

# Orientation of Polydiacetylene and Poly(*p*-phenylene ethynylene) Films by Epitaxy and Rubbing

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**ABSTRACT:** We will focus in this paper on the orientation of thin films of conjugated systems induced either by epitaxy or by rubbing on a polymeric thin layer previously oriented by friction transfer onto glass. In friction transfer, oriented poly(tetrafluoroethylene) (PTFE) onto glass substrates are first prepared, and a layer of the conjugated system is then deposited by vacuum evaporation or by spin-coating. The rubbing technique also enables a mechanical orientation of the thin film of the conjugated system, itself deposited onto glass. We applied both techniques for the preparation of oriented thin films of polydiacetylenes and phenyl-ethynylene oligomers. For an asymmetrically substituted PDA (poly[9-(9-carbazolyl)-5,7-nonadiyne-1-ol ethylurethane] (pCNEU), a very high degree of orientation on aligned PTFE was demonstrated using several techniques, resulting in a high degree of orientation than previous films on potassium acid phthalate (KAP) crystals. For the first time a rather good orientation of soluble poly[1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-dexadiyne] (pDCHD-HS) films was obtained using a rubbing technique. Both epitaxy on PTFE and rubbing were also used for the orientation of phenyl-ethynylene derivative samples. For a sequenced rigid poly(*p*-phenylene ethynylene) ester (sPE5C8) fairly good orientations have been obtained.

## Introduction

In recent years there has been a renewed interest in the study of conjugated polymers due to their possible application in many optical devices. Transistors, waveguides, and light-emitting diodes (LEDs) have been obtained from conjugated polymers, and their development has increased the search for new materials with outstanding optical properties. Among these systems, polydiacetylenes (PDAs) prove to be interesting materials given that the alternation of triple, single, and double carbon-carbon bonds of their backbone ensures a high electronic delocalization. Moreover, they can be prepared from monomers through a solid-state topotactic polymerization<sup>1</sup> induced by thermal or photochemical initiation.<sup>2</sup> Changing of the lateral substituents allows for polymers to be obtained with defined chemical and physicochemical properties. Two classes of PDAs are particularly attractive. The first groups together the derivatives of diacetylene diol urethanes,<sup>3,4</sup> where the urethane group, with the formation of intramolecular hydrogen bonds and a high reactivity of polymerization, ensures the possibility of different conformations as well as a good anchoring to glass substrates. The poly[5,7-dodecadiyne-1,12-diol-bis(*n*-butoxycarbonylmethylurethane)] (p4BCMU) was studied in detail due to its good solubility and interesting thermochromic properties.<sup>5</sup> The second class groups together the carbazolyl-diacetylene derivatives, where at least one of the lateral substituents is a carbazolyl residue, directly or indirectly attached to the backbone.<sup>6,7</sup> The presence of this aromatic group ensures a high polarizability as well as high

thermal and mechanical stability; thus, poly[di(*N*-carbazolyl)-2,4-hexadiyne] (pDCH) exhibits remarkable nonlinear optical properties,<sup>8–10</sup> while, being insoluble, the exploitation of its specific properties still remains at a potential level. To prepare polymers with the same electronic properties as pDCH, long aliphatic chains were placed on the 3,6 position of the carbazolyl rings. These new polymers are soluble in common organic solvents, and they show promising properties both in the solid and in solution states.<sup>11,12</sup> The most attractive of these PDAs, the poly[(3,6-dihexadecyl)-*N*-carbazolyl-2,4-hexadiyne] (pDCHD-HS), proved of great value for the third-order nonresonant optical susceptibility.<sup>13</sup>

Besides PDAs, other conjugated systems are used in optoelectronics.<sup>14</sup> For example, rigid arylene-ethynylene compounds can be applied in this field since the conjugation between the arylene and ethynylene moieties ensures a delocalization of the electrons through the molecule. Several authors have observed that the combination of two or three aryl groups differently alternated to the ethynylene moiety along the same chain results in highly fluorescent polymers, thus yielding materials that can be applied in fluorescent chemical sensors,<sup>15</sup> photoconductors,<sup>16</sup> organic light-emitting diodes (OLEDs),<sup>17–19</sup> etc.

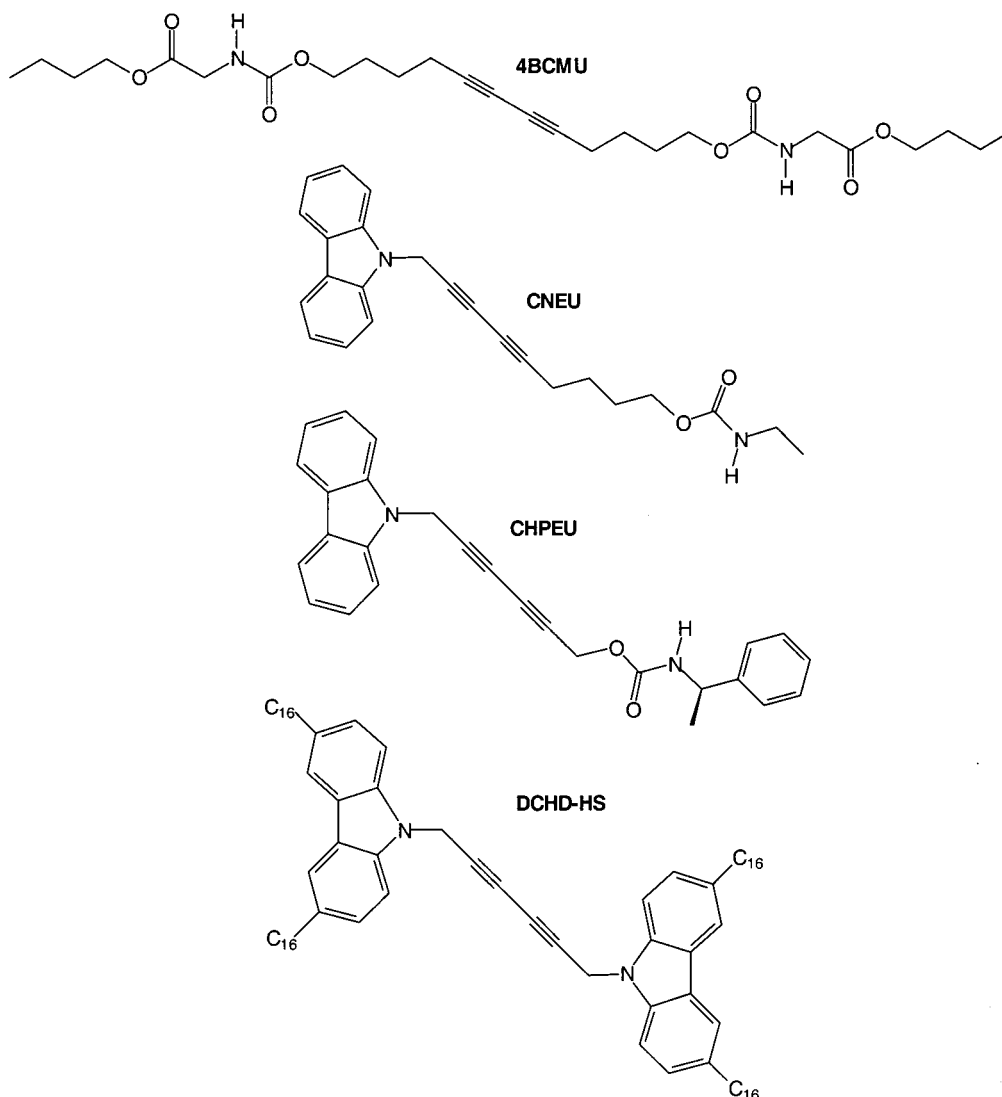
In the expanding field of the application of conjugated systems to optoelectronic and photonic devices, an important point to be developed is the choice of a preparation technique leading to reproducible samples characterized by a good surface order and controlled molecular organization. Moreover, many optical applications need well-oriented films, which can be prepared by techniques such as rubbing,<sup>20</sup> stretching,<sup>21</sup> or epitaxy.<sup>22</sup> This last method proves to be most promising for organic optical devices in terms of thickness control and facility. The orientation degree obtained by epitaxy

