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Formation and transport of polarons in poly[methyl(phenyl)silylene] is discussed. Analytical theory based on the effective medium approach is used to explain the electric field dependence of charge carrier mobility. The obtained value of the polaron binding energy is about 0.29 eV. This result is in agreement with quantum chemical calculations based on the B3LYP method. Charge carrier transport can be described by a small polaron movement in the presence of an energetic disorder. Polaron binding energy represents significant part of the activation energy of the charge mobility.

Keywords Binding energy; charge mobility; hopping transport; polaron; poly [methyl(phenyl)silylene]; polysilane

Introduction

The interest in organic electronics has continuously grown in recent decades since it presents a good prospect for microelectronic applications that are either not covered by conventional silicon semiconductor technology or where the active elements may be manufactured at a reduced cost compared to conventional devices. Possible applications have emerged or are expected to emerge in the domain of sensors,

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electronic papers, memory devices, organic light-emitting diodes, solar cells and integrated optoelectronic devices [1–4]. In such applications, one of the critical parameter is charge carrier mobility which is in the most cases lower than that in inorganic semiconductors. Although molecular materials with the charge carrier mobilities as high as $1\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ have been reported [5], majority of organic semiconductors and polymers in particular, exhibit much lower carrier mobilities. This feature strongly limits the applications. Therefore, there is a strong interest in understanding the charge transport properties in organic materials with the aim to find some possibilities for the increase of charge velocity.

The important features of molecular solids are weak intermolecular interactions, resulting in a facile formation of disordered structures in which, due to the dispersion of polarization energy, energetic transport tail states in the gap are formed. It is generally accepted that charge transport in such structures occurs by disorder controlled thermally activated hopping of charge carriers through a manifold of localized states. In the past decade, the Gaussian [6,7] disorder model [8–11] proposed by Bässler and co-workers has been extensively used to interpret the charge transport properties. The distribution of site energies, referred to as energetic disorder, is characterized by the half width parameter, σ. It can be, together with the positional distribution parameter, Σ, determined from the temperature and field dependences of the charge mobility. The model seems to be universally applicable also to polymeric materials, the structure of which is generally characterized by a high degree of disorder. Transport sites can be of various types, e.g., additive molecules in highly-doped polymers, pendant side groups or conjugated segments in the main chain of the polymer. Local variation in molecular packing and orientation results in the variation of the electronic polarization energy in the vicinity of transport sites and variation in the intersite distances.

During the charge carrier hops, the strong electron-phonon coupling causes carrier self-trapping and creates a quasiparticle, 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, higher than the electron mass. The description was supported by the experiment of Kim *et al.* [12] who measured the migration rate of the excitation energy along the polymer chain. Thus, the charge carrier transport in disordered molecular materials can be described by a small polaron movement in the presence of energetic disorder. 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; concomitantly, the activation energy of charge transport reflects the static energy disorder of the hopping sites. In contrast, the polaron model in its standard form assumes a strong electron-phonon coupling and a negligible contribution of the static energy disorder to the activation energy of carrier mobility. The importance of polaron effects for charge transport in organic materials is still under debate (even though it has been extensively discussed in the literature during last two decades [13–24]) since the deformation energy might be comparable with the energy resulting from the disorder effects.

It was demonstrated [18–20] that the interplay between the polaronic and disorder effects may be responsible for the specific temperature dependence of the charge mobility. Bässler *et al.* [18] suggested that the effective zero-field activation energy of the mobility, $E_a^{(eff)}$, can be approximated by a sum of the polaronic $E_a^{(p)}$

and disorder $E_a^{(d)}$ contributions as

$$E_a^{(eff)}(F \to 0) = E_a^{(p)} + E_a^{(d)} = \frac{E_p}{2} + \frac{4}{9}\frac{\sigma^2}{kT} \tag{1}$$

where σ is the half width of the density of states (DOS) distribution, T is the temperature, k is the Boltzmann constant and E_p is the polaron binding energy (the adiabatic zero electric field ($F \to 0$) activation energy of the polaron mobility is $E_p/2$).

