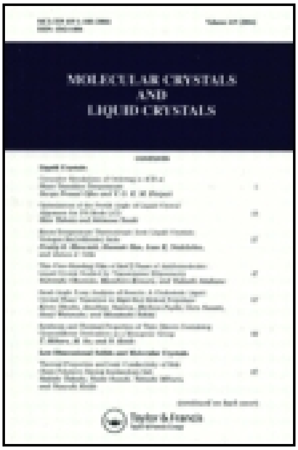

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Bipolar Transport in Aromatic Polyimides

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Bipolar Transport in Aromatic Polyimides

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Electron and hole drift mobilities were measured by the time-of-flight technique in films of aromatic polyimides based on 9,10-*bis*(*p*-aminophenyl)anthracene or 9,10-*bis*(phenylthio)anthracene and a series of diimide fragments. The electric field and temperature dependences of the mobilities were detected. In amorphous films of the soluble polyimide, the drift mobility was found to reach the value of 10^{-4} cm^2 V^{-1}s^{-1} at 5.5×10^5 V cm^{-1}. In the insoluble polyimides films, the mobility was lower by one or two orders of magnitude. This is attributed to the presence of cavities in the films of the insoluble polyimides.

Keywords: aromatic polyimide; disordered medium; time of flight technique; bipolar transport

Some of aromatic polyimides (APIs) are characterized by significant photoelectric sensitivity originating from the electron donor-acceptor interaction between the electron acceptor diimide fragments and the electron donor arylene rests of diamines. In most polymers, the presence of both donor and acceptor functionalities results in charge-transfer complexation with a concurrent decrease in the mobility. Nevertheless, it was suggested that the charge carriers transport in the APIs is defined not only by the presence of both electron donor and electron acceptor units in the polymer chains, but by peculiarities of the chemical structure and also the APIs solid state structure. In this report, the results of an investigation of the electron and hole transport in some APIs based on 9,10-*bis*(aminophenyl)anthracene (Fig. 1) or 9,10-*bis*(phenylthio) anthracene are described. The APIs synthesis, their properties and X-ray diffraction study were described in the preceding paper [1].The API-1 films are highly crystalline and exhibit a planar texture. The API-2 films consist of the mixed crystalline and amorphous phases whereas the soluble API films were found to be fully amorphous.

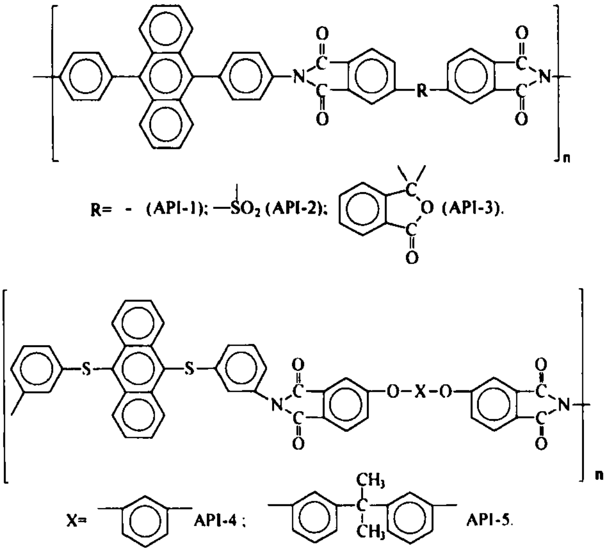

FIGURE 1. Structural formulae of the APIs studied.

Charge carriers mobility, μ, was measured by conventional time-of-flight techniques [2]. Sandwich type samples of the API films with the thickness, *d*, ranged from 3 to 7 μm were prepared for these measurements. The transit time, t_T, was determined from the intersection of the asymptotes to the plateau and the tail of the normal transient. The drift mobility was determined from the conventional expression $\mu = d/(F \cdot t_T)$, where F is the applied field. Figure 2 and 3 show the field dependences of the hole and electron mobilities respectively.

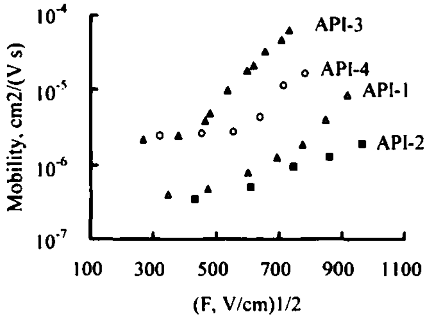

FIGURE 2. Field dependence of the hole drift mobility in API film at 291K.

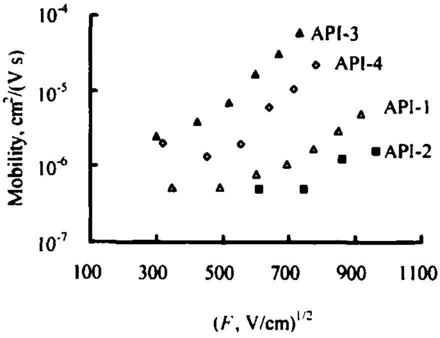

FIGURE 3. Field dependence of the electron mobility in API films at 291K.

