Poly(alkoxyphenylene−thienylene) Langmuir−Schäfer Thin Films for Advanced Performance Transistors

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Solution processed Langmuir−Schäfer and cast thin films of regioregular poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene) are investigated as transistor active layers. The study of their field-effect properties evidences that no transistor behavior can be seen with a cast film channel material. This was not surprising considering the twisted conformation of the polymer backbone predicted by various theoretical studies. Strikingly, the Langmuir−Schäfer (LS) thin films exhibit a field-effect mobility of 5×10^{-4} cm^2/V·s, the highest attained so far with an alkoxy-substituted conjugated polymer. Extensive optical, morphological, and structural thin-film characterization supports the attribution of the effect to the longer conjugation length achieved in the Langmuir−Schäfer deposited film, likely due to an improved backbone planarity. This study shows that a technologically appealing deposition procedure, such as the LS one, can be exploited to significantly improve the inherently poor field-effect properties of twisted conjugated backbones. This achievement could promote the exploitation for electronic, and possibly sensing, applications of the wealth of opportunities offered by the alkoxy substitution on the phenylene units for convenient tailoring of the phenylene−thienylene backbone with molecules of chemical and biological interest.

Introduction

Superior transport properties in organic materials can be reached with planar and highly conjugated chains that are also orderly packed with a strong $\pi-\pi$ interchain interaction in the charge-transport direction. An elegant example is the regioregular poly(3-alkylthiophene) (RR PAT),[1] where both the requirements of chain planarity and good packing are accomplished as the head−tail regiochemistry[1] allows maximizing of chain planarity and conjugation length, while the lipophilic interactions of the alkyl chains cause the formation of a spontaneously ordered solution processed film with a lamellar structure comprising two-dimensional highly conjugated sheets where field-effect mobilities (μ_{FET}) as high as 10^{-1} cm^2/V·s can be reached.[2]

The deposition procedure adopted generally influences the molecular packing as well as the film morphology and thickness uniformity. Soluble molecules can be deposited by casting techniques, such as drop casting, spin-coating, or via layer-by-layer assembly techniques such as the Langmuir−Blodgett (LB; vertical transfer) and Langmuir−Shäfer (LS; horizontal transfer) protocols.[3] Solution casting methods are appealing for large-scale processing; nevertheless, they present the disadvantage of preventing strict thickness control. Conversely, LB and LS techniques allow obtaining polymer films with good thickness control and offer the possibility to easily produce multilayer structured films.[3−5] The LB and LS techniques, usually restricted to amphiphilic molecules, have been employed to obtain thin films of conjugated polymers for electrical and optical devices such

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as LEDs, thin-film resistors, and memory devices.[6,7] The first LB field-effect transistor, based on a regiorandom PAT, reported by Paloheimo et al.,[8] exhibited mobilities in the 10^{-7}−10^{-4} cm^2/V·s range. Device performance improved with RR PAT LS films, with the best mobilities reaching 10^{-2} cm^2/V·s.[9] This figure is, however, 1 order of magnitude lower than that achieved with the solution cast RR PAT films.[2] Recently, RR alkoxyalkyl-substituted polythiophene LB films have been also employed as active layers in thin-film-transistor (TFT) devices, demonstrating conductivity anisotropy, with the highest field-effect mobilities being in the low 10^{-5} cm^2/V·s range.[10] LB blends of nonamphiphilic RR PAT and acrylamide polymers have also been proposed for TFT applications.[11]