In this paper the influence of the polaron contribution to the activation energy of the charge carrier mobility in poly[methyl(phenyl)silylene] (PMPSi) is discussed. The experimental results based on the electric field strength dependencies of charge mobility are supported by quantum chemical calculations.

PMPSi is a member of the large class of silicon backbone solids. The polymer, in addition to crystalline phase, also contains silicon clusters, silane oligomers and poly(organylsilanes). Polysilanes, being σ-conjugated main chain polymers, have attracted much attention as a class of advanced materials on account of their unique photophysical properties [25–27]. Most of them arise from the σ-electron delocalization along the silicon backbone. The high quantum photogeneration efficiency [28,29] and the high charge carrier drift mobility [30,31] of the order of 10^{-4} cm^2 V^{-1}s^{-1}, stimulate research into this class of polymers. The charge carrier transport has been believed to be controlled by charge hopping through intrinsic states derived from domain-like segments of the silicon chain [32,33].

Polarons in Molecular Crystals

Polaron-like particles in organic molecular crystals were extensively studied by Silinsh *et al.* [34]. Figure 1 schematically shows hierarchy of interaction time scales for different processes which take place in the presence of an excess charge carrier.

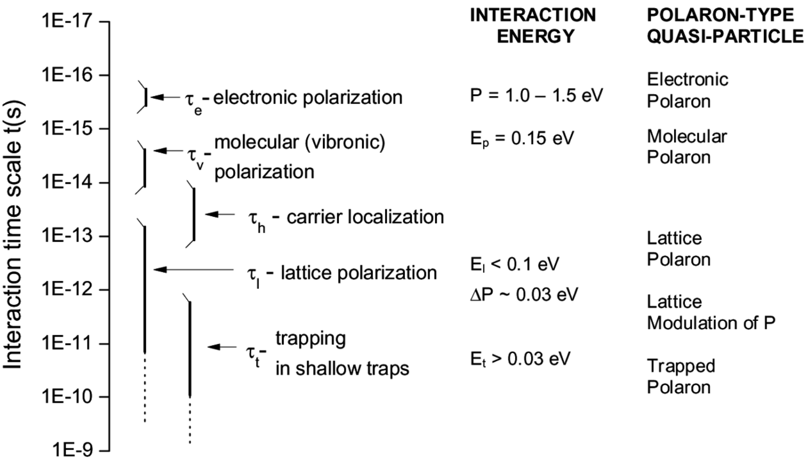

Figure 1. Various types of interactions in anthracene-type crystal (taken from [34]).

Corresponding interaction energies are estimated from uncertainty relation

$$\tau_{Int} = \hbar/\Delta E_{Int} \tag{2}$$

where τ_{Int} is the interaction time, $\hbar$ is the reduced Planck constant and ΔE_{Int} is the interaction energy. Each process creates its own type of polaron quasi-particle. Silinsh *et al.* has introduced and developed the model of the nearly small molecular (vibronic) polaron (MP), formed by the interactions of an excess charge carrier localized on a given molecule with the IR-active vibrations of the molecule itself and the nearest-neighbor molecules [molecular (vibronic) polarization]. The presence of the excess charge results in the position changing of equilibrium configurations of the nuclei in the time scale of vibronic relaxation (schematic illustration in Fig. 2). The formation energy of the MP in anthracene and tetracene is about 0.15 eV; 60% of the value comes from the formation of ionic state of the charged molecule and the rest results from interactions with surrounding molecules. The polarization of lattice vibrations is not included (it is usually much lower than 0.1 eV).

