

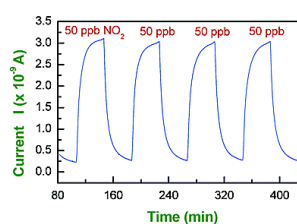
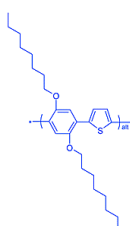
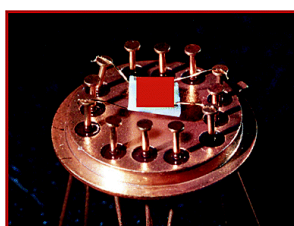
Article

Thin Film Construction and Characterization and Gas-Sensing Performances of a Tailored Phenylene–Thienylene Copolymer

Francesco Naso, Francesco Babudri, Donato Colangiuli, Gianluca M. Farinola, Fabio Quaranta, Roberto Rella, Raffaele Tafuro, and Ludovico Valli

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Thin Film Construction and Characterization and Gas-Sensing Performances of a Tailored Phenylene–Thienylene Copolymer

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Abstract: An alternating copolymer, poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene), has been synthesized and used in this research. The behavior of the floating film at the air–water interface has been investigated by measuring surface pressure versus area Langmuir isotherms and contemporaneously by reflection spectroscopy and Brewster angle microscopy. The floating films were transferred by the Langmuir–Schäfer (horizontal lifting) method onto various substrates. It is apparent from these analyses that the effective conjugation length is larger than those in other electroactive polymers and that a strong coplanarity and interchain association takes place above all in the floating film on the water surface and in the transferred multilayers. Such films were used as the active layers in resistive chemical gas sensor devices, thus revealing excellent sensitivity toward NO₂, reversibility, and time stability of the response.

Introduction

In past decades, conjugated polymers have been paid considerable attention because of their academic importance and capability in technological applications. Their electrical and optical properties are utilized in functional device preparation such as large flat-panel displays, light emitting diodes,¹ and chemical sensors.² However, the correlation between such properties and the structural characteristics of these materials has rarely been performed.³

The rationale for the utilization of soluble polymeric derivatives in such apparatuses is connected to the possibility of modulating materials' characteristics and economical processing requirements. The variation of materials' properties can be obtained through the chemical modification of unsaturated chain units. In this light, the vinylene moiety of PPVs has been replaced by a thiophene ring, thus inducing in some instances improvement of chemical and physical characteristics, such as solubility, adhesion for film formation, and electrical properties.^{1,4} Moreover, the presence of suitable pendant groups allows processible alkoxy substituted copolymers, such as poly(2,5-

dialkoxy-1,4-phenylene-*alt*-2,5-thienylene), to preserve their solubility during conversion procedures, thus making available further chances of easy processibility. Ballauff compared the behavior of lateral substituents to bound solvent molecules, inducing the macromolecules' solubility and fusibility.⁵ Additionally, these rigid main chain materials behave as mesogenic moieties in which the liquid-crystalline characteristics are intimately connected to the optical and electrical properties.³ Upon being heated above their melting points, such electroactive polymers undergo a phase transition, producing a nematic phase.

Unlike the construction of devices containing the inorganic counterpart, usually demanding severe conditions, polymeric coatings could be prepared by different techniques such as spin-coating, casting, Langmuir–Blodgett, self-assembly, or printing methods.⁶

Microelectronics apparatuses are becoming more and more small-scale and elaborate, and consequently the standard of control over orientation and arrangement of molecules becomes more exigent and pressing. The method of deposition univocally considered well fitting with molecular engineering is the Langmuir–Blodgett technique that in this research has been used for the deposition of poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene), POPT (Scheme 1, Supporting Information). The control over the film thickness is of paramount importance to

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pilot properties such as carrier concentration, charge mobility, and conduction and to improve the device performances. Polymeric LB films are usually more stable and physically more robust than those of nonpolymeric amphiphiles that, although sometimes highly ordered, unfortunately are prone to molecular reorganization.