In the present study the conjugation, structural, and field-effect properties of a regioregular alkoxyphenylene−thienylene copolymer, namely poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene), are investigated. This conjugated system was first synthesized, via Pd-catalyzed cross-coupling reaction of 2,5-bis(tributylstannyl)thiophene with 1,4-dibromo-2,5-bis(octyloxybenzene) or the corresponding triflate, by Z. Bao and co-workers,[12] who also investigated its reversible thermochromic properties.[13] Subsequently, a more convenient synthetic methodology, based on Pd-catalyzed cross-coupling reaction of the bis-organomagnesium reagent derived from 1,4-dibromo-2,5-bis(octyloxy)benzene with 2,5-dibromothiophene, which avoids the use of organotin derivatives, was appointed.[14] The resulting polymer, deposited as LS thin film, gives a very sensitive and performing resistive NO_2 sensor.[15] Here, the alkoxyphenylene−thienylene copolymer, synthesized as reported in ref 14, is deposited as drop-cast and LS thin films. Their performances, as organic TFT (OTFT) active layers, are compared. It is shown that LS films exhibit a higher performance level, and in-depth spectroscopic investigation allows correlation of this effect to the occurrence of an LS deposition-induced longer conjugation length of the copolymer chains. As a result, the LS OTFTs exhibit the highest field-effect mobility attained so far with an alkoxy-substituted conjugated polymer.

Results

The chemical structure of regioregular poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene) (henceforth POPT), is shown in Figure 1, along with the thin-film-transistor device scheme.

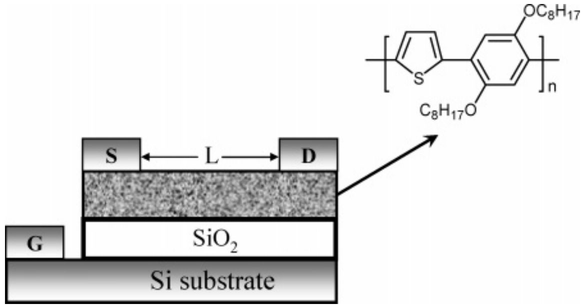

Figure 1. Schematic diagram of a bottom-gate TFT device composed of highly conducting silicon substrate (n-doped, 0.02−1 Ω/cm) coated by 300 nm thick SiO_2 thermal oxide (C_i = 10 nF cm^2). Gold source (S) and drain (D) contacts were defined, by thermal evaporation through a shadow mask, directly on the POPT films. The channel length, *L*, is 200 μm, and the width, *W*, is 4 mm. The gate (G) gold pad was deposited directly on the conducting silicon. The POPT chemical structure is reported on the right.

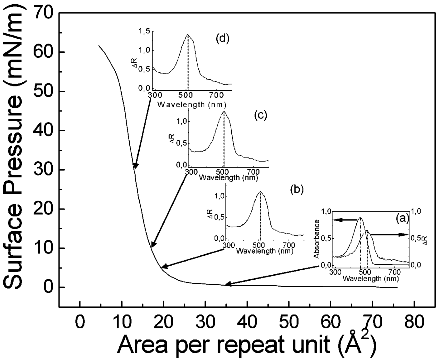

Figure 2. Langmuir curve (Π vs *A*) of POPT (spreading solution of 1.91 mg of POPT in 10 mL of chloroform). The insets show the normalized reflectance spectra of the floating layer at the air−water interface at applied surface pressures of 0.8 (a), 5 (b), 10 (c), and 30 mN/m (d). In the inset (a) the standard UV−vis absorption spectrum of the chloroform POPT solution is reported as well.

The presence of the two alkoxy groups renders the copolymer highly soluble in various organic solvents besides conferring also an amphiphilic character, although very weak. The polydispersity index (M_w/M_n) of 1.67 was indicative of a narrow distribution of chain lengths.

POPT thin films were deposited, either by drop casting or by 10−50 LS horizontal transfers. The casting procedure was carried out by depositing a drop of a POPT chloroform solution on the substrate and leaving the deposit in an N_2 inert atmosphere until the solvent slowly evaporated. This procedure is known to allow regioregular polymers to form fairly ordered films.[1,2] For the LS transfer to the substrate, the POPT molecules are spread as a chloroform solution at the water−air interface and, after the $CHCl_3$ evaporation, they are laterally compressed until a uniform layer is formed. A typical Langmuir curve—pressure (Π) vs area (*A*)—reported in Figure 2 shows a very steep area reduction as the surface pressure is changed by a few millinewtons per meter. This effect, already reported for other nonamphiphilic polymers,[16] is indicative of the polymer's capability to self-organize. As the surface pressure is increased even further, the floating molecules form a densely packed layer and the limiting area per repeat unit (*A*), extracted from the experimental curve, is as low as 18 Å^2. The insets of Figure 2

