Polaronic transport in polysilanes

S Nešpúrek¹, J Nožár¹, A Kadashchuk² and I I Fishchuk²

¹Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
²Institute of Physics, Academy of Sciences of Ukraine, Prospect Nauki 46, 03028 Kiev, Ukraine

E-mail: nespurek@imc.cas.cz

Abstract. Analytical theory based on the effective medium approach is used to explain electric field dependences of charge carrier mobility in poly[methyl(phenyl)silylene]. It is shown that the charge transport can be described by a small polaron movement in the presence of correlated energetic disorder. Polaron binding energy is the main part of the activation energy of the mobility.

1. Introduction

Amorphous silicon is a member of the larger class of silicon backbone solids which, in addition to crystalline phase, also contain silicon clusters, silane oligomers, poly(siloxanes), and poly(organylsilanes). The last mentioned backbone polymers are under considerable research interest because of their unusual optical and electrical properties and possible models for the charge carrier transport in one-dimmensional silicon structures, where quantum dots can be created [1,2].

Charge carrier transport in silicon backbone polymer, poly[methyl(phenyl)silylene] (PMPSi), was discussed by Kepler et al. [3] and by Abkowitz et al. [4]. The experimental results were interpreted in the frame of charge hopping between backbone-derived localized states. These states were associated with domain-like suborganization of the silicon backbone into all-trans segments of approximately 10 – 20 repeat units separated by conformationally disordered regions. An alternative explanation [5] was done on the basis of intragap states which spontaneously arise, even in a perfectly ordered chain, from bond order polaron formation. This is a consequence of the coupling of charge carriers to the quasi-one-dimensional silicon backbone.

Several values of the polaron binding energy is mentioned in literature for PMPSi. In this paper we summarize the published methods suitable for the determination of this energy with some criticism of their use. The second part of the paper deals with our new methods for the polaron detection and the determination of the polaron binding energy.

2. Experimental

Poly[methyl(phenyl)silylene] (PMPSi) was prepared by Wurtz coupling polymerization, as described by Zhang and West [6]. The low-molecular-weight fractions were extracted with boiling diethyl ether. The residual polymer, obtained in c. 17 % yield, possessed a unimodal but broad molar mass distribution, $M_w = 4 \times 10^3$ g mol⁻¹.
Thin films (thickness from 1 to 3 μm) were prepared from a toluene solution by casting on conductive ITO glasses. The top Al or Au electrodes, 40 – 60 nm thick, were prepared by the vacuum evaporation. Before the deposition, the polymer was three times purified by precipitation in methanol and toluene solution and centrifuged (12 000 rpm, 15 min). After the deposition the films were dried in the vacuum of 0.1 Pa at 330 K for at least 4 hours. The film thicknesses were determined by surfometric measurements.

Charge carrier mobility was measured by a time-of-flight method using an electrical circuit consisting of voltage source, sample and oscilloscope (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 penetration depth of the light was 0.13 μm which represents less than 4 % of the sample thickness. The samples were kept in a vacuum cryostat (10⁻⁴ Pa) or under argon during the measurement. In both cases the same experimental results were obtained.

3. Charge carrier transport

The previous experimental results mentioned in literature [4] suggest that in 3D samples the charge carrier transport is realized by hopping through sites distributed both in energy and space [7]. Tails, observed in the current transients (time-of-flight method), suggest the dispersive character of the transport [8].

Recently, Kim et al. [9], from the measurements of the velocity of the excitation energy along the PMPSi chain, have found the excitations are carrying significant distortions of the backbone. One possibility of explaining this behaviour is to use disordered polaronic theory [10]. In this case the activation energy of the charge mobility has contributions both from the dynamic disorder, i.e., the polaronic barrier, and from the static disorder, i.e., the variation of the energy as a result of the environment. Thus, in the first approximation, one can write for the activation energy of the charge carrier mobility the relation [11]

$$E_{a}^{\text{eff}} = E_{a}^{\text{pol}} + E_{a}^{\text{dis}} = \frac{E_{p}}{2} + \frac{8 \sigma^2}{9 kT}$$

where $E_{a}^{\text{pol}}$ and $E_{a}^{\text{dis}}$ represents polaronic and disorder contributions and $E_{p}$ is the polaron binding energy.

We proposed two methods for the polaron detection in polymeric materials:

(i) The first method, published recently [12], is based on the shift of the low temperature thermostimulated photoluminescence (TSPL) peak to higher temperatures after the additional infrared illumination. The idea is based on the following principle. The initial energy distribution of polaron was formed in the course of low-temperature energy relaxation. The polaron formation strongly affects both low-temperature energy relaxation and thermally assisted hopping of charge carriers in disordered material. If the polaron binding energy is comparable with or larger than the density-of-states (DOS) width, the energetically downward hopping is strongly suppressed by the lack of deeper vacant sites, which are only accessible for further jumps at low temperatures. Therefore, after a fast initial polaron relaxation, the energy distribution of polarons remains almost "frozen in" over the entire dwell time between low-temperature photoexcitation of the sample and the onset of the TSPL heating run. The polaronic contribution to the activation energy of every individual upward jump is equal to a half of the polaron binding energy, $E_{p}/2$, while the low-temperature energy relaxation of polarons within the DOS distribution is slowed down because the polaron energy distribution is shifted down by $E_{p}$. IR irradiation causes a local heating in the environment of charged molecules and at low temperatures efficiently stimulates energy relaxation towards the deeper tail states of polarons. Concomitantly, charge carriers get a possibility to occupy those tail states, which would be accessible
for them when there were no polaron effects. This results in the shift of the TSPL peak towards higher temperatures and in a decrease in its intensity.