In recent years, a great research effort has been devoted to the development of suitable gas-sensitive materials to monitor the quality of atmosphere in both work and domestic ambients.² Semiconducting polymers can assume great importance in gas-sensing applications, because their conductivity can be varied over many orders of magnitude by exposing them to specific gaseous species. Concerning thin film-based devices, sensors incorporating these polymers offer important benefits in comparison with the inorganic counterpart, such as their structural versatility and capacity to experience reversible redox chemistry in response to diverse environments.⁷ Usually the main drawback connected with the use of electroactive polymers is the thermal conductivity degradation, due to thermal disordering in the alkyl side chains. This leads to a less coplanar conformation of the polymer backbone, a higher oxidation state of the polymer, and a localization of the polaron or bipolaron. As a result of the instability of the localized charge, polymers undergo chemical reactions and lose conductivity. Yet, in our investigation, by using POPT as the active layer in resistive chemical gas sensors, we have shown evidence of appealing characteristics such as excellent sensitivity and selectivity toward NO₂ toxic gas, reversibility, and time stability of the response.

Results and Discussion

Conjugated macromolecules could be produced through several synthetic methods that allow one to link together different aromatic units to produce electroactive polymers exhibiting novel properties.⁸ A rationalization of this combinatorial method is necessary to choose a derivative exhibiting the aimed characteristics of good filmability, time stability, and mechanical resistance, in addition to high sensibility and selectivity and the adequate response time typical of applications in the field of gas sensors. Such considerations prompted us to synthesize a PPT derivative whose different appealing properties have been investigated in previous reports.^{3,6,9–13}

The Langmuir isotherm of pure POPT is illustrated in Figure 1. It displays a typical behavior reported also for other nonamphiphilic polymers.¹⁴ It shows evidence of a sort of gaseous phase ($\Pi < 1$ mN/m) for areas per repeat unit larger than 25 Å² and a condensed, steep, and rigid region for surface pressures larger than 10 mN/m. The collapse of the floating layer is apparent for $\Pi > 50$ mN/m. The limiting area per repeat

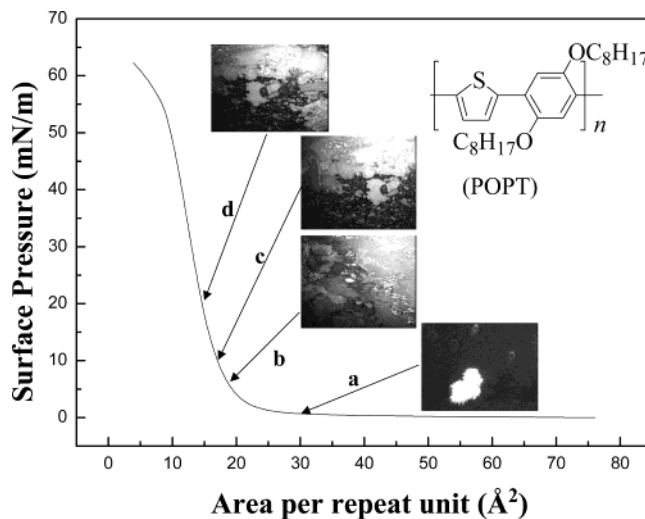


Figure 1. Langmuir curve of POPT (CHCl₃ as spreading solvent, concentration of repeat unit 4.3×10^{-2} M, temperature 293 K) and BAM images of the floating layer at different surface pressures and average area per repeat unit: (a) $\Pi = 0.7$ mN/m and $A = 29$ Å²; (b) $\Pi = 5$ mN/m and $A = 19$ Å²; (c) $\Pi = 10$ mN/m and $A = 17$ Å²; (d) $\Pi = 20$ mN/m and $A = 17$ Å². The field of view along the x axis is 430 μ m.

unit, $A_{\Pi \rightarrow 0}$ (obtained by extrapolation of the steepest portion of the curve to 0 mN/m pressure), is 18 Å². Measurements carried out by space filling molecular models and Cerius2 software have suggested that the area per repeat unit in a densely packed arrangement, with the two octyl chains outside the contact with water, is at least 70 Å². The analysis of the Langmuir isotherm determines that the observed value of $A_{\Pi \rightarrow 0}$ is too small to allow a fully extended configuration of the polymer backbone. An arrangement of the macromolecules in helices or coils could be inferred, but this assumption is probably not consistent with the data obtained by reflection spectroscopy on the floating layers at the air–water interface that, on the contrary, suggest a strong coplanarity and interchain association (vide infra). A plausible rationale is that, upon compression of the floating layer, segments of the polymer chains are forced out of the interface in a coplanar configuration and that eventually film collapse may occur by a process of gradual displacement of macromolecules from the contact with water. It is also probable that each polymer chain has one or a few of its segments fastened at the air–water interface, while the rest of the backbone essentially extends far from the contact with the water subphase because the hydrophobic nature of the whole macromolecule forces the chain out of the interface. We have also tried to improve the floating film homogeneity by waiting for long periods after spreading (at least 2 h) to allow unspread fractions to diffuse to the water surface. Yet, also in these cases, no variations in the behavior of the floating films were monitored.

