Effect of dipoles on carrier drift and diffusion of molecularly doped polymers

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Drift mobilities and diffusion coefficients of molecularly doped polymers, with dipole moment as a parameter, have been measured by fitting a theoretical equation to time-of-flight photocurrent transients. The slope of the logarithm of mobility vs the square root of electric field is proportional to the dipole moment squared. A similar relationship is observed for diffusion coefficients. We analyze the results using disorder formalism and estimate the dipolar contribution σ_d to the width of the density of states. The constant of proportionality in the relation between σ_d and the dipole moment squared coincides with the theoretical value given by the dipole trap model. This result provides an important demonstration of the validity of both the disorder formalism and the dipole trap model. [S0163-1829(97)50430-9]

Carrier transport in molecularly doped polymers (MDP's) has been studied for some decades. This has been important because the characteristics of carrier transport govern the performance of such devices as photoreceptors,[1–6] white-light-emitting organic electroluminescent devices,[7] and photorefractive devices,[8] An MDP is a nonequivalent amorphous system because the organic molecules essentially retain their identity, interacting only weakly through van der Waals forces.[9–10] For this reason, carrier transport cannot be described by the band model and no complete mechanism has been clarified as yet.

One means of investigating carrier transport properties is to measure photocurrent transients. Transit times have usually been determined from the intersection of the asymptotes to the plateau and the trailing edge of the transients.[1,4,5,11] The mobility obtained using this method sometimes exhibits a thickness dependence and negative field dependence at low electric fields.[12–14]

Other definitions of drift mobility[15–19] are also in use. One is derived by assuming that the drift velocity of a packet is constant while its width spreads out because of a constant diffusion coefficient.[18,19] The drift mobility and diffusion coefficient are obtained simultaneously by fitting a theoretical equation for current to the experimental photocurrent transients. This derivation describes carrier transport well. The negative field dependence at low electric field and thickness dependence of mobility obtained using the previous method can be explained by a superimposition of drift and diffusion in this definition. Thus, the analysis of carrier transport in terms of mobilities and diffusion coefficients obtained using this fitting method can be considered physically more meaningful than that based on mobility obtained using the previous method.

The mobility of an MDP is very low and depends on electric field and temperature, as well as on the structure of donor and acceptor functionality.[1] Many studies have been described by a formalism based on disorder due to Bässler[3] in the same manner as Gill's empirical equation.[1] This formalism is based on the assumption that charge transport occurs by hopping through manifolds of localized states with superimposed positional disorder. Recently, it has been

found that mobility decreases exponentially as the dipole moment of the molecule increases.[4] Furthermore, it has been estimated using simulations that the width of the variance of localized states can be described by an argument based on dipolar disorder (the dipole trap model).[20,21] However, the validity of both the disorder formalism and the dipole trap model has not been demonstrated experimentally. In this Rapid Communication, we will report on the dipole moment dependence of mobilities and diffusion coefficients obtained by fitting. The results will demonstrate the validity of both the disorder formalism and the dipole trap model.

We investigated carrier transport in donor-doped bisphenol-A-polycarbonate. Figure 1 shows the structure of the donors and their dipole moments. The donor doping concentration was 26.3% in molar units. Consequently, the average intermolecular distance in all samples was the same value, 12 Å. Measurements were made by conventional time-of-flight techniques at 293 K.[1] the 6.0–8.5 μm MDP was sandwiched between a semitransparent Al-coated quartz glass substrate and an Au electrode. This sandwich structure was connected in a circuit with a voltage source and a resistance (R, 200 Ω). The MDP's were excited through the alu-
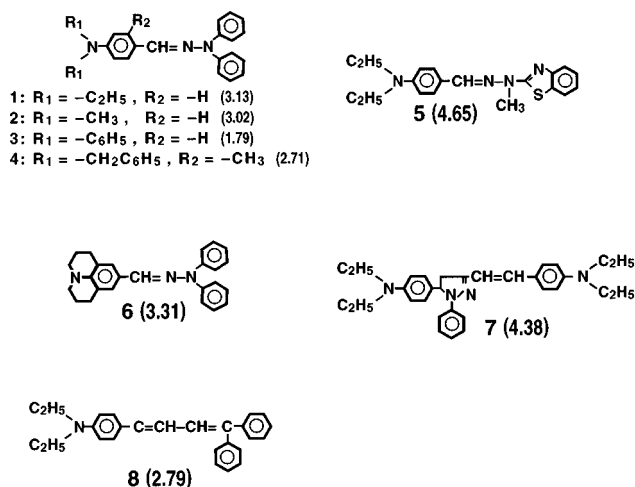

