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High-Temperature Rubbing: A Versatile Method to Align π -Conjugated Polymers without Alignment Substrate

Laure Biniek,[†] Stéphanie Pouget,[‡] David Djurado,[‡] Eric Gonthier,[†] Kim Tremel,[§] Navaphun Kayunkid,^{†,||} Elena Zaborova,^{||} Nicolas Crespo-Monteiro,^{†,#} Olivier Boyron,[⊥] Nicolas Leclerc,^{||} Sabine Ludwigs,[§] and Martin Brinkmann*,[†]

[†]Institut Charles Sadron, CNRS- Université de Strasbourg, 23 rue du loess, 67034, Strasbourg, France

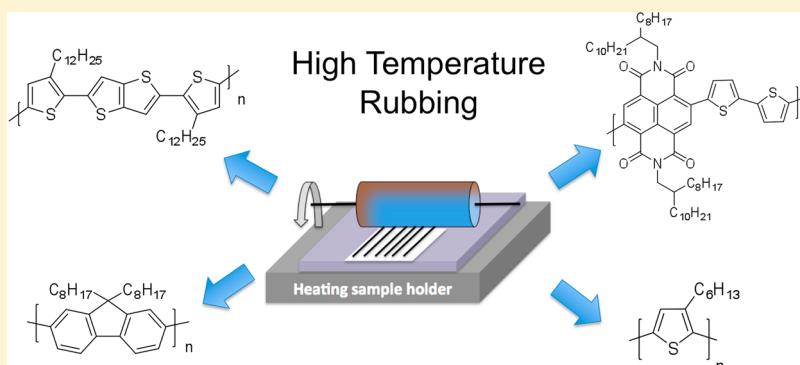
[‡]UMR SPrAM 5819 (CEA-CNRS-UJF) and SP2M, CEA Grenoble/INAC, 38054, Grenoble Cedex, France

[§]Institute of Polymer Chemistry (IPOC), University of Stuttgart, Pfaffenwaldring 55, Stuttgart, Germany

^{||}ICPEES, ECPM, Université de Strasbourg, 25 rue Becquerel, 67087, Strasbourg, France

[⊥]Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), CPE Lyon, CNRS UMR 5265, Université de Lyon 1, Bat 308F, 43 bd du 11 Novembre 1918, 69616 Villeurbanne, France

Supporting Information



ABSTRACT: Mechanical rubbing of polymer films has been widely used in the liquid crystal display industry to prepare oriented alignment layers of polyimides. We show that this fast orientation method can be successfully applied to a large palette of different π -conjugated systems, i.e., p- and n-type semiconducting homopolymers and alternating copolymers. Transmission electron microscopy, grazing incidence X-ray diffraction and UV-vis absorption spectroscopy reveal that both, the temperature of the films during rubbing and the molecular weight of the polymer strongly influence the level of orientation. For polythiophenes and polyfluorenes, the dependence of the orientational order parameter on the rubbing temperature (T_{rub}) was determined. A strong increase of alignment with T_{rub} is explained by the progressive alignment of higher molecular weight fractions at higher T_{rub} . The disordering of alkyl side chains allows the hairy-rod shaped macromolecules to disentangle and align during rubbing. In addition, for certain conjugated polymers, the in-plane orientation, crystallinity, and polymorphism of the rubbed films can be substantially improved/modified by postdeposition thermal or solvent vapor annealing. This high level of orientation results in highly anisotropic optical and electronic properties (UV-vis absorption, fluorescence, charge transport).

1. INTRODUCTION

In π -conjugated semiconducting materials, both molecular and crystalline orientations control optical, electronic, and optoelectronic properties in thin films since these properties are by essence highly anisotropic. This is true in macromolecular systems such as conjugated semiconducting polymers (SCP).^{1–3} Controlling both the in-plane orientation of polymer chains and the contact plane of the crystalline domains in a thin film relative to a substrate and/or an external electric field in a device is therefore of high importance. It determines, for instance, the direction of facile charge transport in a device.³ Alignment of semiconducting polymers can thus be used to enhance charge transport, polarized luminescence, and electro-

luminescence.^{1–7} From a structural point of view, the control of orientation and crystallinity in semiconducting polymer films can further help to understand the macromolecular packing in a crystal and to propose structural models.^{8,9}

On the one hand, alignment of semiconducting polymers and molecular materials was obtained by resorting to some alignment layers. These layers are mostly polymer substrates, such as rubbed polyimide,^{1,10,11} friction-transferred poly(tetrafluoroethylene) (PTFE),¹² hot-drawn polyethylene,¹³ or

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rubbed polycarbonate.¹⁴ Alignment procedures may imply high temperatures (~ 200 °C for polyimides and 300 °C for the friction-transfer of PTFE) that are not compatible with flexible plastic substrates such as polyethylene terephthalate (PET). Moreover, in many cases, the presence of the insulating alignment layer complicates the device architecture. This holds true for organic field effect transistors (OFET) or polarized organic electroluminescent diodes (OLED) with inverted device structures.⁷ On the other hand, alignment strategies were developed to avoid the use of an alignment substrate. For example, friction transfer,^{15–18} directional epitaxial crystallization,^{19,20} and directional zone casting^{21,22} yield very high orientations and controlled crystallinity of the SCP films on different types of substrates. However, they imply a forbiddingly slow oriented growth with characteristic growth rates of only ~ 20 $\mu\text{m}/\text{s}$.

