

Structural Study of a *n*-Alkylthiophene Polymer Grown in an Oriented Ultrathin Matrix of Alkylcellulose

C. Henry,^{†,‡} F. Armand,^{*,†} O. Araspin,[†] J.-P. Bourgoin,[†] and G. Wegner^{*,‡}

CEA/DSM/DRECAM, Service de Chimie Moléculaire, CE Saclay,
91191 Gif-sur-Yvette Cedex, France, and Max-Planck-Institut für Polymerforschung,
Ackermannweg 10, D-55128 Mainz, Germany

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A thin conducting film of an organic composite material made of *n*-butylcellulose and polythiophene has been fabricated. Thin oriented films of *n*-butylcinnamoylcellulose were deposited on a conducting substrate by the Langmuir–Blodgett technique and stabilized by cross-linking through UV irradiation. Subsequent exposure to a solution of 3-pentylthiophene followed by electropolymerization led to the formation of poly(pentylthiophene) (PPT) within the alkylcellulose matrix. The structure of the composite material has been characterized by various spectroscopies, microscopies, and microanalysis techniques. The composite material is made of domains of PPT oriented along the cellulose backbones. In the case of large domains (up to $35 \times 150 \mu\text{m}^2$) there is a segregation between cellulose and PPT. However, for small domains (a few square microns), the two polymers seem to be intimately mixed and PPT is oriented at the molecular level. In all cases, the alkylcellulose stabilizes the PPT film in organic solvents and does not worsen the PPT conducting properties.

Introduction

One of the most promising applications of organic conducting materials is their use for the fabrication of flexible screens.¹ This requires materials with good mechanical properties and high conductivity. Although conjugated polymers are among the best organic conductors, their conductivity is still rather low, even in the doped state,² compared to inorganic compounds; moreover, the rigidity of their structure drastically limits their applications. Their conductivity can, however, be improved if the polymer chains are not only doped but also oriented:³ it was shown that the conductivity of polyacetylene films increased by a factor of 10^5 along one direction⁴ when they were stretched. However, this technique can only be used for thick films whereas the development of very thin systems necessarily involves thin film formation.

To improve simultaneously the conductivity, the mechanical properties, and the availability as ultrathin films, the following strategy was considered: an ultrathin oriented matrix was built and used as a template for the growth of a conducting polymer. The

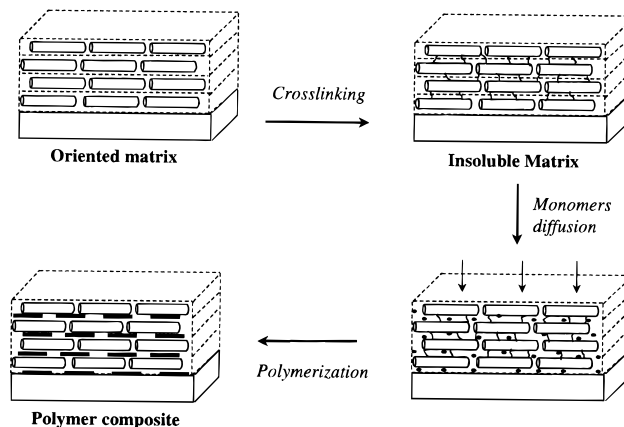


Figure 1. Strategy applied to obtain the polymer composite.

Langmuir–Blodgett (LB) technique applied to rigid rod polymers^{5–6} allows the formation of oriented films of nanometer-scale controlled thickness; therefore, it was used as a starting point to realize our strategy outlined below (Figure 1).

The first step is the fabrication of the oriented matrix of controlled thickness by the LB transfer of rigid rod polymers on a conducting substrate. In a second step, the film is stabilized by cross-linking.⁷ The third step is the diffusion of electroactive monomers into the matrix. In the fourth step, the monomers are electrochemically polymerized so as to provide a better control on the characteristics (conjugation length, amount, etc.) of the conjugated polymer that is formed.