Brewster angle microscopy (BAM) investigations were made during the compression of the floating layer and gave further confirmation about the presence of large aggregates on the water surface. The contemporaneous subsistence of three-dimensional aggregates and the clean water surface was observed even just after solvent evaporation and at low surface pressures and low area densities. It is possible to distinguish bright regions of 3D aggregates and dark areas of pure water surface. One large aggregate of POPT at 0.7 mN/m (area per repeat unit of about 29 Å²) on the water subphase is clearly apparent in Figure 1a,

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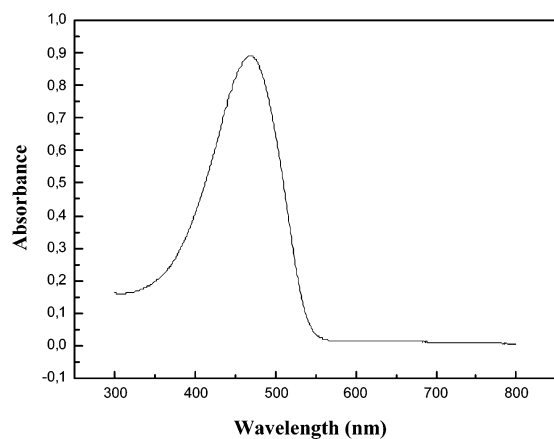


Figure 2. Absorption spectrum of POPT in chloroform solution (concentration of repeat unit 1.91×10^{-2} mg/mL, temperature 293 K).

and its average length along the x -axis is about $100 \mu\text{m}$. During compression, such domains coalesce and broaden; they begin to show more clearly facets and different shades of gray. This is illustrated in Figure 1b, taken at a surface pressure of 5 mN/m (area per repeat unit of about 19 \AA^2). Further compression at higher surface pressures permitted evidence of the generation of larger clusters, even though for $\Pi > 10$ mN/m the morphology of the floating film appeared to be not very sensitive to surface pressure variations. Such a trend is illustrated in Figure 1c and d, which refers to $\Pi = 10$ and 20 mN/m (area per repeat unit of about 17 \AA^2). This behavior is also consistent with the pattern shown in the Langmuir isotherm, whose slope is practically constant above 10 mN/m.

The deposition of multilayers was carried out by the horizontal lifting (Langmuir–Schäfer) method onto different substrates. Films containing up to 40 layers were deposited, giving reddish multilayers.

The electrical and optical properties of this class of copolymers could be modulated through the variation of the HOMO–LUMO gap of the polymer, which is strictly connected to the mean conjugation length in the chain and to the degree of π -electrons delocalization. The UV–vis absorption spectrum of POPT (in chloroform solution, concentration of 1.91×10^{-2} mg/mL), illustrated in Figure 2, shows a strong absorption band of the π – π^* transition of the conjugated backbone at 469 nm due to the high delocalization of the π -conjugated thiophene units.¹¹ Such a high value of maximum wavelength suggests that both conjugation degree and size of delocalization with respect to other similar polymers¹¹ have been significantly expanded and, accordingly, the torsional angle between adjacent rings is small; moreover, a contribution from the two electron-donating n -octyloxy pendant groups on each phenylene moiety could be claimed.

The UV–vis absorption spectra of films deposited by the horizontal lifting method and containing different numbers of layers are reported in Figure 3. A significant bathochromic shift of the absorption maximum was monitored ($\lambda_{\text{max}} = 494 \text{ nm}$) in comparison with the solution spectrum. The rationale is an expansion of the mean conjugation length in the solid polymer.¹⁵ It most likely derives from the enhanced coplanar conformation of the conjugated chains in the multilayers with respect to the

