Growth and morphology properties of bis (2-phenylethynyl) end-substituted oligothiophenes based thin films

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Growth mechanism of bis(2-phenylethynyl) end-substituted oligothiophenes (**diPhAc-*n*Ts**, n = 2, 3) based organic thin films deposited by high vacuum deposition on Si/SiO$_2$ substrates have been investigated. Especially the influence of acetylenic (-C≡C-) *vs.* olefinic (-C=C-) spacers in thiophene-phenylene derivatives on the growth process was studied in details. While olefinic containing oligomers, distyryl-oligothiophenes (**DS*n*Ts**) show a Stranski-Krastanov mechanism, dependence of thin film morphology on thickness and substrate temperature by atomic force miscrocopy (AFM) reveals a Volmer-Weber mechanism in **diPhAc-*n*Ts**. These results underline the importance of molecular structure on growth mechanism and resulting thin film morphology for future electronic applications such as charge transport in organic thin film transistors (OTFTs).

1. Introduction

In order to further investigate the application of compounds with carbon-carbon triple bonds in electronic applications, herein, the structure-morphology relationship of new semiconductors with carbon-carbon triple bonds (-C≡C-) as π-spacers in the aromatic backbone of thiophene-phenylene derivatives, bis(2-phenylethynyl) end-substituted bithiophene and bis(2-phenylethynyl) end-substituted terthiophene (**diPhAc-2T** and **diPhAc-3T** in Fig. 1 [1,2]) is reported.
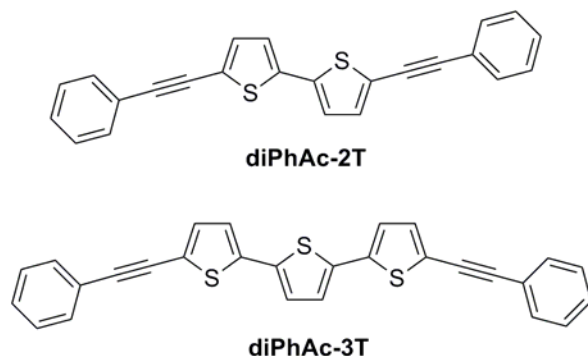

Fig. 1. Chemical structures of diPhAc-2T and diPhAc-3T.

Recently, we have reported that distyryl-oligothiophenes (**DS*n*Ts**, with *n* = 2, 3, 4) exhibit a hierarchical organization across length scales with higher crystallinity in thin films and corresponding carrier mobility values by increasing substrate temperature during thin film deposition [3,4]. Of main interest are oligomers capable of self-assembly in highly ordered structures in the solid state and giving high-performance organic thin film transistors (OTFTs). Growth process in organic thin films is controlled by several factors as (i) molecular structure, (ii) substrate surface energy, (ii) the interaction between molecules and substrate and/or the intermolecular interaction, (iv) deposition rate and (v) substrate temperature. The objective of this paper is to discuss some general trends in the growth and morphology properties of end-capped oligothiophenes on introducing structural modifications on the conjugated backbone by spacers, as acetylenic (-C=C-) and olefinic (-C≡C-), and to understand the property/structure relationship.

2. Experimental part

The synthesis of **diPhAc-2T** and **diPhAc-3T** has been described elsewhere [1,2]. The organic layers were vacuum deposited onto Si wafers covered by a SiO$_2$ layer (300 nm thick). Si/SiO$_2$ substrates were chosen because they represent relevant substrates for future electronic applications such as OTFTs. Si/SiO$_2$ substrates present a

hydrophobic character. Vacuum deposition was realized under a pressure of $1\text{-}2\times10^{-6}$ mbar, where the deposition rate and the thin film thickness were controlled with an in situ quartz crystal monitor. A low deposition rate of 0.2 Å/s was used for both oligomers; while a higher deposition rate of 1.2 and 0.83 Å/s was used for **diPhAc-2T** and **diPhAc-3T**, respectively. Substrate temperature (T_{sub}) was controlled during deposition by thermic sensor integrated in the block on which the substrates are mounted. The block is kept at the internal vacuum chamber temperature ($T_{sub} = 25°C$) or heated ($T_{sub} = 50°C$). Atomic force microscopy (AFM) measurements were done on thin films in air with a SII NanoTechnology inc., S-image operating in the tapping mode. The used cantilever was made of silicon, the resonance frequency being 300 kHz.