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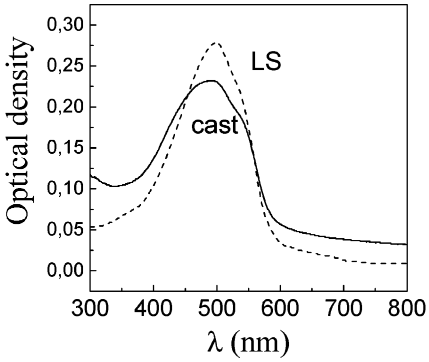

Figure 3. UV−vis spectra of a cast film (solid line) and a 10 horizontal transfer LS (dashed line) POPT film.

show the reflectance spectra of the floating layer at the air−water interface at different applied surface pressures. The abscissa values (Δ*R*) are the difference in reflectivity between the signal coming from the floating layer and the baseline from the water subphase.

In the inset (Figure 2a) the UV−vis absorption spectrum of a chloroform POPT solution is reported for the purpose of comparison. The peak of the POPT floating film at the water−air interface is significantly red shifted, falling at 512 nm, with respect to that of the polymer in solution (469 nm). Comparing the spectra shown in the insets, it is also apparent that the floating layer bathochromic shift is persistent and does not depend on the applied surface pressure. As the compression process was completed, the film was deposited through the horizontal transfer of several subsequent layers. A linear dependence of the LS POPT film adsorption peak intensity on the number of transferred layers was reported, proving that the LS films are built up in a multilayer structure.[15] The LS film with a 50-layer deposit was about 280 nm thick, while the average thickness of the cast one was about 250 nm.

A highly conductive silicon wafer covered by thermal silicon dioxide (Si/SiO_2) was used as POPT film substrate for all the measurements other than for the UV−vis and IR characterization, where glass slides and intrinsic infrared transparent Si were employed, respectively. OTFT devices were also fabricated on a Si/SiO_2 substrate covered by a POPT film. Bare SiO_2 surface is hydrophilic mainly due to the presence of polar OH groups (dangling bonds). Exposure to 1,1,1,3,3,3-hexamethyldisilazane (HMDS) vapors for a night is known to alkyl functionalize the SiO_2 surface, improving its hydrophobicity.[17] An extensive description of all the experimental procedures adopted in this study is given in the Supporting Information.

The evaluation of the POPT molecules' $\pi-\pi^*$ optical transition was performed by measuring the UV−vis absorption spectra of the copolymer cast and LS thin films. The relevant spectra are reported in Figure 3. The $\pi-\pi^*$ peak of the POPT LS film is centered at 500 nm, exhibiting a full width at half-maximum (fwhm) of about 140 nm. The position of such a peak endured a certain variability, and the spectrum reported here exhibits the strongest bathochromic shift observed. The absorption band of the cast film presents a quite flat maximum centered at about 486 nm with a fwhm of almost 190 nm. This band is blue-shifted and much broader than the LS film one, this being indicative of a longer and less dispersed average conjugation length in the LS deposit. The UV−vis bands of both the LS film and the cast film exhibit a shoulder at approximately 536 nm, attributed to the vibronic fine structure.[18]

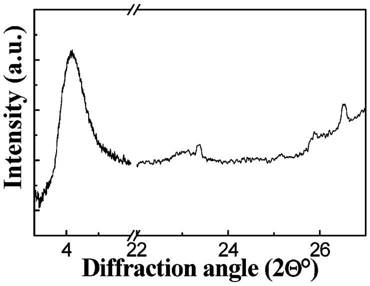

Figure 4. X-ray diffractograms of POPT LS film.

