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On the complex electrical conductivity of poly(2,5-furandiylvinylene)

I. Boro and G. Hinrichsen

Technical University of Berlin, Institute of Nonmetallic Materials, Polymer Physics,
Englische Strasse 20, D-10587 Berlin, Germany

SUMMARY

The presented paper deals with the ac-conductivity of undoped and doped poly(2,5-furandiylvinylene) (PFV). It is shown that the electrical conductivity as a complex physical quantity has to be splitted into a real and an imaginary part. Both parts depend on frequency, temperature, type and concentration of doping agents, and external pressure applied to the test specimens.

INTRODUCTION

Since about 15 years a worldwide interest - both in academia and in industry - in the synthesis, characterization, and physical properties of electrically conducting polymers has been revealed by many thousands of scientific papers. Studies have been made on organic conjugated polymers such as poly(acetylene), poly(p-phenylene), poly(phenylene sulfide), poly(thiophene), poly(pyrrole), poly(aniline), their derivates, and others. It has been discovered that many of these polymers, which have an intrinsic conductivity of less than 10^{-5} S cm^{-1}, could be transformed into semiconducting or conducting materials (up to 10^5 S cm^{-1}) by exposing them to oxidizing or reducing agents. This process is often, but in a misleading way, referred to as "doping" in analogy to the doping of inorganic semiconducturs.[1)]

EXPERIMENTAL

MATERIALS

Poly(2,5-furandiylvinylene) was synthesized by self-condensation of 5-methylfurfural[2)]. The polymer was a granular product with an average grain diameter of 3 µm, a density of 1.42 g/cm^3, and a brown-black colour. In the undoped state PFV is highly crystalline as measured by X-ray wide angle scattering, but by doping with $FeCl_3$ the crystal structure disappears completely. The degree of polymerization could not be quantified directly because of insolubility of PFV in solvents, but from IR spectra a higher degree of polymerization could be assumed. PFV was doped by $FeCl_3$, I_2, AsF_6, and BF_4, respectively. For dielectric measurements the powdery products were pressed into tablets with a diameter of 13 mm and a thickness of 0.2 - 1.0 mm.

The complex electrical permittivity was measured in the frequency interval from 5 Hz to 13 MHz using an impedance analysator Hewlett-Packard HP 4192 A. The analysator was controlled by a microcomputer which stored and analyzed up the measured data. The measurements in dependence on temperature (80 - 480 K) and pressure (0 - 750 MPa) were performed using self-constructed equipments, which are described elsewhere[3].

THEORY

The electrical current I flowing through a polymeric material placed in a parallel-plate capacitor is given by

$$I = i\omega\varepsilon^* C_0 U \tag{1}$$

where

ω angular frequency

ε^* complex dielectric constant or relative permittivity

C_0 vacuum capacitance per unit of electrode

U applied voltage.

The complex dielectric constant is defined by the following equations

$$\varepsilon^* = D/\varepsilon_0 E \tag{2}$$

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{3}$$

where

ε_0 permittivity of free space (= 8.85×10^{-12} F m^{-1})

E electric field

D electric displacement

ε' real part of dielectric constant

ε'' imaginary part of dielectric constant.

Combining eq. (1) and (3) one gets

$$I = \varepsilon''\omega C_0 U + i\omega\varepsilon' C_0 U = I_R + I_C, \tag{4}$$

where

I_R the resistive component of the current, which is in phase with the voltage

I_C the capacitive component of the current, which leads the voltage by 90 °.