* To whom correspondence should be addressed.

[†] Service de Chimie Moléculaire.

[‡] Max-Planck-Institut für Polymerforschung.

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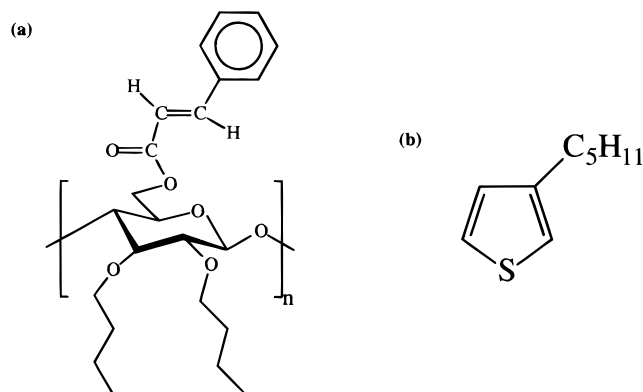


Figure 2. Molecules used in this study: (a) *n*-butylcinnamoylcellulose for the matrix; (b) 3-pentylthiophene as the monomer.

In this paper we analyze and describe the structural aspects of the composite material that has been obtained. The chemical structure has been investigated by UV spectroscopy, X-ray analysis, and X-ray photoelectron spectroscopy (XPS) while atomic force and scanning electron microscopies provided a visual description of the composite.

Experimental Section

Synthesis of the *n*-Butylcinnamoylcellulose. The cellulose derivative was synthesized as reported previously,⁸ following the method described by Isogai et al.⁹ for the alkylation. Of the three hydroxy groups per repeat unit of the unsubstituted cellulose, 2.6 on average were alkylated by a butyl group; of the remaining 0.4 groups on average, only 0.14 were esterified by a cinnamoyl chloride. Figure 2a is a schematic description of the cellulose derivative that is used, which in essence, is a randomly substituted material.

Synthesis of 3-Pentylthiophene. The monomer, presented in Figure 2b, was obtained by Grignard coupling using a nickel catalyst, as described by Kumada et al.¹⁰ It was subsequently isolated, purified, and characterized by nuclear magnetic resonance (NMR) as reported previously.¹¹

Fabrication of Conducting Substrates. The substrates for the LB transfer were made of glass covered with a gold or indium tin oxide (ITO) electrode. The samples for structural studies were bearing a gold electrode, whereas most of the electrochemical studies were realized on commercial ITO electrodes of 200 nm thickness on glass, the area resistance of which was around 20 Ω per square.

ITO-covered substrates and bare glass for gold deposition were prepared according to the following procedure. They were first cleaned with 2-propanol, sonicated 15 min with dichloromethane, and treated for 2 h at 150 $^{\circ}\text{C}$ in a mixture of H_2O_2 (30%)/ HNO_3 (25%)/Millipore water in a ratio of 1/1/5 (CAUTION: dangerous mixture). Finally, the substrates were rinsed 15 min in a stream of Millipore water.

Substrates subsequently used for the structural study of the composite material were covered with gold electrodes of 200 \AA thickness, making use of a Alybold evaporator at a pressure of 10^{-5} mbar and a deposition rate of 0.5 nm/s. To increase the adhesion of gold to the glass substrate, a 25 \AA thick layer of chromium was first evaporated at a deposition rate of 0.2 nm/s.

Before transfer of the LB film, all substrates were made hydrophobic by a 30 min exposure at 100 $^{\circ}\text{C}$ to a saturated atmosphere of hexamethyldisilazane (HMDS).

