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Field-Effect Transistors Based on a Benzothiadiazole−Cyclopentadithiophene Copolymer

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Organic field-effect transistors (OFETs) open the pathway to flexible, large-area electronic devices such as bendable displays or electronic paper.[1] One important aspect of OFETs is the ability to be fabricated by easy patterning techniques and at low cost. Solution processed polymers are particularly well suited for fulfilling these requirements as compared with vacuum deposition of low molecular weight materials, which in general does not allow efficient patterning and shows great device sensitivity to structural defects.[2] However, only a few polymers are known to exhibit good transistor performance, especially with charge carrier mobilities approaching 0.1 cm^2/Vs or higher.[3] Therefore, exploring new polymers with a high charge carrier mobility remains still of great interest and challenge.

We present here a benzothiadiazole (**BTZ**) and cyclopentadithiophene (**CDT**) copolymer **P1** (shown in Chart 1) that exhibits a pronounced transistor performance after simple solution casting. During our study, an excellent photovoltaic efficiency of 3.2% for this copolymer derivative was reported.[4] **CDT**-based materials have attracted considerable attention recently for their semiconducting properties. This kind of fused ring thiophene derivatives lowers the reorganization energy, a factor that has been shown to strongly affect the rate of intermolecular hopping and hence the charge carrier mobility in organic semiconductors, making this kind of compound a potential candidate for organic electronics.[5a] In these regards, alternating **BTZ**−**CDT** copolymer **P1** was designed and synthesized (Supporting Information). Gel-permeation chromatography (GPC) analysis with PPP standard exhibited a number-average molecular mass (M_n) of 1.02 × 10^4 g/mol. The absorption spectra of **P1** in THF displayed two absorption bands at 418 and 718 nm, which were attributed to the **BTZ** and **CDT** segments in the main chain, respectively[5] (Figure S1(a) in Supporting Information). Furthermore, the absorption spectrum of **P1** thin films was broader and red-shifted (426 and 750 nm), indicating that the interchain interactions in the solid state arose from $\pi-\pi$ stacking.[6] This aspect was also supported by the concentration-dependent photoluminescence (PL) spectra of **P1** in solution (Figure S1(b) in Supporting Information).

Bottom contact FETs were fabricated by drop-casting from a hot 1 mg/mL **P1** 1,2,4-trichlorobenzene solution on a highly *n*-doped silicon wafer with a 150 nm thermally grown and HMDS treated silicon dioxide layer. The transistor substrate was held at 100 °C during film formation. Without annealing, the transistors showed a mobility of $\mu_{sat} = 4 \times 10^{-4}$ cm^2/Vs in the saturation regime and $\mu_L = 7 \times 10^{-5}$ cm^2/Vs in the linear regime, together with an on/off ratio of 10^2. Annealing the devices at 200 °C for 2 h led to improved charge carrier mobilities of up to $\mu_{sat} = 0.11$ cm^2/Vs and $\mu_L = 0.02$ cm^2/Vs, as extracted from the transistor curves illustrated in Figure 1. The on/off ratio increased to 10^5 as well. When drop-casting from a 10-fold more concentrated solution followed by the same annealing step as mentioned above, we observed an elevated saturated mobility of $\mu_{sat} = 0.17$ cm^2/Vs and an on/off ratio of 10^5. We assume that this higher μ_{sat} arose from the increased number of charge carriers induced in the saturation regime due to the larger amount of material deposited. The thicker the deposited film, the more charge carriers can be accumulated from the bulk in the saturated regime at higher gate voltages. However, the linear mobility of $\mu_L = 0.001$ cm^2/Vs was 1 order of magnitude lower than that for the less concentrated solution. This effect might result from the more severe contact resistance as revealed by the nonlinear behavior of the output curves at low source-drain voltages (Figure S2(a) in Supporting Information). We attribute the lower linear mobility to the higher molecular disorder at the electrodes and possibly in the first few monolayers caused by the stronger polymer aggregation during film formation from the more concentrated solution. The pronounced self-aggregation was also implied in the concentration-dependent PL spectra, where λ_{max} red-shifted from 765 to 837 nm as the **P1** concentration increased 10-fold (Figure S1(b) in Supporting Information). It is reasonable to assume that, during film deposition from a solution with a lower concentration, self-aggregation took place only on the surface during solvent evaporation resulting in enhanced (local) ordering.