Introducing the formula of the parallel-plate capacitor

$$C_0 = \varepsilon_0 A/d \tag{5}$$

with

A plate area

d distance between the plates,

one gets the current density J

$$J = I/A = (\varepsilon''\varepsilon_0\omega + i\varepsilon'\varepsilon_0\omega)E. \tag{6}$$

The expression in the brackets of (6) corresponds according to Maxwell to a complex electrical conductivity, σ^*, given by

$$\sigma' = \varepsilon_0 \varepsilon'' \omega \qquad \text{(real part)} \qquad (7)$$

$$\sigma'' = \varepsilon_0 \varepsilon' \omega \qquad \text{(imaginary part).} \qquad (8)$$

which are connected by the loss factor tan δ

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sigma'}{\sigma''} \qquad (9)$$

RESULTS AND DISCUSSION

Fig. 1 shows in a very idealized manner the real part of the complex electrical conductivity, σ', in dependence on frequency. Conducting materials like metals are characterized by a high elctrical conductivity, which is independent of the frequency of applied voltage. On the other hand, the real part of the complex conductivity of insulating materials like most polymers is low and increases monotonically with frequency. Semiconductors exhibit a behaviour which is in between that of conducting and insulating materials, i.e. constant conductivity at low frequencies and increasing values at higher frequencies, see e.g. the results of Epstein[4][5] and Ezquerra[6][7]. The imaginary part of the conductivity of semiconductors and insulators increases with frequency. In general, the absolute values of the imaginary part are higher with semiconductors than with insulators. The imaginary part of electrical conductivity of conductors is nearly equal to zero and becomes noticeable just at very high frequencies.

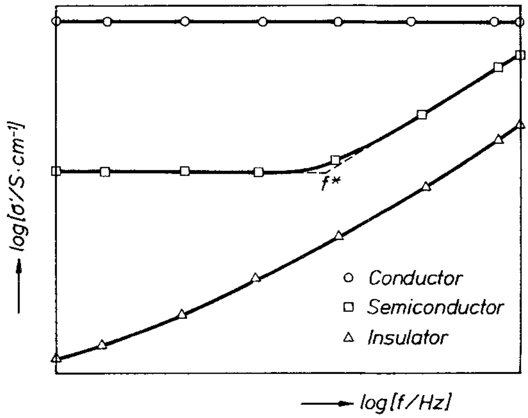

Fig. 1 Schematic course of the real part of complex electrical conductivity, σ', of a conductor, a semiconductor and an insulator, respectively in dependence on frequency.

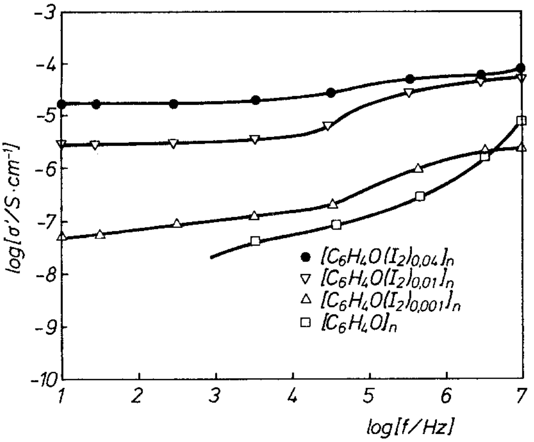

Fig. 2 Real part of complex electrical conductivity, σ', of PFV, undoped and doped with I_2 to different percentages, in dependence on frequency.

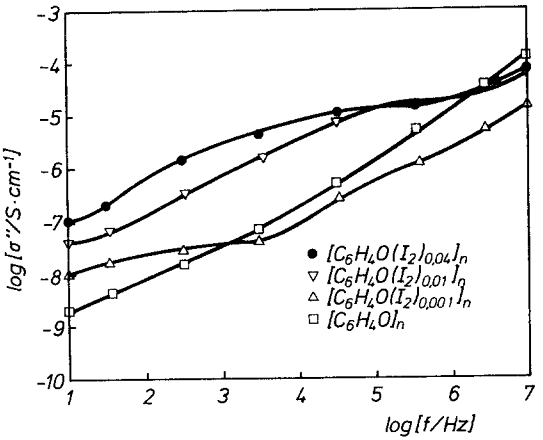

Fig. 3 Imaginary part of complex electrical conductivity, σ'', of PFV. Same specimens as in Fig. 2.