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**Figure 1.** List of the symmetrical and unsymmetrical diacetylenes used in this work: 5,7-dodecadiyn-1,12-diol-bis(*n*-butoxycarbonylmethylurethane), 4BCMU; 9-(*N*-carbazolyl)-5,7-nonadiyne-1-ol-1, ethylurethane, CNEU; 6-(*N*-carbazolyl)-2,4-hexadiyn-1-ol-1 phenyl-ethylurethane, CHPEU; 1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne, DCHD-HS.

depends, however, on an appropriate choice of both the substrate and evaporation conditions.<sup>23</sup> On the whole, some crystallographic surfaces such as metal, ionic, or covalent crystals have been used as substrates,<sup>22,23</sup> but their high costs make them unattractive for applications. On glasses, the orientation is possible by epitaxial growth on an intermediate layer, previously oriented by either friction transfer<sup>24</sup> or rubbing.<sup>25</sup> For friction transfer, good orientations have already been obtained for thin films of some conjugated systems such as poly(diacetylenes) grown on poly(tetrafluoroethylene) (PTFE).<sup>26</sup> For rubbing, only a few experimental details and data are reported in the literature available.<sup>20</sup>

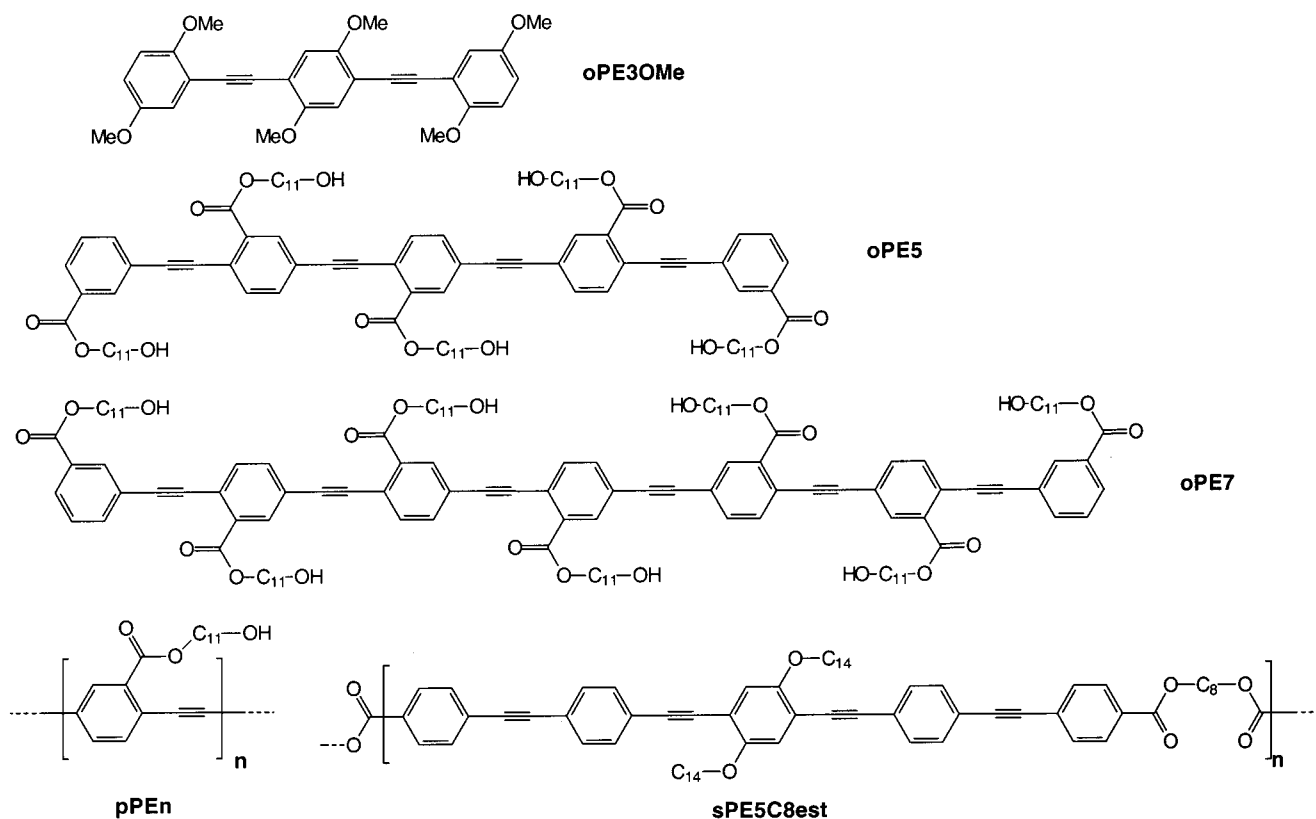
The challenge of this work was to establish a procedure and investigate the experimental parameters involved in friction transfer and rubbing. We thus focused our attention on the preparation and characterization of oriented thin films of two types of conjugated polymers, i.e., PDAs and phenylene ethynylene oligomers or polymers. We are reporting here on the structure, morphology, and orientation relationships of the oriented films, analyzed by UV-vis and micro-Raman spectroscopies and by electron diffraction and electron microscopy.

## Experimental Section

**Materials.** Figures 1 and 2 show respectively the chemical formula of the diacetylenes and phenyl-ethynylene derivatives investigated in this work.