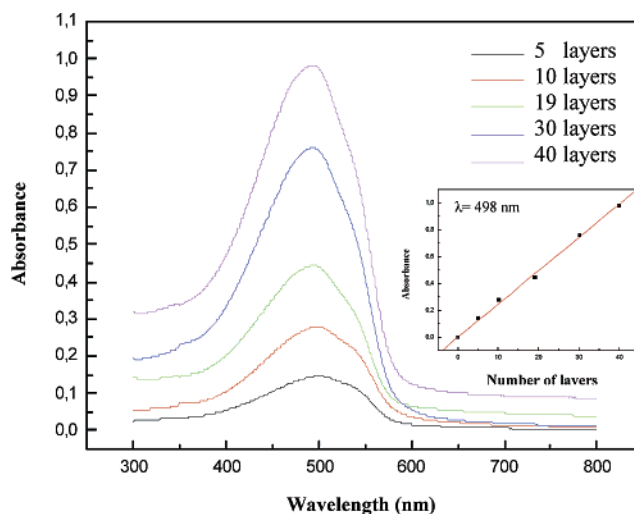


Figure 3. Absorption spectra of LS films of POPT with different numbers of layers. The inset shows the dependence of the film absorption on the number of transferred layers.

solutions. The interchain interactions in the solid state probably could promote coplanar organization of the aromatic rings in the polymer sequence and account for the experimental increased conjugation.¹⁶ The competitive interplay between the attractive forces among different chains and repulsive interactions mainly due to sterical hindrance determines in a major proportion the preferred conformation and consequently the HOMO–LUMO gap height. DiCésare et al. calculated for the gas phase (i.e., without mutual interactions among different polymer backbones) a small energy threshold value of less than 2.2–2.3 kcal/mol per repeat unit for the conformational transition from twisted to planar arrangement.^{12,17} Moreover, it has already been reported that the coplanar organization is favored by the stacking (very probable during the multilayer deposition) above all when the threshold value is small.¹⁸

The inset in Figure 3 exhibits the dependence of the film absorption on the number of transferred layers; the straight line was drawn using a least-squares fit and reproduces well the experimental data. Such a behavior implies that the transfer is reproducible, a constant amount of POPT is on the average picked up at each run, and the molecular environment of POPT in each layer is practically constant during deposition.

The molecular organization of the polymer floating layers at the air–water interface was investigated by spectroscopic measurements through reflection of light under normal incidence.^{19,20} This method is particularly tailored for this purpose because only chromophores at the interface contribute to the enhanced reflection. The difference ΔR in reflectivity from the chromophore floating layer on the subphase and reflectivity from the bare subphase surface was monitored as a function of wavelength. The corresponding reflection spectra from the

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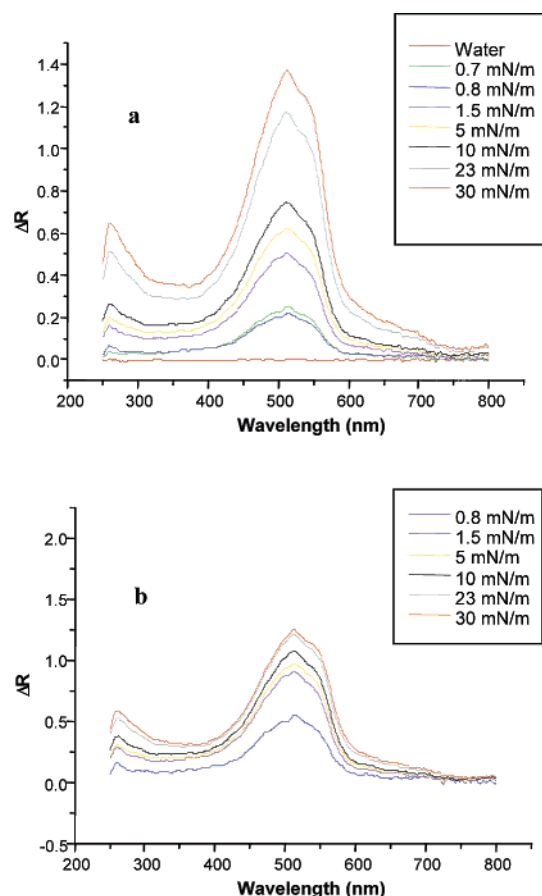


Figure 4. Absolute reflection spectra (a) and normalized reflection spectra (b) from the polymer floating film on the water surface at different fixed surface pressures after equilibrium.

polymer on the water surface at different fixed surface pressures after reaching equilibrium (i.e., no variation in surface pressure and enhanced reflectivity) are shown in Figure 4a. It is apparent that, upon compression, the reflection enhances because on the average the surface density grows, while its profile does not change. The reflection spectra were then normalized to the same surface density of polymer by multiplying ΔR by the surface area, that is, $\Delta R_{\text{norm}} = \Delta R \times A$, where A (nm^2 per repeat unit) is taken from the Langmuir isotherm at the relative value of surface pressure. The normalized spectra are illustrated in Figure 4b. The continuous increase in ΔR_{norm} , together with the constancy of the maximum wavelength, suggest that, after initial aggregation after solution spreading, the self-organized and associated clusters are dragged on the water surface and coalesce, while consequently the surface density of the floating layer enhances. As can be detected, the normalized reflection spectra of POPT undergo smaller and smaller variations during the compression process. This could also be rationalized considering that, after initial preaggregation, the 3D domains of aggregated polymers are constrained together, but reorganization of POPT chains on the water surface is progressively less important and pronounced during compression. This spectral behavior is also consistent with the poor amphiphilic character of the polymer and the BAM images.