Recently, some of us investigated the possibility to align directly the active layers of semiconducting polymers via mechanical rubbing.⁶ First rubbing experiments on regioregular poly(3-alkylthiophene)s were conducted at room temperature. Significant alignment was observed for poly(3-hexylthiophene) (P3HT) with low molecular weight ($M_w = 6.4$ kDa or 7.9 kDa) that crystallizes with extended chains. By contrast, rubbing high- M_w P3HT with $M_w \geq 50$ kDa at room temperature did not induce any orientation. Chain entanglements and tie-chains linking crystalline domains through amorphous domains seem to impede reorientation of domains upon rubbing for high- M_w P3HT.⁶ Recent studies on rubbing of poly(2,5-bis(3-dodecylthiophene-2-yl)thieno[3,2-*b*]thiophene) (C12-pBTTT) and poly{[*N,N'*-bis(2-octyldodecyl)-1,4,5,8-naphthalene-dicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} (p-(NDI2OD-T2)) demonstrated that the temperature of the polymer films during rubbing (T_{rub}) is a key parameter to enhance alignment.^{23,24} As an example, high orientation of C12-pBTTT could only be observed for films rubbed for $T_{\text{rub}} \geq 100$ °C (*vide infra*). It was proposed that the increase of in-plane orientation of C12-pBTTT and p-(NDI2OD-T2) with T_{rub} is related to the higher plasticity of the films upon disordering of the alkyl side chains that gives sufficient molecular mobility for the reorientation of crystalline domains.

In the current manuscript, we demonstrate that high temperature rubbing is a versatile method to prepare oriented and crystalline films of *p*- and *n*-type SCP including various polythiophenes, polyfluorenes and alternated copolymers. We show that the role of temperature during rubbing is essential for various SCP. Importantly, this study demonstrates that the impact of rubbing temperature on alignment is a function of the molecular weight of the polymer. Moreover, the structure, orientation and the polymorphism of the rubbed films can be further modified by postdeposition annealing.

2. EXPERIMENTAL SECTION

Polymer Samples. The macromolecular parameters of all polymer samples used in this study are collected in Table 1. PFO was purchased from American Dyes (ADS329BE). The synthesis of PF2/6 is reported elsewhere.¹² P3HT was purchased from Merck and used as received ($M_w = 43$ kDa). Additional molecular weight fractions were obtained by Soxhlet extraction successively in *n*-hexane, dichloromethane and tetrahydrofuran. In this study, we have used the *n*-hexane ($M_w = 7.9$ kDa) and the THF ($M_w = 53.7$ kDa) fractions. Two polymer syntheses of C12-pBTTT were performed according to ref 23, yielding two different batches. Each of these two batches was subsequently fractionated by Soxhlet extraction giving two M_w fractions in each case (see Table 1).

Table 1. Size Exclusion Chromatography Parameters of the Semi-Conducting Polymers Used for Mechanical Rubbing

polymer	M_w (kg/mol equiv PS)	M_n (kg/mol equiv PS)	polydispersity index
P3HT^a			
low- M_w (<i>n</i> -hexane fraction)	7.9	6.9	1.1
medium- M_w (Merck)	43	24	1.8
high- M_w (THF fraction)	53.7	35.7	1.5
C12-pBTTT^b			
low- M_w (CHCl ₃ fraction of batch 1)	13	8.3	1.57
medium- M_w (CB fraction of batch 1)	45	27	1.67
high- M_w fraction (CB fraction of batch 2)	81	36	2.25
PFO	56	23.3	2.4
PF2/6 ^a	147	38	3.9
P(NDI2OD-T2) ^c	19.3	9.1	2.1

^aP3HT and PF2/6: GPC performed in THF at 40 °C. ^bC12-pBTTT: GPC performed in 1,2,4 trichlorobenzene at 150 °C. ^cp(NDI2OD-T2): GPC performed in chloroform.

Low molecular weight p(NDI2OD-T2) was synthesized via Ni-catalyzed chain-growth polymerization following the procedure described in the literature.^{24–26}

Thin Film Preparation and Orientation. Orientation of the films by mechanical rubbing follows the procedure described in an earlier work for the preparation of polycarbonate alignment layers.^{14,6,19} It involves mainly two steps: (i) the preparation of a polymer film by the doctor blade method and (ii) rubbing of the as-deposited films with a microfiber tissue. The films of P3HT, C12-pBTTT and p(NDI2OD-T2) were prepared by doctor blading a 4–5 wt % solution in *ortho*-dichlorobenzene (*o*-DCB) on glass substrates at 180 °C whereas for polyfluorenes, a 4–5 wt % chloroform solution was deposited on the glass substrates at 45 °C. It is worth noting that rubbing of PFO films prepared from chlorobenzene did not afford aligned layers, indicating that the initial structure of the films is important for the efficiency of alignment by rubbing.

For the alignment of the films, a homemade rubbing machine was used. It is composed of a rotating cylinder (4 cm diameter) covered by a microfiber cloth. The rubbing is performed by applying the rotating cylinder with a 2 bar pressure on the translating sample holder (1 cm/s). The sample holder can be heated to the desired temperature during the rubbing process. The sample temperature is allowed to equilibrate for 1–2 min before rubbing. A rubbing cycle is characterized by the so-called rubbing length, i.e., the length of the rubbing tissue applied on a given point of the sample. In the present case, it is 50 cm. Postalignment thermal annealing was done in a Linkam hot stage under inert atmosphere at the required temperature for 1 min. Heating and cooling rates were 20 °C/min and 0.5 °C/min, respectively. A closed glass container with 10 mL of toluene was used for the solvent vapor annealing of PFO films.

Structural Analysis. TEM: Oriented areas were identified for TEM analysis by optical microscopy (Leica DMR-X microscope). The polymer films were coated with a thin amorphous carbon film and removed from the glass substrate by floating on a diluted aqueous HF solution (10 wt %) and subsequent recovery on TEM copper grids. TEM was performed in bright field, high resolution, and diffraction modes using a CM12 Philips microscope equipped with a MVIII (Soft Imaging System) charge coupled device camera. Calibration of the reticular distances in the ED patterns was made with an oriented PTFE film.

Grazing incidence X-ray diffraction (GIXD) was performed at the ESRF on line BM02 using a monochromated X-ray beam at 23.14 keV. Samples suited for the GIXD measurements were prepared on Si(100) substrates (Silchem mbH). The sample to detector distance was 30 cm.