Polarons in Poly[Methyl(Phenyl)silylene]

In this section we will summarize the published data concerning the polaron binding energy of PMPSi. Polymers are usually amorphous materials; we do not consider the crystalline phase and therefore lattice vibrations will be neglected in the forthcoming discussion. Instead of the lattice vibrations we must, due to the electron-phonon (vibronic) interactions, take into account deformation of the macromolecule; this term in a soft polymer chain is expected to be quite high.

The polaron binding energy in PMPSi was estimated as $E_p = 0.16$ eV [18] by the linear extrapolation of the temperature dependence of the activation energy of the charge carrier mobility to zero temperature. However, the dependence is not generally linear and, therefore, the E_p value given above can be only taken for rough estimate. For polaron-exciton, the value of $E_p = 0.08$ eV was determined by Pan *et al.* [35]. Owing to the fact that in molecular crystals defects of the same type form

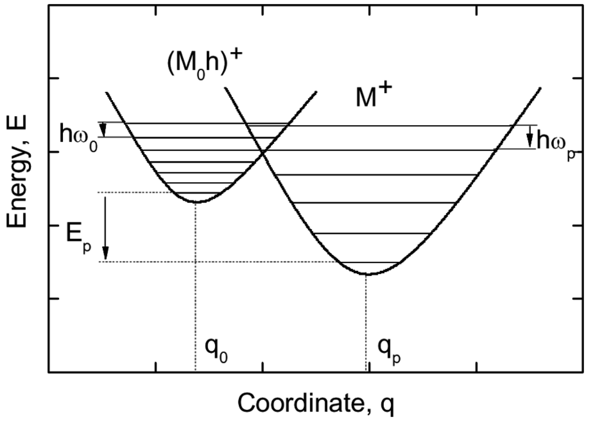

Figure 2. Schematic energy diagram of molecular ion $(M_0h)^+$ and molecular polaron (M^+) (see details in the text).

traps for charge carriers about 3 times deeper than those for singlet excitons [36], one can take for the polaron binding energy the value $E_p = 0.24\,\mathrm{eV}$. The estimated average value is thus $E_p = 0.20\,\mathrm{eV}$. Even if the polaron binding energy is higher than the width of the density of states [37], the disorder seems to be still an important contributor to the temperature and field dependencies of the charge carrier mobility in PMPSi where inter- and intramolecular hopping takes place.

Note that the simplified jump rate equation used in Ref. [18]. for polaron hopping transport has no theoretical justification. Paris *et al.* [17] demonstrated that the problem related to physical parameters can be solved assuming the small polaron transport which occurs in the presence of correlated energetic disorder. A detailed discussion of the problem for the general case of the Marcus jump rate can be found in Ref. [24].

Experimental

Material

Poly[methyl(phenyl)silylene] (PMPSi) was prepared by Wurtz coupling polymerization, as described by Zhang and West [38]. The low-molecular-weight fractions were extracted with boiling diethyl ether. The residual polymer, obtained with ca. 17% yield, possessed a unimodal but broad molar mass distribution, $M_W = 4 \times 10^4\,\mathrm{g\,mol^{-1}}$.

Thin films (thicknesses 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 deposited by the vacuum evaporation. Before the deposition, the polymer was purified three times by precipitation from methanol and toluene solution and centrifuged (12 000 rpm, 15 min). After the deposition the films were dried in vacuum of 0.1 Pa at 330 K for at least 4 hours. The film thicknesses were determined by surfometric measurements.

Measurements and Quantum Chemical Calculations

Charge carrier mobility was measured by the 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. During the measurements, the samples were kept in a vacuum cryostat (10^{-4} Pa) or under argon. In both cases the same experimental results were obtained.

Quantum chemical calculations were performed using B3LYP method [39–41], programs G03 and G98 [42], basis 6–31G*.