The structure of the LS POPT films were analyzed by means of $\theta-2\theta$ X-ray difractometry (XRD), and the spectrum, reported in Figure 4, shows a broad band falling at about 4.5° diffraction angle, corresponding to interlayer spacing of ca. 20 Å. Very small but sharp peaks can be observed in the LS film spectrum at 23.3° and 26.5° incidence, corresponding to diffraction planes separated by 3.8 and 3.3 Å, respectively. The features of such a spectrum are very similar to those reported for a POPT film deposited by casting from chloroform.[18] Such cast POPT films have been reported to hold a lamellar-type structure with the backbone planes spaced by 20−22 Å.[18] The sharpness of the main XRD peak, assigned to the (100) Bragg diffraction, is gradually lost as the POPT cast film is heated to 150 °C and the lamellar spacing becomes eventually higher.[18] This is correlated with the thermochromic reversible properties reported for this POPT polymer.[12,13] The XRD spectrum of the LS film shown in Figure 4 resembles the features of an heated cast film mainly because of the broad nature of the main reflection. This could be ascribed to the fact that no precaution was taken to avoid thermal stress on the samples. On the basis of such results and in analogy to the structure of the RR PAT films,[2,9] a molecular packing involving edge-on POPT backbones, i.e., with the conjugated lamellae oriented normal or nearly normal to the substrate, could be proposed for the POPT LS films, although the film holds a fairly low degree of overall order. The lamellar spacing of 20 Å is consistent also with the length of interfaced octyloxy chains,[19] and the peaks at higher diffraction angles correspond to the π-staking distances between the aromatic rings.[20]

An extensive investigation of polarized infrared transmission spectra of the cast and LS POPT films was carried out and compared to the standard transmission Fourier transform infrared spectra of POPT in the apolar CCl_4 solution and in a KBr pellet. In Figure 5 the spectra of the cast and LS films, along with those of the POPT solution and KBr pellet, in

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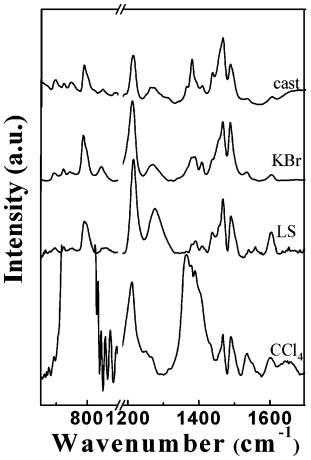

Figure 5. Unpolarized transmission spectra in the 650−1700 cm^{-1} range of CHCl$_3$ POPT solution and POPT KBr pellets along with polarized infrared transmission spectra of cast and LS POPT films.

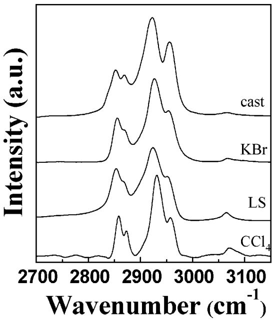

Figure 6. Polarized infrared spectra in the 2700−3200 cm^{-1} range of cast film and LS film along with unpolarized spectra of POPT KBr pellet and CHCl$_3$ POPT solution.

the 650−1700 cm^{-1} range are reported. Here the absorption bands at about 780 cm^{-1} are attributed to the 2,5-disubstituted thiophene ring C−H out-of-plane bending vibration,[21,22] while the bands at about 840 cm^{-1} are attributed to the 1,4-disubstituted benzene rings.[22,23] The absorption at about 1215 and 1270 cm^{-1} can be attributed to C−O stretching-type vibrations and to the conjugated backbone stretching, the latter in analogy with bands falling at the same position in a poly(octylthiophene).[22] The band falling at ca.1380 cm^{-1}, having a shoulder at higher wavenumbers (ca. 1411 cm^{-1}), is attributed to the CH$_2$ and CH$_3$ deformation bending vibrations, although attribution to thienyl group intracycle C−C stretching can be given as well. The two peaks at 1468 and 1490 cm^{-1} are assigned to symmetric and asymmetric thiophene ring stretching, while those falling at ca. 1535 and 1603 cm^{-1} are relevant to the same vibration modes for the phenylene ring. In Figure 6 the spectra of the cast and LS films in the 2700−3200 cm^{-1} range are reported along with the spectra of the POPT CCl$_4$ solution and KBr pellet. The four main structures present in all the spectra are attributed to CH$_2$ and CH$_3$ symmetric (ca. 2850 and 2870 cm^{-1}) and asymmetric (ca. 2930 and 2955 cm^{-1}) stretching, respectively.[9,23,24] A table of all the IR peaks positions is reported in the Supporting Information.