Optical Absorption. The orientation of the polymer films was probed by UV-visible absorption (300–900 nm) using a Shimadzu UV-2101PC spectrometer with polarized incident light and spectral resolution of 1 nm.

3. RESULTS

a. Versatility of the Alignment Process. The applicability of high-*T* rubbing to π -conjugated polymers was investigated for various classes of polymers ranging from the more flexible regioregular poly(3-hexylthiophene) to more rigid “hairy-rod” polymers such as polyfluorenes. Figure 1a exemplifies the case of a semirigid and semicrystalline polymer, regioregular P3HT with a high molecular weight ($M_w = 53$ kDa). Rubbing P3HT films at 180 °C affords highly oriented films with a dichroic ratio above 25. The quality of the alignment and the crystallinity of the films is reflected in the sharpness and intensity of the 002 meridional reflection. It implies significant order along the rubbing direction and a much higher crystallinity than for high- M_w films grown, for example, by epitaxy on 1,3,5-trichlorobenzene.^{19,20} The rubbed high- M_w P3HT films have a characteristic and regular periodic lamellar structure with a 13 nm lamellar periodicity (see Figure ESI1 in the Supporting Information), i.e., much smaller than the 25–28 nm period observed in oriented P3HT films grown by directional epitaxial crystallization.¹⁹ For the more rigid thienothiophene based polymer C12-pBTTT, a very high orientation is also obtained for $T_{rub} = 125$ °C (see Figure 1b). For both C12-PBTTT and P3HT, the ED patterns indicate that rubbing induces a change of the crystal contact plane from initially “edge-on” in as-prepared films to mainly “face-on”²³ i.e. the chain axis (*c* axis) becomes aligned in the direction of the rubbing R and the π -stacking direction along the substrate normal.

To further assess the large-scale alignment achieved in the high-*T* rubbed films, we also performed grazing incidence X-ray diffraction (GIXD) measurements on rubbed films. GIXD probes orientation over large areas (several square millimeters) as opposed to the more local analysis by electron diffraction. Figure 2 shows representative 2D GIXD maps for P3HT (43 kDa) and C12-pBTTT (45 kDa) recorded for the incident X-ray beam q_i oriented parallel and perpendicular to the rubbing direction. In agreement with ED results, for both the rubbed P3HT and C12-pBTTT films, GIXD shows equatorial $h00$ reflections ($h = 1–3$) for $q_i \parallel R$ whereas all these reflections are absent for $q_i \perp R$. These reflections are typical of the face-on oriented domains of P3HT and C12-pBTTT on the Si(100) substrate. Interestingly, for C12-pBTTT, edge-on oriented domains are also present as the $h00$ reflections are seen also along q_z . For P3HT, a small population of edge-on oriented domains is suggested from the presence of a very weak 100 reflection along q_z . Whereas for P3HT, the 002 reflection is very difficult to see, when $q_i \perp R$, the 003 reflection in C12-pBTTT is well observed on the equator.

The in-plane orientation of the rubbed P3HT films was further quantified by performing φ scans of the (100)_{P3HT} reflection which is shown in Figure 3. The level of alignment achieved by high-*T* rubbing is characterized by a full width at half-maximum (fwhm) of 14 degrees for P3HT. This level of orientation is similar to that observed by Nagamatsu et al. for films oriented by friction transfer¹⁷ and only slightly lower compared to that found in thin films grown by directional epitaxial crystallization.²⁷