The data for API-5 are not plotted as they are similar to those for API-4. As the electric field, F, increases the transit time decreases exponentially and the drift mobility increases accordingly. The $F^{1/2}$- lgμ plot yields straight lines at $F^{1/2} >$ 400 (V/cm)$^{1/2}$. For the soluble API-3, the mobilities of both electrons and holes are higher than those obtained for the other APIs and reach the value of 10^{-4} $cm^2/(V{\cdot}s)$ at 5.5×10^5 V/cm. In the insoluble polyimide films including crystalline phase, the mobility was lower by one or two orders of magnitude.

One may suppose that relatively high drift mobility in soluble APIs is connected with the absence of structure traps in fully amorphous films. Films API-1 and API-2 are prepared from poly(amid acid) by thermal imidization which causes the loss of two water molecules per one monomer link unit. This process may form microcavities, microcracks etc. disordering electron transport paths. It is known [3] that defects of up to 100-200 A in size are present in polyimide films prepared by thermal imidization. The lower drift mobility of API-1 and API-2, compared with other APIs, is most probably due to these defects. For hopping charge carrier transport the following relationship for the drift mobility is valid:

$$\mu \propto R^2 \exp\left(-\frac{2R}{R_0}\right) \tag{1}$$

where R is the distance between the neighboring transport sites and R_0 is the wave function decay constant. In API-1 and API-2, the mean distance is longer than that in other APIs. The assumption agrees with the microcavity structure of the crystalline films.

Another reason for the relatively high electron drift mobility in API-3 may be the presence of a phthalide moiety in diimide fragment. It is useful to compare API-3 with poly(3,3'-phthalidylidene-4,4'-biphenylene), denoted PPB. Both API-3 and PPB have a phthalide moiety in the monomer link. It was found [4] that PPB has an energetic stable state which corresponds to an opening of the lactone ring leaving a -(CO_2)- group on the side benzene ring and causes high conductivity of PPB. Furthermore, API-3 diimide moiety consists of three electron-acceptor groups: one is a phthalide group and the others are phthalimide groups. The electron-acceptor groups are single bonded with a thetrahedral carbon atom; thus they have no effect on each others electronic properties.

These groups are characterized by similar electron affinity values. Hence, the effective concentration of electron transport sites is higher in API-3 compared with other APIs. It is possible that all the above reasons create suitable conditions for charge carrier transport in API-3.

For API-3 films, drift mobility dependences on temperature and electric field were investigated in more details. The dependences obtained fit well the Gill equation:

$$\mu = \mu_0 \cdot \exp\left[-\frac{E_a}{k}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \qquad (2)$$

where μ_0 is the preexponential factor, k is the Boltzmann constant, T_0 is a characteristic temperature, and $E_A = E_A(0) - \beta F^{1/2}$ where $E_A(0)$ is an activation energy at zero field and β is a coefficient.

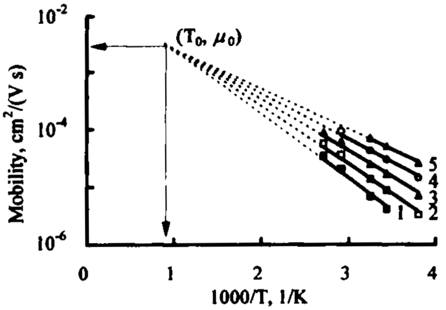

FIGURE 4. Temperature dependence of the hole drift mobility in API-5 at different fields ($\times 10^5$ V/cm): 2.14 (curve *1*), 2.85 (*2*), 3.57 (*3*), 4.28 (*4*), and 5.0 (*5*).

The plot in Fig.4 shows $\mu_0 \approx 5\times10^{-3}$ cm^2/(V s) at $T_0 \approx 1110$K. The activation energy E_a which is calculated in accordance with Equation (2) decreases as the field F increases. For API-3 the parameters Δ and β defined from the plot in Fig.4 are equal to 0.42 eV and 3.8×10^{-4} eV(cm/V)$^{1/2}$, respectively. The coefficient β in Equation (2) is usually compared with the Poole-Frenkel coefficient $\beta_{P\text{-}F} = e[e/(\pi\varepsilon\varepsilon_0)]^{1/2}$, where

$\varepsilon\varepsilon_0$ is the permittivity. For API-3 (ε=3.7) the coefficient $\beta_{P\text{-}F}$ is equal to 4.0×10^{-4} eV(cm/V)$^{1/2}$. The calculated values of β and β_{PF} are closely matched, so it may be assumed that the process of the charge carrier transport is described in terms of a model similar to that of Poole and Frenkel. The correlated disorder (CD) model [5] appeared to fit the obtained experimental data obtained quite well. The CD model describes the relation (2) without assuming that there are charged traps in the medium. Unlike the Poole-Frenkel model, the CD model requires the existence of a permanent dipole moment of a transport site. The CD approach to the problem is quite consistent with the structure of API molecules.

In summary, for amorphous films of soluble APIs, both hole and electron drift mobilities were found to be higher than those for other API films. This may be attributed to the absence of microcavities and other similar defects which form in the process of thermal imidization of insoluble APIs.

Acknowledgments

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