Charge Transport in a π-Stacked Poly(dibenzofulvene) Film

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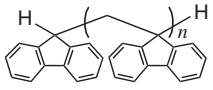
Hole drift mobility of poly(dibenzofulvene) was found to be 2.7×10^{-4} cm^{2}V^{-1}s^{-1} at 299 K at a field strength of 7×10^5 Vcm^{-1} by the time-of-flight (TOF) measurement on a cast film containing 2,4,7-trinitrofluorenylidene-9-malononitrile as an electron acceptor. This value is higher than that of main-chain π-conjugating poly(π-phenylenevinylene) (1×10^{-5} cm^{2}V^{-1}s^{-1}), is comparable to that of main-chain σ-conjugating poly(methylphenylsilane) (1×10^{-4} cm^{2}V^{-1}s^{-1}), and is slightly lower than that of Se (10^{-4} cm^{2}V^{-1}s^{-1} order), an inorganic semiconductor.

Conducting polymers are an important class of material required for organic electronics and optoelectronics.[1] While most conducting polymers so far studied have a long electronic conjugation system in the main chain, a few vinyl polymers with no main-chain conjugation indicate intriguing electronic properties as represented by poly(*N*-vinylcarbazole) (poly(NVCz)), which finds practical applications based on its photoconductivity.[2,3] In this communication, we report the electronic properties of poly(dibenzofulvene) (poly(DBF)), a vinyl polymer with a characteristic conformation in which the side-chain chromophores are regularly stacked.[4,5] The hole drift mobility measured by a time-of-flight (TOF) method[6] was much higher than the existing photoconductive vinyl polymers, including poly(NVCz), and was comparable to some main-chain conjugated polymers. In addition, cyclic voltammetry measurements indicated that holes may be delocalized over the π-stacked side groups.



$\overline{M}$n 1070

poly(**DBF**)

The poly(DBF) was synthesized by the anionic polymerization of dibenzofulvene (DBF) using 9-fluorenyllithium in tetrahydrofuran (THF) at -78 °C at $[DBF]_o/[Li]_o = 5$.[4,5] MeOH-insoluble, THF-soluble part was used for the measurements (Mn = 1070, Mw/Mn = 1.38, SEC using oligo(DBF)s as the standard sample. Poly(DBF) (20 mg) and 2,4,7-trinitrofluorenylidene-9-malononitrile (TNFMN) (1.0 mg) as an acceptor were dissolved in chloroform (1.0 mL), and the solution was cast on an indium-tin oxide (ITO) glass plate and slowly dried under air to afford a thin film (thickness 5 μm). A circular Au electrode (thickness 20 nm, diameter 5 mm) was vacuum deposited onto the 5-μm thick film to produce a sandwich-type cell for the drift mobility measurement.

In order to investigate the interaction between poly(DBF) and the acceptor molecule, absorption spectra were taken in a chloroform solution and in film (Figure 1). Both in the solution and in the film, a weak band, probably due to donor–acceptor interaction, appeared around 520 nm in the mixture of poly(DBF) and TNFMN in addition to the bands due to poly(DBF) and TNFMN. These results indicate that TNFMN is an effective electron accepting dopant toward poly(DBF). In addition, the spectra indicate that pure poly(DBF) absorbs much less than TNFNM and the mixture at 337 nm. This means that N_2 laser irradiation in TOF experiments will mainly excite the acceptor band or the donor-acceptor band to induce charge separation.

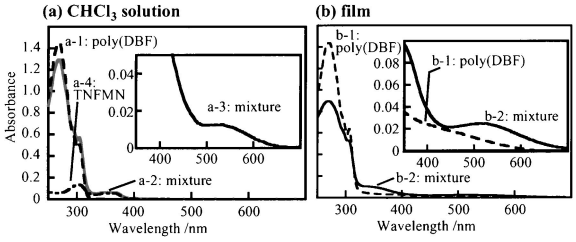


Figure 1. Absorption spectra of poly(DBF) in $CHCl_3$ solution (cell length 0.1 mm) (a) and poly(DBF) film (0.5 μm) (b): (a-1) poly(DBF) in $CHCl_3$ ([DBF unit] 1.1×10^{-2} M), (a-2) poly(DBF)–TNFMN mixture in $CHCl_3$ ([DBF unit] 1.1×10^{-2} M, [TNFMN] 2.8×10^{-4} M), (a-3) poly(DBF)–TNFMN mixture in $CHCl_3$ ([DBF unit] 1.1×10^{-1} M, [TNFMN] 2.8×10^{-3} M), (a-4) TNFMN in $CHCl_3$ (2.8×10^{-4} M), (b-1) poly(DBF) film, and (b-2) poly(DBF)–TNFMN film ([DBF unit]/[TNFMN] = 20).