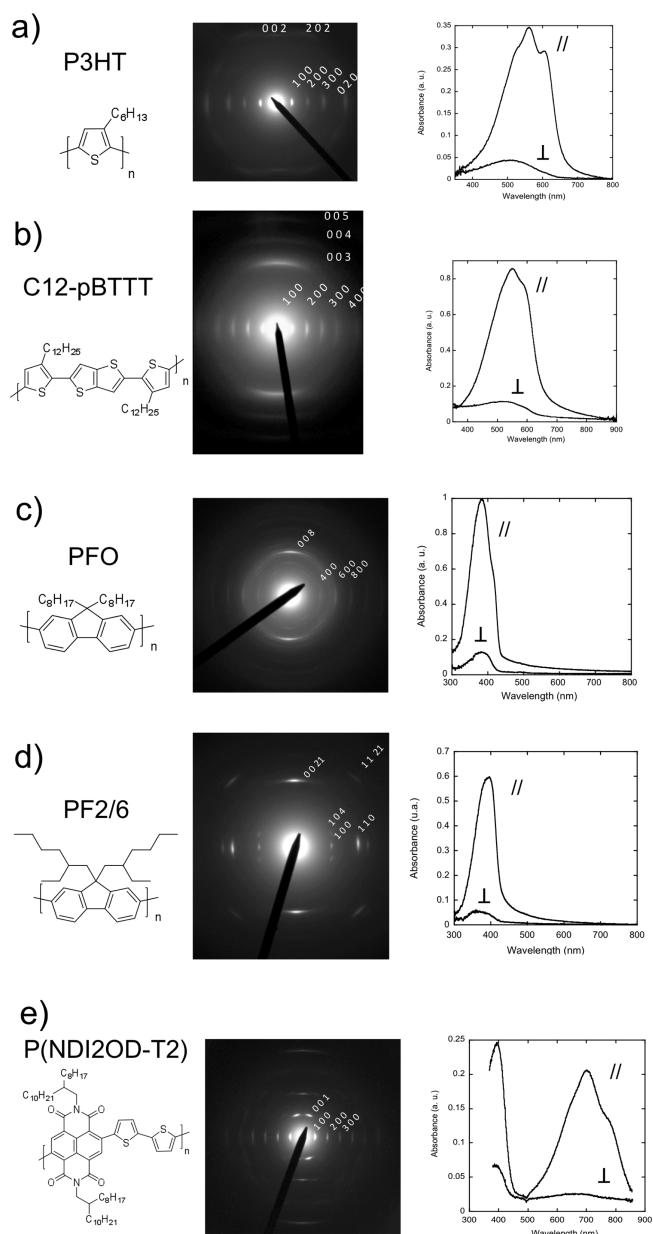


Figure 1. Electron diffraction patterns and polarized UV-vis absorption spectra (for parallel (||) and perpendicular (⊥) orientations of the incident light with respect to the rubbing direction) of highly oriented thin films of semiconducting π -conjugated polymers prepared by high-temperature rubbing. The chemical structures of the polymers are shown on the left. The P3HT films ($M_w = 53$ kDa) were rubbed at 180 °C, C12-pBTTT films ($M_w = 45$ kDa) were rubbed at 125 °C, p(NDI2OD-T2) films ($M_w = 19.3$ kDa) were rubbed at 80 °C and annealed at 280 °C, PFO films ($M_w = 56$ kDa) were rubbed at 125 °C and annealed at 210 °C. PF2/6 films ($M_w = 147$ kDa) were rubbed at 190 °C and annealed at 200 °C. Indexing of the electron diffraction patterns was performed using the structures published in the literature.^{8,9,12}

Successful alignment for rubbed polythiophenes (P3HT and C12-pBTTT) films became an incentive to test the alignment method with other families of conjugated polymers, in particular polyfluorenes. The conjugated backbone of polyfluorenes is more rigid than P3HT and the polymers tend to crystallize in the form of extended chain lamellar crystals.^{9,12} Polyfluorenes have blue-emitting properties which make them

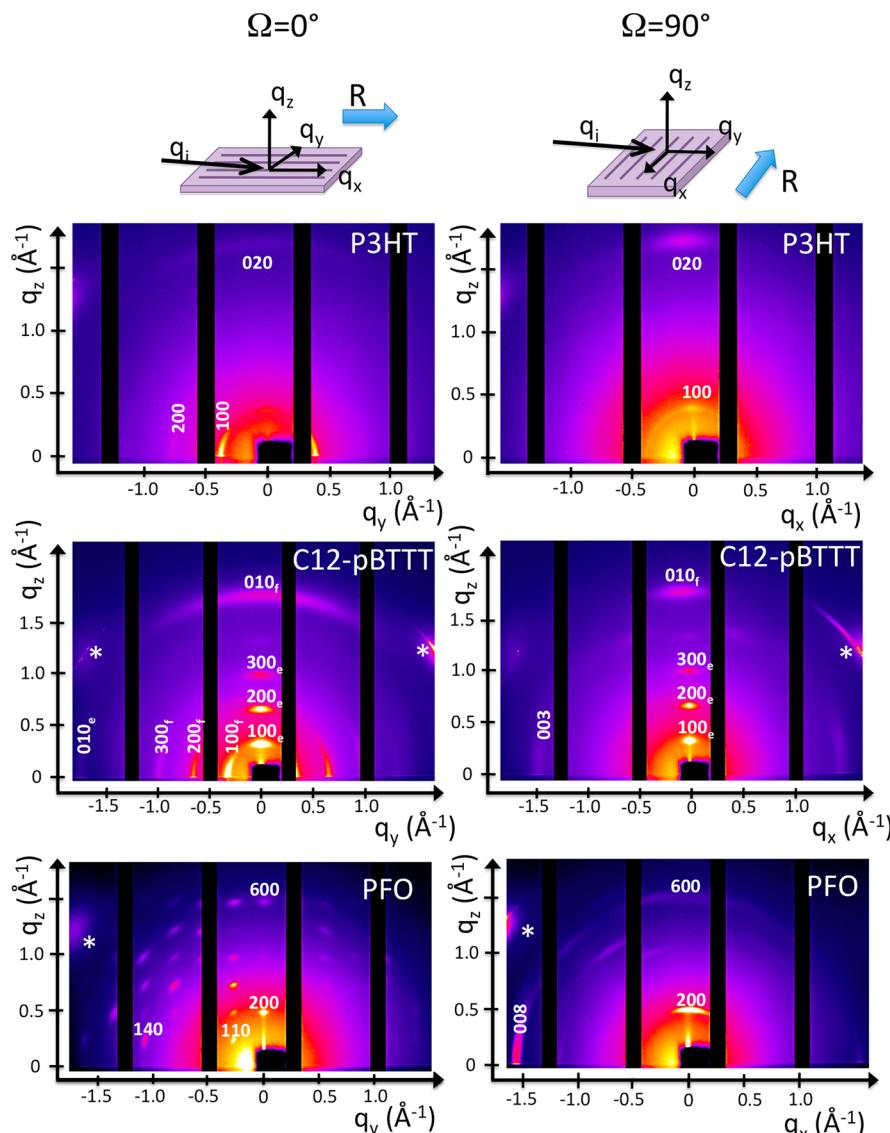


Figure 2. GIXD 2D maps obtained for rubbed films of P3HT (43 kDa, $T_{\text{rub}} = 180^\circ\text{C}$), C12-pBTTT (45 kDa, $T_{\text{rub}} = 100^\circ\text{C}$, Trub=125 °C, annealed at 210 °C). The 2D maps are recorded for the incident X-ray beam oriented parallel ($\Omega = 0^\circ$) and perpendicular ($\Omega = 90^\circ$) to the rubbing direction R as illustrated in the top sketches. In the case of C12-pBTTT, the main reflections are indexed with labels corresponding to the population of face-on (f) and edge-on (e) domains. The asterisk indicates reflections from the Si(100) substrate.

interesting candidates for OLED.^{20,21} We have chosen two different poly(dialkylfluorene)s, namely poly(9,9-di(*n*-octyl)-fluorene-2,7-diyl) (PFO) with linear *n*-octyl side chains and poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF2/6) with branched 2-ethylhexyl side chains. As seen in parts c and d of Figure 1, even for these very rigid “hairy-rod” polymers, the use of rubbing temperatures above 100 °C yields highly aligned but not highly crystalline films. Post-rubbing annealing is necessary to increase the crystallinity of the rubbed polyfluorene films as is also the case for friction-transferred PFO films.¹⁷ It is also worth noting that the structure of the initial PFO films prior to rubbing impacts the efficiency of high-*T* rubbing. Indeed, films of PFO prepared from chlorobenzene solutions did not align well whereas those from chloroform showed high alignment. We anticipate that the initial crystallinity of the films prior to rubbing can play an important role on the alignment level. For PFO, the higher crystallinity of the PFO films prepared from high boiling point solvents seems to hamper subsequent reorientation of the PFO chains during high-*T* rubbing. This

result suggests that amorphous films of SCP are preferred to achieve a good alignment upon rubbing.