The results of the measurements of ac-conductivity of PFV specimens undoped and doped with I_2 are plotted in Fig. 2 (real part) and Fig. 3 (imaginary part). As expected the real part, σ', increases with growing content of doping agent from ~ 10^{-8} S cm^{-1} for the undoped PFV up to ~ 10^{-5} S cm^{-1} for the specimen doped with 4 mole-% I_2 (at frequency 10^3 Hz). The increase of σ' with frequency depends on the degree of doping showing little increase for samples with higher conductivity and significant increase for less conducting specimens. The small step in the course of the σ' - log f diagrams at about f = 10^5 Hz is described and explained in more detail elsewhere[3].

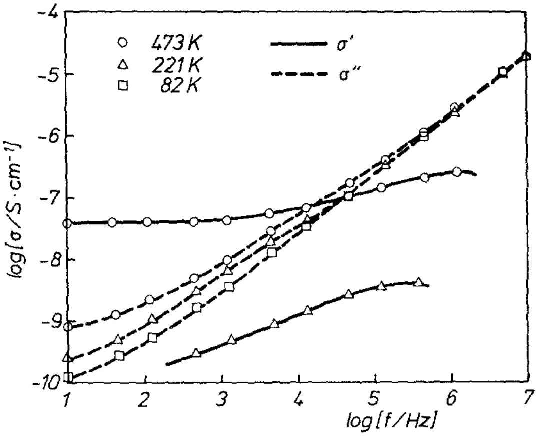

Fig. 4 Real and imaginary part of complex electrical conductivity, σ' and σ'' resp., of undoped PFV in dependence on frequency at different temperatures. The measured σ'-values at 82 K are less than 10^{-10} Scm^{-1}.

The imaginary part of complex conductivity, σ'', of PFV reveals a stronger dependence on frequency as compared to the respective real part, see Fig. 3. Within the frequency interval of investigation between 10 Hz and 10 MHz σ'' increases by 3 - 5 decades. At constant frequency the differences of σ'' values for undoped and doped specimens are in the range of 2 decades.

The temperature dependence of both σ' and σ'' of undoped PFV as a function of frequency can be gathered from Fig. 4. It is well known from many investigations on electrically conducting polymers that the temperature has a strong influence on σ', see for example the results of Epstein on trans-poly(acetylene)[4]. At frequencies above 10^5 Hz the measured values of σ'' exceed those of σ'.

Investigations in the time-frame of this work proved that no ageing effects were observed with undoped but with doped specimens. Figs. 5 and 6 represent the real part, σ', and the imaginary part, σ'', of PFV doped with 13 mole-% $FeCl_3$ in dependence on frequency for various ageing times up to 22 months. The decrease of σ' due to ageing time is very high while significantly lower for σ''. Such a process which is also observed in other conducting polymers like polyacetylene and polypyrrole has been called degradation of electrical conductivity[8)-10)].

Regarding the powdery state of the material it was presumed that the application of pressure to the specimens during the measurement would influence the electrical conductivity because the contact beween the particles will be enhanced, and improved. This effect will result in an improved hopping of charge carriers from grain to grain. Fig. 7 proves this assumption: σ' is increased by at about one decade applying a pressure of 750 MPa to the specimen. The influence of pressure on σ'' is less significant; pecularities of the σ''-curve at very low and very high frequencies are dicussed elsewhere[3)].