Results and Discussion

In Figure 3 the charge carrier mobility (μ) as a function of electric field strength (F) is shown. The log μ vs. $F^{1/2}$ dependencies are linear, their slopes are weak decreasing functions of temperature. The saturation and even decreasing dependence $\mu(F)$ of the mobility at low applied fields can be explained by an increasing influence of the

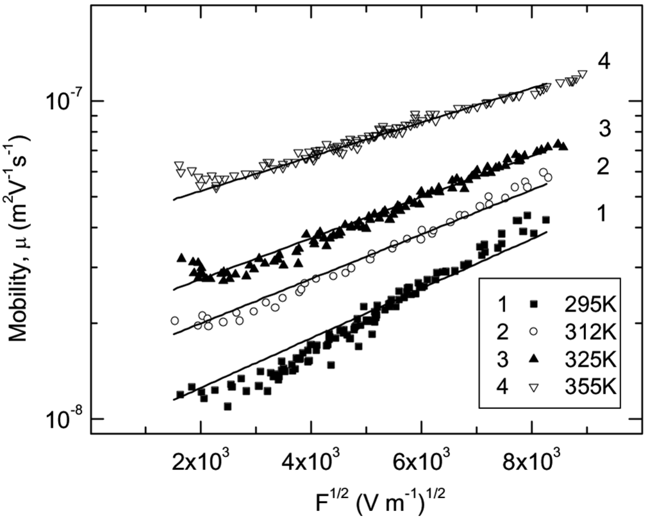

Figure 3. Electric field dependences of the charge carrier mobility of PMPSi parametric in temperature; $T = 295$ K (curve 1), 312 K (curve 2), 325 K (curve 3), 355 K (curve 4), 358 K (curve 5). Lines represent the best common fit using Eq. (3).

charge diffusion. According to effective medium approach, for the symmetrical charge jump rate the mobility can be approximated by the expression [24]

$$\mu \propto \exp\left[-\frac{E_p}{2kT} - \frac{1}{8}\left(\frac{\sigma}{kT}\right)^2 + \left(\frac{\sigma}{kT} - 1\right)\sqrt{\frac{erF}{8kT}}\right], \tag{3}$$

where e is the unit change, F is the electric field strength and r is the average distance between neighboring hopping sites. This equation represents a good approximation to the electric field dependence of the charge carrier mobility. The parameters of the fits obtained from the curves shown in Figure 3 are summarized in Table 1. Note that the polaron binding energy slightly depends on temperature. Room temperature value is about $E_p = 0.29$ eV.

From the electric field and temperature dependencies obtained from the measurements on the samples prepared from another synthetic run, after a simultaneous fitting of both dependencies, the following values were obtained [24] using Eq. (3): energy distribution parameter of hopping states $\sigma = 0.089$ eV, polaron binding energy

Table 1. Half-width of the hopping states distribution σ and the polaron binding energy E_p obtained by fitting curves from Figure 2 ($1+2$ means the fitting of the curve 1 and 2 together)

Combination of fitted plots	σ (eV)	E_p (eV)
$1+2$	0.099	0.285
$2+3$	0.091	0.296
$3+4$	0.083	0.341

$E_p = 0.28$ eV, the most probable hopping distance $r = 1.2$ nm, and nearest-neighbor transfer integral $J = 0.008$ eV. The values were obtained under the assumption of the polaron movement in the presence of an energetic disorder. It follows from a detailed analysis that the polaron term represents a significant part of the activation energy of the charge mobility. Note that the existence of polarons can be proved by two experiments: (*i*) Thermostimulated photoluminescence [23], (*ii*) Temperature dependence of the Poole-Frenkel factor $\alpha = \partial \ln(\mu/\mu_0)/\partial\sqrt{F}$ (determined from the dependence of the charge carrier mobility on electric field). As was shown in [24], α should vary almost linearly with $T^{3/2}$ in the case of polaron-free transport, whereas it should significantly deviate from the $T^{3/2}$ dependence in the case of the transport controlled by polaron motion.