The 5,7-dodecadiyn-1,12-diol-bis(*n*-butoxycarbonylmethylurethane) (4BCMU) and unsymmetrical substituted carbazolyldiacetylenes, 9-(9-carbazolyl)-5,7-nonadiyn-1-ol-ethylurethane (CNEU), and 6-(9-carbazolyl)-2,4-hexadiyn-1-ol-[1-phenylethylurethane] (CHPEU) were synthesized using procedures already published.<sup>5,27,28</sup> The syntheses of both the 1,6-bis(3,6-dihexadecyl-*N*-carbazolyl)-2,4-dexadiyne (DCHD-HS) and phenyle-ethynylene oligomers (oPEn) and polymers (pPEn) were published elsewhere.<sup>12,29</sup> The sequenced phenyl-ethynyl ester polymer (sPE5C8) was polymerized by polycondensation using the modified chemical route with respect to that of oligomers.<sup>29,30</sup>

**a. Route to (sPE5C8) Ester: 4,4'-(1,4-Diethynyl-2,5-bis(tetradecanoxy)benzene Diethyne.** The general diprotective method described in the literature was followed without modification to synthesize 4,4'-(1,4-diethynyl-2,5-bis(tetradecanoxy)benzene diethyne. The crude product was recrystallized in methanol and dried in a vacuum. A yellow solid (1.00 g, mp 90 °C, yield 71%) was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.45 (s, 8H, -PhH end); 7.05 (s, 2H, PhH center), 4.07 (t, 4H, O-CH<sub>2</sub>), 3.18 (s, 2H, -C≡CH), 1.88 (q, 4H, -CH<sub>2</sub> β ether), 1.30 (s, 44H, CH<sub>2</sub>), 0.89, (t, 6H, -CH<sub>3</sub>). Anal. Calcd % for C<sub>54</sub>H<sub>70</sub>O<sub>2</sub>: C,



**Figure 2.** Oligomers and polymers based on phenylene ethynylene units used in the present work: the trimer (2,5-methoxyphenylethyne), oPE3OMe; (11-undecanol) benzoate containing pentamer, oPE5; (11-undecanol) benzoate containing heptamer, oPE7; (11-undecanol) benzoate containing polymer, pPE<sub>n</sub>; the sequenced poly 5(*p*-phenylene ethynylene) ester, sPE5C8 ester.

86.35; H, 9.39; Si, 6.27; O, 4.26. Found: C, 85.95; H, 9.41.

**b. Octyl-4,4'-dibromodibenzoate-1,6-diyl.** To a solution of 4-bromobenzoic acid (7 g, 35 mmol, 2 equiv), 1,8-octanediol (2.55 g, 17.5 mmol, 1 equiv) and DMAP (175 mg) in 100 mL of CH<sub>2</sub>Cl<sub>2</sub>, cooled at 0 °C, a DCCI solution (8.20 g, 40 mmol, 2.3 equiv in 80 mL of CH<sub>2</sub>Cl<sub>2</sub>) was slowly added and stirred for 3 h at room temperature. Urea was filtered off, and the filtrate was washed with a 0.5 M HCl solution followed by a saturated solution of NaHCO<sub>3</sub>. The solution then dried on Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed, and the crude product was finally purified by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>). White crystals (6.54 g, yield 73%, mp 60 °C) were obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.95 (m, 4H, PhH), 7.60 (m, 4H, PhH), 4.32 (t, 4H, COOCH<sub>2</sub>), 1.80 (m, 4H, CH<sub>2</sub> β ester), 1.40 (8H, s, -CH<sub>2</sub>-). Anal. Calcd % for C<sub>22</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>4</sub>: C, 51.59; H, 4.72; Br, 31.20; O, 12.49. Found: C, 51.42; H, 4.68.

**c. Polymer (sPY5C8) Ester** (500 mg, 0.9 mmol, 1 equiv), PdCl<sub>2</sub> (3 mg, 0.02 equiv), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (3.6 mg, 0.02 equiv), TPP (23 mg, 0.10 equiv) in 25 mL of triethylamine, 25 mL of THF (**2**) (670 mg, 0.09 mmol, 1 equiv). Crude polymer, yellow solid, 1.10 g. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.05 (d, 2H, PhH<sup>3'</sup>) and 7.56 (m, 4H, AA'BB'), 7.92 (d, 4H, PhH 3), 7.50 (d, 8H, Ph 2+2'), 7.00 (s, 2H, PhH), 4.35 (m, 4H, COOCH<sub>2</sub>), 4.05 (t, 4H, OCH<sub>2</sub>), 1.84 (m, 6H, -CH<sub>2</sub>- β ester and ether), 1.30 (m, 52H, -CH<sub>2</sub>-), 0.89 (t, 6H, -CH<sub>3</sub>). Anal. Calcd % for C<sub>76</sub>H<sub>92</sub>O<sub>6</sub>: C, 79.37; H, 8.88; O, 11.75. Found: C, 78.57; H, 8.06; O, 8.16; Br, 4.44.

**Films Preparation and Characterization. a. Glass Treatment.** Microscope glass slides<sup>31</sup> were used as a mechanical support. Prior to the film deposition, two types of treatment of the glass surface were carried out. For PTFE deposition, the glass slides (Corning) were cleaned in ethanolic KOH at room temperature (5 min), washed, and then dried in a dry nitrogen flux. For evaporation or spin-coating deposition of diacetylenes and phenylethyne, the glass slides were cleaned with CH<sub>2</sub>Cl<sub>2</sub> and acetone and then treated in a basic surface active solution at 60 °C for 4 h (4% v/v DECON 90). After washing with Milli-Q water (~10 times), the glasses were dried under Ar flux and heated for 15 h in an oven at 160 °C.

**b. Films Epitaxially Oriented on PTFE.** On the cleaned glass slides described above, an oriented PTFE film was deposited following the Wittmann and Smith method.<sup>32</sup> A PTFE block was set on the glass kept at 290 °C, and after 15 min, the PTFE block was slid at 0.3 mm s<sup>-1</sup> under a pressure of 2.1 MPa. For TEM, the thin films were prepared by sliding the PTFE block at 16 mm s<sup>-1</sup> on the glass surface kept at 300 °C and under a pressure of 50 MPa. On glass slides coated with oriented PTFE the deposition of the film was adapted for each case as described below:

**PDA Films.** Diacetylene monomer films (CHPEU, CNEU, 4BCMU) with a thickness ranging from 10 to 100 nm were obtained by vacuum vapor deposition (pressure about 3 × 10<sup>-6</sup> Pa) of the monomer. The CHPEU films were annealed at 120 °C and then polymerized under UV irradiation (254 nm). Polymerization of CNEU film was carried out either *with or without annealing* at 100 °C of the monomer film, prior to UV irradiation. Thermal treatments led to different polymeric forms of the pCNEU, a blue or violet form; when no annealing was carried out, a red form was obtained, while a violet form was observed upon UV polymerization of the annealed monomer film. For 4BCMU films two procedures were used, the evaporation and spin-coating of the monomer solution, followed by the polymerization of 4BCMU films using UV irradiation.

**oPE Films.** Oriented films of oPE3OMe with the same range of thickness as for PDA films were obtained using the experimental conditions described above, vaporization under vacuum on oriented PTFE.

**c. Films Oriented by Rubbing.** Orientation by rubbing was performed on films deposited directly on glass substrates. Depending on the nature of the conjugated system, different film deposition techniques were used: vacuum evaporation or spin-coating from solutions in the case of diacetylene monomers, Langmuir-Blodgett or spin-coating methods for oPE oligomers and pPE. Rubbing was performed directly on the conjugated system film by using a homemade installation consisting of a cylinder rotating at a speed of 400 rpm on the substrate with the organic layer, while the latter is slid at a



rate of 10 mm/s. The cylinder was lined with a polyacrylonitrile fibrous cloth (fibers diameter = 26  $\mu\text{m}$ ) with a disordered texture, chosen from a series of cloths with fibers of different textures and natures as it provided the best orientation degree of the films. To ensure a close contact between the cloth and the film, a force of 9.6 N was applied to the cylinder. The corresponding pressure at the interface is estimated to have been around  $6 \times 10^4$  Pa.

