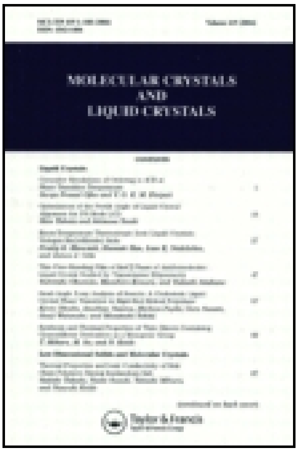

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CHARGE CARRIER TRANSPORT IN CONJUGATED POLYMERS

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Abstract The pecularities of charge carriers transport in conjugated polymers are discussed.

The polymers in which the electronic mobility μ_h can be measured by a straightforward time-of-flight method can be divided into the following groups: 1. molecularly doped polymer systems, such as aromatic amines in polyesters; 2. carbochain polymers with chromophoric aromatic pendant groups, e.g. poly(N-vinylcarbazole) (PVK); 3. polymers with transport sites in the backbone, such as poly(hydroxyaminoesters)(PHAE)[1]; 4. σ- and π-conjugated polymers, e.g. polysilylenes[2] and poly(p-phenylene vinylenes) (PPV)[3]. In groups 1-3 the localized transport sites are associated with N-atoms conjugated with phenyl groups. In polymers of group 4 the transport sites are domain like suborganization of the chain[2] or so-called effectively conjugated segments[3]. The common feature of the systems listed above is the similar depedences of μ on the electric field F and temperature T which are described by the empirical equation proposed by Gill[4]:

$$\mu_h = \mu_o exp\{(1/k)[-(\Delta-\beta F^{0.5})](T^{-1}-T_o^{-1})\} \qquad (1)$$

The similarity of transport parameters allowed one to suggest that the same common but uncompletely elucidated mechanism of electronic transport by thermal emission from localized states that has been established for molecularly doped polymers operates also in π-and σ-conjugated polymers[2]. Eq. (1) is often connected with the Poole-Frenkel effect for two reasons. First, μ depends on F as $\log \mu \sim \beta F^{0.5}$ as it is predicted by the Poole-Frenkel effect; second, the experimental values of coefficient β approximately correspond to the values calculated from equation for the Poole-Frenkel factor:

$$\beta = e^{1.5}/(\pi\varepsilon\varepsilon_0)^{0.5} \qquad (2)$$

The last equation gives an additional possibility to elucidate mechanism of charge carrier transport, so far as it contains another variable that is dielectric constant ε. We changed the dielectric constant by introducing into polymer matrices *o*-dinitrobenzene (*o*-DNB) that had the large dipole moment (6.0 D). For the 1-3 groups the increase of ε of polymer systems results in decreasing μ_h and increasing activation energy Δ which, it would seem, corresponds to eqs.1 and 2 [3]. However, as shown for polysterene doped by triphenylamine, β calculated from the $\log \mu$ vs $\beta F^{0.5}$ dependences *increases* with increasing ε which is contrary to eq.(2)[5]. Hence for the polymer systems with localized transport sites the Poole-Frenkel effect fails. Indeed, there are a number of models namely small-polaron hopping[6], hopping in a Gaussian density of states[7], escaping dipole traps[8] and others which provide a successful description for the field and temperature dependences of the mobility. These models don't require the charged traps presence, as the Poole-Frenkel model does.

The temperature and field dependences of the mobility in conjugated polymers are analogous to the cited above ones. However, contrary to groups 1-3 of the polymer systems in PPV, for instance in poly [1,4-phenylene-1,2-di(4-metoxyphenyl)vinylene] (DMOP-PPV), μ_h increases and activation energy decreases with the increase of the *o*-DNB concentration and consequently ε. In accordance with eq.(2) the Poole-Frenkel coefficient β *decreases* with increasing ε, the calculated values of β and experimental ones practically coinciding as it is shown in Table 1.
It was found[3] that all mobility data concerning PPV can be

fit with the phenomenological relationship suggested by Pfister[9]:

$$\mu_h = \mu_o exp[(\beta/k)(F^{0.5}-F_o^{0.5})(T^{-1}-T_o^{-1})], \qquad (3)$$

where F_o is a new fitting parameter which has the following relationship to Δ : $\Delta = \beta F_o^{0.5}$. The parameters of eq.(3) calculated from experimental data are the same for the o-DNB doped and undoped films of DMOP-PPV. The values of μ_o, T_o and F_o are given in Table 2.