FIG. 1. Structures of the donors used in this study and their permanent dipole moments in debye.
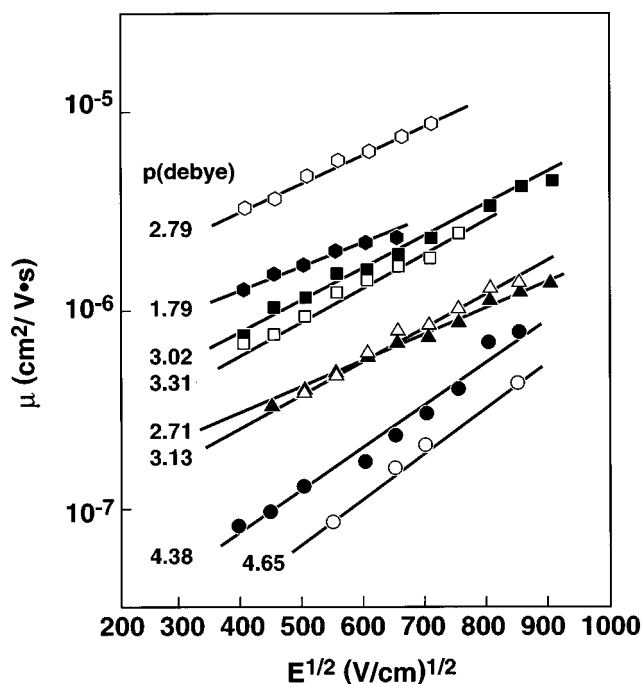
FIG. 2. Logarithm of mobility vs square root of applied electric field, with dipole moment as a parameter.

minum electrode using a 0.9-ns nitrogen laser pulse (NDC, JS-1200). The pulse penetrated less than 0.1 μm into the MDP, so penetration was sufficiently small compared with the thickness of the MDP. The energy incident on the MDP per pulse was adjusted such that the maximum charge generation in the MDP was less than $0.03 C_s V$, where C_s is the capacitance of the sample and V is the applied electric field. Current transients were measured with a voltage amplifier (NF Electronic Instruments, BX-31A) and a digitizing oscilloscope (Tektronix, model 11403). Over the range of fields investigated, the transients were reversible, with no signs of hysteresis. To obtain mobilities and diffusion coefficients, the transients were fitted by a theoretical equation for the photocurrent transients derived by assuming that a carrier packet drifted at a constant velocity and was spread by diffusion.[18,19]

The electric field dependence of mobility is shown in Fig. 2. In all but a few cases, mobility decreases with increasing dipole moment of the charge transport molecule, as is the case for mobility obtained using the previous method.[4] The logarithm of diffusion coefficient increases linearly with the square root of electric field, as shown in Fig. 3, in the same manner as mobility. In most cases, diffusion coefficient decreases as the dipole moment of the molecule increases, as is the case for mobility. Furthermore, the slope of the logarithm of mobility against the square root of electric field is proportional to the dipole moment squared, as shown in Fig. 4. In this figure, the slope is 1.68×10^{-4} $(\mathrm{cm}^{-1/2}\,\mathrm{V}^{-1/2}\mathrm{D}^{-2})$. Further, the slope of the logarithm of diffusion coefficient against the square root of electric field is also proportional to the dipole moment squared, as shown in Fig. 4.