**PDA Films.** To prepare p4BCMU films, the monomer was deposited on a glass slide by vacuum evaporation or by spin-coating from chloroform solutions. The pCNEU and pCHPEU films were then prepared only by vacuum evaporation of the monomers on glass. As a result, highly homogeneous polymer films were obtained by UV irradiation. For pDCHD-HS only spin-coating from toluene solutions could be used to prepare thin films, because DCHD-HS monomer cannot be vacuum-evaporated, and its films deposited by spin-coating from solutions are highly heterogeneous.

**oPE and pPE Films.** oPE5, oPE7, and pPE<sub>n</sub> films were prepared either by Langmuir-Blodgett technique or by spin-coating from methylene chloride solutions. sPE5C8 ester films were prepared by spin-coating from xylene solutions. For all these samples, orientation by rubbing was performed as described for PDA films.

The effect of annealing on the orientation degree of the films was also studied. For vacuum-deposited monomers and oPE films, an annealing temperature below their melting points was used. The PDA films oriented by rubbing were annealed at the melting point of the corresponding monomers while in the case of oPE and pPE, annealing was carried out at a temperature corresponding to their liquid crystal (LC) transitions.

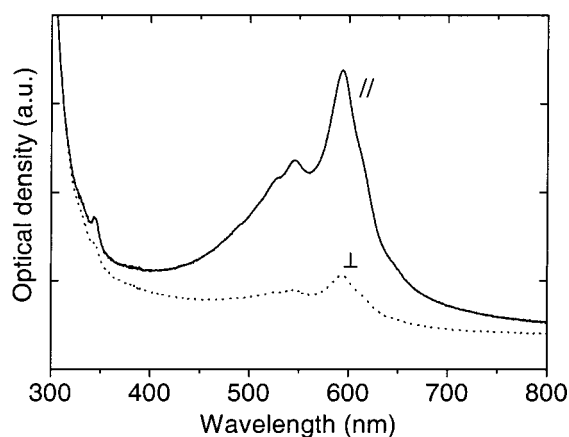
**d. Films Characterization.** UV-vis spectra were recorded on a Hitachi U-3000 spectrophotometer equipped with polarizers. The chain orientation was evaluated by the order parameter  $OP = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + A_{\perp})$ , where  $A_{\parallel}$  and  $A_{\perp}$  were the absorbance in parallel and normal polarization of light relative to the alignment direction, that is, the sliding direction of PTFE rod or the rubbing direction. Micro-Raman measurements were performed with a Dilor Labram spectrometer equipped with a linearly polarized He-Ne laser ( $\lambda_{\text{ex}} = 632.8$  nm) coupled to an Olympus BX40 microscope with 10 $\times$ , 50 $\times$ , and 100 $\times$  objectives. Scanning electron microscopy (SEM) was carried out using a JEOL JSM-840 microscope.

The morphology and quality of the film orientation were viewed at with a Philips CM12 STEM microscope operated under 120 kV for both bright field imaging and electron diffraction. The polymer film, Pt/C shadowed when needed, was backed by a carbon film. The sample was removed from the glass support via the well-known poly(acrylic acid) (APA) method. The whole system (polymer, Pt/C, C, dried APA) was floated on distilled water which dissolves APA. The remaining sample [polymer, (Pt/C), C] was then transferred on the TEM grid.

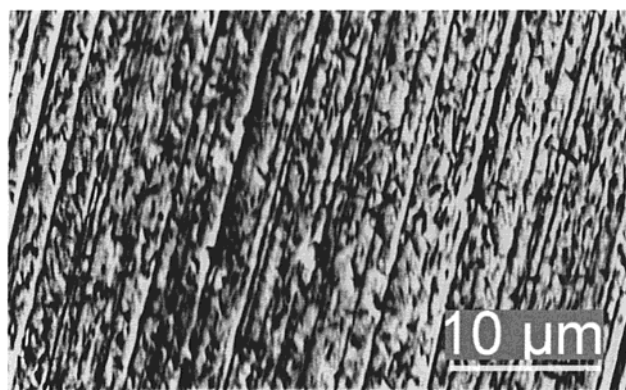
## Results and Discussion

**Epitaxial Growth of Diacetylenes on PTFE.** As experimental references prior to the characterization of our new samples, we first checked the orientation of p4BCMU films prepared by vacuum vapor deposition of the monomer on PTFE followed by UV polymerization. Our results coincided with the literature data in terms of orientation, with an increase of the dichroism related to the annealing of the deposited monomer film close to the melting point of 4BCMU.<sup>26</sup>

The polymerization of CHPEU thin films can be achieved only by annealing at 120  $^{\circ}\text{C}$  before UV irradiation as previously reported for films of the same molecule grown on KAP.<sup>16</sup> Figure 3 shows the UV-vis spectra of a pCHPEU film on PTFE taken with light polarized parallel and perpendicular to the PTFE friction direction. The two spectra exhibit a main peak at

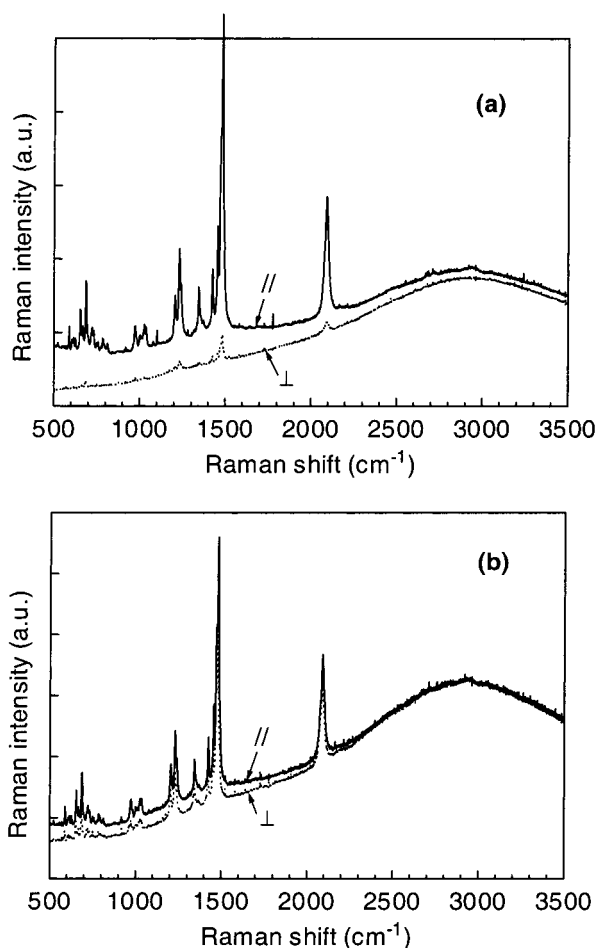


**Figure 3.** Polarized UV-vis spectrum of a pCHPEU film on PTFE: full line, parallel polarization of light relative to the PTFE rows; dotted line, normal polarization of light relative to the PTFE rows.