The rubbed films of PFO are in the characteristic α polymorph. The domains have a pure (010)_{PFO} contact plane after thermal annealing at 210 °C and slow cooling to room temperature (0.5 °C/min). The selected area diffraction pattern of rubbed and annealed PFO films is nearly single-crystalline (see Figure ESI2). GIXD was also used to quantify the quality of the alignment of rubbed and annealed PFO films. The GIXD pattern observed for $q_i \parallel R$ (see Figure 2) shows only (*hk*0) reflections and is similar to the ED pattern observed for PFO films with standing chains on mica.⁹ For $q_i \perp R$, the pattern displays exclusively (*h0l*) reflections ([010] zone), indicating that all crystals have the same (010)_{PFO} contact plane and a high in-plane orientation of the chains parallel to the rubbing direction R. As seen in Figure 3, the φ -scan performed on the (008)_{PFO} reflection yields a fwhm of only 6.7 deg, which points at a remarkable in-plane orientation of the crystalline domains in the films over large areas.

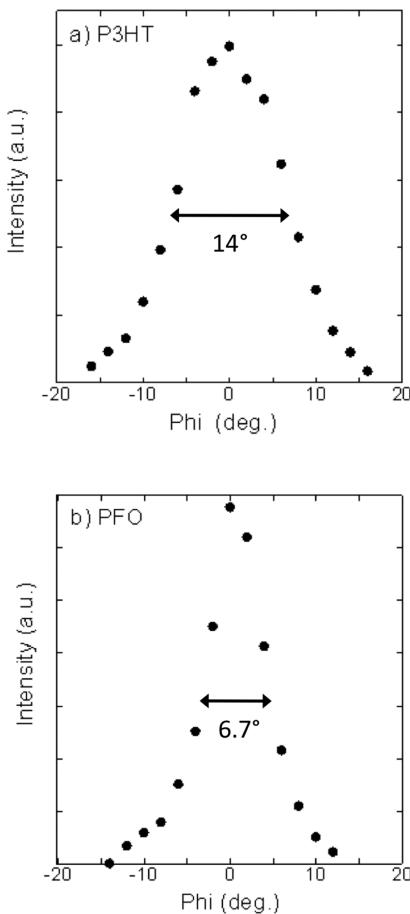


Figure 3. In-plane orientation of the high- T rubbed thin films as probed by GIXD. Phi scans are performed on the (100) reflection of P3HT (a) and the (008) reflection of PFO (b). The P3HT (43 kDa) films were rubbed at 180 °C. The PFO films were rubbed at 125 °C and subsequently annealed at 210 °C for 1 min.

Concerning PF2/6, the 21₄ helical conformation of the chains¹² does not hinder alignment by rubbing but the annealed films show the coexistence of (010)_{PF2/6} and (1–10)_{PF2/6} crystal contact planes as indicated by the presence of both the 100 and the 110 reflections on the equator of the ED pattern (see Figure 1d). By contrast, PF2/6 oriented on PTFE substrates has mostly a (010)_{PF2/6} contact plane.¹²

For both polyfluorenes, orientation sets in close to the transition temperature between the crystalline and the nematic liquid crystal phase.²⁸ However, to limit mechanical damaging of the layers, rubbing must be done in the crystalline state, as noted also for C12-pBTM.²³

For the ease of comparison between the different alignment levels of the SCP investigated herein, we decided to plot a 3D order parameter as a function of T_{rub} (see Figure 4). The order parameter S is equal to 0 for an isotropic distribution of chain orientations and 1 for a system of perfectly aligned chains, respectively. Selecting a 3D order parameter S is appropriate because the layer thickness (50–100 nm) exceeds the average segmental Kuhn length of the different polymers (a few nanometers).¹ S is defined as $(R - 1)/(R + 2)$ with R the dichroic ratio in absorption measured at the maximum of absorption.²⁹ Figure 4 displays the dependence of the order parameter S with T_{rub} for the polythiophenes and polyfluorenes investigated in this study. The same trend is observed for all semiconducting polymers: S increases gradually with T_{rub} . The

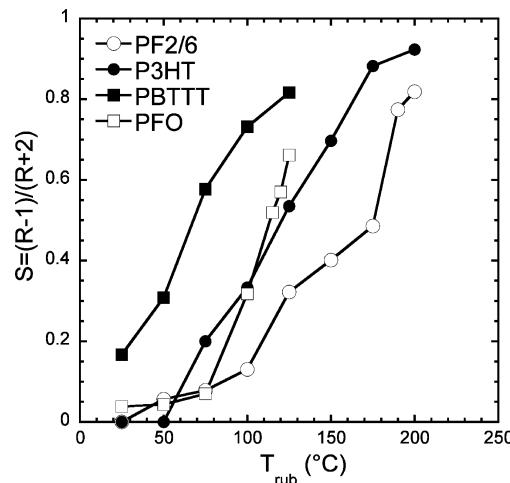


Figure 4. Evolution of the order parameter $S = (R - 1)/(R + 2)$ calculated from the UV-vis absorption dichroic ratio R for rubbed semiconducting polymer films as a function of T_{rub} , the temperature of the sample during rubbing. S values are calculated for P3HT ($M_w = 53$ kDa), C12-pBTM ($M_w = 13$ kDa), PFO ($M_w = 56$ kDa), and PF2/6 ($M_w = 147$ kDa) samples.

highest orientations in as-rubbed films are observed for both polythiophene films (P3HT and C12-pBTM) with S in the range 0.80–0.85. The alignment observed in PFO is somewhat lower. It is worth mentioning again that rubbing could not be realized at T_{rub} too close to the temperature of the C → LC phase transition because the PFO films are easily damaged. As a matter of fact, for polyfluorenes and C12-pBTM that show a transition from a crystalline to a liquid crystalline phase at high temperature (around 150 °C), the highest orientation is obtained when the rubbing temperature is 10–20° below that C → LC transition. Accordingly, the orientation efficiency is limited since the rubbing must be performed further away from the melting of the polymer.