Charge drift mobility (μ) was estimated by TOF transient photocurrent measurement under vacuum under N_2 pulse laser irradiation (337 nm, pulse duration 3 nsec, 50 μJ). The value of μ was calculated according to $\mu = d/(t_\tau \cdot F)$ (cm^{2}V^{-1}s^{-1}), where d is the film thickness, t_τ is the transit time determined by the TOF experiment, and F is the field strength. By switching polarity in the measurement, it was confirmed that holes mediate the charge drift in the present systems. Figure 2 indicates the μ values at different F's and different temperatures. Overall, a higher field strength led to a higher drift mobility; however, a reversed relationship was observed in the field strength range below 2×10^5 V/cm. In this range, holes may transport in a different path from that predominantly used at the higher field strength, suggesting that the polymer sample is somewhat heterogeneous in terms of molecular structure and/or intermolecular arrangement. The hole drift mobility was higher at a higher temperature at all field strengths, indicating that the charge drift is thermally activated.

The observed charge drift mobility was as high as 2.7×10^{-4} cm^{2}V^{-1}s^{-1} at 299 K at F = 7×10^5 V/cm. This value is

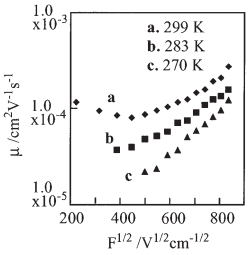


Figure 2. Hole drift mobility of poly(DBF) film (4 μm): (a) at 299 K, (b) at 283 K, and (c) at 270 K.

higher by the order of 10^3 than those for other side-chain aromatic vinyl polymers including poly(NVCz) and poly(1-vinylpyrene) (10^{-7} $cm^2V^{-1}s^{-1}$ order),[7] and is the highest so far reported for a vinyl polymer although mobility values higher than 10^{-2} $cm^2V^{-1}s^{-1}$ have been reported for some other types of organic polymers.[8] The hole drift mobility is even higher than that of main-chain conjugating poly(*p*-phenylenevinylene) (1×10^{-5} $cm^2V^{-1}s^{-1}$),[9] is comparable to that of poly(methylphenylsilane) (1×10^{-4} $cm^2V^{-1}s^{-1}$),[10] and is slightly lower than Se (10^{-4} $cm^2V^{-1}s^{-1}$ order),[2] an inorganic semiconductor.

In the film sample, both intramolecular and intermolecular charge transfers may take place, and the observed charge mobility will mainly reflect the slower process. Because the poly(DBF) chains used in this study appear to have disordered intermolecular alignments on the basis of the almost linear field dependences of mobility in the higher field ranges,[11] the major limiting step of the drift mobility will be the intermolecular charge transfer. This suggests that intramolecular charge transfer may be faster than the bulk mobility characterized by $\mu = 2.7 \times 10^{-4}$ $cm^2V^{-1}s^{-1}$. This idea was supported by cyclic voltammetry measurements of poly(DBF). The oxidation potential for the poly(DBF) measured in a THF solution (0.1 M tetrabutylammonium perchlorate) was 1.49 V (vs Ag/AgCl), which was significantly lower than that for fluorene, a model of monomeric side chain (1.70 V).[5] This indicates that a hole may be readily delocalized over the π-stacked fluorene groups in the side chain, leading to fast intramolecular charge transfer. The ordered π-stacked structure of the poly(DBF) may act as a charge transport pathway.

From the data in Figure 2, field-dependent activation energies for the charge transport were calculated to be 0.22 eV at $F = 7.0 \times 10^5$ Vcm^{-1}. This value is much smaller than that of poly(NVCz) (0.4–0.7eV)[2] and is comparable to that of poly(methylphenylsilane) (0.24 eV).[10] For poly(NVCz), locally π-stacked chromophores are trap sites for charge drift,[12,13] and the activation energy corresponds to the thermal hopping-up of charges from the π-stacked trap sites.[2] The smaller activation energies of the poly(DBF) support that the hole transport mechanism in poly(DBF) is completely different from that in poly(NVCz).[14]

In summary, we found that the charge mobility of poly(DBF) film was as high as some main-chain conjugating polymers. In addition, fast intramolecular charge transport was suggested to take place through the stacked π-electron systems. Charge transport through regularly stacked heteroaromatic systems have been proposed for DNAs where the stacked systems serve as a "π-way"[15] although there is controversy as to whether they really conduct.[16] Poly(DBF) may be recognized as a new, synthetic "π-way" molecule. Further studies are under way, to establish the charge transport through single molecule of π-stacked poly(DBF), and to expand the π-stacked molecular design to other versatile synthetic polymers.

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