**Figure 4.** Morphology of pCHPEU film on PTFE. SEM micrograph.

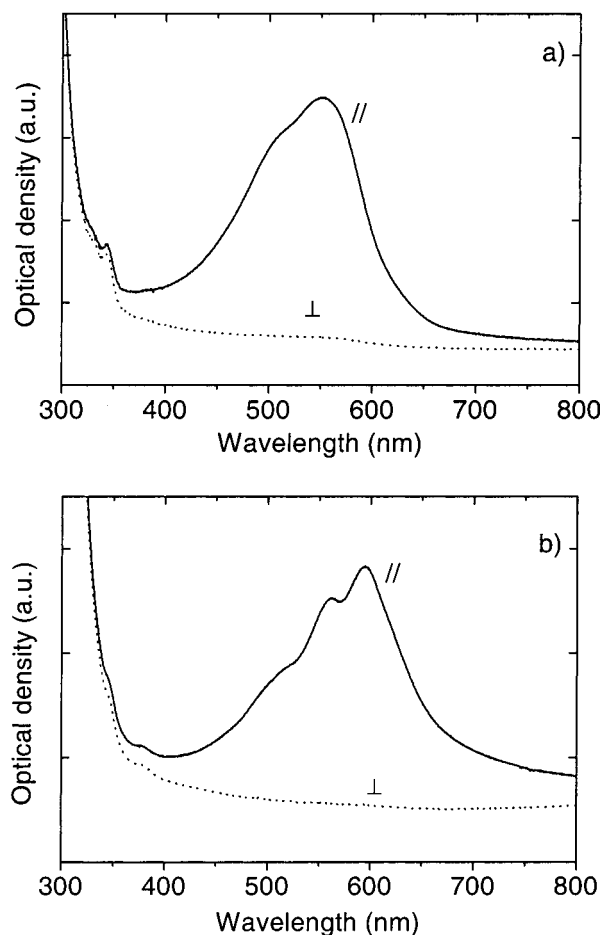
595 nm (2.08 eV, 16821  $\text{cm}^{-1}$ ), a lower absorption at 545 nm (2.27 eV, 18332  $\text{cm}^{-1}$ ), and a shoulder at about 530 nm. A shoulder is also observed around 610 nm. According to previous assignments proposed for other polydiacetylenes,<sup>33</sup> we can assign the energy band at 595 nm to the singlet excitonic transition and the other two, centered at lower wavelengths, to the vibronic replica of the double and triple carbon-carbon bonds, respectively. The film absorption at the exciton is more intense in light polarized parallel to the PTFE friction direction than for the perpendicular polarization of light. The OP value around 0.6 at 595 nm indicates that only a partial orientation has been obtained in this sample. This result is identical to the electron scanning microscopy images, which show that the CHPEU deposition on PTFE did not occur in regular arrangement (Figure 4). Micrograph pictures (not shown here) obtained by micro-Raman confirm this. Different zones are evident: dark areas where well-oriented crystals are observed and brighter ones where almost no orientation can be detected. The Raman scattering spectra relative to the dark areas are reported for the two different polarizations of the exciting radiation in Figure 5a. It is interesting to notice that the vibrational stretching modes corresponding to both the triple (2092  $\text{cm}^{-1}$ ) and double bonds (1481  $\text{cm}^{-1}$ ) exhibit a rather high dichroic ratio. However, the same modes observed in the Raman spectra recorded in the brighter regions (Figure 5b) exhibit a much lower dichroism. The importance of microspectroscopy techniques which allow the orientation at microscopic scale to be detected is well demon-



**Figure 5.** Polarized micro-Raman spectra of pCHPEU on PTFE: (a) dark domains of polymer and (b) bright domains of polymer. The polarization axes are parallel and perpendicular to the PTFE sliding direction.

strated by the results obtained for the pCHPEU films. These results can in fact explain the modest OP value measured by the standard spectroscopic methods that provide only average characteristics.

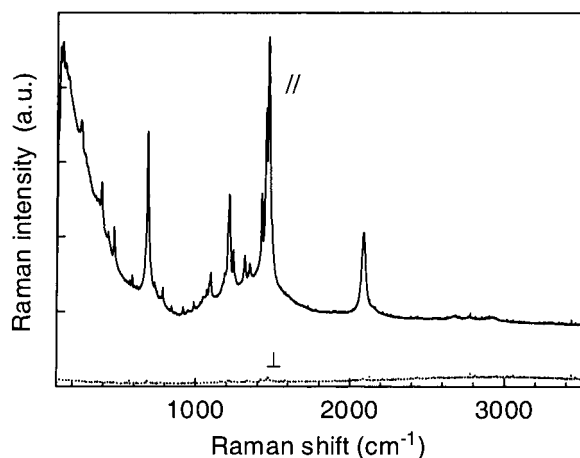
Polymerized CNEU samples on PTFE can be obtained either with or without annealing of the monomer film at 100 °C, before UV irradiation. Thermal treatments lead to different polymeric forms characterized by different UV-vis spectra. When no annealing is carried out, a red form is obtained, while a violet form is observed after annealing upon UV polymerization. The same result is observed when the monomer is evaporated on cleaned glass, when both the red and violet forms are observed. In Figure 6, we see the absorption spectra of both forms of pCNEU samples on PTFE in light polarized parallel and perpendicular to the sliding direction. In perpendicular polarization almost no absorption occurs in the visible range for red or violet samples. In parallel polarization, the spectrum of the *red form* is characterized by a single broad band at 554 nm (2.23 eV, 18505 cm<sup>-1</sup>) with a poorly defined feature at higher energy. The spectrum of the *violet form*, however, is more resolved and shows two peaks centered at 595 nm (2.08 eV, 16807 cm<sup>-1</sup>) and 562 nm (2.20 eV, 17780 cm<sup>-1</sup>) as well as a vibronic feature at 513 nm (2.42 eV, 19490 cm<sup>-1</sup>). Presumably, the two clearer peaks are a result of having mixed red and blue forms of the polymer. A very high dichroism is observed for both samples: an OP value equal to 0.90 at 554 nm for