3. Results and discussion

In order to get correlation between ordering in organic thin films and molecular structure, atomic force microscopy (AFM) experiments are crucial. By increasing successively the thickness from 5 to 50 nm, the growth mechanism can be identified. For both oligomers, **diPhAc-2T** and **diPhAc-3T**, dependence of thin film morphology on temperature and deposition rate was also investigated by AFM measurements.

Figs. 2 and 3 show the thickness dependence of **diPhAc-2T** and **diPhAc-3T** thin films deposited on Si/SiO$_2$ with a low deposition rate (0.2 Å/s) at $T_{sub} = 25°C$ and 50°C, respectively. At $T_{sub} = 25°C$, **diPhAc-2T** based thin films consist of separated islands with a longitudinal shape and a high value of the average height, typically 140 nm and 280 nm for 5 and 10 nm thick films.
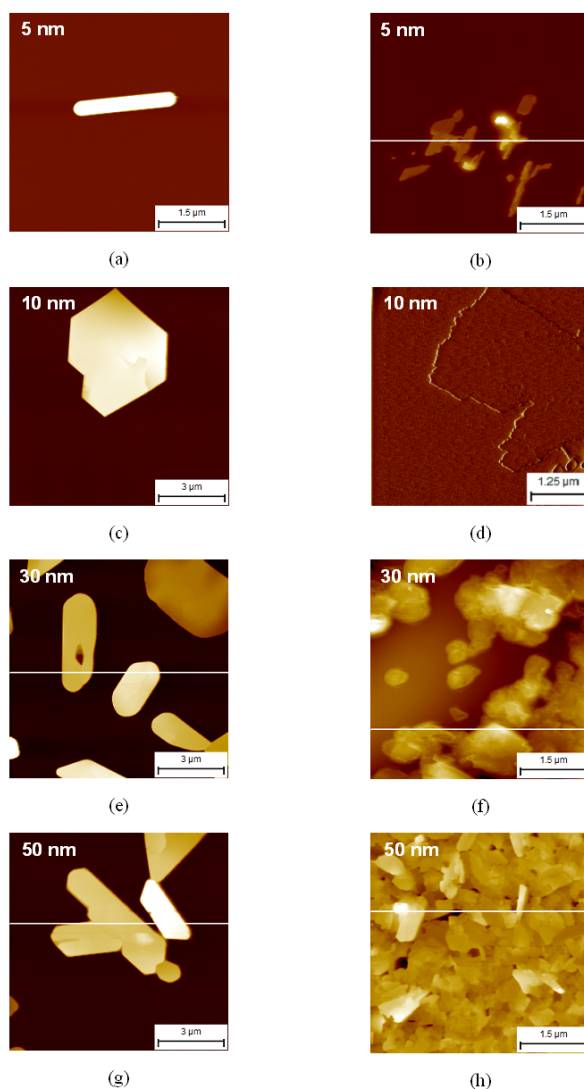

Fig. 2. Thickness dependence of AFM pictures of diPhAc-2T (a, c, e, g) and diPhAc-3T (b, d, f, h) thin films deposited at $T_{sub} =$ 25°C on Si/SiO$_2$ with a low deposition rate of 0.2 Å/s.