Quantum Chemical Calculation of the Polaron Binding Energy

The schematic energy diagram of potential energies of molecular ion and polaron is shown in Figure 2. The curve of the potential energy of positive molecular ion $(M_0h)^+$ has a minimum at the coordinate q_0, the position of the potential minimum of polaron is located at q_p. The energy difference of the minima is polaron binding energy E_p. $\hbar\omega_0$ and $\hbar\omega_p$ are the vibration quanta of the positive (unrelaxed) molecular ion and of the positive molecular polaron, respectively. Thus, the charge carrier localized for some time on a molecule affects equilibrium energies of vibrational modes, resulting in changes of vibration frequencies ($\omega_0 \rightarrow \omega_p$) and coordinates of energy minima ($q_0 \rightarrow q_p$).

According to our model the polaron binding energy consists of three terms

$$E_p = E_{def} + E_{e-ph} + \Delta E_{e-ph} \tag{4}$$

where E_{def} is the deformation energy of the molecule, which represents the shift of the equilibrium positions of nuclei, $E_{e\text{-}ph}$ is the electron-vibration (phonon) coupling energy and $\Delta E_{e\text{-}ph}$ is the dynamic electron-phonon coupling which represents the energy needed for the change of vibration modes between the neutral and charged molecule. Note that E_p in Eq. (4) corresponds to the molecular (vibronic) polarization as usually used in literature. The difference between the nearly small molecular polaron (MP) and the polaron determined by the quantum chemical calculations is that the latter does not include the interaction with the nearest neighbors.

Each term can be evaluated with quantum chemical calculations. The deformation energy can be determined from the optimized geometries and potential energies of the molecular ion and polaron (see below). Energy of the electron-phonon coupling can be calculated using the equation

$$E_{e-ph} = \frac{1}{2}\sum_{k=1}^{3N-6} \hbar\left(\omega_0^{(k)} - \omega_p^{(k)}\right) \tag{5}$$

where $\omega_0^{(k)}$ and $\omega_p^{(k)}$ are the angular frequencies of the kth vibration modes of the neutral and positively charged molecule, respectively (PMPSi is a p-type semiconductor); the summation is performed over all vibration modes of the molecule (N is the number of atoms in the molecule). Dynamic electron-phonon coupling term is expressed by the following equation (approximation valid for high temperatures)

$$\Delta E_{e-ph} = \sum_{k=1}^{3N-6}\left(\frac{e^{\frac{\hbar\omega_0^{(k)}}{kT}}}{\left(e^{\frac{\hbar\omega_0^{(k)}}{kT}}-1\right)^2}\frac{\left(\hbar\Delta\omega^{(k)}\right)^2}{kT}+\left(\frac{1}{e^{\frac{\hbar\omega_0^{(k)}}{kT}}-1}+\frac{1}{2}\right)\hbar\frac{(\Delta\omega^{(k)})^2}{\omega_0^{(k)}}\right) \qquad (6)$$

where $\Delta\omega^{(k)} = \omega_0^{(k)} - \omega_p^{(k)}$.

The molecular geometries were optimized for neutral (charge 0, multiplicity 1) and positively charged (charge 1, multiplicity 2) molecules. The polymer chain was taken in all-trans conformation which was found to have the lowest potential energy. The deformation energy was calculated in the following manner. Energy of the neutral molecule (configuration: charge 0, multiplicity 1) (E_{hot}) was considered to be the energy of the hot state of the molecule (the state which already contains excess charge carrier but its geometry is still the same as for the neutral molecule). Further, the energy of the positively charged molecule (charge 1, multiplicity 2) was taken as the energy of a relaxed state (E_{relax}). The deformation energy was taken as the