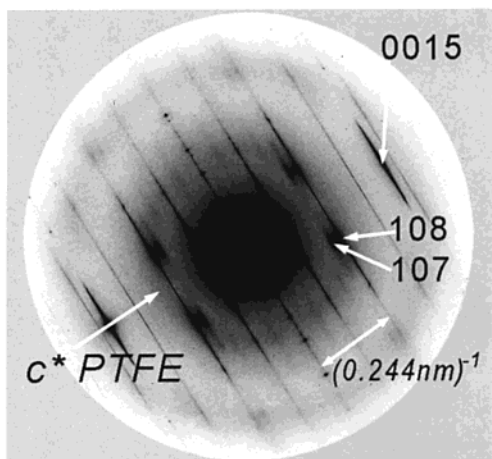
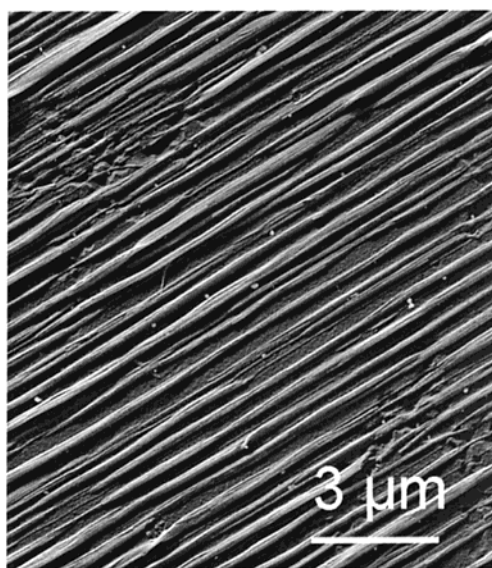
**Figure 6.** Polarized UV-vis spectra of pCNEU samples on PTFE: (a) prepared by UV polymerization of as-deposited monomer film (red form); (b) prepared by UV polymerization of an annealed monomer film (violet form). Full lines: parallel polarization of light relative to the PTFE rows. Dotted lines: normal polarization of light relative to the PTFE rows.

the red sample (Figure 6a) and to 0.995 at 595 nm for the violet form (Figure 6b). For this polymer OP values are generally obtained in the range 0.85–0.995 for the two types of treatments.

Since the annealing procedure yields the most oriented samples, the morphological details were studied by micro-Raman spectroscopy and TEM techniques on the violet pCNEU samples. The optical microscopy image shows a homogeneous distribution of the material and a very good alignment of microcrystals. The polarized micro-Raman spectra of the microdomains exhibit a very high and reproducible dichroism as shown in Figure 7. The C=C and C≡C stretching vibrations detected at 1469 and 2084 cm<sup>-1</sup>, respectively, are typical of the blue form of the polymer due to the Raman resonance conditions of this form at the excitation wavelength. These values, when compared with those observed for a blue unoriented sample at 1465 and at 2076 cm<sup>-1</sup>, confirm the presence of a high-wavelength component in the absorption spectra. Similar effects in the excitonic energy transition were observed for another PDA<sup>34</sup> and were attributed to different intermolecular interactions for different supramolecular structures of the same material. The Raman spectra obtained with the light polarized perpendicular to chain alignment show no signal, except for the weak luminescence background due to the substrate. The anisotropy of the micro-Raman spectra confirms the very high degree of



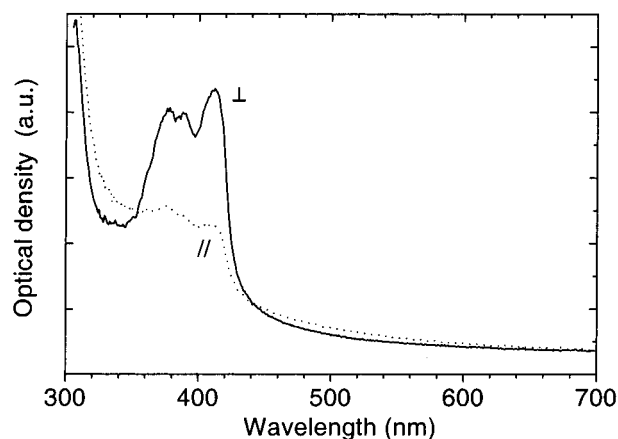
**Figure 7.** Polarized micro-Raman spectra of pCNEU on PTFE. The polarization axes are parallel and perpendicular to the PTFE sliding direction.



**Figure 8.** (a, top) Bright field TEM micrograph of the pCNEU on PTFE and (b, bottom) corresponding electron diffraction pattern of the composite pCNEU/PTFE.

orientation of the conjugated polymeric chains.

The TEM bright field image reported in Figure 8a shows well-organized parallel rows of the PDA along the sliding direction of PTFE and, between the rows, a background of tiny crystals. From this image it is impossible to distinguish the individual crystals of



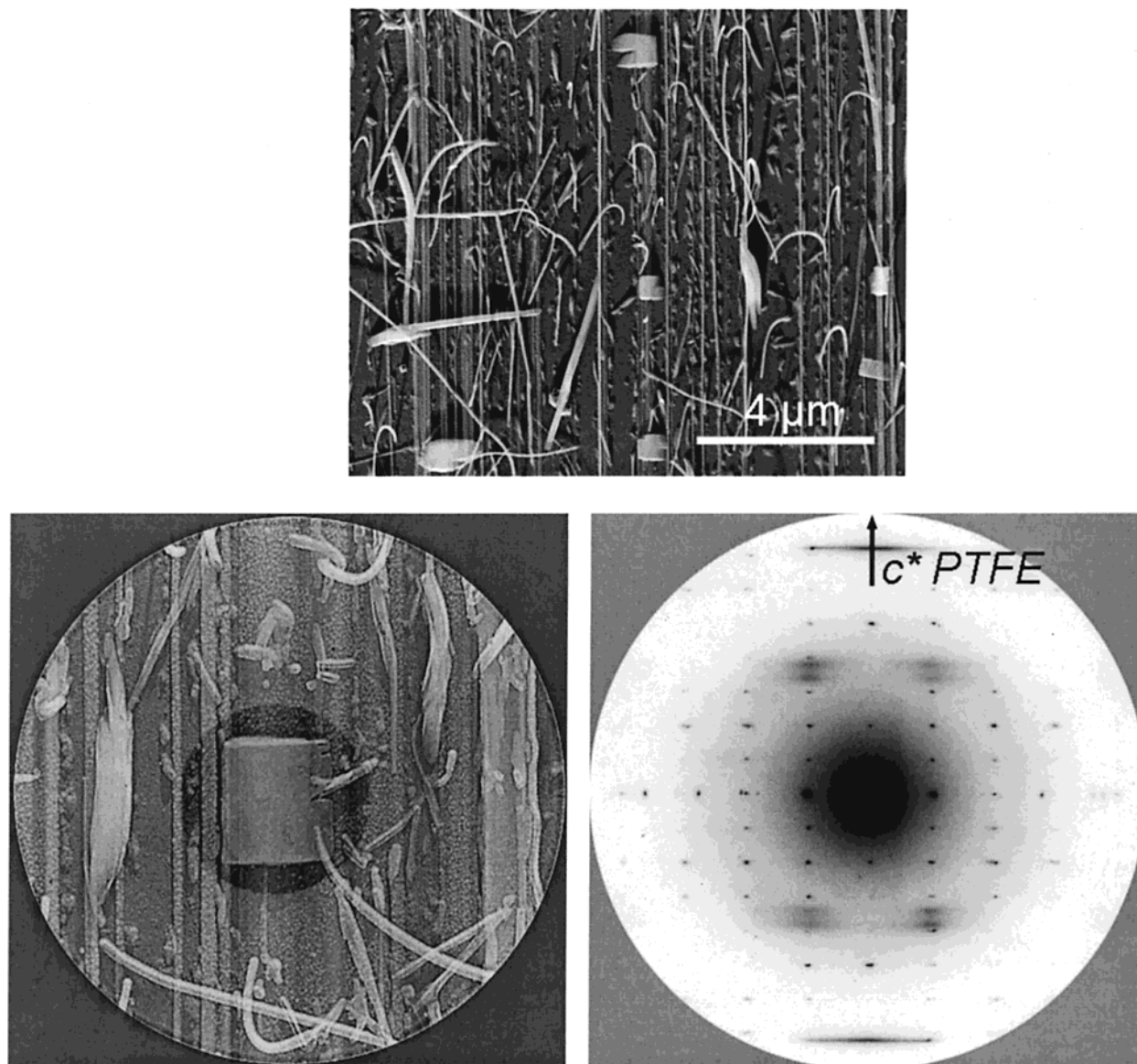
**Figure 9.** Polarized UV-vis spectra of oPE3OMe sample on PTFE: full line, parallel polarization of light relative to the PTFE rows; dotted line, normal polarization of light relative to the PTFE rows.

