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Electrical Properties of σ-Conjugated Polymers with Additives and Their Applications in Sensors

*Stanislav Nešpůrek,**[1,2] *Geng Wang,*[1] *Stanislav Böhm,*[3] *Marek Kořínek,*[3] *Hans-J. Adler*[4]

[1] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
E-mail: nespurek@imc.cas.cz
[2] Chemical Faculty of Technical University, Purkyňova 118, 612 00 Brno, Czech Republic
[3] Department of Organic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
[4] Institute of Macromolecular Chemistry and Textile Chemistry, Dresden University of Technology, Mommsenstr. 13, 01062 Dresden, Germany

Summary: The charge carrier transport in poly[methyl(phenyl)silylene] (PMPSi) proceeds predominantly along the σ-delocalized Si backbone with participation of interchain hopping and polaron formation. The charge carrier mobility increases with increasing electron affinity of acceptor dopands having zero dipole moments. On the other band, the hole drift mobility is influenced by the dipole moment of the dopand. The electrostatic charge-dipole interactions cause a broadening of the energy distribution of transport states, which results in a decrease in the charge carrier mobility. An addition of organic salts leads, under the conditions of increased humidity, to an increase in electrical conductivity and capacitance. This is demonstrated on the layers PMPSi/1,5-dimorpholino-1,5-diphenylpentamethinium perchlorate.

Keywords: polysilylenes, charge transport, doping, humidity sensors

Introduction

Polymers offer lots of advantages for sensor technologies: they are relatively low-cost materials, their fabrication techniques are quite simple and they can be deposited on various types of substrates. Sensors with electrical responses are usually fabricated in the form of vacuum-evaporated, cast or spin-coated thin films, Langmuir-Blodgett films, printed films of inks consisting of polymer matrix and particles of sensing additives, or spin-coated films prepared from a conjugated polymer, in which the sensing material is dispersed on molecular level. In the

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last case usually π-conjugated polymers are used as charge-transporting media. In this contribution, we will show that also σ-conjugated polymers (e.g. polysilylenes) are suitable for the preparation of polymeric sensitive inks.

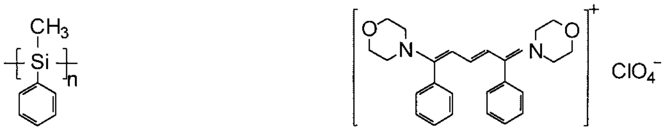
Experimental

Materials

Synthesis of poly[methyl(phenyl)silylene] (PMPSi; see Scheme 1): Oxide-free sodium was dispersed in boiling toluene under argon and a small amount of diglyme was added. Freshly distilled dichloro(methyl)phenylsilane in toluene solution was dropped into the dispersion. After the 2 h reaction at 140 °C, the reaction was quenched at room temperature by addition of a butyllithium solution. The residual sodium was reacted, under ice cooling, first with ethanol and then with H_2O. Crosslinked and insoluble portions were separated by centrifugation. The polymer was then precipitated by addition of isopropyl alcohol. The low-molecular-weight portion was separated by 1 h extraction with boiling ether. The polymer was then dried at 13 mbar for 48 h. The polymer, obtained in *ca.* 17% yield, possessed a unimodal but broad molar mass distribution ($M_w = 4 \times 10^4$ g mol^{-1}, $M_w / M_n = 2.7$; SEC averages, polystyrene standards).

Synthesis of 1,5-dimorpholino-1,5-diphenylpentamethinium perchlorate (MDPPMClO; see Scheme 1): Commercially available (Aldrich) 4-(trimethylsilyl)morpholine was after purification added to a solution of 2,6-diphenylpyrylium perchlorate in dry acetonitrile under nitrogen atmosphere. The reaction mixture was stirred for 4 h at room temperature and complete consumption of the starting material was checked by TLC. After evaporation to dryness in vacuum the solid residue was crystallized from ethanol.

Scheme 1. Chemical structures of materials used for humidity sensor fabrication.



poly[methyl(phenyl)silylene] (PMPSi)

1,5-dimorpholino-1,5-diphenylpentamethinium perchlorate (MDPPMClO)

Thin film formation

Before deposition of films, the polymer was reprecipitated three times from a toluene solution with methanol and centrifuged at 12000 rpm for 15 min. After deposition (spin coating, 3000 rpm) on glass substrates from a toluene solution, the films were dried in vacuum (10^{-3} Pa) at 330 K for at least 4 h. Then, for the sensor element (the polymer system was deposited on a ceramic substrate), the system of interdigital gold electrodes (distance 1 mm) was vacuum evaporated on the top of the film. Samples for the time-of-flight (TOF) measurements were prepared in the form of sandwich structures ITO/sample/Al; Al electrode 60 nm thick was prepared by vacuum evaporation. The doped samples were prepared in the same way by spin coating of the corresponding mixed toluene solutions.

