PHYSICAL REVIEW B **74**, 113203 (2006)

Enhanced charge-carrier mobility in β-phase polyfluorene

Paulette Prins,[1] Ferdinand C. Grozema,[1] Benjamin S. Nehls,[2,*] Tony Farrell,[2] Ullrich Scherf,[2] and Laurens D. A. Siebbeles[1]
[1]*Opto-Electronic Materials Section, DelftChemTech, Delft University of Technology, Delft, The Netherlands*
[2]*Department of Chemistry and Institute for Polymer Technology, Bergische Universität Wuppertal, Wuppertal, Germany*

(Received 8 March 2006; revised manuscript received 3 May 2006; published 27 September 2006)

Alkyl substituted polyfluorenes are promising candidates for use in organic display applications due to efficient, pure blue (polarized) luminescence, high charge carrier mobility, and good processabilty. Poly(9, 9′-dioctylfluorene) (PFO) is an especially interesting polyfluorene derivative, because of its self-organization into distinct supramolecular structures at room temperature. In addition to the amorphous glassy phase, PFO exhibits a unique packing behavior, the so-called β-phase formation, which leads to a higher degree of organization. We show that the β-phase is an energetically favorable environment for charge carriers. We look into the migration of charges from glassy polyfluorene to areas where PFO exhibits β-phase organization and find that the charge carrier mobility is higher in β-phase polyfluorene than in glassy polyfluorene. Our results illustrate that the order on a supramolecular scale determines the conductive properties of conjugated polymers to a large extent. We conclude that the performance of devices based on polyfluorene can be significantly improved by the enhancement of the supramolecular order.

DOI: 10.1103/PhysRevB.74.113203 PACS number(s): 72.80.Le, 72.20.Jv

Alkyl substituted polyfluorenes are promising candidates for use in organic display applications due to efficient, pure blue (polarized) luminescence,[1,2] high charge carrier mobility,[3] and good processabilty.[4] Poly(9, 9′-dioctylfluorene) (PFO, see inset of Fig. 1) is an especially interesting polyfluorene derivative, because of its self-organization into several distinct supramolecular structures at room temperature. In addition to the amorphous glassy phase, PFO exhibits a unique packing behavior, the so-called β-phase formation, which leads to regions with a higher degree of organization.[5,6] Furthermore, crystalline or α-phase regions can form in the glassy PFO matrix upon specific thermal treatment.[7,8] With this morphological diversity, PFO offers a unique possibility to study the optoelectronic properties for different supramolecular organizations, without the need to chemically modify the polymer. The extent to which the conductive properties of conjugated polymers are determined by the order on a supramolecular scale is nicely illustrated by the hole mobility in glassy films of PFO: The (already relatively high) time of flight mobility of 3×10^{-4} cm^2/V s for isotropic glassy films[3] can be increased by an order of magnitude to 8.5×10^{-3} cm^2/V s by homogeneous alignment.[9] β-phase polyfluorene is found to be an energetically favorable environment for excitons.[5,10,11] The change in optical properties for PFO upon β-phase formation is widely discussed in the literature, e.g., for single PFO chains,[12] for the polymer in solution,[13] and for PFO films.[2] In this contribution we show that the β-phase is an energetically favorable environment for charge carriers. It was found that charges migrate from glassy polyfluorene to areas where PFO exhibits β-phase organization and that the charge carrier mobility is higher in β-phase polyfluorene than in glassy polyfluorene.

β-phase organization occurs within the glassy polyfluorene matrix in condensed phase PFO upon thermal treatment[14] and upon exposing PFO films to solvent vapors.[15] The β-phase domains are relatively small (tens of nanometers) (Ref. 6) as compared to the dimensions of the polymer film, which is often in the order of several hundred nanometers. In a standard device setup (such as a field effect transistor or a sandwich configuration used for time of flight measurements and space charge limited current measurements), the charge carriers have to migrate over the entire thickness of the polymer film to contribute to the conductivity signal. Therefore, it is not possible to exclusively study the charge carrier motion in β-phase polyfluorene with a device setup.

The time resolved microwave conductivity (TRMC) (Ref. 16) technique is a contact-less measurement method that probes the conductive properties of a solid sample using an oscillating electromagnetic field. All mobile charge carriers present in the sample contribute to the conductivity signal. Thus, the motion of charge carriers in β-phase polyfluorene can be probed even if only part of the sample exhibits β-phase organization.

The polyfluorene derivative poly(bis(2-ethyl)hexylfluorene) (PF2/6, see inset of Fig. 1) is known to exhibit a

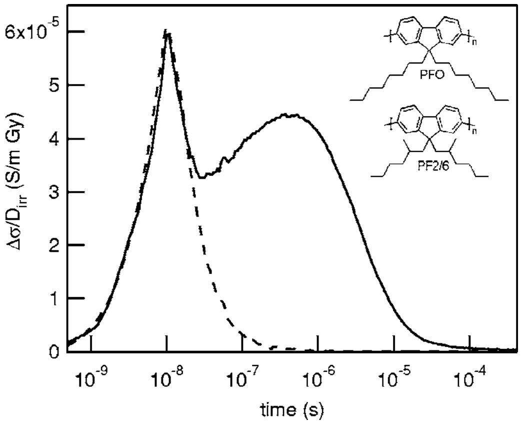

FIG. 1. Dose normalized change in conductivity after creation of charge carriers in PFO (solid line) and PF2/6 (dashed line) for an irradiation dose (D_{irr}) of 35 Gy and a sample density (ρ) of 0.30×10^3 kg/m^3. The inset shows the chemical structure of the two polyfluorene derivatives.