By increasing the substrate temperature to 50°C, still separated islands are observed, but as their number increased their size and height decreased (height = 30-90 and 50-120 nm for 5-and 10 nm-thick films). At T_{sub} = 50°C, **diPhAc-2T** based-thin films are formed of more circular-shape blocks (Fig. 3 (a), (c) and (e)).
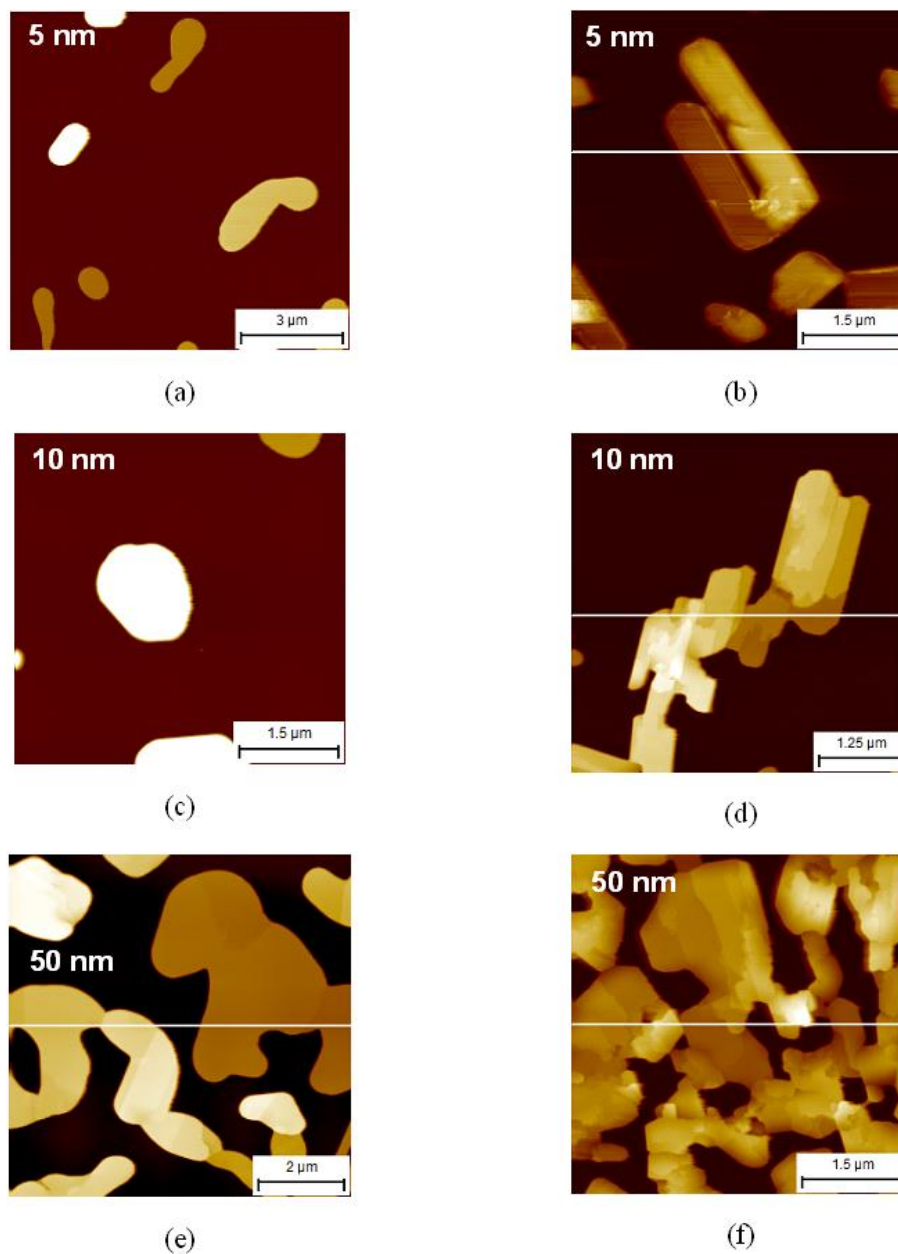

Fig. 3. Thickness dependence of AFM pictures of diPhAc-2T (a, c, e) and diPhAc-3T (b, d, f) thin films deposited at T_{sub} = 50°C on Si/SiO₂ with a low deposition rate of 0.2 Å/s.

For both substrate temperatures, 50-nm thick films are formed by high organic grains separated by large grain boundaries. As revealed by the corresponding AFM profiles (Fig. 4 (a) and (c)), no surface structure, as a layer-by-layer profile, is observed on top of grains conferring a 3-dimensional (3D) aspect to the grains.
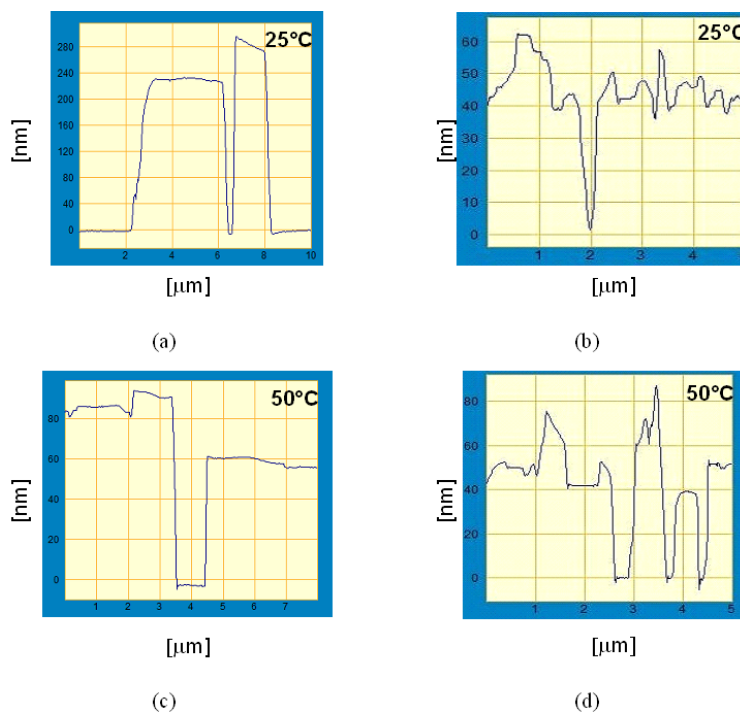
(a)