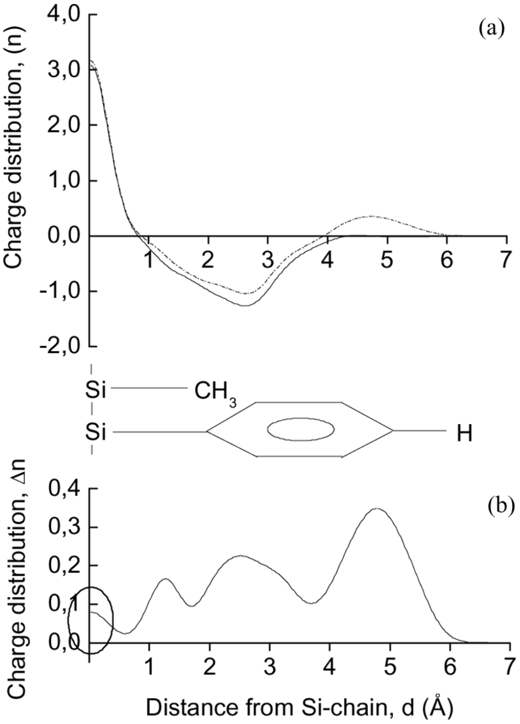

Figure 4. (a) Charge distribution on side phenyl and methyl groups of neutral (full line) and positively charged (dash-and-dot line) monomer unit of MPSi tetramer. (b) Difference between the charge distributions on side groups during the transformation from neutral to positively charged MPSi tetramer.

difference of both energies. Calculated vibration frequencies were used for the evaluation of the electron-phonon term.

According to our expectations and obtained results, the Si chain of PMPSi is positively charged. An addition of a positive charge results in a charge redistribution during the relaxation process. A major fraction of the charge is localized at the ends of the side groups due to the Columbic repulsion. Figure 4a shows the charge distribution on the phenyl and methyl side groups for neutral and positively charged monomer unit. Figure 4b shows the difference between the charge distributions on the monomer unit during the transformation from neutral to positively charged molecule. Note that the charge on silicon atoms corresponds with the value of the deformation energy.

In contrast to the charge densities in the presence of the excess charge, the spin density is mostly localized on the backbone and increases with the chain length. Figure 5 displays the difference between the spin distributions on the phenyl and methyl side groups for hot and relaxed state of MPSi tetramer. The dependence of the total spin on the chain length (expressed as the number of Si atoms in the chain) is demonstrated in Figure 6.

As mentioned above, the polaron binding energy E_p consists of three terms (see Eq. (4)), the deformation energy E_{def}, static electron-phonon term $E_{e\text{-}ph}$ (see Eq. (5)) and term $\Delta E_{e\text{-}ph}$ (see Eq. (6)). Their magnitudes are given in Table 2 for oligomers of different lengths (expressed by the number of monomers (N) in the chain). As one

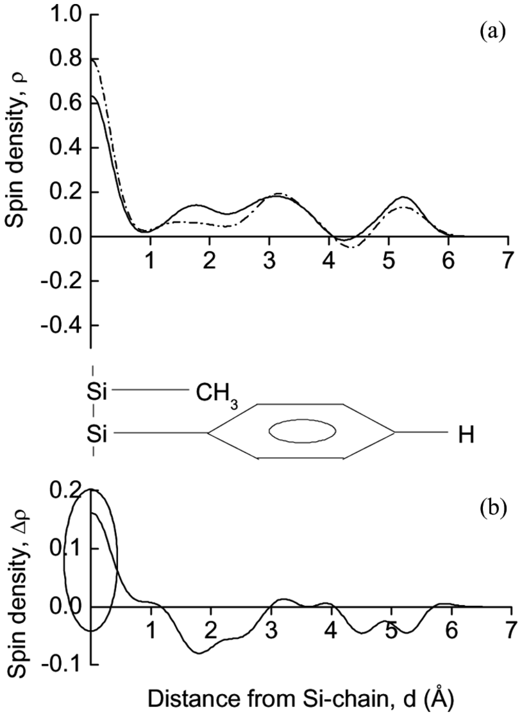

Figure 5. (a) Spin distribution on side phenyl and methyl groups (per monomer unit) of MPSi tetramer during the transformation from hot (full line) to relaxed (dash-and-dot line) form. (b) Difference between spin densities of the hot and relaxed state.