TABLE 1 The values of β in DMOP-PPV films.

Polymer	Concentration o-DNB, weight %	$\beta, 10^{-5}$ eV $V^{-0.5}m^{0.5}$		ε
		experimental	expression (2)	
DMOP-PPV	0	4.4	4.4	3.0
DMOP-PPV	3	3.6	3.5	4.5
DMOP-PPV	5	3.2	3.1	6.2

TABLE 2 The values of parameters of expression (3)

Polymer	μ_o, $m^2/V\ s$	T_o, K	F_o, V/m
DMOP-PPV	$1.0\cdot10^{-7}$	400	$2.45\cdot10^{8}$
PVK	$1.8\cdot10^{-7}$	454	–
PPPT	$1.6\cdot10^{-7}$	386	$2.56\cdot10^{8}$
PPC	$1.5\cdot10^{-7}$	386	$1.92\cdot10^{8}$

From the independence of F_o on ε it follows that Δ decreases with increasing ε in the case of PPV. These results allow one to accept the Poole-Frenkel mechanism for the electronic transport in PPV. The polyionic products which appear by synthesis of PPV can be charged traps. As it was shown[10] in polymers with conjugated double bonds in the main chain the energy structure is defined by the effective length of conjugated segments $2l$. In this case the condition of applicability of the band mechanism has the following form:

$$\mu_o \geq 0.1\beta'/(kTl^{\alpha'}) \qquad (4)$$

where β'- resonance integral in the places of conjugation break($\beta' \approx kT$), α is a coefficient which changes from 1 to 3. Near the border of the band, where transport occurs,

α=3. From different sources $l \gtrsim 10$, then $\mu_o \geq 10^{-8} m^2/V \cdot s$ is the condition of applicability of band model. The value of μ_o for PPV are larger than $10^{-8} m^2/V \cdot s$, therefore the band model is applicable.

Thus many investigations were carried out on polymers with carbazolyl and other chromophoric pendant groups and there are results on the transport characteristics of conjugated polymers. But polymers, which in addition to chromophoric groups include the conjugated double bonds in the main chain, have not been studied enough. There is no any information about charge carrier transport in such polymers. In this paper we present the results of investigations of charge carrier transport in poly(N-(2-propynyl) carbazole) (PPC) and poly (N-(2-propynyl) phenothiazine) (PPPT)[11]. In these polymers the side aromatic chromophores are separated from conjugated main chain by methylene groups. The large mobility of side chromophoric groups may promote charge carrier transport in PPC and PPPT similarly to charge carrier transport in PVK and other polymers with side chromophores. The time-of-flight measurements on PPC and PPPT showed, that hole transient currents for both polymers are observed at positively biased illuminated electrode after photoexitation.

In Fig.1 the T^{-1} dependences of $\log \mu$ are shown for films of PPPT with and without the addition of different concentration of o-DNB. The data fall on straight lines which have a common intersection. The important experimental result obtained is that the values of μ are constant over the range of o-DNB concentration from 0 to 5 weight%. The values of μ_o, T_o, F_o are shown in Table 2. In Fig.2 the $F^{0.5}$ dependences of $\log \mu$ for films PPPT are shown. Straight lines which have a common intersection can be drawn through appropriate sets of data points. One can see the dependence $\log \mu \sim F^{0.5}$ is fulfilled.

The similar temperature and field dependences are observed for transport in films PPC. Thus charge carrier mobility data obtained for PPPT (and PPC) can be also fit with eq.(3), however all *log* μ vs T^{-1} curves don't depend on the o-DNB concetration, that is ε, within the experimental error.