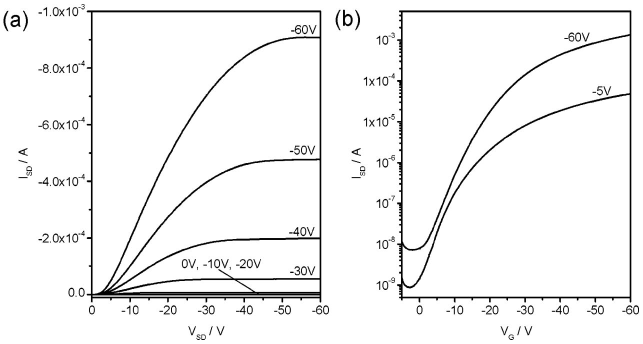
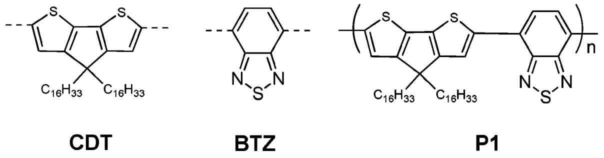


Figure 1. FET performance of **P1**: (a) output curves taken at different gate voltages; (b) transfer curves displaying the saturation regime for $V_{SD} = -60$ V, resulting in $\mu_{sat} = 0.11$ cm^2/Vs, and the linear regime for $V_{SD} = -5$ V, giving $\mu_L = 0.02$ cm^2/Vs.

Chart 1. Structures of **CDT**, **BTZ**, and alternating copolymer **P1**



To gain an insight into the supramolecular organization of **P1** on the surface, large-area X-ray diffraction in reflection mode was carried out. Therefore, the films were prepared in the same way as for the device and deposited on a HMDS modified glass substrate.

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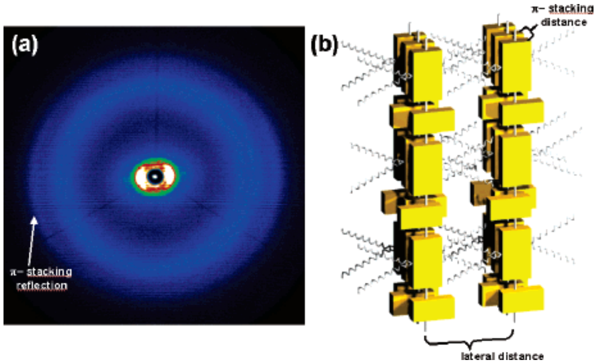

Figure 2. (a) Two-dimensional WAXS pattern of filament extruded **P1**; (b) schematic illustration of the arrangement of **P1** (corresponding reflections are indicated in the drawing).

The experiments were performed on films before and after annealing. Surprisingly, no scattering intensities were observed, indicating considerable macroscopic disorder and thus an amorphous structure in both thin layers (Figure S3 in Supporting Information). Consequently, we assign the significant mobility increase by annealing to the elimination of the residual solvent molecules which act as trapping sites. Since differential scanning calorimetry (DSC) did not display any phase transition up to 300 °C (thermal stability up to 450 °C) and additionally the thin films did not show any birefringence in the polarized optical microscopy, the lack of reorganization after annealing indicated by the X-ray study was in good agreement.

As an additional approach, two-dimensional wide-angle X-ray scattering (2D-WAXS) was performed on filament extruded samples of **P1** to reveal the supramolecular arrangement.[7] Indeed, reflections appeared in the pattern, which were characteristic for organization (Figure 2a). However, relatively diffuse reflections and the lack of higher order ones implied pronounced disorder. The equatorial scattering intensities at small angles described the orientation of the polymer chains along the shearing direction. The position of the reflections was related to the lateral distance of 2.66 nm between the polymer chains. They are arranged in a lamella structure consisting of the aromatic rigid backbone separated by disordered aliphatic side chains filling the periphery, as schematically presented in Figure 2b. More crucially, the wide angle located also in the equatorial of the pattern was attributed to the exceptionally small π-stacking distance of 0.37 nm between macromolecules in comparison to other conjugated polymers. This distance coincided with similar values reported for all conjugated polymers, revealing also a high performance in a device.[1,8] Temperature-dependent measurements of the extruded sample also did not show any annealing effect on the position and intensity of the reflections.

Since the macroscopic order of the film was extremely poor in the presented case, only the small π-stacking distance has a major contribution to the pronounced FET mobility. This directly highlights the great importance to control and thus increase the intermolecular interaction by the variation of the chemical design and to decrease the gap between building blocks. Furthermore, in many other cases, it was necessary to post-treat the thin layers in the FET geometry after solution deposition in a controlled way to achieve remarkable mobilities.[9] Since the amorphous film structure of **P1** does not require any controlled and complex processing proceedings, this behavior makes the copolymer an attractive candidate for low-cost electronics.

In summary, we have presented a **BTZ−CDT** alternating copolymers **P1**, which exhibited an ability to self-assemble into a lamellar superstructure. It has provided functionally desirable FET performance characteristics with mobilities up to 0.17 cm^2/Vs, when solution deposited, which was related to a close π-stacking distance. Particularly, this pronounced performance was observed for thin films with no macroscopic order, making the presented conjugated copolymer an attractive active material for low-cost organic electronics, without the need for difficult processing techniques.

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Supporting Information Available: Experimental procedures, DSC, TGA, UV/vis absorption and concentration-dependent PL spectra of **P1**, FET performance of films prepared at higher concentration, X-ray diffraction of the thin films, and equatorial scattering intensity distribution of the 2D pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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