Thin Film Characteristics and FET Performances of β-Octyl-substituted Long Oligothiophenes

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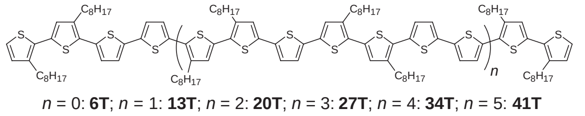
A series of β-octyl-substituted oligothiophenes from 6-mer to 41-mer was examined for active layers of organic filed-effect transistors. Upon spin-coating from chloroform solution, the 20-mer and the longer oligomers formed homogenous thin films composed of stacked lamella structures. Top-contact devices fabricated using these films showed good p-channel FET characteristics with mobilities of $10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ which gradually increase with the extension of chain length.

Organic filed-effect transistors (OFETs) are currently attracting much attention, and a growing number of new organic semiconductors have been actively developed.[1] The impressive performances of OFETs largely depend not only on the intrinsic characters of organic semiconductors but also on the morphologies of thin films produced from them. Good films that can allow fabrication of high-performance field-effect devices can be conventionally formed by vacuum deposition of vaporizable small molecules. For practical application, however, film-deposition by solution processing techniques is recommended, and accordingly, the development of solution-processible, high-grade semiconductors is an important topic. In this regard, regioregular poly(3-alkylthiophene)s (PATs) are particularly notable.[2] The PAT chains tend to form two-dimensional planar structures known as "lamellae," which are oriented perpendicular to the substrate, and the close stacks of these lamellae are believed to be responsible for the high field-effect mobility.[2,3]

We have recently developed a series of structurally well-defined long oligothiophenes **6T–41T**, in which pendent octyl groups are attached at β-positions to provide solubility (Figure 1).[4] These oligothiophenes have been allowed us to elucidate the effective conjugation length and conduction mechanism of doped polythiophenes. Considering systematic extension of these oligomers up to polymer sizes, we have anticipated that these oligothiophenes would be also very useful for investigating the ordered lamella films and field-effect mobilities of polythiophene systems. We report here on thin film characteristics and FET performances of **6T–41T**.

Oligothiophenes **6T–41T** were synthesized according to the references.[4] Thin films were prepared on a quartz or an OTS-modified $\mathrm{Si/SiO_2}$ substrate by spin-coating using a 0.4 wt % solution of the oligothiophenes in chloroform at 2000 rpm for 1 min. All these operations were carried out without taking any precaution against exposure to ambient air, moisture, or light.



n = 0: **6T**; n = 1: **13T**; n = 2: **20T**; n = 3: **27T**; n = 4: **34T**; n = 5: **41T**

Figure 1. Structures of oligothiophenes.

Optical microscopic analyses have revealed that the morphologies of the thin films deposited on a $\mathrm{Si/SiO_2}$ substrate greatly depend on the chain lengths of the oligomers. Immediately after the film of **6T** was formed by spin-coating, crystalline islands appeared, resulting in an inhomogeneous film (for the microscopic image, see Figure S1 in Supporting Information). This is in sharp contrast to the formation of homogeneous films from β,β'-dihexylsexithiophene.[5] The film of **13T** was somewhat stable, but aggregation occurred forming numerous crystalline domains in several hours (Figure S2). On the other hand, the higher homologues **20T–41T** formed quite stable, homogeneous films with no time-dependent morphological changes (Figures S3–S6).

All the UV–vis spectra of **6T–41T** in THF solution (Figure S7) showed a broad π–π^* transition absorption band, which was bathochromically shifted with chain elongation of the oligomer up to the icosamer: $\lambda_{\max}$ of **6T**, 378 nm; **13T**, 453 nm; **20T**, 461 nm. On the other hand, as shown in Figure 2, the spectra measured in the thin films are quite different. When compared to the solution spectrum, the film spectrum of **13T** has a similar broad absorption band with a small bathochromic shift ($\lambda_{\max}$ 480 nm). In contrast, the film spectra of the longer oligothiophenes are characterized by vibronic splitting bands as well as marked bathochromic shifts (ca. 100 nm). This, in connection with the above microscopic analyses, suggests that the thin films of **20T–41T** are composed of highly ordered structures.

Figure 3 shows X-ray diffractograms of the thin films of **13T–41T**. For the film of **13T**, no diffraction pattern is observed, corroborating the inhomogeneous morphology. On the other hand, the films of **20T–41T** show a series of peaks assignable to (00*l*) reflection. Evidently, the long oligomers are composed of ordered layered structures. From the diffraction pattern, *d* spacings were determined to be 15.5 Å for **20T**, 15.0 Å for **27T**, 14.8 Å for **34T**, and 14.7 Å for **41T**. It should be noticed

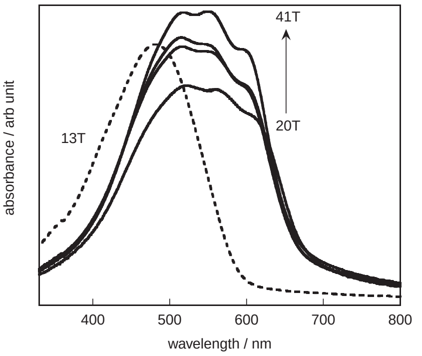


Figure 2. UV–vis spectra of spin-coated thin films of **13T–41T**.