Realization of the Matrix by the LB Technique. The cellulose derivative was spread from chloroform solution at a concentration of approximately 0.4–0.6 g/L, at the surface of pure Millipore water. The Langmuir trough was a Lauda FW-1. Up to 800 monolayers of cellulose could be transferred at a speed of 1 cm/min with a stop of 10 s under the water surface and 1 min in the air. To achieve the cross-linking of the matrix, the films were irradiated by a low pressure 50 W mercury lamp with the help of an aluminum mirror which cuts the shortest wavelengths of the lamp spectrum. The reaction, that is, the cycloaddition of the cinnamoyl groups, was followed by UV spectroscopy;¹² it was stopped when 25% of the cinnamoyls had reacted, which corresponded to approximately 2.5 h of irradiation.

Electropolymerization of 3-Pentylthiophene. A 20 cm^3 three-compartment electrochemical cell was used. The reference electrode was the Ag/AgCl system; the counter electrode was a platinum foil and the working electrode was an ITO or gold electrode on top of which the cellulose was deposited by the LB technique. All experiments were performed at room temperature using acetonitrile as the solvent and tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) as the electrolytic salt. The concentration of the solution was around 0.1 $\text{mol}\cdot\text{L}^{-1}$ for the salt and 0.2 $\text{mol}\cdot\text{L}^{-1}$ for the 3-pentylthiophene.¹³ Before each polymerization experiment, nitrogen was bubbled through the solution for several minutes. The potentiostat was computer-controlled with PAR 270 software and PAR 173 interface. The electropolymerization of the 3-pentylthiophene was performed in a galvanostatic mode with current densities of 2–5 mA/cm^2 ¹⁴ in order to obtain an anodic potential of approximately 1.90 V.

Characterization Techniques. The polymer composite was characterized by UV spectroscopy (Perkin-Elmer Lambda 9) and atomic force microscopy (Digital Instrument nanoscope IIIa used in the tapping mode). Scanning electron microscopy and X-ray microanalysis were realized on a JEOL JSM-840 A microscope; the acceleration voltage was 3–5 kV and the current intensity was maintained at low level, from 10^{-9} to 10^{-11} A, to avoid destruction of the films.

Results and Discussion

Fabrication of the Polymer Composite. Obviously, the cross-linking efficiency of the *n*-butylcinnamoylcellulose was sufficient to form a stable matrix. Indeed, X-ray reflectivity carried out on multilayer preparations before and after immersion in acetonitrile clearly shows the absence of dissolution. However, the fitting of the Kiessig fringes¹⁵ suggests an increase of the surface roughness from 5 \AA to around 11 \AA . Considering the proportion of the cinnamoyl groups in the matrix (less than 5% of the available substitution sites) and their cross-linking percentage (around 25%), the mean dimension of the mesh size of the network available inside the matrix for the diffusion of molecules can be calculated. The result, $1.2 \times 14.6 \text{ nm}^2$, is consistent with the assumption that small molecules such as alkylthiophenes can readily diffuse in and out.

The substitution of the thiophene by an alkyl chain is an important element to favor its diffusion into the cellulose matrix. Moreover, considering the Hildebrand

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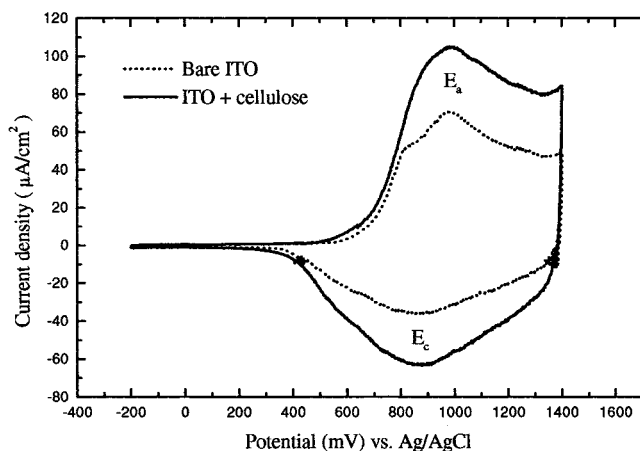