(ii) We present here a new method based on the electric field ($F$) and temperature ($T$) dependencies of the charge carrier mobility ($\mu$). The ln($\mu$) versus $\sqrt{F}$ dependence is linear. From detail calculations [13] follows that Poole-Frenkel factor $\alpha = \partial \ln(\mu/\mu_0) / \partial \sqrt{F}$ varies almost linearly with $T^{-3/2}$ in the case of polaron-free transport. Alternatively, this dependence deviates significantly from a straight line in the case of polaron model.

The polaron binding energy in PMPSi was estimated by Bässler et al. as $E_p = 0.16$ eV [11] by the linear extrapolation of the temperature dependence of the activation energy of the charge carrier mobility to zero temperature. Pan et al. [14] obtained the value of $E_p = 0.08$ eV for exciton-polarons. Regarding to the fact that in molecular crystals the defects of the same feature form about 3 times deeper traps for charge carriers than for singlet excitons [15], one can write for the charge-polaron binding energy $E_p = 0.24$ eV. Even if the polaron binding energy is higher than the width of the density of states, the disorder seems to be still an important contributor to the temperature and field dependencies of the mobility in macroscopic systems where inter- and intramolecular hopping takes place.

Let us put some comments to the facts mentioned above:
(i) The plot of the dependence of the charge carrier mobility on temperature is not usually linear. Thus, $E_p$ value is only the rough estimation.
(ii) The simplified jump rate equation used in Ref. [11] for polaron hopping transport has no theoretical justification. Paris et al [16] demonstrated that the problem related to physical parameters can be solved assuming the small polaron transport occurs in the presence of correlated energetic disorder. In this case the coefficient $(8/9)$ - see Eq. (1) - in the disorder term must be changed to $(1/4)$ [13]. Discussion of the problem for general case of the Marcus jump rate is discussed in Ref. [13]. According to our effective medium approach for the symmetrical jump rate the mobility can be approximated by the expression [13]

$$\mu \approx \exp \left[ -\frac{E_p}{2kT} - \frac{1}{8} \left( \frac{\sigma}{kT} \right)^2 + \left( \frac{\sigma}{kT} - 1 \right) \sqrt{\frac{eF}{8kT}} \right], \quad (2)$$

where $e$ is the unit charge, $F$ is the electric field strength and $r$ is the average distance between neighboring hopping sites of the disordered polaron transport. Equation 2 represents a good approximation for the electric field dependences of the charge carrier mobility.

![Figure 1](image)

**Figure 1** Electric field dependences of the charge carrier mobility of PMPSi parametric in temperature; $T = 295$ K (curve 1), 312 K (curve 2), 325 K (curve 3), 355 K (curve 4).

Lines represent the best common fit according to Eq. 2.
After the fitting the electric field dependencies (see Fig. 1) using Eq. 2, the following parameters were obtained: energy distribution parameter of hopping states $\sigma = 0.09$ eV, $E_p = 0.29$ eV, the most probable hopping distance $r = 1.2$ nm. The common fit for all dependencies is represented by straight lines in Fig. 1. From this result follows that the polaron binding energy is about two times higher (compare $E_p = 0.16$ eV vs. 0.28 eV). In the latter case the small polaron transport in the presence of correlated energetic disorder was assumed. Thus, the activation energy of the charge mobility is not only a simple sum of the contributions due to the polaron formation and energetic disorder. The contribution of the disorder to the activation energy of the mobility is only 26 % (0.076 eV).

Acknowledgements
This work was supported by the grants No. IAA100100622 and KAN400720701 from the Grant Agency of the Academy of Sciences of the Czech Republic.

[1] Nešpůrek S, Toman P and Sworakowski J 2003 Thin Solid Films 438-439 268
[2] Nešpůrek S, Sworakowski J and Kadashchuk A 2001 IEEE Trans. Die. Electr. Insul. 3 432
[3] Kepler R G, Zeigler J M, Harrah L A and Kurtz S R 1982 Phys. Rev. B 35 2819
[4] Abkowitz M A, Rice M J and Stolka M 1990 J. Philos. Mag. B 61 25
[5] Rice M J and Philpot S R 1987 Phys. Rev. Lett. 58 937
[6] Zhang X-H and West R 1984 J. Polym. Sci., Polym. Chem. Ed. 22 159
[7] Bässler H 1991 J. Philos. Mag. B 63 587
[8] Nešpůrek S, Eckhardt A 2001 Polym. Adv. Technol. 12 427
[9] Kim Y R, Lee M, Thorne J R, Hochstrasser R M and Zeigler J M 1988 Chem. Phys. Lett. 145 75
[10] Kenkre V M and Dunlop D H 1992 J. Philos. Mag. B 65 831
[11] Bässler H, Borsenberger P M and Perry R J 1994 J. Polym. Sci. Polym. Phys. 32 1677
[12] Arkhipov V I, Emelianova E V, Kadashchuk A, Blonsky I, Nešpůrek S, Weiss D S and Bässler H 2002 Phys. Rev. B 65 165218
[13] Fishchuk I I, Kadashchuk A, Bässler H and Nešpůrek S 2003 Phys. Rev. B 67 224303
[14] Pan L, Zhang M and Nakayama Y 1999 J. Chem. Phys. 110 10509
[15] Silinsh E A 1980 Organic Molecular Crystals: Their Electronic States (Berlin: Springer-Verlag)
[16] Paris P E, Kenkre V M and Dunlap D H 2001 Phys. Rev. Lett. 87 126601