1098-0121/2006/74(11)/113203(3)

disordered glassy phase if no thermal treatment is applied.[17] In contrast to PFO no β-phase formation has been observed for PF2/6.[18] Comparison of the conductivity for PFO and PF2/6 should give insight into the effect of β-phase ordering on the conductive properties of PFO.

PFO (Ref. 19) and PF2/6 (Ref. 20) were prepared via a nickel-mediated Yamamoto coupling reaction in THF by using 2,7-dibromo-9,9′-dioctylfluorene and 2,7-dibromo-9, 9′-di-2-ethyl-hexylfluorene as the monomer, respectively.[21] The molecular weights of the polymers were determined by routine size exclusion chromatography measurements giving number averaged molecular weights of 190×10^3 and 152×10^3 g/mol with polydispersity indexes of 2.4 and 1.9, respectively. Since PFO was precipitated from the relatively polar solvent ethyl acetate, this polyfluorene is likely to contain a considerable fraction of β-phase.[10] The presence of β-phase organization is confirmed by the fluorescence excitation spectrum.[21] No special heat treatment was used during the preparation, therefore the presence of crystalline or α-phase polyfluorene is very unlikely. About 10 mg of solid polymer samples was compressed manually into a perspex container with a tight fitting polyethylene rod. Subsequently, the container was placed in the microwave wave guide, where the samples were irradiated with 10 ns pulses of 3 MeV electrons, which results in the generation of electron-hole pairs with a uniform concentration close to one micromolar. The change in conductivity that results from the generation of these positive and negative charge carriers is monitored using the TRMC technique on a time scale ranging from nanoseconds to milliseconds. It is not possible to distinguish between the contribution of positive or negative charges to the conductivity signal.

In Fig. 1 the transient conductivity is shown for PF2/6 and PFO. For both polymers, the conductivity increases while charge carriers are created during the 10 ns electron pulse. For PF2/6 the conductivity decays to zero on a time scale of hundred nanoseconds. For PFO, however, a delayed increase in conductivity is observed on a time-scale from tens of nanoseconds up to microseconds. This increase in conductivity indicates a delayed formation of charge carriers and / or a delayed increase in charge carrier mobility. A delayed formation of charges can result from bimolecular annihilation of triplet excitons that are formed by nongeminate recombination of charges. A delayed increase in charge carrier mobility can result from the migration of charge carriers to regions with an enhanced charge carrier mobility.

The similarity between the conductivity for PFO and PF2/6 on a time scale up to tens of nanoseconds shows that the conductivity for PFO is dominated by charge carriers in the glassy phase on this short time scale. The difference between the conductivity for PFO and PF2/6 on a longer time scale must be attributed to the presence of β-phase regions in PFO. The observed increase in conductivity can be explained by the migration of charges to β-phase regions. These charges can be generated directly during the electron pulse, or can be the result of triplet-triplet annihilation in the glassy phase.[21] The increase of the transient conductivity in PFO shows that the mobility of charges in β-phase polyfluorene is higher than the mobility of charge carriers in glassy polyfluorene. Moreover, the migration of charges to regions with β-phase organization directly indicates that the β-phase is an energetically favorable environment for charge carriers. This is consistent with the higher degree of organization observed for β-phase polyfluorene.[5,6] The faster decay of the conductivity at higher dose for PF2/6 shows that charges in the glassy phase decay (at least in part) via second order charge recombination. In contrast, the decay rate of the conductivity for PFO is dose independent, indicating that charges in β-phase regions decay via a first order process (most likely trapping of charges).[21] Since the fraction of polyfluorene that exhibits β-phase organization is unknown, it is not possible to determine the ratio between the mobility of charges in the two phases.

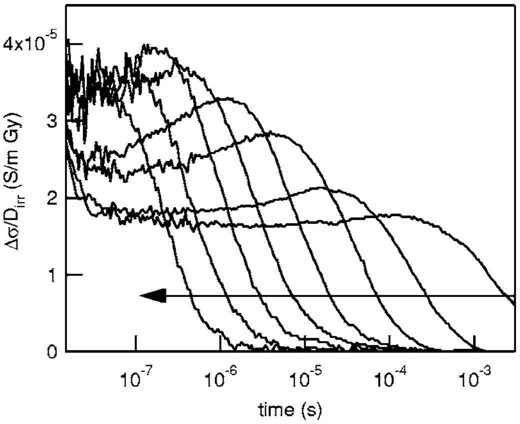

FIG. 2. Dose normalized change in conductivity after creation of charge carriers in PFO for various temperatures (D_{irr}=35 Gy, ρ=0.66×10^3 kg/m^3). The temperature changes from 173 K to 383 K in 30 K steps in the direction of the arrow.