Tapping-mode scanning force microscopy (SFM) images of the cast and LS POPT films are reported in Figure 7. The SFM images reveal the expected different surface morphology of the cast films compared to the LS one. In particular, the root-mean-square roughness, on a scale of about 30 μm, falls in the range of 50−70 nm for the cast films while it goes down to 30−40 nm for the LS ones. Also, on a smaller scale (2−5 μm) differences are evident in the morphology of the two films, with the LS film showing a much more regular and granular-type structure.

The organic semiconductor TFT structure is the typical bottom-gate, top-contact one, as sketched in Figure 1. Thermal evaporation of the gold top source and drain contacts was performed through a shadow mask after thin-film deposition. This is a very convenient and easy thin-film-transistor fabrication procedure as no lithographic patterning is required. However, it has the disadvantage that a leakage current can add to the source-drain current (I_{ds}) flowing in the channel region. The POPT OTFTs were operated in the common source mode, and both V_{ds} and V_g biases were imposed negative with respect to the grounded source as this class of materials were expected to be p-type semiconductors, in analogy to the behavior of thiophene−phenylene oligomers.[25] The current−voltage (I_{ds}−V_{ds}) characteristics of OTFTs relevant to both cast and LS deposited POPT thin films were measured in the 0−100 V range, and the results are reported in Figure 8. Lower operating voltages, down to −5 V, were used on devices comprising a SiO$_2$ gate dielectric as thin as 25 nm.[26,27] From the curves reported in Figure 8, it is immediately recognized that the cast film behaves like a resistor, as no current modulation can be observed when the gate bias is ranged between 0 and −100 V. The behavior of the LS film appears remarkably different as the OTFT current−voltage characteristics exhibit a clear field effect, and fairly good I_{ds}−V_{ds} characteristics could be measured. The best value of μ_{FET} extracted, using standard OTFT equations and assuming ideal behavior,[28] is 5×10^{-4} cm^2/V·s, although routinely achieved values are in the range (2−4) × 10^{-4} cm^2/V·s. A quite high off-current (I_{ds} at $V_g = 0$ V) is measured, similar to what was observed in other alkoxy-substituted conjugated polymers.[29] This is probably related to the low oxidation potential and highly stable p-type conductive state of alkoxy-substituted conjugated systems.[30] This figure of merit improved with OTFT with ultrathin active layers.[31] It is important to note the critical dependence

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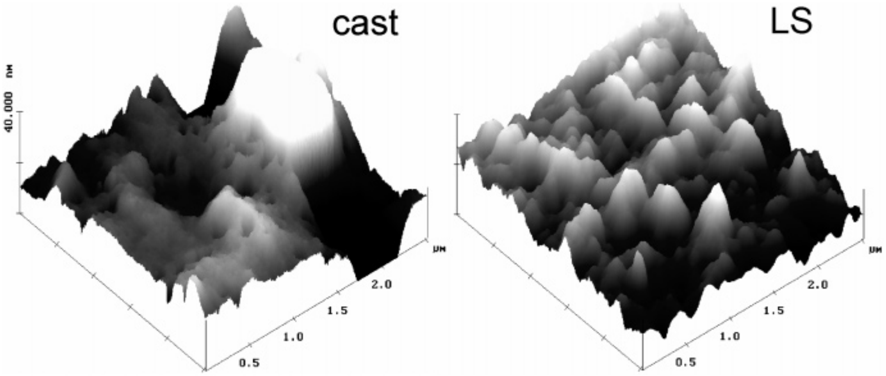

Figure 7. Scanning force microscopy of drop cast and LS films.