(b)

(c)

(d)

Fig. 4. Temperature dependence of AFM profiles of diPhAc-2T (a, c) and diPhAc-3T (b, d) thin films deposited on Si/SiO$_2$ with a nominal thickness of 50 nm at a low deposition rate of 0.2 Å/s.

While **diPhAc-3T** shows more disordered small grains at T$_{sub}$ = 25°C (Fig. 2), the same bulky form in the grains is observed on heated substrates as shown on Fig. 3. At T$_{sub}$ = 50°C, 10 and 50 nm-thick films (Fig. 3 (d) and (f)) show long crystals with a pyramidal profile. Nevertheless, the height profiles of **diPhAc-3T** in Fig. (b)

and (d) reveal no terrace step as already observed for DSnT oligomers [3,4]. Fig. 5 shows the thickness and temperature dependences of AFM pictures of **DS3T** thin films deposited on bare Si/SiO$_2$ with a nominal thickness of 50 nm at the low deposition rate (0.2 Å/s).
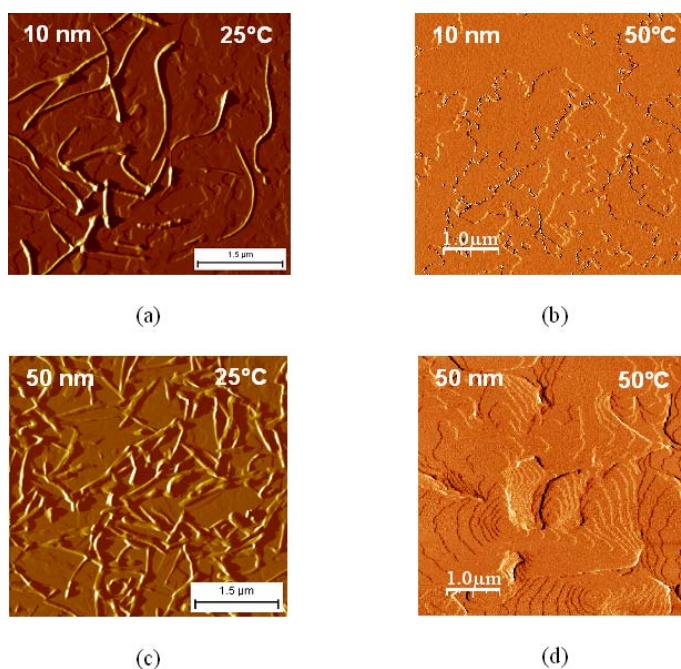

(a)

(b)

(c)

(d)

Fig. 5. Thickness and temperature dependences of AFM pictures of DS3T thin films deposited on Si/SiO$_2$ with a nominal thickness of 50 nm at a low deposition rate of 0.2 Å/s.

