organic groups can be enhanced by several orders of magnitude by doping with acceptors.

It should, however, be kept in mind that the observed effect may also be due to electron delocalization and solid state order.

CONCLUSION

The effect of introducing organic groups into a SN chain is overviewed in Figure 2. Discussion is based exclusively on structural arguments, morphological effects are not taken into account.

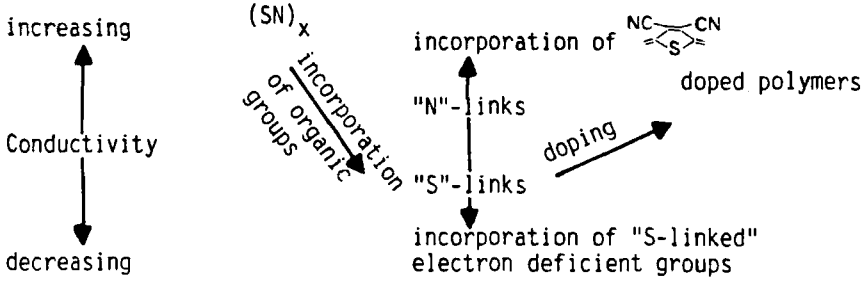


FIGURE 2 Effect of introducing organic groups into a SN chain

The conductivity of microcrystalline $(SN)_x$, synthesized (by our method) from $(Me)_3SiNSNSi(Me)_3$ and SCl_2 is $5 \cdot 10^{-2}$ $^{-1}$ cm^{-1}, i.e. five orders of magnitude lower than the conductivity of solid state polymerized $(SN)_x$. According to Wudl[2] the comparatively low conductivity values may be due to a "wrong" morphology, i.e. extremely insoluble powders instead of solid state polymerized $(SN)_x$.

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