We analyzed this dipole moment dependence of mobility using the disorder formalism.[3] In this formalism,

$$\mu(T,E) = \mu_0 \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right]\exp\left\{C\left[\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]\sqrt{E}\right\},$$
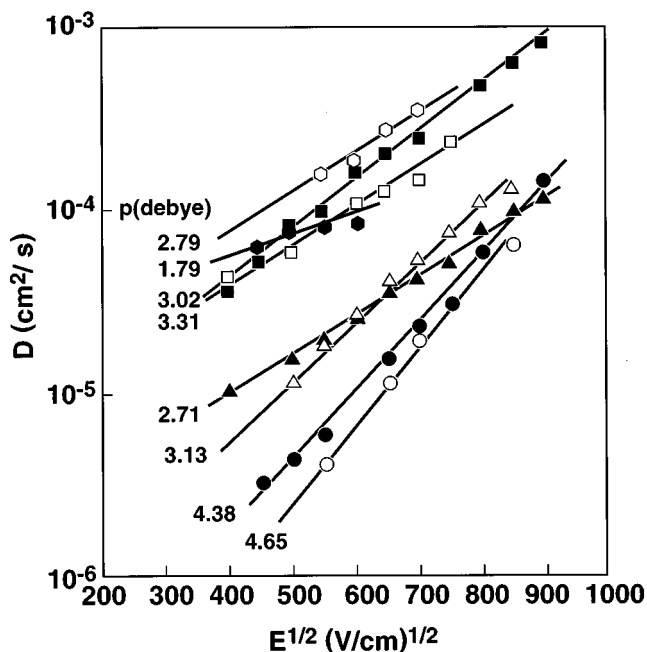$$(1)$$

FIG. 3. Logarithm of diffusion coefficient vs square root of applied electric field, with dipole moment as a parameter.

where σ is the width of the density of states (DOS), Σ is a parameter that describes the degree of positional disorder, μ_0 is the prefactor mobility, and C is an empirical constant, typically 2.9×10^{-4} $(\mathrm{cm/V})^{1/2}$. It has been reported that σ can be described on the basis of dipolar disorder.[20,21] The assumption is that a random distribution of permanent dipoles associated with the donor molecule generates fluctuations in electrostatic potential that add to local variations in potential resulting from van der Waals interactions. Therefore, the total σ can be written in terms of a van der Waals component σ_{vdw} and a dipolar component σ_d. Assuming that the van der Waals component can be described using Gaussian statistics,
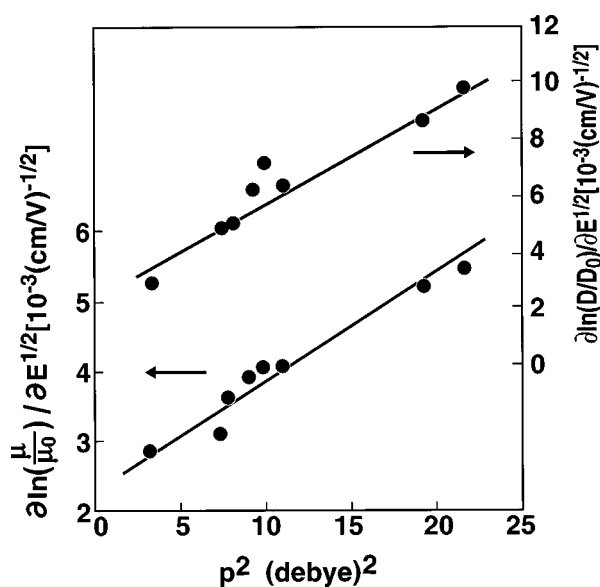

FIG. 4. Slope of logarithm of mobility and diffusion coefficient to square root of electric field vs dipole moment squared.