Figure 3. Cyclic voltammograms obtained after 5 s of polymerization on ITO substrates with/without cellulose. The speed was 50 mV/s.

solubility parameter of acetonitrile ($\delta = 24.0 \text{ MPa}^{1/2}$), we can expect the cellulose matrix ($\delta = 18.6 \text{ MPa}^{1/2}$) to be swollen by the solution,¹⁶ a phenomenon that should further favor the diffusion of the electroactive monomer. This was confirmed by quartz crystal microbalance experiments: the 3-pentylthiophene diffusion is rapid and stabilizes in less than 1 min to give a concentration 11 times higher in the cross-linked cellulose than in the acetonitrile solution (0.1 M). Therefore, it seems that the chemical system chosen for our experiments, that is, cross-linked alkyl cellulose/3-alkylthiophene/acetonitrile, is a convenient system to favor the formation of a composite at the molecular level.

To evaluate the influence of the matrix on the formation of the 3-pentylthiophene (PPT), the polymerization was carried out for 5 s on bare ITO substrates and on ITO substrates covered with 40 layers, that is, around 30 nm, of the cross-linked cellulose derivative. The cyclic voltammograms which characterize the formed polymer are presented in Figure 3. The quantity of PPT formed being proportional to the charge density,¹⁷ it is possible, from the area of the reduction peak and the density of pure PPT, to give an approximate value of the mean thicknesses of PPT: around 22 nm in the case of the bare ITO substrate and around 50 nm when the cellulose matrix is present. In both samples, the PPT polymer has the oxidation and reduction peaks located at the same potential which suggests that the chemical structure is quite identical in both cases. UV-visible spectroscopy did confirm these results: there is twice as much PPT formed on the cellulose-covered substrate than on the bare one and the PPT exhibits the same spectrum in both cases, with a $\pi\pi^*$ transition located at 475 nm.¹⁸ Therefore, the cellulose network does not apparently disturb the conjugated polymer during its formation and does not influence its final structure. Moreover, the matrix not only favors high concentrations of 3-pentylthiophene but also, like a molecular net, avoids dissolution of the

initially oligomeric PPT formed at the electrode interface. In contrast, similar experiments carried out on unsubstituted thiophene shows that the polythiophene films of highest thickness are obtained on bare substrates. Obviously, there is a high chemical compatibility between the 3-pentylthiophene electroactive monomer and the *n*-butylcinnamoylcellulose matrix.

The effect of the number of cellulose layers was checked on samples consisting of 2, 10, 40, 100, and 800 layers. The results show that the presence of cellulose does lead to an increase of the amount of PPT per unit area only for a number of layers higher than 10. Moreover, when the thickness becomes larger than 100 layers, the increase of the amount of PPT formed in the cellulose matrix compared to the amount formed on a bare substrate reaches a plateau. To optimize the electropolymerization efficiency, we chose a particular case: 40 layers of cellulose, 5 s of 3-pentylthiophene polymerization. This gave a sample that was fully characterized from the structural point of view.

Structural Characterization of the Polymer Composite. The matrix thickness of samples made of 40 layers of the dry cellulose derivative is around 30 nm; after 5 s of 3-pentylthiophene electropolymerization, the amount of PPT formed is equivalent to a 50 nm thick film on the ITO electrode while it is around 70 nm thick on the gold surface. When ITO was used as an electrode, structures consisting of small domains (a few square microns) were obtained. However, under strictly identical experimental conditions, the samples bearing gold electrodes led to two different types of structures; some were made of small domains similar to those obtained with ITO electrodes and others were made of large domains (up to $35 \times 150 \mu\text{m}^2$). In both cases, the domains, observed by optical microscopy, were anisotropic and oriented along the LB transfer direction of the cellulose matrix.¹⁸ This is very surprising since the cellulose was not expected to play a role in inducing orientation at the macroscopic scale.