The specified trend is confirmed by the plot of $\Delta(\Delta R_{\text{norm}})/\Delta\Pi$ versus Π in correspondence of the maximum wavelength ($\lambda = 512$ nm), illustrated in Figure 5. The steepest portion of the curve is in the range $0 < \Pi < 10$ mN/m according to the

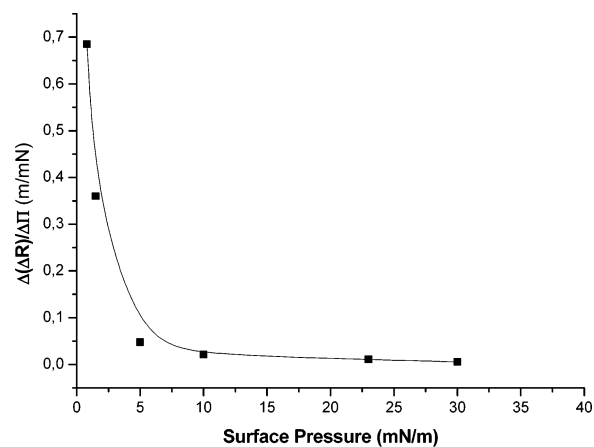


Figure 5. Plot of $\Delta(\Delta R_{\text{norm}})/\Delta\Pi$ vs Π in correspondence of the maximum wavelength $\lambda = 512$ nm.

observed behavior in the Langmuir isotherm, whose slope is practically constant for surface pressures larger than 10 mN/m. The expected rapid decrease of the variation of ΔR_{norm} (normalized to the surface pressure Π) versus Π at the beginning of compression is in fact monitored.

The reflection spectrum at the air–water interface shows evidence of the same band as that in solution and when deposited as an LS multilayer, although with some noteworthy peculiarities. First, the band is significantly broader and less resolved in the case of the ΔR spectrum on the water surface and of the LS film absorbance spectrum in comparison with the chloroform solution absorption. This behavior is typically symptomatic of association among different polymer chains. Second, the peak wavelength of the floating film at 512 nm and of the LS films onto quartz substrates at 494 nm is red-shifted with respect to the solution (469 nm). The rationale is that on the water surface the mean conjugation length is even larger than that in the multilayer: the coplanar conformation of the conjugated chains probably derives from the interchain interactions and accounts for the experimental increased conjugation and smaller HOMO–LUMO gap. The bathochromic shift of the band of the floating films is apparent even at low surface pressures, thus giving further evidence that attractive interchain interactions are sufficiently energetic that significant preaggregation can take place just after the spreading of the solution on the subphase surface and prior to compression of the film.

At last, a shoulder is apparent above all in the case of the floating film at the air–water interface (irrespective of the surface pressure) and faintly for the LS film. The shoulder proposes the existence of a second aggregation state and organization of the polymer backbones. Moreover, it does not seem to be a dependence of the relative intensities of the main peak and the shoulder on the surface tension, thus suggesting that correspondingly the number of POPT macromolecules in the two different associated states does not vary significantly.

Further evidence of the decrease in the HOMO–LUMO gap comes from the optical spectra reported in Figure 6, where the absorption in the UV–vis spectral range is showed for as-deposited and thermal annealed LS thin films. As one can see, the typical absorption spectra of the as-deposited film show a blue shift after thermal annealing at about 373 K. The rationale for this phenomenon is that polymer chain disorganization and high temperature promote the contraction of conjugation and