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$$\sigma = (\sigma_d^2 + \sigma_{\text{vdw}}^2)^{1/2}, \tag{2}$$

the dipolar component can then be estimated with an expression due to Dieckman, Bässler, and Borsenberger[21] as

$$\sigma_d = \frac{A c^{2/3} p}{a^2 \varepsilon_r}, \tag{3}$$

where c is the relative concentration of dipoles, a is the intersite distance (in Å), ε_r is the relative dielectric constant, p is the dipole moment (in debye), and A is the constant 3.06. Young *et al.*[22] have recently derived an expression similar to Eq. (3) which differs only in the value of A. The width of the Gaussian DOS σ_d can be also calculated as the second moment of the DOS originating in interactions between the carrier and dipole moments as follows.

Consider the hopping of a positive charge carrier (hole) of charge e in the presence of an electric field of strength E directed along the positive Z axis, as shown in Fig. 5. The angles θ, ϕ, ψ, and ω are defined in the coordinates shown in the figure. The potential U given by the dipole moments against the hole at (0,0,0) is obtained by

$$U = \frac{ep}{4\pi\varepsilon r^2} \left(\sin\theta \, \cos\phi \, \sin\omega \, \cos\psi + \sin\theta \, \sin\phi \, \sin\omega \, \sin\psi \right.$$
$$\left. + \cos\theta \, \cos\omega \right), \tag{4}$$

where ε is the dielectric constant, and r is the distance between the hole and the dipole center. The potential for orientation of the dipole along the electric field is $pE \cos\omega$. The degree of freedom is restricted,[23] because the dipole of the molecule is surrounded by polymer and other molecules. In order to simulate this effect, we assume that the orientation is restrained by a bounding energy Δ_0. Under these conditions, the weighting W for the probability that a dipole orients in a direction ω degrees from the direction of the applied electric field is obtained by

$$W = \frac{1}{W_0}; \quad pE \, \cos \, \omega < \Delta_0$$
$$\tag{5}$$
$$= \exp\left(-\frac{pE \, \cos \, \omega - \Delta_0}{kT} \right) / W_0; \quad pE \, \cos \, \omega \geq \Delta_0,$$

where W_0 is a normalizing factor. We assume that the probability of a dipole existing in the region below the most probable nearest-neighbor distance between hole and dipole r_c is zero and that it is a constant in other regions. The Nth moment of Eq. (4) is given by

$$\langle U^n \rangle = \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^\pi d\omega \int_0^{2\pi} d\psi \int_{r_c}^\infty dr \, U^n W \rho, \tag{6}$$

where ρ is the density of dipole moments per unit volume. The relation between r_c and the intrinsic distance a_c ($\equiv \rho^{-1/3}$) is reported[24] as

$$r_c = 0.54 a_c. \tag{7}$$

From Eqs. (5) and (6), if n is odd $\langle U^n \rangle = 0$, and if n is even
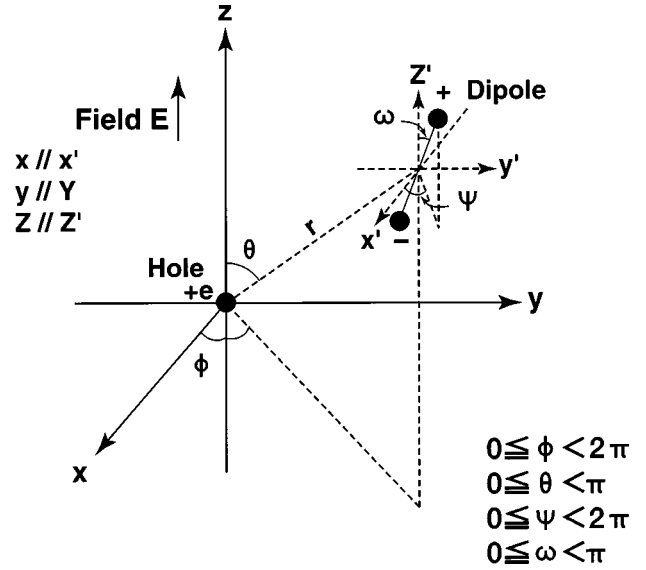