The effect of the number of cellulose layers on the size of PPT domains has been checked. It appeared that, under 10 layers, no domains are observed. The structure of the composite film between 10 and 100 layers is the same as the one of 40 layer samples. For a larger number of layers, 800 for instance, the structure is irregular with large domains covering smaller ones; even in this case, all domains are oriented along the transfer direction of the matrix.

However, at the molecular scale, there is an important difference between samples with small and large domains. Small domain samples exhibit a UV absorption dichroism that is not present in the case of large domain samples. This result was confirmed by optical microscopy experiments between crossed polarizers.¹⁸ In thin layers made of small domains, the PPT main chains are actually lying preferentially parallel to the cellulose backbones. In the case of thin layers made of large domains, only the surrounding area of the domains appeared to be oriented. To further investigate the structure of the composite, atomic force and scanning electron microscopies (AFM and SEM) were carried out on both types of structures.

1. Small-Domain Structure. Figure 4 presents a SEM image of a sample prepared on gold which exhibits

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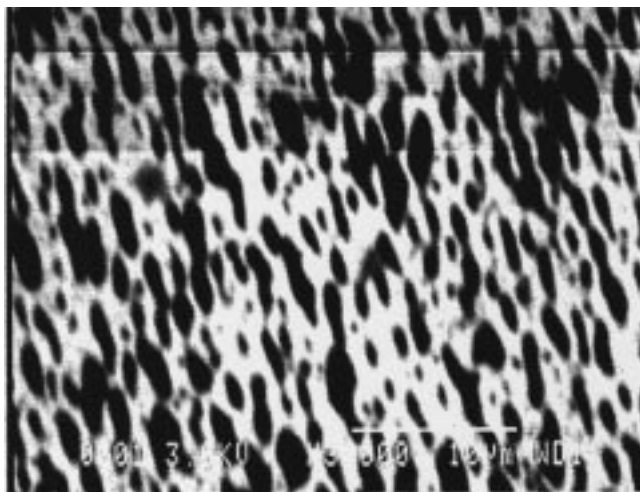


Figure 4. SEM image showing a small-domain structure formed after 5 s of polymerization on cellulose-covered gold substrates. The transfer direction of the cellulose matrix is vertical.

Table 1. Atomic Percentage Deduced from the X-ray Analysis Carried Out on a Small-Domain Structure Sample Formed after 10 s of Polymerization on 40 Layers of the Cellulose Derivative on a Gold Substrate

elements	at. %: white area	at. %: black area
C	38.2	79.5
O	27.0	5.8
Si	10.1	1.2
S		7.8
Au	24.7	5.7

small domains. It shows that the small domains are oriented along the transfer direction of the cellulose LB film. To determine which areas of the film are more concentrated in PPT, energy-dispersive X-ray experiments (EDX) were carried out on the black and the white domains. The results are presented in Table 1. The elements silicon and gold belong to the substrate; the higher percentage of these two elements observed for the white areas clearly indicates that those are less dense and/or less thick than the black ones. The two elements that allow us to quantify PPT are carbon (k_{α} ray at 0.25 keV) and sulfur (k_{α} ray at 2.3 keV). As the sulfur signal is very close to the one of gold (2.1 keV), it is difficult to deconvolute the respective contributions of gold and sulfur. However, the sulfur atomic concentration appears to be lower than 1% (detection limit of the analyzer) for the white areas and carbon is 2 times less concentrated in the white areas than in the black ones. These two results suggest that PPT is mainly present in the black domains. Analysis of several black areas shows that the larger the domains are, the higher the PPT concentration; in contrast, the composition of the white areas is rather independent of size.