The presence of **DS3T** terraces on the grains reveals the crystalline organization of the film on heated substrates. While a layer-by-layer growth together with an island one, characteristic of the Stranski-Krastanov mechanism, was observed for **DS3T** thin films on heated substrates, the formation of the islands in **diPhAc-*n*T** thin films is achieved by the Volmer-Weber mechanism, characteristic of a 3-dimensional (3D) growth [5]. The growth of thin films is here essentially controlled by two types of interaction, the interaction between molecules and substrate and the intermolecular interaction which can be modulated by heating the substrate during the solid state formation of organic thin films. In the Volmer-Weber mechanism (Fig. 6 (a)), the intermolecular interaction is predominant conferring a 3D-growth of islands on the substrate. The Stranski-Krastanov mechanism (Fig. 6 (b)) is characterized by a predominant molecules-substrate interaction during the formation of first organic layers.
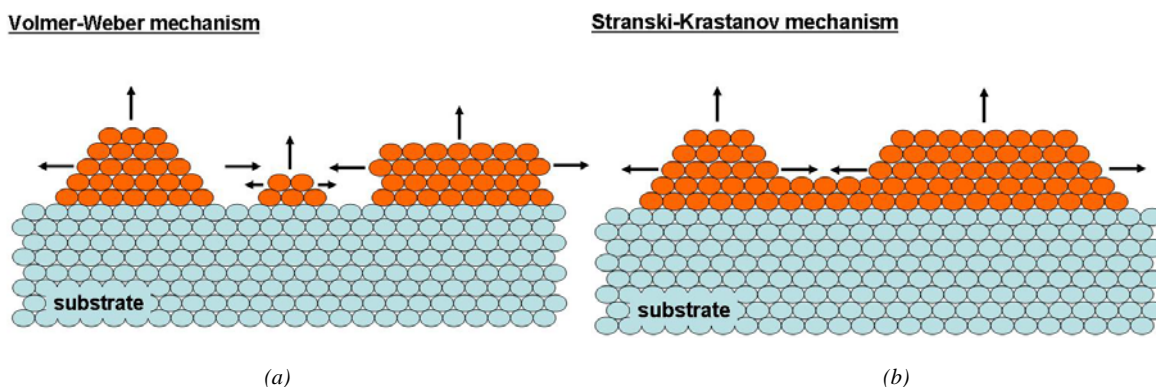

(a)   *(b)*

Fig. 6. Schematic representation of growth mechanisms involving in diPhAc-nT (a) and DSnT (b) thin films.

At high deposition rate (1.2 Å/s and 0.83 Å/s for **diPhAc-2T** and **diPhAc-3T**), Fig. 7 shows the temperature dependence of AFM pictures of **diPhAc-2T** and **diPhAc-3T** thin films deposited on Si/SiO$_2$ with a nominal thickness of 50 nm. For T_{sub} = 25°C, thin films comprise a large number of small crystalline domains randomly oriented on the substrate. At T_{sub} = 50°C, the same 3D-growth of elongated islands as that observed at low deposition rate is observed with in this case interconnection between grains. Such long range interconnected crystalline grains is favorable to charge transport operating by a hopping process in OTFT devices.
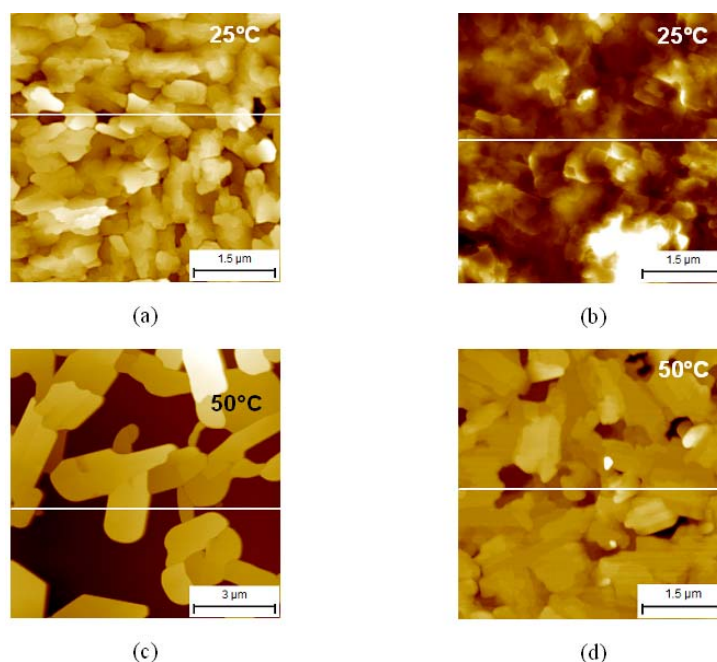

(a)   (b)

(c)   (d)

Fig. 7. Temperature dependence of AFM pictures of diPhAc-2T (a, c) and diPhAc-3T (b, d) thin films deposited on Si/SiO$_2$ with a nominal thickness of 50 nm at a high deposition rate of 1.2 Å/s for diPhAc-2T and 0.83 Å/s for diPhAc-3T.

4. Conclusions

We have described the growth mechanism of bis(2-phenylethynyl) end-substituted oligothiophenes (**diPhAc-nTs**, n =2, 3) based organic thin films deposited by high vacuum deposition on Si/SiO_2 substrates. The results reveal the importance of molecular structure on growth mechanism, while deposition parameters, as substrate temperature and deposition rate, have a great importance on resulting thin film morphology as revealing by AFM pictures.

References

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