Role of the Processing Solvent on the Electrical Conductivity of PEDOT:PSS

Jingjin Dong and Giuseppe Portale*

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is one of the most studied conductive polymers, holding great potential in many applications such as thermoelectric generators, solar cells, and memristors. Great efforts have been invested in trying to improve its mechanical and electrical properties and to elucidate the structure–property relationship. In this work, a systematic and quantitative study of the effect of solvent polarity and solution processing on the film structure and conductivity is presented. By using grazing-incidence wide-angle X-ray scattering (GIWAXS) together with atomic force microscopy (AFM), the importance of the quality of the PEDOT crystal packing is highlighted as a key factor to reach improved electrical conductivity, rather than the overall degree of crystallinity. Moreover, the (re)structuring mechanisms occurring during the film formation and film exposure processes are also studied by in situ GIWAXS. Different intermediate precursor stages and different pathways to reach improved crystallinity are reported depending on the used solvent. The structural results are interpreted looking at the solvent nature and the PSS/solvent affinity. With this contribution, a guidance is hoped to be given not only on how to improve the PEDOT:PSS electrical conductivity, but also on how to tune the film structural or electrical property for different applications.

1. Introduction

Poly(3,4-ethylenedioxythiophene) and its water-soluble complex with poly(styrenesulfonate) (PEDOT:PSS) are the most prominent polymers for various fields like thermoelectrics, organic photovoltaics, and organic field effect transistors.\[1\] The electrical conductivity of PEDOT:PSS was extensively studied and optimized by many researchers to improve the device properties. A level as high as thousands of S cm\(^{-1}\) has been achieved.\[2,3\] Various processing methods were used including solvent addition, solvent-thermal post-treatment, organic–inorganic blending, and even film stretching.\[1\] Different compounds like polar solvents, salt, strong acids, ionic liquids, carbon nanotube, e.g., were utilized as additives, post-treatment agents, or blending components. For example, Saxena et al. post-treated pristine PEDOT:PSS films with various ionic liquids to induce an increased π–π stacking between PEDOT molecules.\[4\] 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) treated films exhibited a record short π–π stacking distance of 3.35 Å due to an enormous bonding effect of TCB to PEDOT and EMIM to PSS and subsequent phase separation. Fan et al. reported an impressive electrical conductivity of 3088 S cm\(^{-1}\) after the exposure of PEDOT:PSS:5% DMSO (dimethyl sulfoxide) films with sulfuric acid.\[3\] Worfolk et al. reported solution sheared PEDOT:PSS films further post-treated with methanol with extremely high conductivity of 4600 S cm\(^{-1}\).\[2\]

Among various strategies, polar solvents addition and post-treatment are among the most used and most efficient ways to improve PEDOT:PSS electrical conductivity.\[3,5–8\] Both processes can induce different effects on PEDOT:PSS thin films, such as π–π stacking distance shortening (i.e., increased π–π orbital overlap), alteration of the crystallite orientation (face-on vs edge-on), overall crystallinity increase, PSS removal, and phase separation.\[9,10\] Polar solvents with high dielectric constants and high boiling points are common additives and post-treatment agents, especially DMSO and EG (ethylene glycol). In 2002, Kim et al. reported for the first time about the use of DMSO as an additive to dramatically increased the conductivity of PEDOT:PSS thin films (about two orders of magnitude higher at room temperature), and since then polar solvents got more and more attention from the research field.\[11,12\] Pipe et al. reported a promising thermoelectric property for PEDOT:PSS by EG dip treatment following pre-doping PEDOT:PSS nanofilms with DMSO or EG.\[13\] The DMSO and EG pre-doped films exhibited σ > 600 S cm\(^{-1}\). After dipping them into an EG bath, conductivities up to 1000 S cm\(^{-1}\) were obtained, which were three orders of magnitude higher than pristine PEDOT:PSS. The effective improvement was mainly attributed to the selective removal of excessive PSS. Palumbiny et al. observed that the in-plane electrical conductivity of PEDOT:PSS increased from 0.2 to 1200 S cm\(^{-1}\) upon EG treatment. The authors drew the emphasis on the formation of larger PEDOT crystallites with more pronounced...
These different film structural variations caused by the polar solvent treatment make a great influence on the electrical property. However, the structure–property relationship, especially the mechanism on how the used solvents alter the structure during film formation is still not fully revealed.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) is a powerful technique to probe the crystalline structure of thin films.\(^{[15,16]}\) GIWAXS data can be fully analyzed to extract information about the overall film crystallinity, average crystalline domain size, intermolecular distances, and crystal orientation, making it one of the most used techniques in studying PEDOT:PSS films. For example, Honma et al. used GIWAXS to successfully reveal the mesoscopic 2D structure of PEDOT:PSS thick films.\(^{[8]}\) Besides the static structure, dynamic structure evolution during film formation can also be studied with in situ GIWAXS. Palumbiny et al. monitored the structure evolution with in situ GIWAXS during the printing process and studied the mechanism on how EG affected the PEDOT:PSS film structure formation.\(^{[34]}\) Parameters like crystal size, edge-on ratio, and π–π stacking distance were analyzed in order to reveal the structure–property relationship. Besides, Yildirim et al. reported a theoretical simulation on the film formation of DMSO-added PEDOT:PSS, trying to explain the mechanism behind.\(^{[17]}\) These works offer a great insight into the principle of the polar solvent effect and help develop new strategies to get electrical conductivity of PEDOT:PSS further improved. However, because of the different film preparation methods employed in the different works, parameters from different literature works are not easily comparable, making it difficult to extrapolate the exact influence of different processing methods on the PEDOT:PSS structure and properties.