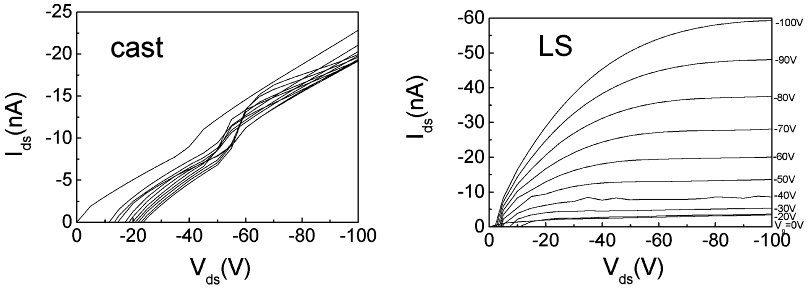

Figure 8. Current−voltage characteristics of cast and LS POPT OTFTs.

on the HMDS SiO_2 treatment observed, as much worse transistor characteristics, with mobilities falling to (2−5) × 10^{-6} $cm^2/V{\cdot}s$, were measured when the POPT LS active layer was deposited on the hydrophilic substrate.[31] All the characteristics were measured in air, and no particular care was taken to handle the samples when transferred to the different laboratories.

Discussion

Theoretical models have predicted phenylene−thienylene systems to have a backbone structural conformation critically dependent on the side groups attached to the phenylene units. A nonsubstituted system, namely 1,4-bis(2-thienyl)benzene, is predicted to exhibit a phenylene−thienylene torsional angle (Φ) of 24.3°.[23] The effect of an alkyl side chain is detrimental, as the 1,4-bis(2-thienyl)-2,5-dimethylbenzene backbone is much more twisted, with Φ becoming as high as 63°. A lower twisting angle can be recovered with a phenylene−thiophene system bearing an alkoxy chain on the phenyl ring; in 1,4-bis(2-thienyl)-2,5-dimethoxybenzene Φ is lowered to 40°, most probably because of the stabilizing sulfur−oxygen interaction.[23,32] A similar scenario is also predicted in the work by Pan and co-workers, although a much less twisted structure ($\Phi = 9°$) is assigned to the alkoxyphenylene−thiophene system.[33] An alkoxyphenylene−thiophene model compound is calculated to hold an absolute energy minimum for a twisting angle of 140°, while a local minimum (energetically very close to the absolute one) is reached for $\Phi \approx 42°$.[18] This model, being in agreement with the elicited study by Reynolds and co-workers,[23] also predicts a very low energy barrier (about 1.3 kcal/mol) for the molecule to flip to an unstable planar or 90° tilted chain conformation.[18] Such a low barrier to conformational changes is said to account for the previously reported POPT reversible thermochromic properties.[12,13] Phenylene−thienylene systems are quite interesting also because sublimed 1,4-bis[2-(5-phenylthienyl)]benzene thin films and solution-processed thiophene−phenylene oligomers functionalized with terminal *n*-hexyl groups have been proven to hold field-effect properties comparable to those of high-performing thiophene oligomers or polymers.[25] Moreover, the phenylene units allow for easy substitution[34] and organometallic synthetic methodologies have been already appointed to obtain tailored conjugated polymers bearing ad hoc chosen side groups, such as simple alkoxy chains and/or glucose molecules bonded through the alkoxy linkage.[14,35,36]

All this calls for a systematic investigation of the solid state structural and field-effect properties of phenylene−thienylene systems, also comparing different thin-film deposition techniques. LB and LS transfer procedures seem particularly promising because they both involve a stage where the polymer molecules interact with the highly polar water surface. In this respect very detailed studies assess the molecular arrangement at the water−air interface for truly amphiphilic regioregular polymers bearing alkyl and polyether chains displayed in opposite directions,[37−39] while much

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less is known, also in this respect, about alkoxy-substituted polymers in which polar and nonpolar sites are not fully spatially separated.

