

Conductivity Changes of Polyacetylene Exposed to SO₂

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ABSTRACT: The conductivity change of polyacetylene foils under exposure with different pressures of sulfur dioxide vapor was measured as a function of time. Adsorption and diffusion are the rate determining steps for the increase of the conductivity. A simple mathematical description of the two processes yields agreement with experiment.

KEY WORDS Polyacetylene / Sulfur Dioxide / Electrical Conductivity /
Diffusion / Doping / Kinetics / Two Probe Method /

Samples of polymers with conjugated double bonds can be prepared as insulators. Their intrinsic conductivity is low and such samples are especially suited for the study of low level doping effects. Changes of the electrical conductivity induced by exposure to oxidizing or reducing gases may form the basis for the application of these polymers as sensors of toxic gases, such as SO_x or NO_x. Previously, we have studied the conductivity changes induced by exposure of polypyrrole, polythiophene, and polyacetylene to various oxidizing or reducing gaseous compounds.¹⁻³ In these studies, the conductivity change was measured as a function of vapor pressure. The results were discussed on the basis of a model which implied the adsorption of the vapor molecules coupled with an increase of the conductivity of the surface.³ Recently, time resolved measurements of the conductivity increase after exposure to various gases or vapors were carried out and a more detailed insight into the processes involved emerged. Here, we wish to report on the conductivity changes of polyacetylene exposed to sulfur dioxide.

EXPERIMENTAL

Polyacetylene was prepared according to the method developed by Ito *et al.*⁴ A strip of approximately $A = d \times h = 5 \times 6 \text{ mm}^2$ area and $\delta = 60 \mu\text{m}$ thickness was attached with silver paste to two tungsten wires serving as the electrodes. The electrode assembly was housed in a glass container which could be evacuated. The conductivity was obtained from measurements of the current, I , as a function of the applied voltage, U . A schematic diagram of the set-up is shown in Figure 1. Over a range of voltages a linear relationship between current and voltage was observed although sometimes the straight line did not go exactly through the origin. The slope $\Delta I/\Delta U$ was taken for the calculation of the conductivity σ , given as

$$\sigma = \frac{\Delta I d}{\Delta U (\delta h)} \quad (1)$$

The conductivities of the samples *in vacuo* were between 3×10^{-8} and $2 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. Sulfur dioxide was quickly admitted up to the desired pressure to the evacuated sample container and the current through the sample

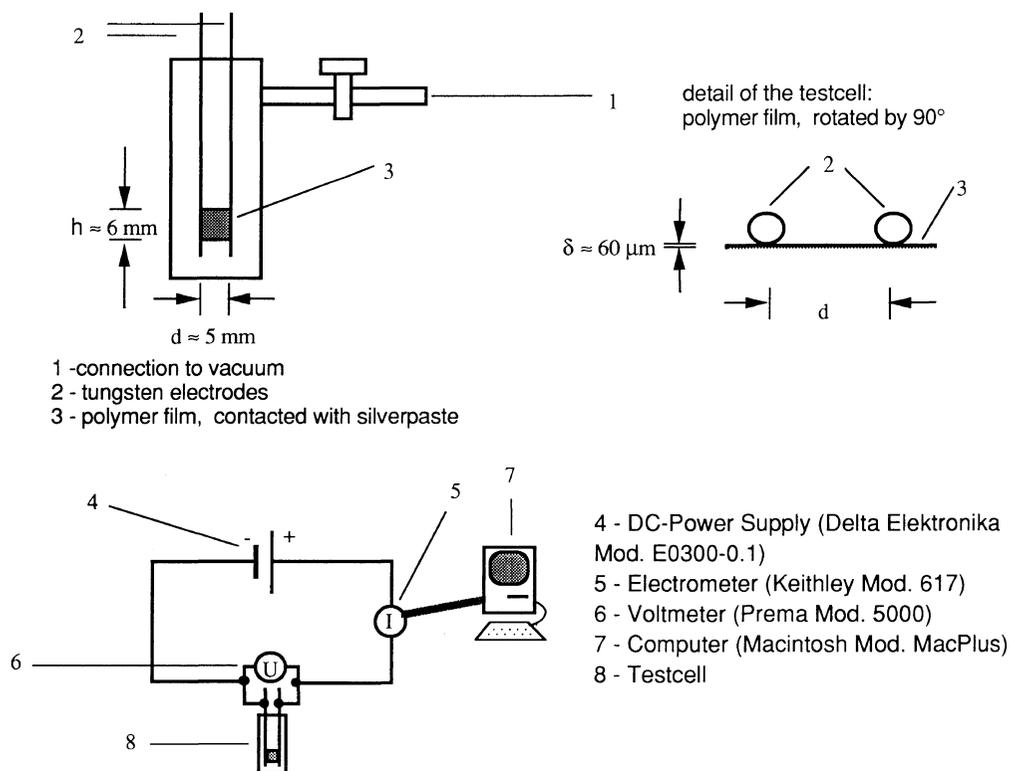


Figure 1. Experimental set-up.