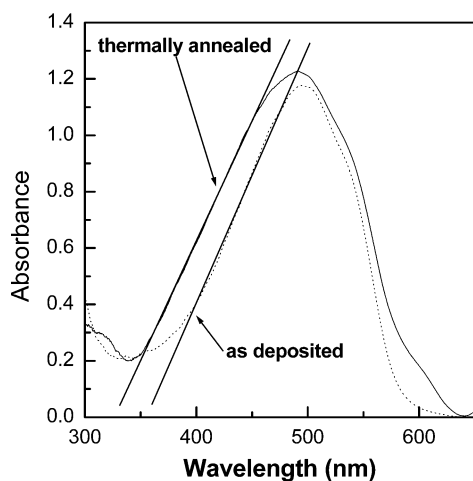


Figure 6. Absorption in the UV–vis spectral range of as-deposited and thermal annealed (373 K) LS thin films.

the consequent blue-shift effect. This behavior justifies the decrease in the electrical conductivity of the thin layer during the tests performed in a controlled atmosphere with the LS film kept at a different working temperature ranging between room temperature and 373 K. In other words, the spectra show evidence of a blue shift in the absorption threshold that gives rise to the decrease in the conductivity of the sensing layer by increasing the working temperature of the sensor.

The conformational rearrangement from a coplanar (π – π attractive interaction among different polymer chains) to a twisted organization of the aromatic rings involves small energy threshold values overcome by the energetic gain deriving from temperature enhancement. In addition, the negligible influence of the length of the pendant group on the polymer skeleton has already been demonstrated by other researchers.^{18,21}

Electrical Characterization. As was reported in recent literature, the electrical properties of a large variety of polymers have been studied.²² Moreover, it is well known that the electronic properties of certain conducting polymers can be modified by the presence of a gas or vapor. Consequently, conducting polymers have been used to make a number of chemically sensitive microelectronic devices such as resistors, diodes, transistors, and coating for quartz crystal microbalance. From a technological point of view, thin films of polymer materials offer several benefits over other gas-sensitive layers. First, the reaction process takes place at room temperature or at a low working temperature of the sensing layer in comparison with the elevated temperature needed in the case of active layers based on metal oxide semiconductors. In this case, a device containing a polymer as the sensing element does not have a high power consumption and can be used in a handheld portable device. Conducting polymers deposited in thin film form by using different deposition techniques such as spin coating, thermal evaporation, and the Langmuir–Blodgett technique²² have been shown to respond reversibly in a few seconds and to be sensitive at the parts per million level and below to volatile organic compounds²³ but also to low levels of reactive gases

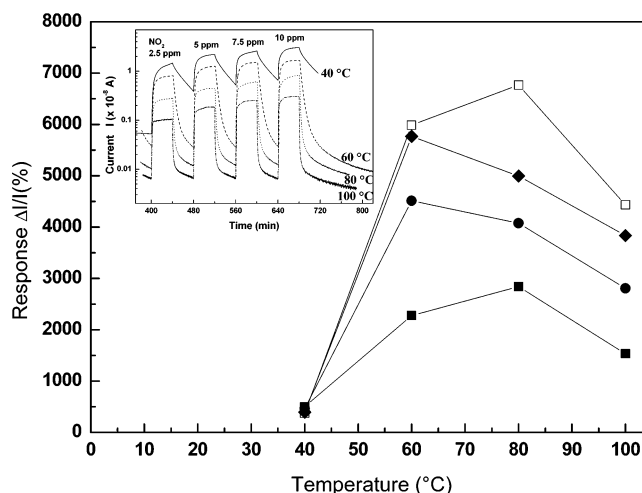


Figure 7. Response of the sensing layer as a function of the working temperature for different NO₂ concentrations: □ 10 ppm; ◆ 7.5 ppm; ● 5 ppm; and ■ 2.5 ppm. In the inset are reported the dynamic responses at different NO₂ concentrations in dry-air, keeping the sensing layer at different working temperatures.

such as ammonia and nitrogen dioxide.²⁴ Generally, the electronic ground state of these polymers is that of an insulator, with a forbidden energy gap between filled and empty energy levels. The conductivity of the polymer thin film is transformed from insulating into conducting through the doping process, with larger conductivities induced by higher doping levels. In our case, the doping mechanism is temporary and is ascribable to the interaction among gas molecules and the surface of the active layer. The doping mechanism induces the creation of extra charges on the chain of the polymer with the formation of charged defects, such as spinless bipolarons, associated with strong modification and the appearance of electronic states in the gap.²⁵ Conductive polymers are generally acknowledged to exhibit behavior which is in accordance with p-type conductive materials; it is reasonable to expect that oxidizing gases, such as NO₂, or reducing gases, such as NH₃, will cause an increase or decrease in the conductivity as a consequence of the formation of additional free carriers within the band structure of the material. However, much work has been focused on the nature of the charge carriers; also, at a high density of conduction electrons at the Fermi level for the highly doped state, the carriers may be spatially localized so that they cannot participate in transport except through the hopping mechanism²⁶ even at a high-temperature condition.