Here, we present a quantitative investigation of the semicrystalline structure of PEDOT:PSS thin films processed using different organic solvents either i) directly added to the casting solution (addition method, AD) or ii) used as immersion solvents for pre-casted films (post-treatment method, PT). Moreover, the evolution of the structural parameters with time during drop casting with the AD method and during drying with the PT method is studied using in situ GIWAXS. Five organic solvents with different boiling points and different dielectric constants are used, including toluene (Tol), iso-propanol (IPA), methanol (MeOH), dimethylformamide (DMF), and DMSO. Using the information about the final structure and the structural evolution with time during the thin film processing, we aim to find out the most critical parameters relevant for tuning the electric conductivity and to unveil the film structuring mechanisms acting in the different solvent processes.

### 2. Results and Discussion

The compounds used in this work, together with a basic description of the experimental configuration used to perform the GIWAXS measurements are reported in **Scheme 1**.

The electrical conductivity of both AD- and PT-processed PEDOT:PSS films is shown in **Figure 1**. Generally, for a given solvent, PT-processed samples exhibit higher conductivity compared to the AD-processed ones. This observation suggests that the properties of the pristine PEDOT:PSS film can be optimized further and because of the relatively large amount of solvent volume used in the PT method, the effect is larger. The remarkable difference in conductivity between MeOH-AD and MeOH-PT films (about two orders of magnitudes) can be attributed to the low boiling point (64.7 °C) and higher volatility of MeOH with respect to water. During the drying process, most of MeOH additive will evaporate before water which makes its conductivity very close to the pristine PEDOT:PSS deposited from pure water. In contrast, the conductivities of DMSO-AD and DMSO-PT samples are relatively close to each other which can be attributed to the high boiling point of DMSO (189 °C). In the DMSO-AD processing, we can infer that DMSO is left inside the film after all water has evaporated and it will influence the PEDOT:PSS structure in a similar way as DMSO-PT processing. This will be further discussed below in the in situ GIWAXS part. With the exclusion of the results for the MeOH-AD sample, a clear correlation between the solvent polarity and the film conductivity can be found. The more polar the solvent, the higher the film conductivity is. Our observation is in agreement with the results reported previously.\(^{[1,11,18]}\) Moreover, we can confirm that high boiling point of solvent is a threshold when the addition method is used. The optical properties of the different films were characterized using UV-vis–NIR (near-infrared) spectroscopy (see Figure S1, Supporting Information). The UV-vis–NIR spectra show that a small intensity increase in the bipolaron range from 900 to 1200 nm occurs when the most polar solvents are used. However, no obvious changes in the polaron states after processing were observed. This observation suggests that the nature of the solvent and processing method used have mainly an impact on the film structure (as it will be commented extensively below), rather than on the PEDOT electronic structure. It should be noted that the conductivity axis in **Figure 1** is displayed logarithmically, thus the difference in conductivity of samples such as DMF-AD and DMF-PT is quite significant (354 and 723 S cm\(^{-1}\), respectively).