The evaluation of the POPT molecules floating at the water–air interface shows that they hold a strongly red-shifted $\pi-\pi^*$ transition as the reflectance spectra are peaked at 512 nm, i.e., at more than 40 nm longer wavelength with respect to the same transition for the molecules in a chloroform solution. This result evidences that a longer average conjugation length is established when the POPT molecules lie on the water surface. This might be an effect of the dense molecular packing reached as the floating layer is compressed at progressively higher surface pressure, or it might be due to the self-organization of the POPT molecules. The latter hypothesis was put forward,[15] being strongly supported by the evidence that the reflectance maximum persistently falls at 512 nm independently of the surface pressure applied, while the normalized optical density ($\Delta R_{\mathrm{norm}} = (\Delta R)A$, where A is the area per repeat unit taken from the Langmuir curve) steadily increases. This evidence, along with the peculiarly steep line shape of the Langmuir curve previously addressed, suggests that an individual spontaneous organization of the POPT molecules readily occurs as they are spread over the water. The barrier compression apparently just drags the formed systems in a more densely packed structure.

A step further in the phenomenological modeling of the POPT molecular arrangement at the water–air interface can be made by discussing whether the floating-layer HOMO–LUMO band gap reduction is mainly due to the previously suggested self-organization of the molecules or to an improved planarity of the chains induced predominantly by the interaction of the POPT molecules with the water surface. The latter hypothesis is substantiated by the much weaker delocalization effect observed for the POPT molecules that spontaneously arrange in the films cast from chloroform. Indeed, the UV–vis peak for the cast film is 26 nm blue-shifted with respect to the molecules at the water–air interface. It could be inferred that the interaction of the POPT twisted polymer backbone with the water subphase forces the molecules to lie flatter on the polar surface, reaching a more planar, though energetically unstable, conformation. A simple electrostatic interaction of the sulfur and oxygen atoms of the POPT molecules with the water surface could be considered as a phenomenological model for the system. By the same token, the long alkyl branches of the side chains are likely to be pulled upward or in any case far from the water surface. The modeling of a densely packed POPT arrangement with the two octyl chains far from the water gives at least a 70 Å^2 occupied area per repeat unit.[15] The actual occupied surface that can be derived from the Langmuir curve (as limiting area extrapolated at zero pressure) is much lower (18 Å^2). This evidence could be explained considering a molecular packing involving an edge-on POPT backbone, in agreement with what was already proposed for PAT systems.[2] A similar arrangement has been proposed for a poly(heptadecyl 3-thiopheneacetate) deposited from chloroform at the air–water interface.[38] It cannot be ruled out, however, that the very small measured limiting area can be also the result of a partial three-dimensional organization of the POPT molecules at the water–air interface under barrier compression. A molecular stacking can, in fact, occur. Further work is in progress to investigate experimentally and theoretically the POPT self-organization at the air–water interface as well as at the solid surface.

The POPT LS film UV–vis absorption peak is 14 nm red-shifted with respect to that of the cast film and its fwhm is 50 nm narrower, showing that a slightly longer average conjugation length along with a more uniform conjugation length distribution is achievable, depositing the POPT molecules with the LS procedure with respect to the cast one. As already pointed out, the bathochromic shift of the LS POPT $\pi-\pi^*$ peak is not constant, and this can be related to the molecular conformational instability previously discussed. The study of the infrared and Raman peaks attributed to the symmetric and asymmetric thiophene ring stretching, being connected to the π-bonding system, is known to deliver also information on the system average conjugation length. The ratio of the intensities of such infrared absorption bands ($I_{\mathrm{sym}}/I_{\mathrm{asym}}$) has been recognized by some authors as an indication, at least for regioregular and regiorandom polythiophene backbones, of improved conjugation length as it decreases.[24] In the present case this figure of merit is slightly less for the LS films (1.3) than for the cast ones (1.7). For the POPT in KBr a value of 1 is reached, and this could be interpreted as a planarization effect on the molecule due to close packing of the polymer chains. It is not clear, however, why the same low value is also reached for POPT in the CCl_4 environment. A preliminary Raman investigation on both the LS and cast films confirms such a trend. All this evidence concurs to prove that an extended mean effective conjugation length is retained when the POPT floating layer is transferred to the substrate as an LS film. This effect was already reported for LB films of organic molecules comprising long-chain esters, although the configuration was addressed as an unstable one.[40]