pCNEU from PTFE, indicating a high degree of nucleation of CNEU on PTFE. Some crystals are protruding from the plane in two zones where PTFE layers present some defects, and small needles can be distinguished here. The main orientation seems nevertheless to be preserved in these needles. Figure 8b shows the composite diffraction of pCNEU on PTFE, which proves the relative orientation of the two polymers. The diffraction pattern of the PTFE is readily observed with its characteristic 0015 (0.13 nm), 108, and 107 spots. The *b* chain axis of the pCNEU is parallel to the *c* chain axis of PTFE. Moreover, we clearly see that the eighth layer of PTFE (0.244 nm) matches well with the second layer of pCNEU (*b* axis) (0.244 nm).<sup>28</sup> Considering the previous ordered parameters and the quality of the diffraction pattern, the present results demonstrate a good orientation by epitaxial growth of pCNEU on PTFE. In the case of pCNEU on KAP<sup>28</sup> we were only able to observe only the first layer of diffraction often with a lot of streaking, indicating some disorder along the *b* axis of pCNEU. Here we can observe up to four layers of diffraction, and on the first and second layers instead of a streaked line in the case of pCNEU on KAP the diffraction spots are resolved. The quality of the pCNEU crystals nucleated on PTFE is thus superior to that of the pCNEU nucleated on KAP, and the order along *b* is better.

The different forms found for pCNEU may be due to different crystal structures of the monomer molecules evaporated on PTFE films. This is likely to occur, considering the possible rotational movements around the spacers, i.e., between the carbazole or the urethane group and the diacetylenic group, which the annealing process can activate. The different monomeric crystal structures could yield polymeric polymorphs characterized by different conjugation length. All these results indicate that the orientation by epitaxial growth on aligned PTFE layers is even better than that obtained by epitaxy on KAP single crystal. More detailed analysis of the film growth is currently in progress.

**Epitaxial Growth of Phenyl-Ethynylene Oligomers (oPE) on PTFE.** The overall orientation of oPEN on PTFE is generally lower than that found for polydiacetylenes. Figure 9 shows the polarized absorption spectra of a film of oPE3OMe grown by epitaxy. It is interesting to note that the long axis of the molecule matches with the perpendicular direction to the PTFE





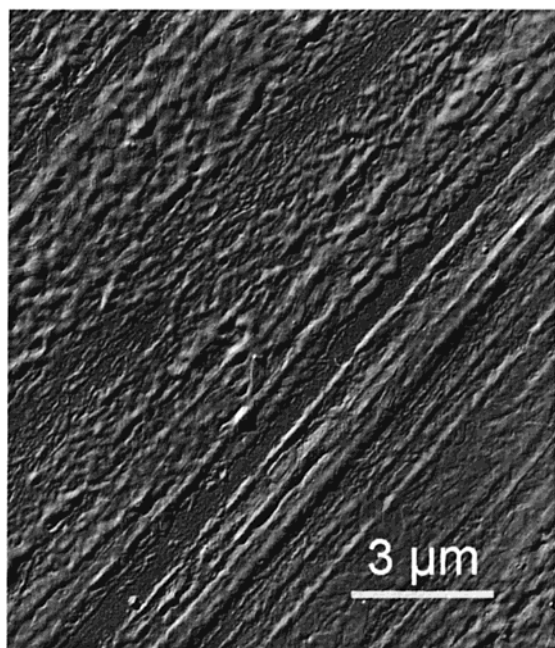
**Figure 10.** (a, top) Bright field TEM micrograph of oPE3OMe, (b, bottom left) zooming on a selected single crystal, and (c, bottom right) corresponding electron diffraction pattern.

sliding direction. Three maxima are observed at 412 nm (3.00 eV, 24 270  $\text{cm}^{-1}$ ), 388 nm (3.09 eV, 25 770  $\text{cm}^{-1}$ ), and 378 nm (3.27 eV, 26 460  $\text{cm}^{-1}$ ) corresponding to the exciton peak and its vibronic replica at 1500 and 2190  $\text{cm}^{-1}$  respectively for the aromatic C–C and C $\equiv$ C stretching. The OP value at 412 nm is 0.35, indicating that only a poor orientation of the crystals has been achieved. The bright field picture of the sample (Figure 10a) observed by TEM shows a coexistence of long crystals and platelets. Some fibrillar crystals are curved and randomly distributed. The platelets are well-defined squared crystals, all oriented along a unique direction parallel to the PTFE sliding direction. The fibrillar crystals are too thin to diffract. However, the developed platelets produce a diffraction pattern consisting of well-defined spots, corresponding to a high molecular order. Furthermore, the relative orientation of this diffraction pattern and the diffraction pattern of the PTFE is always the same. To illustrate this, Figure 10c shows the composite electron diffraction of the platelets as seen in the defocused diffraction picture (Figure 10b). The characteristic diffraction pattern of PTFE (indexed in Figure 8b) can be observed, and although the crystal-

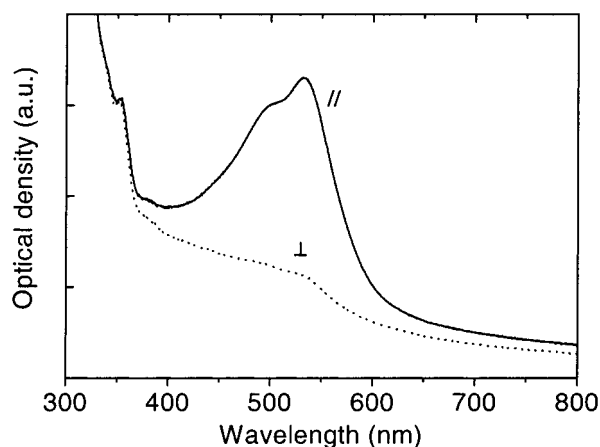
lographic structure of oPE3OMe is not available at present, we can see that the diffraction layers of oPE3OMe are parallel to that of PTFE, indicating a well-defined epitaxial orientation of the platelets on PTFE.

