Short Communication

Water-sensitive sensor based on modified poly(vinyl chloride)

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Abstract

A conducting polymer obtained from chemical modification of poly(vinyl chloride) is presented; it possesses high sensitivity and selectivity to water in the vapour and liquid phase. Water molecules, as associates with hydrogen bonds, appear to form bridges between the conducting fragments of the polymer increasing its conductivity.

Introduction

High interest has been devoted to conducting polymers since their possible application as basic materials in molecular electronic devices with nonlinear characteristics, such as field effect transistors, diodes, intelligent sensors, etc. [1—4]. In some cases, modified conventional polymers can be used for these purposes. It is possible to vary the electrical conductivity of insulating polymers by several orders of magnitude by adding conductive fillers [5, 6]. The conductivity of insulating polymers such as poly (vinyl chloride) (PVC) can also be changed by chemical modification [7, 8]. *trans*-Polyacetylene-type polymers have been obtained from PVC under irradiation [9].

The aim of this work is to fabricate chemically modified PVC and construct resistive sensors which are sensitive to chemical substances.

Experimental

Commercially available PVC films ($70 \times 70 \times 0.05$ mm^3) were treated by fuming sulfuric acid to yield dark brown or black modified films. The

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conductivity of the films at room temperature and humidity was about 10^{-4}—10^{-3} S/cm (two-probe method). Scanning electron microscopy showed the presence of micropores with an average 40 μm diameter and a density of 1×10^5 cm^{-2}.

D.c. studies were carried out by using an active balance bridge with two approximately identical resistive sensor elements with an exposed surface of 2 cm^2. A 10% solution of water in anhydrous acetone injected into the closed volume filled with dry argon was used to register the response on small concentrations of water in the gas medium. The measured sensor sensitivity to NH_3, alcohols, acetone, ethers, etc., was one to two orders of magnitude smaller than to water. Saturated aqueous solutions of different inorganic salts were used to measure the relative humidity.

EPR spectra were registered with 3 cm waveband PS-100X spectrometer using a standard method.

Results and discussion

The modified PVC films exhibited at room temperature a single weak EPR signal, with a Lorenzian lineshape, the width between peaks being ΔH_{pp} = 5.4 G and g = 2.0031, characteristic of π-electron systems. The line-width and signal intensity changed weakly while the temperature decreased to 77 K. Magnetic parameters of this material are close to those of *cis*-polyacetylene, in which a small amount of *trans*-isomer is usually present [10]. Thus, the increase of conductivity and paramagnetic susceptibility in the film can be explained by dehydrochlorination during oleum treatment with the formation of *trans*-polyacetylene regions with unpaired electrons according to the scheme [7, 8]:

$[-CHC1-CH_2-]_m \rightarrow [-CHCl-CH_2-]_m - [CH=CH-]_k$

Being weak electron acceptors, water molecules can partially accept the electron density from the neutral charge carriers, solitons [11], on the surface or in the bulk of the film, thus providing *p*-type conductivity of the sample.

The dependence of sensor conductivity versus time at a sharp 0.4% change of relative humidity is shown in Fig. 1. The arrows up and down indicate the moment of the injection and removal of H_2O (solid line) and D_2O (dotted line), respectively. The increase of film conductivity is not considerable at the initial period of time, when $t < \tau_i$. This corresponds to water diffusion into the bulk of the polymer. The characteristic time r_4 of the quasi-stationary diffusion process is determined by the limited film thickness d and by the effective diffusion coefficient $D[$ [12]:

$$\tau_i = d^2 / \pi^2 D_i^| \tag{1}$$

So the real diffusion coefficient depends on the diameter h of the pores and on their number N in unit area of the film [12]:

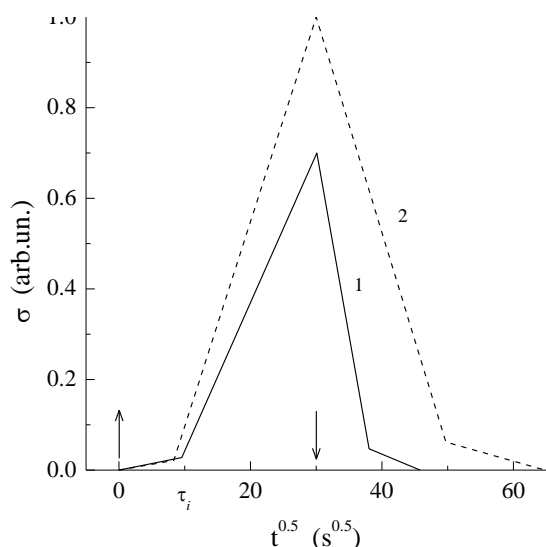$$D_i = 12 D_i^| / \pi N h^2 = 12 d^2 / \pi^3 h^2 N \tau_i. \tag{2}$$