Measurements

DC and AC conductivities were measured using a Keithley 6517A electrometer and Hioki LCR Hitester 3532-50, respectively. The charge carrier mobility was measured by the TOF method in an electrical circuit consisting of a voltage source, sample and osciloscope (HP 54510A, 50 Ω input impedance) connected in series. The samples were illuminated by the 347 nm laser pulses (duration 20 ns) generated by a ruby laser (Korad model K1QS2) in conjunction with a frequency doubler through the transparent ITO electrode. The samples were kept in a vacuum cryostat (10^{-4} Pa) or under argon during the measurement.

Results and discussion

Charge carrier transport

Polysilylene consists of a chain of silicon atoms with three interacting sp^3 hybrid orbitals. Electron delocalization along the silicon backbone results from the interaction of sp^3 orbitals of adjacent silicon atoms[1]. The resonance integral between two sp^3 orbitals located on adjacent silicon atoms and pointing to each other, β_{vic}, is responsible for the formation of a Si-Si σ-bond. The degree of electron delocalization in the backbone is a function of the $\beta_{vic} / \beta_{gem}$ ratio, where β_{gem} is the resonance integral between two sp^3 orbitals localized on the same silicon atom. Electron delocalization is perfect if the ratio equals unity. Thus, the linear Si backbone behaves as a molecular wire due to the σ-conjugation. The mobilities of charges (holes) depend on the chemical nature and size of the side groups[2]. The "on-chain" hole mobility in PMPSi was found to amount to $\mu \sim 2 \times 10^{-6}$ $m^2V^{-1}s^{-1}$ using time-resolved microwave photoconductivity[3,4].

A question arises why the value of "on-chain" mobility is so low. A possible reason is the formation of polarons. The strong electron-phonon coupling causes carrier self-trapping and creates a quasiparticle, a polaron, which can move only by carrying along the associated molecular deformation. The motion of such a charge carrier, dressed into a cloud of local deformation of the nuclear subsystem, can be phenomenologically described by introducing a temperature-dependent effective mass which is higher than the electron mass. A significant distortion of the PMPSi chain was recently found by Kim at al.[5] and by quantum-chemical calculations[6].

The shapes of photocurrent transients obtained by the TOF method were the following: after an initial drop, which is RC-limited, a plateau was reached followed by a tail. Transit time, t_0, was determined from the intersection of the asymptotes to the plateau and tail of the transient signal. Mobilities were determined from the conventional expression, $\mu = L^2/t_0U$, where L is the sample thickness and U is the applied voltage.

Figure 1 illustrates the dependences of the charge carrier mobility, μ, of a PMPSi sandwich sample (thickness ca. 2 μm) on $F^{1/2}$, the square root of the electric field strength, at different temperatures. In all cases, the mobility can be described by an $\exp(\beta F^{1/2})$ dependence for $F > 10^7$ Vm^{-1}. At lower field strengths, $\mu(F)$ becomes constant or increases slightly upon reducing F. These types of dependences are usually treated in the framework of the hopping disorder concept. The essential difference between the polaron and disorder models is that the latter, at variance with the former, implies a sufficiently weak electron-phonon coupling and the activation energy of charge transport reflects the static energy disorder of the hopping sites. In contrast, the polaron model suggests a strong electron-phonon coupling and a negligible contribution of energy disorder to the activation energy of the carrier mobility[7,8]. It was suggested[8-10] that the zero-field activation energy of the mobility, $E_a(F \rightarrow 0)$, obtained from the temperature dependence of the extrapolated charge mobility values to zero field $\mu(F \rightarrow 0)$, can be approximated by the sum of the disorder and polaron contribution as[9,11]

$$E_a(F \rightarrow 0) = E_a^{pol} + E_a^{dis} = \frac{E_p}{2} + \frac{4}{9}\frac{\sigma^2}{(kT)^2} \qquad (1)$$

where E_a^{pol} and E_a^{dis} are the polaronic and disorder contributions, σ is the energy width of the density-of-states (DOS) distribution, k is the Boltzmann constant, and T is temperature. Because it is experimentally difficult to determine energy E_p, the activation energy E_a ($F \rightarrow 0$) is often related to the effective energy width of the DOS distribution σ^*. Usually it is also difficult to distinguish experimental data between $\mu(1/T^2)$ and $\mu(1/T)$ dependences. Then, the right side of Eq. (1) is treated as an apparent (effective) activation energy which can be expressed as E_a^{eff} ($F \rightarrow 0$) = $(8/9)\,\sigma^{*2}/kT$.