Finally, the high- T alignment method was also applied to alternating copolymers, in particular the n-type polymer poly{[N,N'-bis(2-octyldecyl)-1,4,5,8-naphthalene-dicarboximide-2,6-diyl]-alt-5,S'-(2,2'-bithiophene)} (p(NDI2OD-T2)).^{24,30–32} The use of alternated copolymers becomes widespread in OPV and OFET applications because of their unique electronic properties resulting from the association of electron-rich and electron-deficient monomeric units. As seen in Figure 1e, a highly oriented film of p(NDI2OD-T2) is obtained after rubbing at 80 °C and thermal annealing at 280 °C (for 1 min) (the dichroic ratio exceeds 25).²⁴ The ED pattern exhibits very sharp reflections and is characteristic of form I p(NDI2OD-T2).³² As such, this result demonstrates the high potential of the high- T rubbing method for the alignment and structural studies of new alternated donor–acceptor copolymers.

b. Impact of Molecular Weight on Alignment. Whereas the role of temperature during rubbing was highlighted in our previous studies on C12-pBTM and p(NDI2OD-T2), no systematic investigation of the concomitant effects of molecular weight and temperature was proposed so far. However, it is well-known for polyolefins that both crystallization and mechanical properties under shear conditions are highly dependent on molecular characteristics such as molecular weight M_w .³³ As shown hereafter, the polymer M_w and polydispersity are two important parameters in the dependence

of alignment on the rubbing temperature. First, we highlight the importance of these parameters by a comparison of three different P3HT samples: a low- M_w (7.9 kDa, PDI = 1.1), a nonfractionated medium M_w sample (M_w = 43 kDa, PDI = 1.8) and a high- M_w sample obtained after Soxhlet extraction in THF (M_w = 53 kDa, PDI = 1.5). Figure 5 shows the dependence of

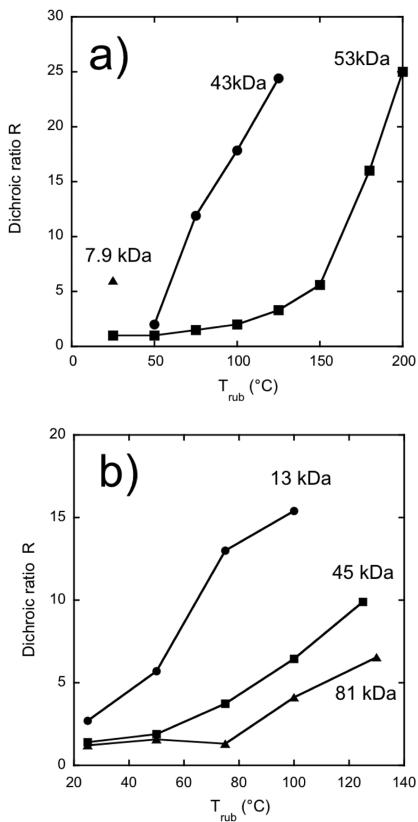


Figure 5. T_{rub} -dependence of the dichroic ratio at 605 nm for P3HT (a) and C12-pBTTT (b) thin films rubbed as obtained for different molecular weights. As a mean of comparison, the DR of a P3HT 7.9 kDa sample rubbed at 25 °C is shown in part a.

the rubbed thin film dichroic ratio as a function of M_w . The low- M_w P3HT exhibits high orientation when rubbed at room temperature. However, both medium- and high- M_w samples show different behaviors with T_{rub} . The nonfractionated medium- M_w P3HT sample shows an onset of alignment already at $T_{\text{rub}} = 75$ °C contrary to the high- M_w fraction which is poorly oriented under identical rubbing conditions. For the high- M_w sample, T_{rub} must be above 150 °C to achieve a similar orientation as observed for the medium- M_w sample at 75 °C. More generally, Figure 5a indicates that for T_{rub} below 125 °C, alignment of high- M_w P3HT is limited.

From a structural point of view, electron diffraction on rubbed P3HT evidence a similar evolution of the patterns with T_{rub} as reported previously for C12-pBTTT.²³ As seen in Figure ESI3, the ED pattern of 43 kDa P3HT films rubbed at 50 °C shows only very weak $h00$ reflections on the equator and a dominant 020 Scherrer ring, indicating that no substantial alignment was induced. For $T_{\text{rub}} = 100$ °C, the ED pattern is characteristic of almost purely “face-on” oriented P3HT domains. For 150 °C, the 002 reflection becomes particularly intense and the equatorial $h00$ reflections tend to be sharper and less arced.

To verify if the impact of M_w on the alignment efficiency versus rubbing temperature is a general trend for other polymers, we performed a similar experiment on three different M_w fractions of C12-pBTTT (see Table 1). As seen in Figure 5.b, the T_{rub} -dependence of alignment is similar to that found for P3HT: for the low- M_w fraction C12-pBTTT (13 kDa), alignment sets in at much lower T_{rub} as compared to the 45 kDa sample. The low- M_w fraction shows a steady increase of alignment already for low rubbing temperatures contrary to the 45 kDa and the 81 kDa samples for which the onset of alignment is clearly shifted to higher temperatures. One possibility could be that the shift is related to the M_w -dependence of the C → LC transition temperature.