was measured as a function of voltage and time. Changing of the polarity of the voltage changed the polarity of the current but not its magnitude. This may serve as an indication that contact problems or inhomogeneity of doping were not encountered. In Figure 2, the current-voltage dependence of a polyacetylene sample after a 30 min exposure to SO_2 is shown. Care has to be taken that the Joule heat dissipated in the sample does not lead to structural changes of the polymer. At 100 V a current of 2×10^{-5} A was measured which gives a thermal load of the sample of approximately 1 W cm^{-3} . The corresponding temperature rise should be of the order of $0.1^\circ \text{C s}^{-1}$. Convection cooling of the sample by the gas and heat flow to the tungsten wires will limit the temperature rise to a few degrees at most. Tests with a thermocouple did not show any temperature rise.

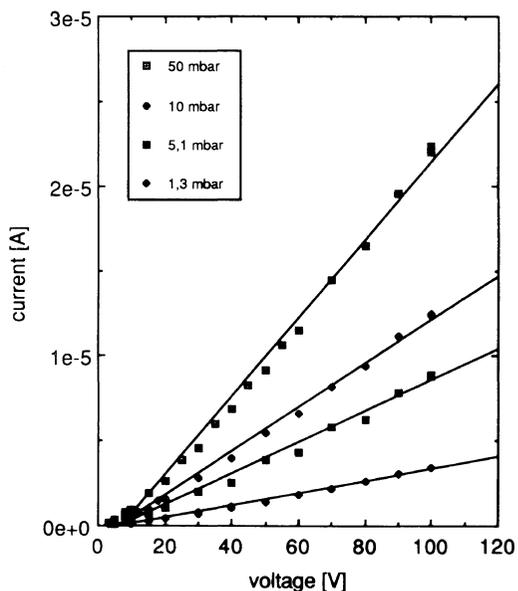


Figure 2. Current-voltage dependence of polyacetylene after 30 min exposure to SO_2 gas.

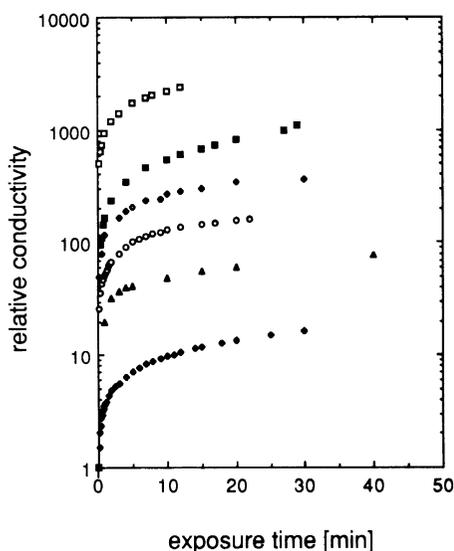


Figure 3. Evolution in time of the current through a sample of polyacetylene after exposure to SO₂: ◆, 1.2 mbar; △, 5.1 mbar; ○, 10 mbar; ◇, 50 mbar; ■, 100 mbar; □, 210 mbar.

After exposure to a given pressure of SO₂ the current increased fast within a minute. This region was followed by a more gradual increase. The data are shown in Figure 3. The increase in conductivity was irreversible. After evacuation of the sample for 120 min the conductivity remained constant and changed little if the sample was exposed to SO₂ again. The maximum conductivity attained was of the order of $10^{-3} \Omega^{-1} \text{cm}^{-1}$ after 12 min exposure to 210 mbar. A stationary state of doping was not reached in these experiments. Thus no information on the concentration of dopant in the polymer can be given.