To test the electrical behavior and response of our LS films, we initially exposed the multilayers to a flux containing parts per million levels of NO₂ gas in a mixture with dry-air. The doping process that takes place during the interaction is completely reversible, as can be seen in the inset of Figure 7. Moreover, the performances of the sensing layer increase in terms of response time and recovery time by increasing the working temperature of the device. In other words, as has been generally observed for every couple of gas and sensitive material, a working temperature exists at which the response of the sensor reaches its best value as it is possible to argue

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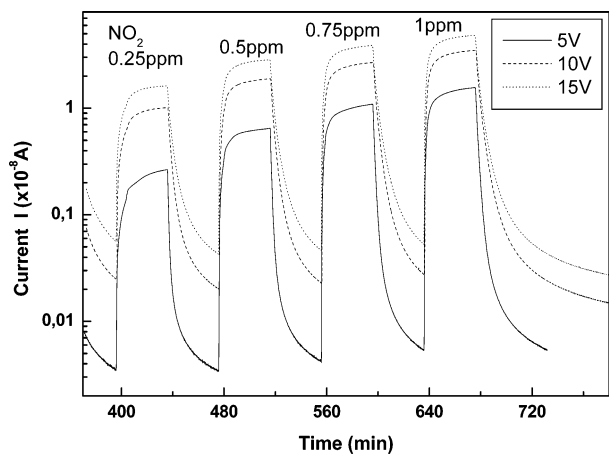


Figure 8. Dynamic responses of the sensing layer to different NO₂ concentrations for different voltages applied to the electrodes.

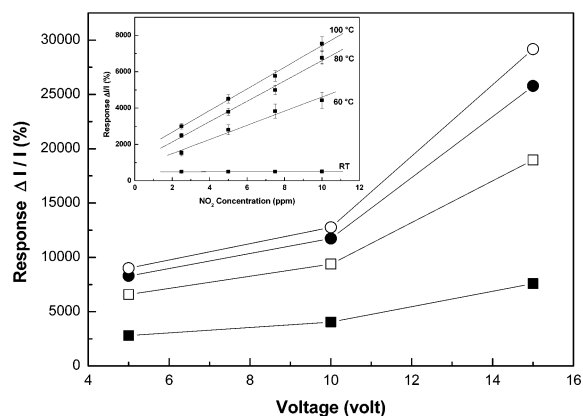


Figure 9. Response $\Delta I/I$ calculated at different voltages applied to the electrodes and in the presence of various NO₂ concentrations in the test chamber: ■ 0.25 ppm; □ 0.5 ppm; ● 0.75 ppm; ○ 1 ppm. The inset shows the calibration curves of the sensor obtained at different working temperatures of the device.

from Figure 7. Here, the response is defined as $\Delta I/I = (I_{\text{gas}} - I_{\text{air}})/I_{\text{air}}$, where I_{air} is the electrical current measured at the electrodes by fixing a voltage of 5 V, and I_{gas} is the electrical current of the sample in the presence of test gas.

The sample shows a maximum response to NO₂ gas in the temperature range between 60 and 80 °C. Figure 8 reports on the variation in the conductivity of the sensing layer along the y-axis in log scale to show evidence of the magnitude of the variation in the electrical current even in the presence of very low NO₂ concentrations. In fact, Figure 7 shows this amplitude in the response of the sensor that varies from 2000% to 6000% in the working temperature range 60–80 °C, depending on the NO₂ concentration in dry-air.

Moreover, the response is linear with the NO₂ concentration, as is illustrated in the inset of Figure 9, where the NO₂ concentration is in the range 2.5–10 ppm. At room temperature, the response of the sensor remains practically constant in the investigated concentration range, because of the interaction mechanism among gas molecules and the active sites of the sensing layer not being activated; however, by increasing the temperature, the response of the sensor increases with the concentration, while the response time and recovery time decrease with values of about 2 and 3 min, respectively. Here, the response time is defined as the time required for the sample variation electrical current to reach 90% of the equilibrium value

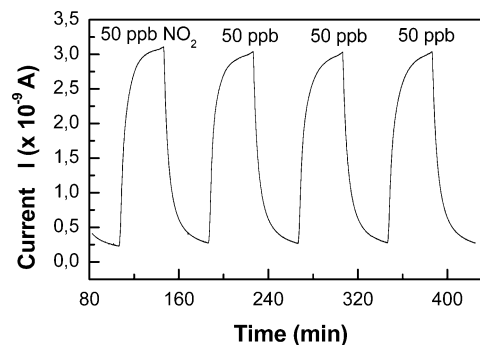


Figure 10. Dynamic response of the sensor in the presence of low NO₂ concentration (50 ppb).

following a step increase in the test gas concentration, while the recovery time is defined as the time necessary for the sample to return to 10% above the original electrical current in air following the removal of the test gas.