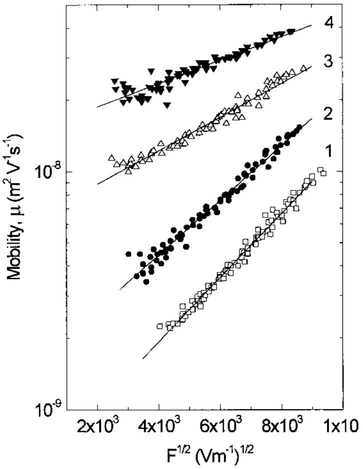


Figure 1. The charge carrier mobility vs. the square root of the electric field strength (F) for PMPSi, parametric in temperature; T = 295 K (curve 1), 325 K (2), 355 K (3), 358 K (4).

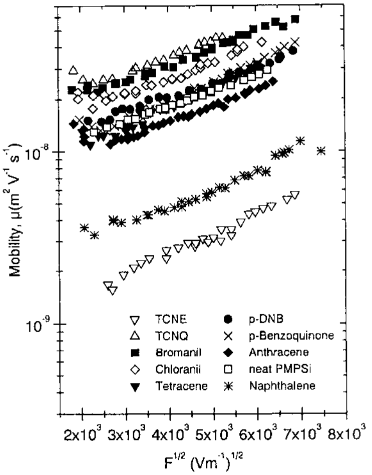


Figure 2. The charge carrier mobility vs. the square root of the electric field strength (F) for neat PMPSi (squares) and PMPSi doped with acceptors (3 mol %).

The polaron binding energy was determined for PMPSi[10] as E_p = 0.16 eV. Recently, Pan et al.[12] reported a smaller value of E_p = 0.08 eV. The E_p values are still an open question and need more measurements and discussions. The zero-field value of the activation energy of the mobility was measured, E_a^{eff} ($F \rightarrow 0$) = 0.29 eV. The effective value of the half-width of the Gaussian distribution of the hopping states σ^* was determined from the above equation to be 0.093 eV (at room temperature). From thermostimulated luminescence studies[13], the value σ^* = 0.096 eV was obtained. The real value of the width of the distribution of hopping sites σ would be lowered by the polaron contribution ($E_a^{eff} - E_p/2 = 8\ \sigma^2/9\ kT$); this yields σ = 0.078 eV.

It is interesting to try to change the transport parameters by doping[11]. The dopands can be divided into three groups:

(i) Materials of acceptor type with high electron affinity and zero dipole moment, like 7,7,8,8-tetracyano-1,4-quinodimethane (TCNQ), 2,3,5,6-tetrabromo-1,4-benzoquinone (bromanil), 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), tetracene, *p*-dinitrobenzene (*p*-DNB), *p*-benzoquinone and anthracene increase the charge carrier mobility and decrease the σ^* parameter. The mobility increases with increasing electron affinity of the acceptor (TCNE is an exception – the behaviour is not fully understood). At the moment it is not clear what is responsible for this effect, a decrease in the polaron binding energy or disorder parameter.

(ii) Dopands with high dipole moments, like *m*- and *o*-dinitrobenzene (*m*- and *o*-DNB), decrease the charge carrier mobility, while the effective σ^* parameter increases (see Table 1). The detail analysis shows that in this case charge-dipole interactions are important. Two effects must be mentioned in this context: (1) A broadening of the energy distribution of hopping states[11,14]; the mobility depends on the dipole moment (decreases with increasing dipole moment), molecular dimensions and concentration of the additive. (2) New local states are formed in the vicinity of dipolar species[15] even though these molecules do not necessarily have to act as trapping sites. However, contrary to the situation encountered in the case of both chemical traps and the "conventional" structural traps, the electron and hole dipolar traps are formed on different molecules: a molecule close to the negative pole of the dipole should be a hole trap, whereas a molecule close to the positive pole should trap electrons. The results of doping experiments are summarized in Table 1 and presented in Fig. 2 (*m*-DNB and *o*-DNB are not included because of the distinctness of the figure).

(iii) Naphthane does not act as an acceptor. Its presence in PMPSi increases the disorder effect.