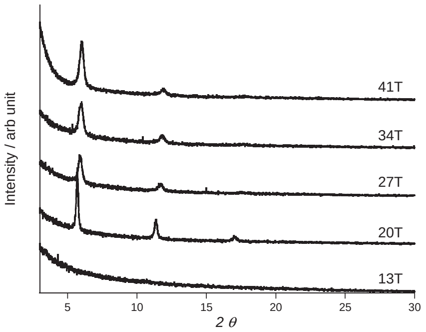


Figure 3. XRD of spin-coated thin film on a Si/SiO$_2$ substrate of **20T**–**41T**. The first peak appears at $2\theta = 5.69°$ for **20T**, 5.87° for **27T**, 5.96° for **34T**, and 6.01° for **41T**.

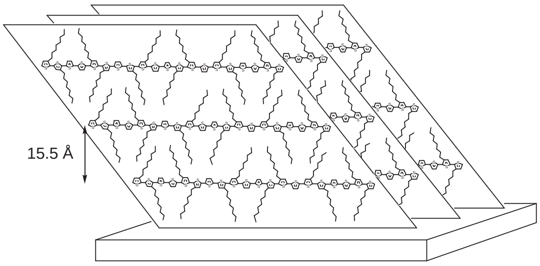


Figure 4. Illustration of the ordered lamella structure of oligothiophene **20T**.

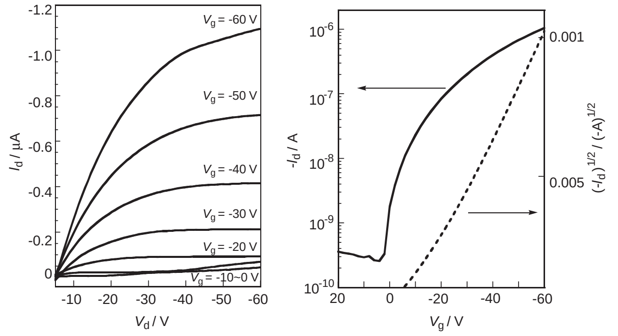


Figure 5. FET performance of the **41T**-based device; output characteristics (left) and transfer characteristics at $V_d = -60$ V.

Table 1. FET performances of oligothiophene-based devices[a]

	μ/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}	V_{th}/V
20T	8.6×10^{-4}	8×10^2	+5.5
27T	8.8×10^{-4}	2×10^3	+4.0
34T	1.3×10^{-3}	2×10^3	+5.1
41T	2.1×10^{-3}	3×10^3	−6.0

[a] "Top-contact" configuration with gold source and drain electrodes was used. The channel length (L) and channel width (W) are 50 mm and 1.5 mm, respectively.

that the monolayer thickness for any oligothiophene is nearly 15 Å despite different molecular length. This can be explained by an ordered layered structure as is shown in Figure 4, where the long oligothiophenes have two-dimensional lamella structures similar to those for regioregular PATs.[2,3] The octyl side chains are extended to the lateral direction so as to interact with the octyl side chains of the neighboring molecules. It is interesting to note that the longer oligomers have a little shorter *d* spacings. Presumably, this indicates enhanced van der Waals interactions due to the increasing number of pendent octyl groups. From these results, it is certain that the van der Waals interaction of octyl groups contributes to the formation of the lamella structures for the long oligothiophenes.

The top-contact OFET devices using **20T**–**41T** thin films as active layers showed typical p-channel FET responses, and Figure 5 represents the FET performance of **41T**-based device. Table 1 lists the hole mobilities, I_{on}/I_{off}, and threshold voltages of **20T**–**41T**. These data were obtained by averaging those measured from more than 20 devices independently fabricated for each oligomer. The filed-effect mobilities of these devices are around 10^{-3} cm^2 V^{-1} s^{-1}, which gradually increase with the chain extension. This result is fairly consistent with mobilities of the order of 10^{-3} cm^2 V^{-1} s^{-1} reported for the low molecular weight part of regioregular poly(3-hexylthiophene) corresponding to twenty to thirty thiophene units.[6]

In summary, we have found that the octyl-substituted oligothiophenes consisting of twenty thiophene units or more have the ability to form ordered films of lamella structures by spin-coating, and the devices using these films showed good p-channel FET characteristics, being reminescent of those observed for regioregular PATs. Considering versatile structural modifications of oligomers as compared to polymers, we thus believe that structurally well-defined long oligothiophenes would be potential semiconductive materials for solution-processible high-performance OFET devices.

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