The morphology of thin films of PFO depends strongly on the history and preparation method of the film. The supramolecular organization of films can be altered by choice of solvent,[13] by exposing the prepared film to solvent vapors[4,13,15] or by thermal treatment of the film.[4,14] In the present experiments it is found that the delayed increase in conductivity for PFO is less pronounced for more compressed samples, i.e., for higher sample density. Since the observed conductivity is directly related to the morphology of the sample, these experiments show that the supramolecular organization of solid samples of PFO is also affected by the sample density.[21]

To gain insight into the mechanism of charge carrier migration between the different phases, the transient conductivity in PFO was studied at various temperatures (see Fig. 2). The transient conductivity is found to be strongly temperature dependent. The time scale on which the conductivity reaches the maximum value decreases by four orders of magnitude as the temperature increases from 173 K to 383 K and is found to be thermally activated with an activation energy of 0.20 eV.[21] This temperature dependence of the transient conductivity is completely reversible, therefore, no permanent changes in the sample morphology occur in this temperature range. The time where the conductivity reaches the maximum value is related to the number of charge carriers present in the β-phase, and thus to the transfer rate of charge carriers from the glassy polymer matrix to the

β-phase, and to the decay rate of charge carriers in the β-phase. The activation energy of 0.20 eV reflects the thermally activated diffusion of the species involved and is comparable to activation energies generally found for the mobility in conjugated polymers.

In conclusion, we have shown that the β-phase in Poly(9,9′-dioctylfluorene) is an energetically favorable environment for charge carriers, with an enhanced charge carrier mobility. The switching times of organic display devices critically depend on the charge carrier mobility in the active layer. Hence, our results show that the performance of display devices based on polyfluorene can be significantly improved by the enhancement of the supramolecular order.

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

---

*Present address: Melville Laboratory, Department of Chemistry, University of Cambridge, Cambridge, England.

[1] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H.-G. Nothofer, U. Scherf, and A. Yasuda, Adv. Mater. (Weinheim, Ger.) **11**, 671 (1999).

[2] M. Ariu, D. G. Lidzey, M. Sims, A. J. Cadby, P. A. Lane, and D. D. C. Bradley, J. Phys.: Condens. Matter **14**, 9975 (2002).

[3] M. Redecker, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, Appl. Phys. Lett. **73**, 1565 (1998).

[4] U. Scherf and J. W. List, Adv. Mater. (Weinheim, Ger.) **14**, 477 (2002).

[5] M. Ariu, M. Sims, M. D. Rahn, J. Hill, A. M. Fox, D. G. Lidzey, M. Oda, J. Cabanillas-Gonzalez, and D. D. C. Bradley, Phys. Rev. B **67**, 195333 (2003).

[6] M. Grell, D. D. C. Bradley, G. Ungar, J. Hill, and K. S. Whitehead, Macromolecules **32**, 5810 (1999).

[7] M. Misaki, Y. Ueda, S. Nagamatsu, Y. Yoshida, N. Tanigaki, and K. Yase, Macromolecules **37**, 6926 (2004).

[8] S. A. Chen, A. C. Su, and C. H. Su, Macromolecules **38**, 379 (2005).

[9] M. Redecker, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, Appl. Phys. Lett. **74**, 1400 (1999).

[10] A. L. T. Khan, P. Sreearunothai, L. M. Herz, M. J. Banach, and A. Köhler, Phys. Rev. B **69**, 085201 (2004).

[11] C. Rothe, S. M. King, F. Dias, and A. P. Monkman, Phys. Rev. B **70**, 195213 (2004).

[12] K. Becker and J. M. Lupton, J. Am. Chem. Soc. **127**, 7306 (2005).

[13] M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. P. Woo, and M. Soliman, Acta Polym. **49**, 439 (1998).

[14] A. J. Cadby, P. A. Lane, H. Mellor, S. J. Martin, M. Grell, C. Giebeler, and D. D. C. Bradley, Phys. Rev. B **62**, 15604 (2000).

[15] S. H. Chen, A. C. Su, and S. A. Chen, J. Phys. Chem. B **109**, 10067 (2005).

[16] P. P. Infelta, M. P. de Haas, and J. Warman, Radiat. Phys. Chem. **10**, 353 (1977).

[17] B. Tanto, S. Guha, C. M. Martin, U. Scherf, and M. J. Winokur, Macromolecules **37**, 9438 (2004).

[18] G. Lieser, M. Oda, T. Miteva, A. Meisel, H.-G. Nothofer, U. Scherf, and D. Neher, Macromolecules **33**, 4490 (2000).

[19] M. T. Bernius, M. Inbasekaran, J. O′Brien, and W. Wu, Adv. Mater. (Weinheim, Ger.) **12**, 1737 (2000).

[20] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H.-G. Nothofer, U. Scherf, and A. Yasuda, Adv. Mater. (Weinheim, Ger.) **11**, 671 (1999).

[21] See EPAPS Document No. E-PRBMDO-74-021639 for online supplementary information. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).