These two examples of high- T rubbing on P3HT and C12-pBTTT illustrate the general and strong dependence of the alignment on both the molecular weight of the polymer and the rubbing temperature T_{rub} . As a general rule, higher rubbing temperatures are necessary to align higher M_w fractions. More generally, this study suggests that the molecular weight distribution is also crucial for the alignment by rubbing. It can be anticipated that polydisperse samples containing a large distribution of chain lengths may show an onset of alignment at lower rubbing temperatures as compared to more monodisperse samples of high M_w .

c. Chain Alignment Scenario. The interesting finding illustrated in this study is the generality of the dependence of the alignment on T_{rub} for all conjugated polymers bearing either linear or branched alkyl side chains. In the case of C12-pBTTT oriented by high- T rubbing, it was proposed that, by increasing the rubbing temperature, 3D crystalline order present in the as-prepared films is disrupted because of the progressive disordering of alkyl side chains whereby conferring a higher plasticity to the films and ease the alignment. Since the alignment of numerous semiconducting polymers was achieved by high- T rubbing, the incriminated mechanism must be more general and must also take into account the M_w distribution of the polymers. We propose the following scenario for the effect of M_w on high temperature alignment of P3HT and C12-pBTTT. We want to distinguish two important roles of rubbing in the orientation of SCP films. First, rubbing is a simple mean to create bundles of aligned chains that can act as seeds for the subsequent growth of oriented crystalline domains. In other words, rubbing is a mean to act on the nucleation of oriented polymer crystals. Second, rubbing is also a mean to disentangle polymer chains, especially at higher rubbing temperatures. As noted in our previous work on P3HT, thin films rubbed at room temperature, the efficiency of alignment is related to the presence of chain entanglements in the amorphous phase between crystalline domains. The amount of entanglements is expected to increase with M_w , explaining the gradual difficulty to align samples with increasing M_w . The progressive increase of R with T_{rub} observed in medium- M_w P3HT can be understood by considering that a larger distribution of polymer molecular weights is impacted by rubbing when T_{rub} increases. In other words, for polydisperse samples composed of short and long chains, only short chains will be aligned at low T_{rub} . When T_{rub} increases, the proportion of longer chains that can be aligned increases, hence the dichroic ratio of the films increases with T_{rub} . Increasing the temperature of the sample during rubbing causes the alkyl side chains to progressively disorder/melt. Because of this, the entangled “comb-shaped” SCP chains in the amorphous parts can progressively disentangle as T_{rub} increases and this leads to the progressive

alignment of the longer chains upon rubbing (see Figure 6). In other words, increasing the temperature of the polymer during

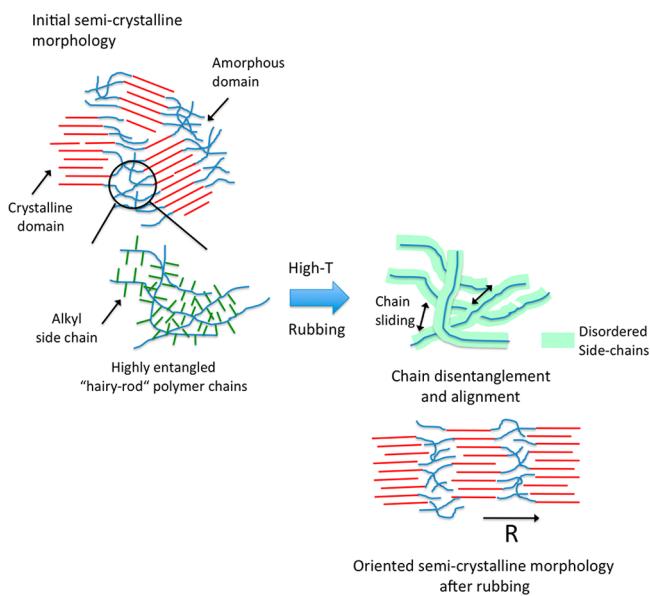


Figure 6. Schematic illustration of the mechanism responsible for the alignment of “hairy-rod” semiconducting and semicrystalline polymers upon high temperature mechanical rubbing.

rubbing allows for the disentanglement of “hairy-rod” polymer chains which is necessary for the efficient alignment of the entire film. Higher M_w fractions showing more chain entanglements require higher rubbing temperatures to undergo alignment.

As such, these results can be linked to a large body of earlier works dealing with polymer alignment using shear or elongational flow, especially concerning polyolefins.³³ As an example, the important role of chain entanglements in the

amorphous regions of semicrystalline isotactic polypropylene (iPP) during uniaxial stretching was recently highlighted.³⁴ In particular, the role of the temperature during stretching was clearly evidenced in the case of iPP, high temperatures favoring chain disentanglements and thus the formation of more folded-chain crystals from coiled segments. However, the present case of π -conjugated polymers is different because: (i) these polymers bear rather long alkyl side chains that make these chains look like “hairy-rods” and (ii) the conjugated backbones are not as flexible as in polyolefins. Therefore, the mechanism of alignment of π -conjugated polymers must imply the disentanglement of chains via a partial melting of the side chains.

The important role of side chain disordering is further supported by the observation that the crystal lattice of both C12-pBTTT and P3HT is subjected to an expansion along the side chain direction (**a** axis) with increasing temperature.^{35,36,23} For C12-pBTTT, this expansion is between 19.4 Å at 25 °C and 20.0 Å at 150 °C whereas for P3HT it is reported between 16.7 Å at 25 °C and 18.0 Å at 240 °C. This lattice expansion would translate to a weakening of the interchain interactions within both crystalline and amorphous domains, favoring thus chain disentanglements and reorganization upon rubbing.

d. Postdeposition Treatments: Temperature and Solvent Vapor Annealing. Although high-*T* rubbing demonstrates already effective alignment without resorting to an alignment layer, it is also possible to improve in-plane orientation, crystallinity and eventually to change the contact plane and/or the structure of the films by postrubbing treatments, e.g., thermal and solvent vapor annealings. We show two examples that illustrate this finding. Figure 7 compares the ED patterns of as-rubbed and annealed films of p(NDI2OD-T2) and PFO. In the case of p(NDI2OD-T2) annealed at 280 °C, the ED patterns display a large number of very sharp reflections contrary to the as-rubbed layers showing only a limited set of arced reflections.²⁴ Annealing at 310 °C result in a reorientation of the domains on the substrate from

