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Charge Carrier Transport in Ether-substituted Poly(1,4-phenylene-1,2-diphenylvinylene) Films

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Electron and hole transport occur simultaneously in oxyphenyl-substituted poly(phenylenevinylene)s; the dependence of the drift mobility of the charge carriers on electric field, temperature and dielectric constant have been interpreted in terms of the Poole–Frenkel model

Oxyphenyl-substituted poly(phenylenevinylene)s (P-PPV) are soluble in organic solvents and give an opportunity to obtain thin films of high quality. P-PPV films have a low dark conductivity ($\sigma < 10^{-15}$ S cm^{-1}) and exhibit photoconductive properties. The main chain of P-PPV consists of segments containing conjugated bonds [the so-called effectively conjugated segments (ECS)], which contain several (k) structural repeating units (it is assumed that $k \approx 4$).[1] For the majority of P-PPVs the charge is delocalized within the ECS.

The investigation of the photoelectrical properties of the original P-PPV is of great interest owing to the prospect of creating electrophotographic materials.[2] In the present communication the charge carrier transport in P-PPVs with structures **1** and **2** is considered.

The P-PPVs were synthesized by methods described previously.[1,3] The films were prepared for measuring by coating solutions of P-PPV onto a quartz substrate which had previously been treated with an electroconductive layer of SnO_2. A second electrode of Ag or Au was deposited on the surface of the film by vacuum thermal evaporation. Using the conventional time-of-flight method, transient current curves were obtained from which the transit times (t_T) of the charge carriers were determined. The drift mobility (μ) of the charge carriers was found according to eqn. (1), where L = film thickness, F = electric field strength.

$$\mu = L/Ft_T \quad (1)$$

The dielectric constant (ϵ) of the films was varied by introducing polar *ortho*-dinitrobenzene (*o*-DNB) into the P-PPV films.[4] For comparison, films containing nonpolar *para*-dinitrobenzene (*p*-DNB) were also prepared. The dipole moments of *o*-DNB and *p*-DNB were 6 and 0.5, respectively. In order to prevent the evaporation of DNB from the films during the temperature measurements, the samples were covered with a thin layer of polyvinyl alcohol (PVA).

It was found that both the holes and the electrons are mobile in film **2**, but only the holes are mobile in film **1**. The field and temperature dependences of the hole mobility (μ_h) are satisfactorily described by the phenomenological relationship of eqn. (2),[5]

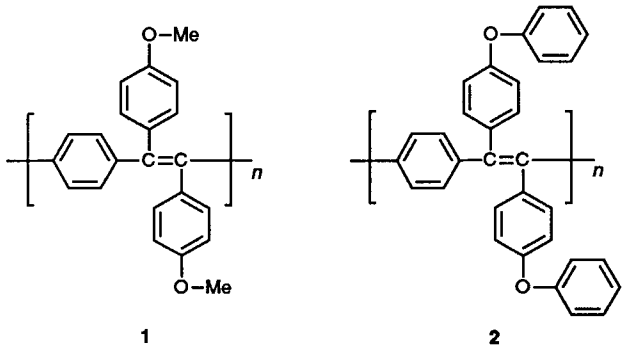
$$\mu_h = \mu_0 \exp[(\beta/k)(F^{0.5} - F_0^{0.5})(T^{-1} - T_0^{-1})] \quad (2)$$

where μ_0, T_0, F_0, β are parameters. We obtained the same magnitudes of $\mu_0 = 1.0 \times 10^{-7}$ m^2 V^{-1} s^{-1} and $T_0 = 400$ K for films **1** both with and without addition of *o*-DNB and for films **2** with and without addition of small concentrations (< 0.5%) of *o*-DNB. The magnitudes of F_0 are 2.45×10^8 and 1.5×10^8 V m^{-1} for films **1** and **2**, respectively. Values of β and of the activation energy of hole mobility (Δ) for different concentrations of polar *o*-DNB are presented in Table 1. The activation energy is given by eqn. (3).

$$\Delta = \beta F_0^{0.5} - \beta F^{0.5} \quad (3)$$

Table 1 Values of β and Δ (at $F = 4 \times 10^7$ V m^{-1}) in films **1** and **2**

P-PPV	Concentration of *o*-DNB (wt.%)	$\beta/10^{-5}$ eV V$^{-0.5}$ m$^{0.5}$		ϵ	Δ/eV
		Experimental	Eqn. (5)		
2	0	4.5	4.4	3.0	0.32
2	0.5	4.2	4.3	3.2	0.29
1	0	4.4	4.4	3.0	0.37
1	5	3.2	3.1	6.2	0.30