Fig. 1. PVC sensor conductivity vs. time with instantaneous increase (↑) and decrease (↓) at 0.4% relative humidity in a mixture of argon with (1) H_2O and (2) D_2O vapour at room temperature.
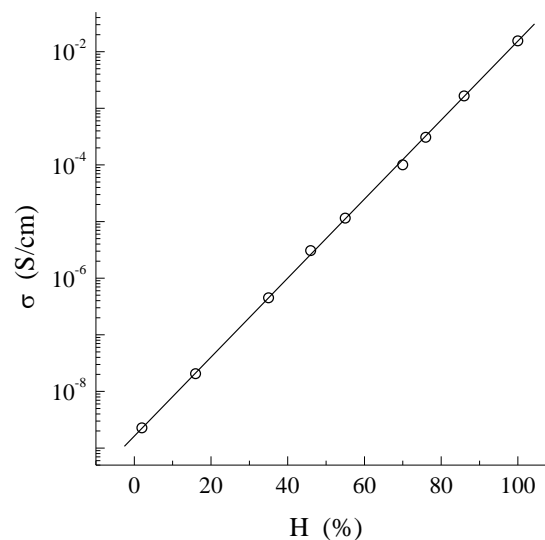
Fig. 2. PVC sensor conductivity vs. relative humidity registered at room temperature.

As the quasi-stationary process is reached, the sensor conductivity changes quadratically with time (Fig. 1). Thus, if the number of molecules diffused into the polymer correlates with that of charged spinless solitons, the process may be considered in terms of molecular diffusion transfer through the membrane. So, the concentration of molecules in the interface being constant, the concentration C of water molecules diffused into the bulk of the polymer to a distance x at time t is equal to

$$C = C_0 \text{erf}(z) \tag{3}$$

where $\text{erf}(z) = \int_0^z \exp(-y^2) dy$ is the error function and $z = x/[2(D_i^| t)^{1/2}]$. For a total number n of water molecules diffusing into the bulk at time t and therefore in a quasi-stationary regime ($t > \tau_i$), the film conductivity σ would be equal to [10]

$$\sigma = kn = kC_0(D_i^| t / \pi)^{1/2} \tag{4}$$

where κ is the coefficient.

As shown in Fig. 1, the sensor conductivity is well described with the $\sigma \sim t^{|0.5|}$ power law. The diffusion coefficient, as determined from the data of Fig. 1 using eqn. (2), was equal to 6.5×10^{-8} cm^2/s for H_2O molecules and 1.2×10^{-7} cm^2/s for D_2O molecules. The Figure shows that the diffusion coefficient of D_2O changes insignificantly with the change in direction of molecular diffusion. The rate of direct diffusion of H_2O molecules is almost one order of magnitude smaller than that of the reverse process. Moreover, the rate of direct diffusion of H_2O molecules is less than half that of D_20 molecules. This fact can be interpreted by considering the larger degree of association of usual water entering the polymer as compared with D_2O because

of higher polarity. When water vapour interacts with the polymer the association degree decreases, resulting in a higher diffusion rate of the water being expelled.

Figure 2 shows the dependence of the conductivity of one of the sensors under study on relative humidity H, registered at room temperature and under the condition $t > \tau_i$. There is an exponential dependence of these values:

$$\sigma = \sigma_0 \exp(k'H) \tag{5}$$

where k' is the coefficient. The k' value varies in the range of 0.07-0.12 $(\%)^{-1}$ for different films. Such dependence is characteristic of interchain hopping charge transfer with activation energy E_a, which decreases with increase of reagent concentration [13]. Thus, the sensor conductivity in the quasi-stationary regime can be generally presented as

$$\sigma = k_1 \sigma_0 (D_i^| t)^{1/2} \exp[-E_a(1 - k_2 H)/kT] \tag{6}$$

where k_l and k_2 are coefficients, and k is the Boltzmann constant.

The sensor also exhibits high sensitivity and selectivity to water molecules in nonpolar liquid medium. The conductivity of the sensor in hexane solution depends exponentially on water concentration; the k' value being equal to 0.41 $(\%)^{-1}$.

The following scheme of dynamic processes occurring in the film of modified PVC is proposed. The PVC modification results in the formation of polyacetylene conjugated fragments. The initial conductivity of the modified polymer in dry atmosphere is determined by the length and packing of the conjugated fragments; charge transfer along the conjugated chains is realized by solitons [11]. Charge transfer between conjugated fragments is realized in the framework of the interchain electron hopping mechanism. When the water molecules diffuse into the polymer bulk, they form bridge-type bonds between the conjugated chains. As a result, the solitons acquire a positive charge in the ircms-polyacetylene-like fragments. Moreover, solitons which may occur in the spreading water associate [14] may also participate in charge transfer between polymer chains. Thus, the macroconductivity of the sample increases considerably as a result of both intra- and interchain charge transfer. Other molecules are not able to form such associations which determine the selectivity of the sensor to water molecules only.

Conclusions

The modified PVC keeps its conducting and water-sensitive properties for at least three years and can be potentially used as a cheap humidity sensor, electrostatic screen or floor and other elements of low-current electronic equipment. Further progress involves the fabrication in a controlled manner of thin-film sensitive elements with small area; the study of their reproducibility, stability and response time will be also necessary.

This polymer is also convenient for the study of structural and electrodynamic properties of separate conjugated chains in an insulating matrix.

References

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