Humidity sensor

Thin films for humidity sensors were deposited by spin coating on glass substrates. Both PMPSi and MDPPMClO were dissolved in toluene and mixed. After deposition, the sensor was kept in vacuum for 4 h at 330 K.

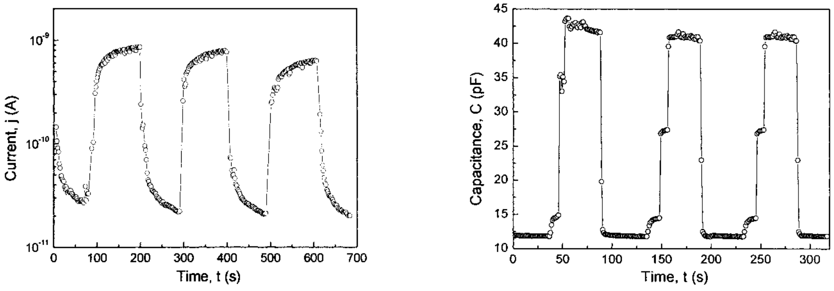
The humidity sensors are usually fabricated using hydrophilic polymers with some ionic groups[16], or polymeric matrices containing inorganic salts[17] like $FeCl_3$. Here, our sensing material, MDPPMClO, was prepared as an organic salt. Under the influence of humidity one can expect dissociation of the molecule and formation of two types of species: ion-pairs and free charge carriers after full dissociation in external electric field. The formation of dipolar species results in the broadening of the transport hopping state distribution, as it follows from Table 1. Thus, the charge carrier mobility decreases and electric permittivity increases. On the other hand, full dissociation results in the formation of free charge carriers, which can move in the transport polymer matrix. Because electrical conductivity is the product of the unit charge, charge carrier mobility, μ, and free charge carrier concentration, n, the final change of the conductivity under the humidity exposure depends on the equilibrium of the changes $\Delta\mu$ and Δn. In our case the

Table 1. Values of hole mobilities, μ, their effective activation energies at zero electric field, E_a^{eff} $(F \to 0)$ and effective values of the half-widths of DOS, σ^*. PMPSi films doped with 3 mol % additive.

Dopant	$10^8\mu^{\#}$	E_a^{eff} $(F \to 0)$	$A^{\dagger}$	σ^*	$m^{\ddagger}$
	(m^2/Vs)	(eV)	(eV)	(eV)	(D)
TCNQ[1]	5.71	0.241	1.7 ~ 1.8	0.084	
Bromanil	4.80	0.242	1.4	0.084	
Chloranil	4.12	0.247	1.3 ~ 1.4	0.085	
Tetracene	3.06	0.275	0.9 ~ 1.0	0.089	
p-DNB[2]	3.10	0.283	0.7	0.091	0.0
p-Benzoquinone[3]	2.74	0.286	0.7 ~ 1.8	0.091	
Anthracene	2.57	0.285	0.5	0.091	
None (neat PMPSi)	2.28	0.298	–	0.093	
m-DNB[4]	1.20	0.340	0.3	0.099	3.8
Naphthalene	0.77	0.375	0 ~ 0.15	0.104	
o-DNB[5]	0.50	0.460	0	0.116	6.0
TCNE[6]	0.43	0.463	2.2 ~ 2.9	0.116	

[1] 7,7,8,8-tetracyano-1,4-quinodimethane, [2] 1,4-dinitrobenzene, [3] 1,4-benzoquinone, [4] 1,3-dinitrobenzene,
[5] 1,2-dinitrobenzene [6] tetracyanoethylene, [#] measured at T = 295 K and F = 36 MV/m,
[†] electron affinity and [‡] dipole moment of the dopands.

contribution to the conductivity of the increase in free charge carrier concentration is higher than the decrease in charge mobility; thus, both AC and DC conductivity increase. The changes of the steady-state current and capacitance for relative humidity changes from 45 to 96 % (fast change during about 2 s realized by the switching between dry and wet flowing air) are given in Fig. 3 The change of the current was about two orders of magnitude (thickness of the film was ca. 500 nm); for thinner layers even larger changes could be detected. Similar changes were also observed in AC conductivity. Figure 3(b) shows the capacitance changes. It could be pointed out that both current and capacitance changes were stable and fully reproducible.



(a) (b)

Figure 3. Changes of the steady-state current (a) and capacitance (b) of the system PMPSi : MDPPMClO (4 : 1 weight) for relative humidity changes from 45 to 96 %.

Acknowledgements

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