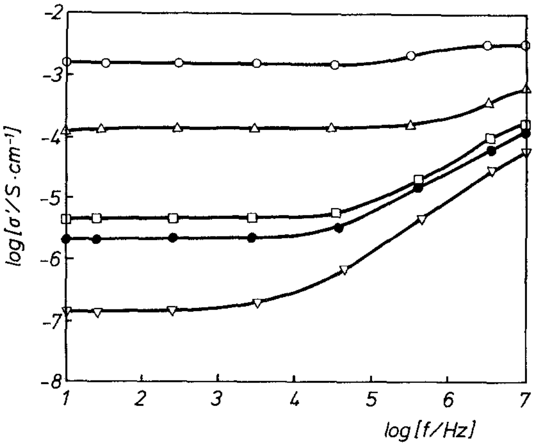

Fig. 5 Real part of complex electrical conductivity, σ', of PFV doped with 13 mole-% $FeCl_3$ in dependence on frequency, after different ageing time.

○ immediately after 2 months; △ after 5 months; □ after 10 months;

● after 11 months; ▽ after 22 months.

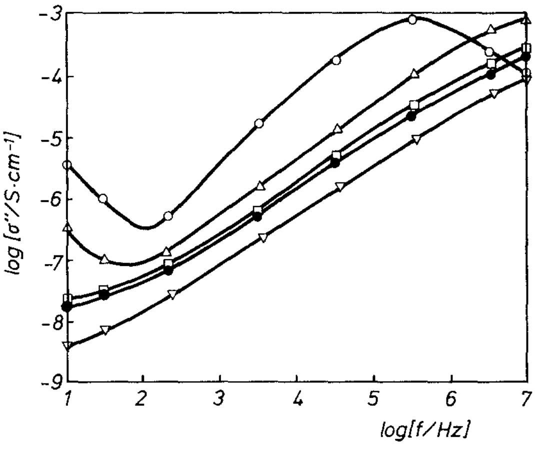

Fig. 6 Imaginary part of complex electrical conductivity, σ'', of PFV doped with 13 mole-% $FeCL_3$ in dependence on frequency after different ageing time. Same specimens as in Fig. 5.

The electrical transport phenomena in conducting polymers are described by the theoretical concept of solitons and polarons[11)-13)]. These solitons or polarons contribute only in an indirect way to the electrical conductivity by hopping or tunneling within one chain or from one chain to the neighbouring one[14)]. Moreover, in a powdery polymeric material the charge

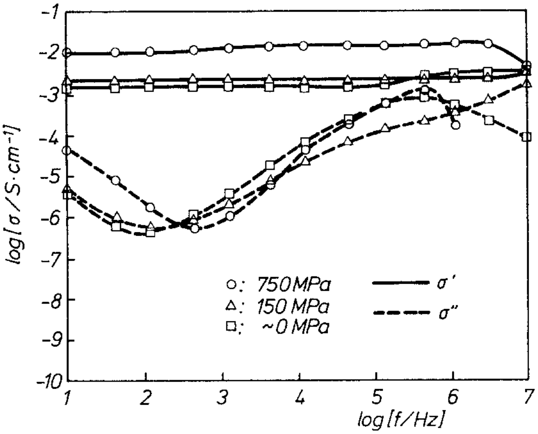

Fig. 7 Real and imaginary part of complex electrical conductivity, σ' and σ'', of PFV doped with 13 mole-% $FeCl_3$ in dependence on frequency.
Parameter: Applied pressure.

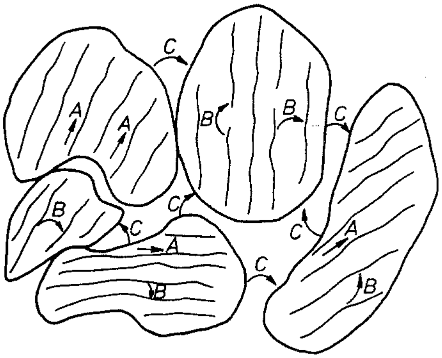

Fig. 8 Schematical drawing of the transport paths in a powdery conducting polymer, according to (13).

transport consists of different contributions, an interparticle (C) and an intraparticle charge transport (A + B). The latter can be divided into an intrachain (A) and an interchain (B) transport mechanism, which may be understood from the schematical drawing in Fig. 11 according to[14].

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