**Rubbing of Polydiacetylenes.** Among the symmetric polydiacetylenes tested here, very good results were obtained for p4BCMU. The quality of the orientation can be improved by repeating rubbing and annealing. The polarized optical microscopy of a film oriented by only one rubbing (OP  $\sim$  0.28) shows the coexistence of two regions: well-oriented and unoriented zones. These unoriented parts can be removed by repeating rubbing as we observed by SEM; thus, the OP increases to 0.80. Finally, annealing for 3 h at 70  $^{\circ}\text{C}$ , near the melting point of the monomer,<sup>26</sup> greatly improves the surface morphology and anisotropy; the OP at the excitonic peak (530 nm) reaches the excellent value of 0.99.

The polymer morphology was controlled by TEM. A bright field image of a p4BCMU rubbed film (Figure 11) shows a rough surface with stripes mainly stretched along the rubbing direction as well as a few ribbons



**Figure 11.** Bright field TEM micrograph of a rubbed p4BCMU film on glass.



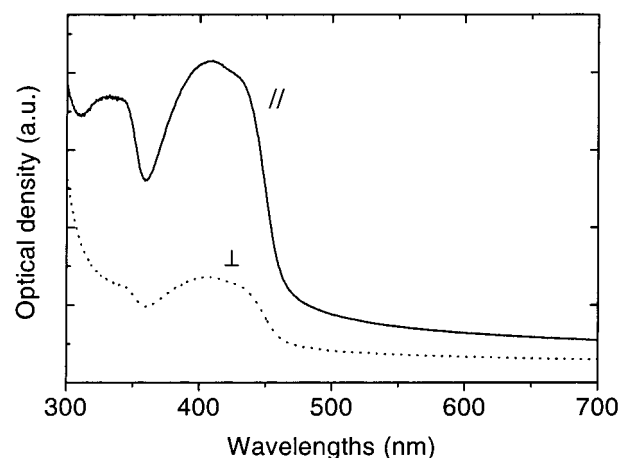
**Figure 12.** Polarized UV-vis spectra of a rubbed pDCHD-HS sample. Full and dotted lines: parallel and perpendicular polarization of the light relative to the rubbing direction.

elongated nearly at 45° of the rubbing direction. Given that the corresponding diffraction pattern is very weak, it was impossible to see the diffraction pattern of the latter orientation. Nevertheless, these observations confirm the good orientation revealed by the high OP value.

The same rubbing conditions were applied to other PDAs. We therefore studied the orientation of pDCHD-HS films. Figure 12 shows a polarized absorption spectrum of a rubbed pDCHD-HS sample. The overall picture, characterized by the presence of the excitonic peak at 534 nm followed by the vibronic replica at around 500 nm, is similar to that already observed for isotropic films.<sup>35</sup> The OP value at 534 nm is around 0.60. Even if this is a moderate value, this is the first time that oriented samples of this molecule have been prepared. In fact, on PTFE pDCHD-HS only gives isotropic samples. This lack of orientation is probably caused by the paraffinic moieties, which screen the aromatic ordering. Among unsymmetrical polydiacetylenes, the pCNEU and pCHPEU were poorly aligned by the rubbing technique. From our experience on the

**Table 1. Order Parameters (OP) of the Oligomers oPEn and Polymer pPEn**

phenyl-ethynyl derivative	order parameter
oPE5	0
oPE7	0.47
pPEn	0.58



**Figure 13.** Polarized UV-vis spectra of a rubbed sPE5C8 ester sample. Full and dotted lines: parallel and perpendicular polarization of the light relative to the rubbing direction.

orientation of PDAs induced by rubbing, we infer that the interactions at the interface, such as the molecular interactions between the film and the rubbing cloth and between the film and the glass substrate, are very important. The molecular surface structure of the material is a parameter to be evaluated. Indeed, we obtained the best results for a poly(acrylonitrile) cloth and for p4BCMU.

**Rubbing of oPE and pPE Polymers.** We applied the same rubbing conditions for the more rigid chains of oligomers oPE5 and oPE7 and polymers pPEn. Table 1 collects the OP values for samples of the same original thickness. An increase of orientation is observed, the OP values ranging from 0 to 0.58 from the pentamer to the polymer. We would suggest that the orientation increases with the length of the rod molecule. As for all the other conjugated systems, orientation also decreases with increasing thickness; for pPEn, the maximum value of OP ~ 0.66 is relative to a 10 nm thick film, whereas for a 50 nm thick film, the OP value is only 0.45. This proves the importance of the interface interactions in the orientation induced by rubbing.

In the micro-Raman spectra the C=C and C≡C bonds stretching vibrations are observed at 1591 and 2206 cm<sup>-1</sup>, respectively. In addition, a small dichroism is detected in agreement with the modest OP values obtained in the polarized absorption spectra.

For the sequenced (sPE5C8) ester, a good dichroism was observed after drying under vacuum and annealing at the critical temperature corresponding to the liquid crystal (LC) transition (110 °C – 15 h). Figure 13 shows the polarized spectra of a sPE5C8 ester sample after this treatment. The absorption peak is considerably broadened and centered at 412 nm. For an oriented film with an optical density of 0.59 in parallel polarization, the OP value rises to 0.62. We should note that the order parameter obtained by rubbing of thin films is in the same range as those obtained by orientation on PTFE but for thicker films. On PTFE, an oriented film whose optical density in parallel polarization is 1.27, the OP rises to 0.59 at 412 nm after annealing.



## Conclusions

Oriented thin films of conjugated oligomers and polymers were prepared on glass by deposition on aligned PTFE layers or by rubbing. For the *epitaxial growth* on PTFE, very high orientations (up to 0.99 for ordered parameter) were observed for some polydiacetylenes. For these samples, annealing of the monomer film definitely improves the orientation degree. The best results were obtained for pCNEU, for which the OP values were *even higher* than those measured previously for epitaxial films on KAP.

For the *rubbing*, after an optimization of the experimental parameters on the basis of the results of p4BCMU, we studied the orientation of pDCHD-HS samples. Even if further improvement in the orientation has to be gained for this polymer, our preliminary results could lead to the investigation of nonlinear optical properties of anisotropic samples of pDCHD-HS in order to compare them with those already measured for isotropic films. The series of oPE and polymers with increasing molecular size allowed the study of the effect of the length of the molecules on the orientation achieved by rubbing. Since the best results were obtained for the polymer, we can conclude that rubbing is more efficient on systems which can be assembled as long rods. Comparing the results also obtained for the same class of conjugated systems oriented by the two main techniques, we found that oPE oligomers and polymers can be *better oriented by rubbing than by other methods* probably because their LC structure is more favorable to the mechanical alignment induced by this method. The evidence that annealing at the LC transition increases the dichroism confirms our conclusions. Moreover, with well-defined molecular size, the orientation increases with the number of repeating units.

For the PDAs used in the present study, which bear as lateral substituents at least one carbazolyl residue, the rubbing technique does not give good results probably because of the stiffness or bulkiness of the aromatic moiety. On the other hand, orientation by epitaxy occurs for the PDAs with lateral substituents whose periodicity in the monomer crystal is comparable to that of the PTFE substrate.<sup>17</sup> This can also explain the very high and reproducible dichroism here reported for pCNEU on PTFE.

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