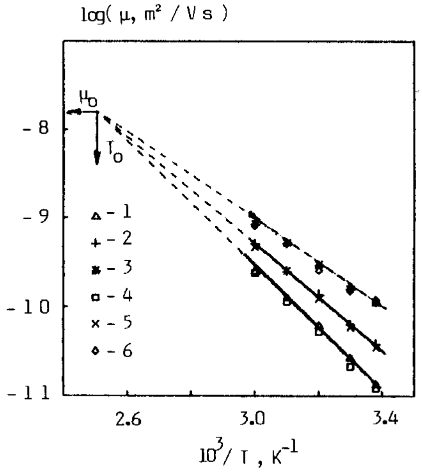

FIGURE 1. The temperature dependences of μ in films PPPT with (4,5,6) and without(1,2,3) addition of 5 weight% o-DNB at $F=2\cdot10^7$ (1,4), $4\cdot10^7$ (2,5) and $6\cdot10^7$ V/m (3,6).

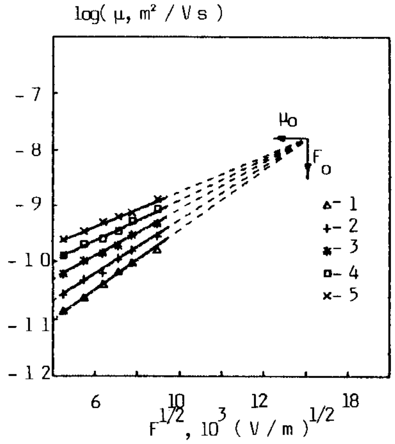

FIGURE 2. The dependences of *log* μ vs.$F^{0.5}$ in PPPT at T=294(1),303(2),313(3), 323(4),333K (5).

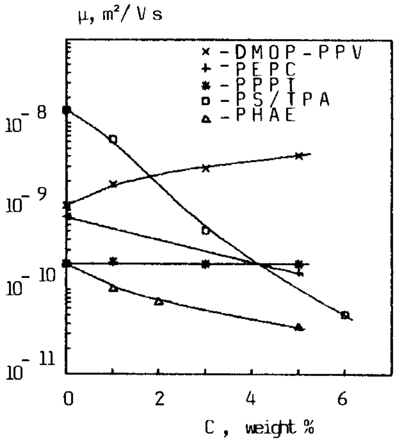

FIGURE 3. The dependence of μ on concentration of o-DNB in DMOP-PPV, PEPC, PPPT , PS/TPA (33 wt.%) and PHAE.

It is possible to suppose the accetable explanation of this phenomenon. In PPC and PPPT the carbazolyl and phenothiazine chromophores are not conjugated with the main chain. In this case these groups represent localized transport sites, which are similar to the transport sites in molecularly doped polymers and other polymers of the 1-3 groups. The transport along such sites occurs in accordance with eq.(1), for instance by polaron mechanism. The independence of μ and Δ on ε in PPPT films may be explained by transition from one transport mechanism to another. At low ε (without addition of o-DNB) the hole transport is defined by charge carrier movement along side groups, and at high ε polaron mobility decreases, but band mobility increases (eq.(3)) and band transport with multiple trapping becomes dominant. There is not observed any significant change of μ and Δ when this transition occurs at changing ε. This fact may be explained by the close values of μ_0 and T_0 for polymers with polaron and band transport mechanisms. Table 2 contains the values of these parameters for PVK, DMOP-PPV, PPC and PPPT.

In Fig.3 the dependences of μ on the o-DNB concentration are shown for films PS doped by TPA, poly(epoxypropylcarbazole) (PEPC), PHAE, DMOP-PPV and PPPT.

So depending on the structure of polymer systems and the transport mechanism hole mobility increases or decreases or remaines costant at increasing matrix polarity. In its turn changing ε allows one to clear up the mechanism of electron transport in the polymer systems.

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