The AFM experiments carried out on the small-domain samples did confirm what has been derived from electron microscopy. An AFM picture and a topographic profile are presented in Figure 5. The films appear to be composed of thick domains oriented in the transfer direction. The height of the domains varies from 10 to 50 nm. In a very few cases a height over 100 nm was observed. Since the average thickness of the formed PPT is 66 nm in this particular case and since EDX experiments did show that the PPT was mainly present inside the domains, these height values are too small to

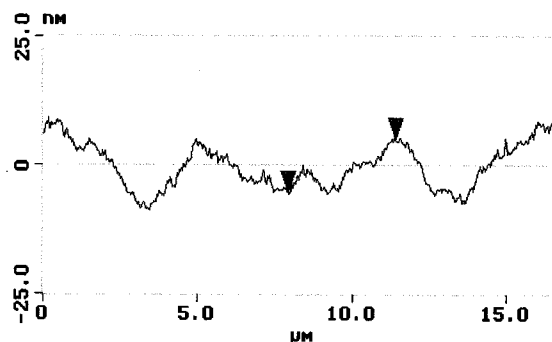
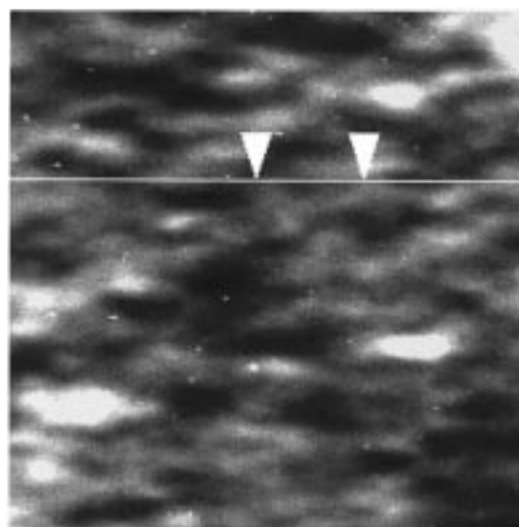


Figure 5. AFM image and topographic profile showing a small-domain structure obtained after 5 s of polymerization on cellulose-covered gold substrates. The transfer direction of the cellulose matrix is horizontal. The white areas correspond to the highest domains; they are the same as the black areas of the SEM in Figure 4.

consider that PPT and cellulose are completely segregated. Moreover, from the results of the microscopic study of the film between crossed polarizers, we already know that the PPT chains are aligned with regard to the cellulose backbones; a large part of PPT is, therefore, mixed close to molecular dispersion with cellulose. If all the PPT formed was mixed homogeneously with the matrix material, this would result in a small increase of the film thickness corresponding to the thickness difference between the dry cellulose, 32 nm, and the swollen cellulose, 48 nm. For the sample presented here, we probably have, at the same time, some segregated PPT and a large part of it homogeneously mixed with cellulose.

To locate the PPT in the volume of the composite film, an XPS analysis was carried out. The sulfur and carbon signals was collected for different angles between the sample and the analyzer (resolved angle XPS). The angles were of 90°, 40°, 30°, and 15°. For 90°, the angle for which a deeper thickness of the sample is characterized, the sulfur signal was present. On the contrary, for smaller angles, lower than 40°, which corresponds to the characterization of a thinner thickness, the sulfur signal was absent and the carbon signal of cellulose was observed. These results clearly indicate that, at least, the PPT is not more present at the film surface than close to the substrate.