The assessment of the alkyl chain arrangement in the POPT films is a critical point. The degree of order of such chains can be investigated by looking at the position of the stretching CH_2 vibration. This band is clearly blue-shifted for the POPT in KBr and in CCl_4 solution with respect to the same band in the cast film that is peaked at 2922 cm^{-1}. A blue shift of such a band is indicative of alkyl chain disorder increase,[9] meaning in the present study that the cast film exhibits a higher degree of side chain order and this feature increases with the film thickness (data not shown). No such conclusion can be drawn for the LS films as the elicited band falls at 2928 cm^{-1} independently of the film thickness. The rationale for this evidence can be given considering that in the cast film a self-assembly of the polymer chains takes place thanks mainly to the interaction of the side chains, which that eventually reach an interdigitated configuration. This can have an effect on the backbone

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planarity, and further studies are in progress to clarify this point.

The systematic investigation of the OTFT electrical characteristics shows that LS POPT active layers always exhibit a source–drain current modulation with the gate bias and the *I*–*V* characteristics are fairly good, as can be seen in Figure 8. The highest field-effect mobility extracted from such curves was 5×10^{-4} cm^2/V·s; this was the best value reported so far for an alkoxy-substituted conjugated system.[29] On the other hand, no transistor behavior could be seen with the cast POPT films. Such a striking difference is not to be ascribed to solid state structural/molecular packing difference of the POPT LS and cast films, as the XRD spectra are very much the same. Also, the morphological dissimilarities cannot account for the different field-effect properties, because in the case of the RR PAT OTFTs a comparable level of performance was observed although morphologically different cast or LB films were deposited as active layers. In fact, in this case the LB OTFTs were even less performing.[9] Also, the very small divergence in the LS and cast film thickness should not account for the field-effect different properties which have been demonstrated to be thickness independent in OTFTs.[41] The field effect observed for the LS film is further and the most striking evidence that a molecular planarization effect is achieved with the LS deposition procedure; this is clear proof of molecular conformational control achieved through the deposition procedure. For such systems thermal stability is expected to be an issue, and proof for this is given by the fact that the LS transistor performances drastically degenerated to the level of the cast films, when the device was annealed at up to 150 °C under nitrogen flux. No performance improvement was seen, on the other hand, for the cast film OTFT upon the same annealing procedure. Despite such a high thermal instability, the devices stored under nitrogen in the lab did not degrade for several weeks, if the temperature was controlled.

Conclusions and Perspectives

The present study sheds light on the conjugation and field-effect properties of a regioregular alkoxy-substituted phenylene–thienylene polymer deposited as cast and Langmuir–Schäfer thin films. It is demonstrated that the LS transferring technique leads to POPT films that, differently from other regioregular systems, strikingly outperform the cast one, exhibiting also the best field-effect properties reported so far for an alkoxy-substituted conjugated system. The effect is ascribed to a molecular more planar conformation achieved with the LS deposition method. It can be envisaged that this study could open perspectives to the use of this technologically appealing deposition technique to improve also the organic semiconductor conductivity properties, controlling the molecule conformational state and eventually the conjugation length. Moreover, the regioregular alkoxyphenylene–thienylene conjugated copolymers are a class of materials that have been poorly investigated so far, despite the wealth of opportunities offered by the alkoxyphenylene unit, for convenient tailoring by molecules of chemical and biological interest. This study can also open an interesting perspective to the use of properly substituted phenylene–thienylene semiconductors as selective active layers in chemical and possibly biological sensing thin-film transistors.[26,27,29,42–45]

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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