DISCUSSION

In conjugated polymers, the electric conductivity is enhanced by many orders of magnitude by doping with electron acceptor or donor molecules. However, the dynamic process has not been clarified as yet. Conductivity changes in organic semiconductors or insulators induced by gases or vapors

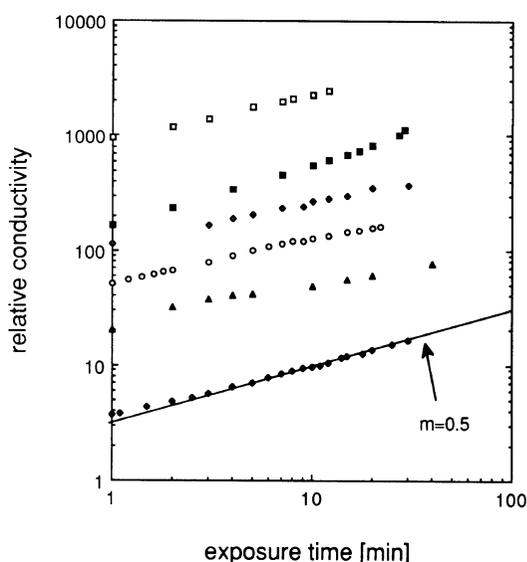
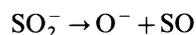


Figure 4. Double logarithmic plot of our data of Figure 3: ◆, 1.2 mbar; △, 5.1 mbar; ○, 10 mbar; ◇, 50 mbar; ■, 100 mbar; □, 210 mbar.

have been attributed to a modification of the surface conductivity. For insulators, weak chemisorption and formation of a charge transfer complex was invoked.^{5,6} If the gas molecules possess a dipole moment reduction of the band gap of the material near the surface and increased charge carrier formation is thought to occur.⁷ In addition to this surface effect, diffusion into the bulk of the material should take place connected with formation of additional charge carriers.

In the case of SO₂/polyacetylene, reaction of SO₂ with the double bond of PA is thought to occur leading to the formation of SO₂⁻ and PA⁺. Studies on electron attachment to three-atomic molecules containing oxygen have shown that dissociation of the initial negative ion with formation of O⁻ is a likely process.⁸ Here, we would speculate that the reaction,



leads to the observed irreversibility of the conductivity change.

If we plot our data of Figure 3 in a log-log plot (see Figure 4), the second time domain of

conductivity increase seems to follow a $t^{1/2}$ -dependence. Such a time dependence is characteristic of diffusion processes. Recently, Tansley and Maddison⁹ investigated the conductivity degradation in oxygen-aged polypyrrole. A decrease of the conductivity of doped polypyrrole is observed when the sample is exposed to atmospheric oxygen. Also in this case the change in time of the conductivity consisted of two regions which could be attributed to adsorption and diffusion.

The kinetics of the adsorption process can be described by the following differential equation,

$$\frac{dC}{dt} = \frac{C_0 - C}{\tau} \quad (2)$$

where C denotes the actual concentration of molecules adsorbed at the surface and C_0 denotes the saturation concentration. τ is the characteristic time constant of the process. At time $t=0$, $C=0$ and the solution of eq 2 is obtained as,

$$C(t) = C_0(1 - e^{-t/\tau}) \quad (3)$$

We assume that the variation in time of the surface conductivity $\sigma_s(t)$ is proportional to $C(t)$, *i.e.*,

$$\sigma_s(t) = K_1 C_0(1 - e^{-t/\tau}) \quad (4)$$

where $\sigma_0 = K_1 C_0$ denotes the maximum conductivity produced by a certain surface coverage at a given pressure. Generally, the dependence of the bulk conductivity of polymers on the dopant concentration is rather complex. From measurements on iodine/polythiophene, proportionality between bulk conductivity and dopant concentration may be inferred at low levels.¹⁰ Here, we are dealing with a conductivity, σ_s , of surface layers induced by a small quantity of dopant. Proportionality of σ_s and C is assumed for this case, too.

The diffusion of gas molecules into the material and doping of the polymer molecules

in the bulk proceeds on a longer time scale. The diffusion process can be considered as one-dimensional with the coordinate x directed perpendicularly away from the surface. The governing equation is given as,

$$\frac{\partial C}{\partial t} = D_b \frac{\partial^2 C}{\partial x^2} \quad (5)$$

D_b is the diffusion coefficient of SO_2 in PA. The solution $C(x, t)$ of eq 5 is given by the complementary error function. The time-dependent number density of infused species per unit surface area $N(t)$, is given as the integral,⁹

$$N(t) = \int_0^\infty C(x, t) dx = 2C_0 \sqrt{D_b \frac{t}{\pi}} = 2C_0 \lambda \quad (6)$$

In principle, the limits of the integral should be taken from 0 to the thickness of the sample ($60 \mu\text{m}$). Since the diffusion coefficients of small molecules in crystalline organic solids are of the order of 10^{-10} to $10^{-12} \text{cm}^2 \text{s}^{-1}$, the diffusion distance, λ , of the gas molecules into the film during the time interval of our experiment is of the order of 10^{-4} to 10^{-5}cm which is small compared to the thickness of the sample. This distance is not small when compared to the diameter of the fibrils (20nm).