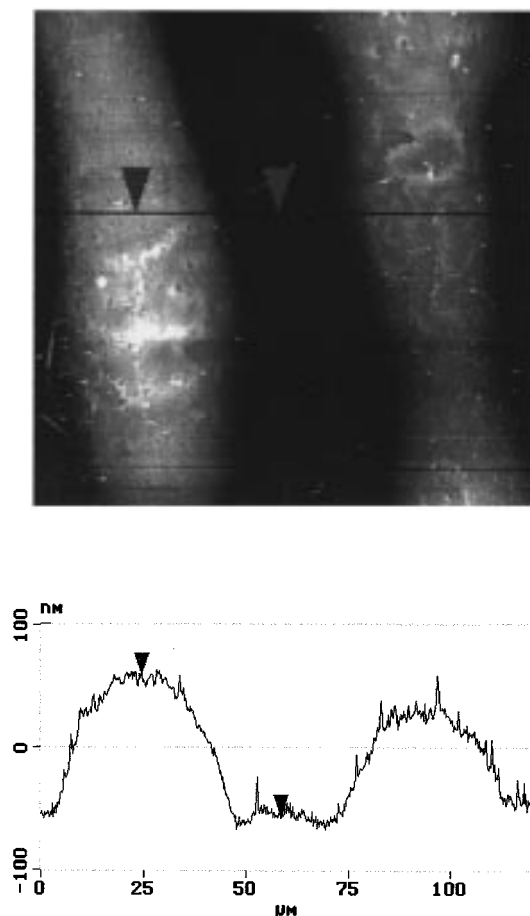


Figure 6. AFM image and topographic profile showing a large-domain structure formed after 5 s of polymerization on cellulose-covered gold substrates. The transfer direction of the cellulose is vertical.

2. Large-Domain Structure. In contrast to what was observed for samples with small domains, the AFM profile of large domains, shown in Figure 6, indicates that they are very high protrusions with steep sides; indeed, the height of the domains is more than 100 nm. Since the average PPT thickness per unit area in this particular case is 79 nm, such results strongly suggest a phase segregation between the cellulose and the PPT polymer.

When observed with SEM (see Figure 7), the large domains appear to be made of smaller units which do not present any orientation. These smaller structures may be PPT polymer chains protruding through the cellulose matrix; this is not unexpected since the large amount of PPT synthesized in the domains must induce large strain on the matrix.

The EDX experiments carried out on the different parts of the film gave similar results to the ones obtained for small domains: PPT was not present between the large domains.

3. Models. The various results discussed previously allow us to build a model of the composite structure in the plane of the film surface (Figure 8) and in the plane perpendicular to it (Figure 9).

If we consider the structure in the plane of the surface, for both types of films, PPT is concentrated in domains oriented along the LB transfer direction of the cellulose matrix. This is what is shown in Figure 8, parts

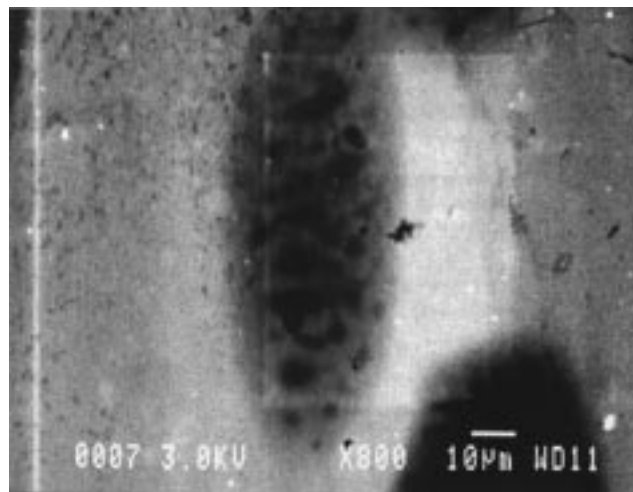


Figure 7. SEM image showing a large-domain structure obtained after 5 s of polymerization on cellulose-covered gold substrates. The transfer direction of the cellulose is vertical. The black areas correspond to the white ones visualized by the AFM microscopy.