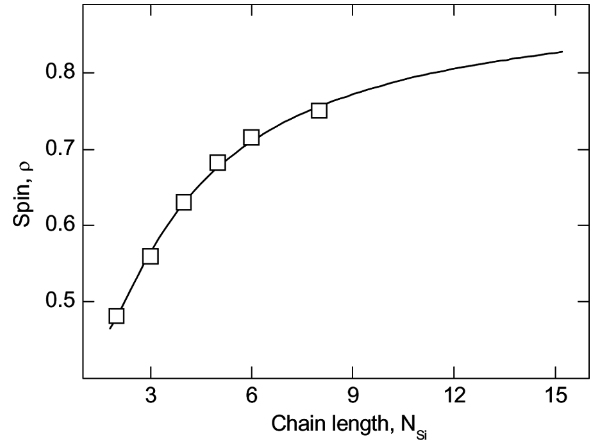

Figure 6. Dependence of the total spin on the chain length (number of Si atoms).

Table 2. Calculated values of the polaron binding energy E_p for different polymer chain lengths (N is the number of monomers in the polymer chain). The polaron binding energy contains contributions from the deformation energy E_{def}, the static ($E_{e\text{-}ph}$) and the dynamic ($\Delta E_{e\text{-}ph}$) electron-phonon coupling terms

N	E_p (eV)	E_{def} (eV)	%	$E_{e\text{-}ph}$ (eV)	%	$\Delta E_{e\text{-}ph}$ (eV)	%
2	0.470	0.421	95	0.000	0	0.026	5
3	0.334	0.295	89	0.014	4	0.025	7
4	0.314	0.294	94	0.000	0	0.020	6
5	0.288	0.277	96	−0.016	−5	0.027	9
6	0.263	0.251	96	−0.014	5	0.026	9
8	0.232	0.224	96	−0.039	−16	0.047	20

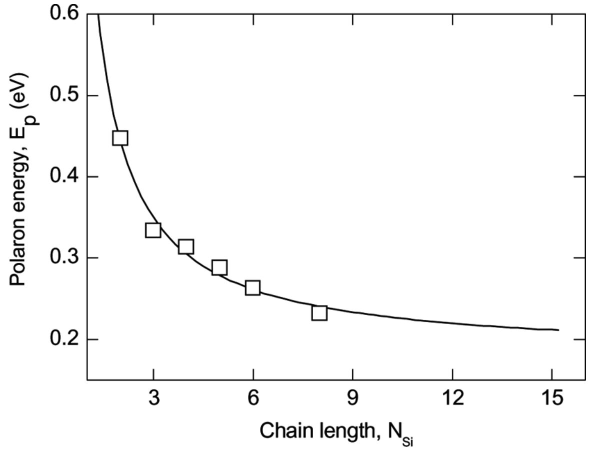

Figure 7. Dependence of the total polaron energy on number of Si atoms.

can see, the value of the polaron binding energy depends on the chain length (cf. Fig. 7); the main contribution coming from the deformation. The average conjugation length in PMPSi was determined as 15–30 monomer units from spectral measurements [32]. Taking into account the results shown in Figure 7, the polaron binding energy can be estimated as 0.21 eV for 15 monomer units.

Conclusion

Polaron binding energy decreases with increasing conjugation length. It consists of three terms: deformation energy, static and dynamic electron-phonon coupling terms. The main contribution follows from the deformation energy; electron-phonon coupling plays a secondary role. This is caused by the softness of the polymer chain. The decrease of the deformation energy with the increasing conjugation length results from the charge distribution on the polymer chain. Extrapolated calculated value of the polaron binding energy for the conjugation length of 15 monomer units is $E_p = 0.21$ eV. This value does not contain the contribution of the correlated energetic disorder. The result is in a good agreement with the experimental value 0.29 eV.

Acknowledgments

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