To increase the recoil efficiency of the charge carriers, and consequently the electrical current of the device in dry-air at the working temperature of the maximum response, the electrical potential applied to the electrodes was varied in the range 5–15 V. Figure 9 shows the response curves thus obtained by using a NO₂ concentration between 0.25 and 1 ppm in dry-air. It can be inferred that not only the current is enhanced by increasing the voltage applied to the electrodes, but also the response in the presence of nitrogen dioxide in very low concentration (0.25–1 ppm) is increased.

Consequently, to optimize the performances of the device in terms of electrical current, it is possible to select a suitable voltage. The measurements reported in Figure 10 also show evidence of a very interesting aspect of our sensing layer, a very low threshold of sensitivity; for this purpose, experimental tests were performed in the presence of 50 ppb of nitrogen dioxide in a mixture with dry-air, taking the sensing layer at the working temperature of maximum response. Measurements performed in the presence of potential interfering gases, such as ammonia, carbon monoxide, or sulfur dioxide in the test chamber, show evidence of a peculiarity in the behavior of our sensing layer regarding the selectivity to very low concentrations of NO₂ (1 ppm), even in the presence of mixtures containing large concentrations of other possible interfering gases (100–200 ppm). Further investigations concerning the selectivity and the responses of the sensor in the presence of different humidity conditions will be the subject of future communications.

Finally, it is important to emphasize three peculiarities induced by the polymer structure and the deposition technique:

(a) Two similar derivatives – poly(2,5-dioctyloxy-1,4-phenylenevinylene) and poly[2,15-dioxabicyclo[14.2.2]icosal(19),16(20),17-trien-17,19-ylenevinylene] – do not exhibit the same sensing characteristics.²⁷ The replacement of the vinylene moiety by a thiophene ring has substantially enhanced the physicochemical and sensing properties.

(b) Active layers of POPT deposited by other techniques, such as simple solvent-casting or spin-coating, do not show evidence of the same electrical behavior. Applying voltages in the same range (5–15 V), we determined that the measured currents were at least 2 orders of magnitude smaller and the response to NO₂

(27) Babudri, F.; Farinola, G. M.; Giancane, S.; Naso, F.; Rella, R.; Scarpa, A.; Valli, L. *Mater. Sci. Eng., C* **2002**, *22*, 445–448.

was practically negligible in the range from room temperature to 100 °C. In our opinion, the rationale is that the LS procedure induces larger coplanarity of rings, conjugation, and interchain association, thus magnifying the electrical behavior. Moreover, the coplanar arrangement of the rings renders π -electron density available for thorough contact with NO₂ gas molecules.

(c) LS active layers of POPT exhibit improved sensing behavior in comparison with usual metal oxide semiconductors, above all concerning selectivity toward NO₂ gas at relatively low temperatures (60–100 °C), even though the inorganic counterpart shows evidence of high mechanical and thermal stability at high temperatures.

Conclusions

Floating films of poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene) have been disposed at the air–water interface and investigated by Brewster angle microscopy and reflection spectroscopy. Experimental data show evidence that interchain association and magnitude of delocalization and conjugation are mainly regulated by ring coplanarity. The observation that the bathochromic effect is more pronounced in the case of the floating film on the water surface than in the LS multilayer is

remarkable, suggesting a loss of association upon the transfer by the horizontal lifting method, probably induced by the disorganizing effect of the two *n*-octyl chains in each repeat unit. Moreover, interchain interaction is clearly ascertainable even just after solution spreading and solvent evaporation. Multilayer conductivity has been demonstrated to be very sensitive to very low concentrations of NO₂ down to a parts per billion order of magnitude. A sensitive device was realized, and the electrical parameters used allowed the realization of a single NO₂ sensor. Further study will be performed to optimize the response time and recovery time, the selectivity, and the sensitivity of the device in different atmosphere conditions.

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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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