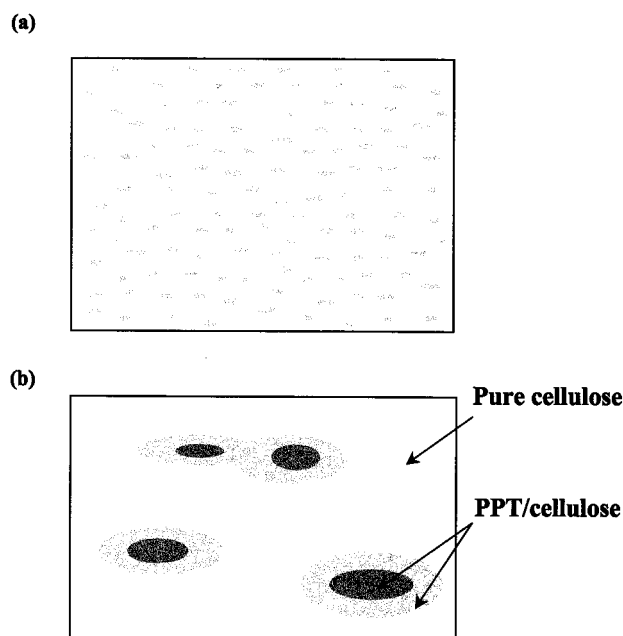


Figure 8. Proposed in-plane models for (a) the small-domain structure and (b) the large-domain structure. The transfer direction of the cellulose matrix is horizontal.

a and b. Inside the small domains and in the surrounding area of the large ones, cellulose behaves as a template and the PPT chains are dispersed and aligned at the molecular level; however, inside the large domains, there is a segregation between the two polymers constituting the composite and no molecular orientation is observed for PPT.

If we analyze the structure perpendicular to the substrate surface, small domains are rather flat and mostly made of intimately mixed PPT and cellulose (see Figure 9a). In contrast, large domains appear as high hills; moreover, PPT is present close to the electrode and mainly separated from the cellulose polymer. The center of those large domains appears to be made of smaller isotropic structures that could be PPT polymer chains protruding through holes of the cellulose matrix (see Figure 9b).

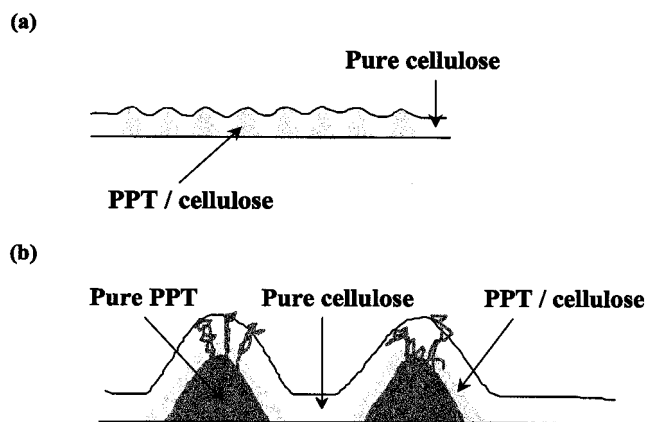


Figure 9. Proposed out-of-plane models for (a) the small-domain structure and (b) the large-domain structure.

Conclusion

These results validate the possibility to fabricate a material which has a composite structure at the sub-micron level and which is made of a conducting polymer and a polymer with good mechanical properties. The role of the cellulose matrix to orient PPT at the molecular level has been observed. This confirms the success of the template approach for the synthesis of oriented conjugated polymers.¹⁹ However, two problems remain. First, the observed orientation of the PPT domains at

the micron level is an unexpected characteristic of the composite which could not be explained so far. Second, although it is clearly related to the gold electrode surface, the formation of small or large domains could not be controlled experimentally.

The cellulose matrix has a positive role toward the other part of the composite. It favors high concentration of 3-pentylthiophene at the electrode interface and, at the same time, behaves as a molecular net and therefore stabilizes the formed PPT in organic solvents.

Conductivity measurements are under investigation. It already appears that the cellulose does not worsen the PPT conductivity and allows enhancement of the anisotropy between in-plane ($\sigma = 10^{-8} \text{ S}\cdot\text{cm}^{-1}$) and out-of-plane ($\sigma = 10^{-9} \text{ S}\cdot\text{cm}^{-1}$) conductivities.

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