1 **2**

1; Poly[1,4-phenylene-1,2-di(4-methoxyphenyl)vinylene] $M_n = 19\,200$

2; Poly[1,4-phenylene-1,2-di(4-phenoxyphenyl)vinylene] $M_n = 16\,000$

M_n = average molecular weight

Scheme 1

As shown in Fig. 1 (curves 1, 2) and Table 1, μ_h increases, but Δ decreases with increasing concentration of *o*-DNB and, consequently, ϵ. The observed dependences of μ_h and Δ on F and ϵ for film **1** over the whole range of concentrations of *o*-DNB and for film **2** at concentrations of *o*-DNB < 0.5% can be interpreted in terms of the Poole–Frenkel model. According to this model the applied electric field influences the release of charge carriers from their traps to the conduction band. In this model the lowering of the Coulomb barrier is given by eqn. (4), where β [eqn. (5)] is the Poole–Frenkel coefficient. The

$$\Delta_{FP} = \beta F^{0.5} \quad (4)$$

$$\beta = e^{1.5}/(\pi\epsilon\epsilon_0)^{0.5} \quad (5)$$

application of the Poole–Frenkel model is possible because the transport sites are delocalized onto extended ECSs that include several structure units, and the calculated values of β coincide

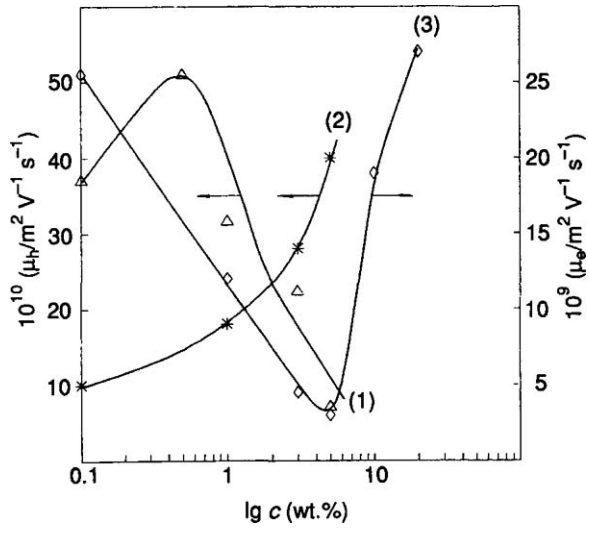


Fig. 1 Dependence of μ_h (curves 1, 2) and μ_e (curve 3) on the concentration of *o*-DNB in films **1** (2) and **2** (1, 3) at $F=4\times10^7$ V m^{-1}, $T=294$ K (1, 2) and $F=6\times10^7$ V m^{-1}, $T=278$ K (3); $L\simeq4$ μm

with the experimental ones for the entire ϵ range considered (Table 1). This is the main evidence for the applicability of the Poole–Frenkel model. The polyionic products which appear during the synthesis of P-PPV may act as charge traps.[6]

At concentrations of *o*-DNB > 0.5% the shape of the graph showing the dependence of μ_h and Δ on the concentration of *o*-DNB in film **2** changes sharply and is different from the shape of a similar graph of this dependence for film **1** (Fig. 1, curves 1, 2). This can be qualitatively explained by the appearance of additional traps for holes in the system due to the increase in the concentration of *o*-DNB. Electrons accepted by *o*-DNB molecules are thus trapped. Electrons in film **2** are mobile, therefore the probability of their acceptance by molecules of *o*-DNB increases as compared with film **1**. This assumption was confirmed by an investigation of electron transport and the measurement of electron transient current at various concentrations of *o*-DNB (Fig. 1, curve 3).

It can be seen from Fig. 1 that μ_e decreases with increasing *o*-DNB concentration up to 5 wt.% due to trapping of electrons by *o*-DNB molecules. At higher concentrations of *o*-DNB (> 5%) electron hopping occurs, predominantly on the *o*-DNB molecules and the P-PPV then serves as a neutral polymer matrix. The absence of any influence of *p*-DNB on μ_h and Δ is connected with the difference in the electron affinities of *p*- and *o*-DNB. Electrons which are accepted on molecules with a greater electron affinity form traps for holes of a smaller depth. In the experiment traps connected with molecules of *p*-DNB are not apparent. Therefore, the dependence of μ_h on the concentration of *o*-DNB, plotted for film **2** in Fig. 1, can be explained in terms of competition between the process of release of the carriers from the charged traps according to the Poole–Frenkel mechanism and the trapping of the holes by additional traps, formed when the concentration of *o*-DNB is increased.

In the oxyphenyl-substituted poly(phenylenevinylenes), the appearance of narrow bands is possible due to the presence of conjugated double bonds in the polymer chain. In this case the transport of charge carriers, which is controlled by trapping on charged traps (charge-trap limited band transport) leads to the use of the Poole–Frenkel model. At the same time, owing to the limited dimension of the ECS (~4 repeated units) electron transfer in P-PPV has the features of hopping transport. It should also be pointed out that **2** is one of the few polymers in which both electron and hole transport occur simultaneously. The magnitudes of both electron mobility and hole mobility in P-PPV are higher ($\mu_e=2.6\times10^{-8}$ m^2 V^{-1} s^{-1} at $F=6\times10^7$ V m^{-1} and $T=278$ K, $\mu_h=7\times10^{-9}$ m^2 V^{-1} s^{-1} at $F=6\times10^7$ V m^{-1} and $T=294$ K) than those in other polymer systems.

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