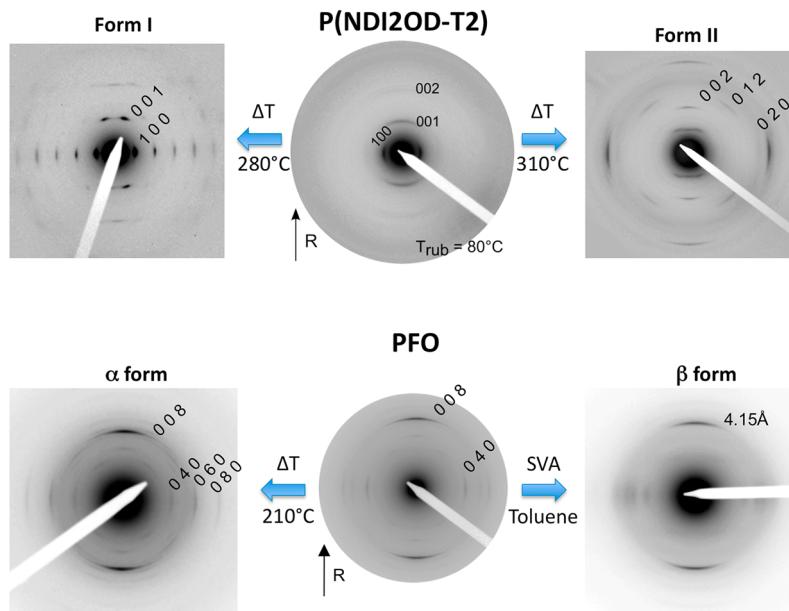


Figure 7. Controlling the contact plane and/or the structure in rubbed π -conjugated polymer films after thermal annealing (ΔT) for p(NDI2OD-T2) and solvent vapor annealing (SVA) for PFO. The electron diffraction patterns of the as-rubbed films are shown in the central column and the rubbing direction **R** is indicated by an arrow.

"face-on" to "edge-on" together with a structural transition to form II.^{24,32} The reorientation of crystalline domains preserves the in-plane direction of the chains imparted by the rubbing. A similar improvement of crystallinity is observed in PFO films annealed at 210 °C as seen in Figure 7. Again, the in-plane orientation is not lost upon annealing at temperatures close to the melting of these polymers.

A change of the structure of oriented films of PFO can also be induced by a solvent vapor annealing (SVA) of the rubbed films. SVA is made with toluene and maintains the in-plane orientation generated by rubbing. It is well-known that exposure of PFO films to toluene vapors generates the β form.^{37,38} Inducing this structure in thin films is very interesting, especially for polarized OLEDs, since the devices show an enhanced luminance efficiency.³⁷ After SVA in toluene (10 min), a PFO film rubbed at $T_{\text{rub}} = 125$ °C shows a marked change in the UV-vis absorption spectrum (see Figure ESI4). The 399 and 433 nm signatures of the β form are clearly observed and have a marked dichroism ($R = 6$ at 433 nm). The corresponding ED pattern of these β -PFO films is in agreement with the one reported for shear-oriented β -PFO (see Figure 7).³⁹ It displays a very limited set of reflections on the equator. The most intense reflection on the meridian at 4.15 Å corresponds to half the monomer repeat period along the rubbing direction. The ED pattern of β -PFO hints at poor fiber-like order contrary to α -PFO obtained after thermal annealing at 210 °C. Both examples on p(NDI2OD-T2) and PFO indicate that the phase transformation induced either by annealing at temperatures close to the melting or by solvent vapor generates films that show a different structure and/or orientation of crystalline domains than the initial as-rubbed films while preserving high in-plane orientation.

4. CONCLUSION

High-T rubbing is a promising and general method to align conjugated polymers without resorting to an alignment substrate. Numerous p- and n-type semiconducting polymers show a gradual increase of orientation with increasing temperature during rubbing. The optimum rubbing temperature depends on molecular weight and the molecular weight distribution, as evidenced for P3HT and C12-pBTBT, and it can be limited by a transition to a LC phase. Higher molecular weight polymers require higher rubbing temperatures. This trend indicates an alignment mechanism whereby the progressive disordering of alkyl side chains allows the hairy-rod-like macromolecules to disentangle and align during rubbing. The role of the alkyl side chains on the efficiency of high-T rubbing still needs further investigations. In particular, it is necessary to distinguish the influence of side chains from that of molecular weight distribution. Post-rubbing treatments of the films using thermal or solvent annealing help to improve the film crystallinity, control the contact plane of the domains and eventually to change the polymorph in the films while maintaining high in-plane orientation. Moreover, the polymorphism of some polymers can also be controlled by combining high-T rubbing with adequate thermal and solvent vapor annealing procedures. This method of orientation can be of high interest to align donor–acceptor block copolymers so as to create continuous and oriented domains of each block. Preliminary results show that high-T rubbing is also particularly efficient for the alignment of donor–acceptor co-oligomers as well as polymer blends.

■ ASSOCIATED CONTENT

● Supporting Information

Low dose HRTEM image and bright field image, selected area electron diffraction pattern, Evolution of the ED pattern, and polarized UV-vis absorption. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*(M.B.) E-mail: martin.brinkmann@ics-cnrs.unistra.fr.

Present Addresses

¹College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang (KMITL), Bangkok, 10520, Thailand.

[#]Université de Lyon, F-42023 Saint-Etienne, France; CNRS, UMR 5516, Laboratoire Hubert Curien, 18 rue Pr. Lauras F-42000 Saint-Etienne; Université de Saint-Etienne, Jean-Monnet, F-42000 Saint-Etienne.

Notes

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