FIG. 5. Illustration of coordinates used.

$$\langle U^n \rangle = \left(\frac{ep_c}{4\pi\varepsilon} \right)^n \rho S_0 \int_{r_c}^\infty r^{2-2n} dr, \tag{8}$$

$$S_0 = \frac{4\pi}{n+1} \sum_{l+m+r=\frac{n}{2}} \frac{(l+m+r)!(2l)!(2m)!}{(l!m!)^2(l+m)!2^{2l+2m}} S_1,$$

$$S_1 = \sum_{s=0}^{l+m} \frac{(-1)^s(l+m)!}{s!(l+m-s)!} \left(\frac{\alpha^{2r+2s+1}}{2r+2s+1} \right.$$
$$+ \sum_{t=0}^{2r+2s} \frac{(2r+2s)!}{(2r+2s-t)!} \beta^{t+1}(\alpha^{2r+2s-t} - \gamma) \right)$$
$$\times \frac{1}{1+\alpha+\beta-\beta\gamma},$$

$$\alpha = \frac{\Delta_0}{Ep}, \quad \beta = \frac{kT}{Ep}, \quad \gamma = \exp\left(-\frac{Ep-\Delta_0}{kT} \right)$$

is obtained. The variance is equal to the second moment and corresponds to the width of the Gaussian distribution. Therefore, σ_d is given by the square root of the second moment. Substituting Eq. (7) for Eq. (8), we obtain

$$\sigma_d = 8.35 \frac{c^{2/3} p}{a^2 \varepsilon_r}. \tag{9}$$

This equation demonstrates that the theoretical width of the DOS distribution resulting from a random distribution of permanent dipoles does not depend on the dipole bounding energy Δ_0. This means that the width of the DOS does not depend on the orientation of the dipoles. Equation (9) is similar to Eq. (3), with the only difference being the value of A.

In experimental results, the slope of the logarithm of mobility against the square root of electric field is proportional to the dipole moment squared, as shown in Fig. 4. Therefore, from Eqs. (1), (2), and (3), the slope of the logarithm of mobility against the square root of electric field, β, is obtained by

$$\beta = C \left(\frac{Ac^{2/3}}{a^2 \varepsilon_r kT} \right)^2 p^2 + C\left[\left(\frac{\sigma_{vdw}}{kT} \right)^2 - \Sigma^2 \right]. \qquad (10)$$

Then, the value A is obtained as 8.32 by substituting $C = 2.9 \times 10^{-4}$, $kT = 0.0253$ (eV), $\varepsilon_r = 3.0$, $a = 12$ (Å), and $\partial\beta/\partial p^2 = 1.68 \times 10^{-4}$ into Eq. (10). This experimental value is similar to the value in Eq. (9) and much larger than that in Eq. (3). This coincidence between the experimental value using the disorder formalism and the theoretical value demonstrates the validity of both the disorder formalism and the dipole trap model. Further, the dipolar component of the width of the DOS is found to be much larger than estimated. Hopping occurs in the potential field originating from a random distribution of dipoles.

The finding that the slope of the logarithm of diffusion coefficient against the square root of electric field is proportional to the dipole moment squared suggests that diffusion occurs in a potential originating from randomly distributed dipoles. The fluctuations in potential are larger than the thermal fluctuations in this system. This results in a large diffusion coefficient[18,19] from the fluctuation-dissipation theorem.[25]

To conclude, we have observed a dipole moment dependence of drift mobility and diffusion coefficient by fitting a theoretical equation of time-of-flight photocurrent transients. The slope of the logarithm of mobility against the square root of electric field is proportional to the dipole moment squared. This result was used to estimate the dipole contribution to the width of the density of states using the disorder formalism. The constant of proportionality in the relationship between dipole contribution to density of state width and the dipole moment squared coincides with the theoretical value. This verifies that hopping takes place in a potential originating from randomly distributed dipoles. The experimental results clarify the effect of dipoles on charge transport and the disorder formalism describing charge carrier migration in a disordered system.

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