The infused molecules form charge transfer complexes with the polymer and thus produce an additional bulk conductivity σ_b which varies in time as,

$$\sigma_b(t) = K_b C_0 \sqrt{D_b t} \quad (7)$$

K_b is a constant. The total conductivity of the sample σ_{tot} , is given by the sum of the intrinsic conductivity σ_{vac} , the surface conductivity σ_s and the bulk conductivity σ_b , *i.e.*,

$$\sigma_{\text{tot}} = \sigma_{\text{vac}} + \sigma_0(1 - e^{-t/\tau}) + K_b C_0 \sqrt{D_b t} \quad (8)$$

In Figure 4, the ratio $\sigma_{\text{tot}}/\sigma_{\text{vac}}$ is plotted as a function of time. The two time domains corresponding to adsorption and diffusion can be identified particularly well for the data of 210 mbar. In Figure 5 we compare the

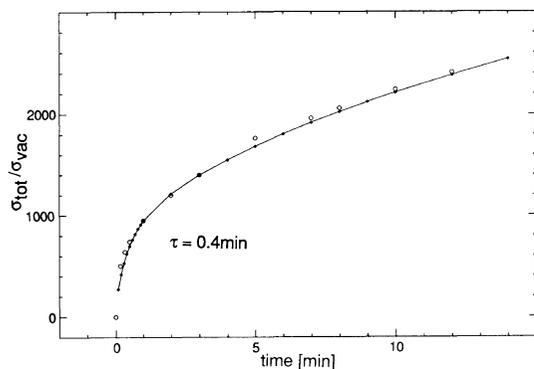


Figure 5. Comparison of the experimental data (○ for 210 mbar) and the dependence given by eq 8 (◆, $\tau = 0.4$ min; $\sigma_0/\sigma_{\text{vac}} = 411$; $(K_b C_0 \sqrt{D_b})/\sigma_{\text{vac}} = 568.5$ [$\text{min}^{-0.5}$]).

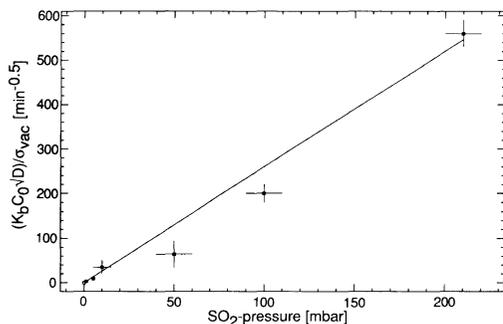


Figure 6. Slope m^* (see eq 9) of the data of Figure 4 as a function of pressure.

experimental data with the dependence given by eq 8. Adsorption approaches saturation with a time constant of $\tau \approx 0.4$ min while for longer times diffusion becomes the rate determining step. For lower gas pressures, the separation in time of the two mechanisms is not so apparent. Since $\sigma_{\text{tot}}/\sigma_{\text{vac}}$ follows a \sqrt{t} -dependence over the whole time range measured we may assume that for lower pressures τ becomes smaller. At longer times, the increase of the conductivity is determined entirely by the diffusion term of eq 8. The slope m^* is given as,

$$m^* = \frac{(K_b C_0 \sqrt{D_b})}{\sigma_{\text{vac}}} \quad (9)$$

From the data of Figure 4, m^* -values were obtained. Since D_b and K_b are independent of pressure, m^* is proportional to C_0 , the surface coverage. In Figure 6, m^* is plotted as a function of pressure. In the pressure range investigated here, the surface coverage increases proportionally with pressure. Langmuir's adsorption isotherm predicts such a dependence for small pressures.

Whether the diffusion process observed here, corresponds to diffusion of the gas into the polymer fibrils or into the interior of the polymer foil which has a porous structure, formed by the fibrils,¹¹⁻¹³ cannot be decided. Measurements on the recently developed N-type film which has a high bulk density of 1.0 to 1.1 g cm⁻³ might answer this question.

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