The surface morphology and bulk structure of the films were investigated using atomic force microscopy (AFM) and GIWAXS in order to establish a correlation between the conductivity and the film structure. AFM images for all the samples are reported in **Figure 2**. The AFM image of the pristine film reflects the so-called core–shell structure where conductive PEDOT chains are surrounded by an insulating PSS shell.\(^{[19,20]}\) As expected, Tol-AD and Tol-PT films exhibited similar morphology to the pristine film due to the little effect on the structure of this low polarity solvent. For IPA-AD and MeOH-AD films, the surface morphology exhibits clear difference with respect to the pristine film and bigger grains are visible (highlighted in **Figure 2** with white dash box). This indicates an increase in the relative crystallinity (RC), which is confirmed by X-rays and will be discussed in the GIWAXS part below. In contrast, IPA-PT and MeOH-PT showed different surface morphology. Compared with the pristine film, there is only a minor elongation of the grains which is visible in the IPA-PT film (highlighted in **Figure 2** with white circle). Similar but more significantly elongated structures are observed on the surface of the MeOH-PT film as well as of some other films exhibiting higher conductivity, namely, DMSO-AD and DMSO-PT. Due to the high polarity and sufficient contact time with the solvent, the DMSO-PT film developed a clear phase separation and
showed a fibrillar-like structure (highlighted in Figure 2 with white circle). The formation of such elongated structures is well reported in literature and is inferred to the strong affinity of DMSO toward PSS.\textsuperscript{[21,22]} The increased phase separation may be also ascribed to a decreased PSS–PSS interactions, as proved by theoretical simulations.\textsuperscript{[17]} The transition from a globular core–shell structure to an elongated fibrous network dramatically increases the carrier mobility, causes percolation, and thus leads to a high conductivity as reported by many researchers.\textsuperscript{[6,8]} The conductivity and AFM results presented here suggest that polar solvents with relative dielectric constant higher than 17.9 (the value of IPA) would trigger film morphology restructuring and thus lead to better charge mobility. Notably, DMF\textsubscript{AD} and DMF\textsubscript{PT} did not show any elongated nanodomains or fibrous network structure. Their high conductivity cannot be thus explained based on their surface structure.

GIWAXS measurements were performed in order to detect how these solvents change the overall film structure. The GIWAXS patterns are shown in Figure 3a and the related line cuts along the vertical quasi out-of-plane direction ($q_z$) and along the horizontal in-plane direction ($q_y$) are reported in Figure S2 in the Supporting Information. In the high angle region, the pristine

\[ \text{Scheme 1. a) Materials under study and b) In situ GIWAXS experimental setup.} \]
sample showed a broad peak at $q ≈ 1.77 \, \text{Å}^{-1}$ which belongs to the $\pi-\pi$ stacking of PEDOT chains and another broad peak located at $q ≈ 1.23 \, \text{Å}^{-1}$ which is assigned to randomly distributed PSS chains. In addition, along the $q_z$ direction and in the low angle part of the patterns, the pristine film exhibited two peaks located at $q_z ≈ 0.26$ and $0.52 \, \text{Å}^{-1}$ which represent the first and the second order of the layered structure (the 100 and 200 reflection, respectively) of the PEDOT nanocrystals. Similar peaks are also observed for most of the solvent-treated films, indicating that none of the solvents employed here destroyed the basic layered nanocrystal structure of PEDOT:PSS. The increase in peak intensity observed here may be attributed to a higher film crystallinity. Notably, the DMF-AD-processed film exhibited a different ratio between the two reflections located at low angles (see Figure S2a, Supporting Information). The peak located at $q_z ≈ 0.51 \, \text{Å}^{-1}$ has a surprisingly high intensity if compared to all the other samples. Moreover, conversely to what observed for all the other samples, the ratio between the location of the first and second peak in the DMF-AD film is different than 1/2. According to recent observations, the signal at $q_z ≈ 0.51 \, \text{Å}^{-1}$ can be attributed to a different type of lamellar stacking of alternating PEDOT and PSS chains. This more compact lateral stacking could lead to an enhanced charge transport in the 100 direction between the different PEDOT-rich domains, owed to the reduced interchain distance. At the same time, a shift to smaller angles of the free-PSS peak is observed for DMF-AD, suggesting a less dense free-PSS structure (see Figure S2c, Supporting Information). Moreover, a significant shift in the position of the 010 diffraction signal of the treated films is also observed in the wide-angle range. The $d$-spacings calculated from the 010 peak position ($q$ values) and associated with the PEDOT $\pi-\pi$ stacking is listed in Table S1 in the Supporting Information. For the Tol-AD, IPA-AD, and MeOH-AD films, little change is observed in the $d$-spacing around 3.53 Å with respect to the pristine film, while DMF-AD and DMSO-AD had significantly smaller $d$-spacing of about 3.49 and 3.48 Å, respectively. This observation explains the high conductivity of the DMF-AD and DMSO-AD films, as a shortened $\pi-\pi$ stacking distance between the PEDOT molecules indicated a larger $\pi$-orbital overlap and helps the de-localization of the hole carriers, increasing charge transport along the (010) direction. Moreover, due to simultaneous presence of both face-on and edge-on PEDOT crystallites in the film, both the in-plane and out-of-plane carrier mobility will be enhanced. A similar shift is observed for the MeOH-PT, DMF-PT, and DMSO-PT films too, where the 010 $d$-spacing decreased to 3.46, 3.49, and 3.47 Å, respectively. The enhanced interchain interactions caused by the 010 $d$-spacing also suggest an increase of the average film crystallinity as reported by previous research. The crystal correlation length ($\text{CCL}$) was calculated from the full-width at half-maximum (FWHM) of the PEDOT $\pi-\pi$ stacking peak ($\text{CCL} = \frac{2\pi}{\text{FWHM}}$). The CCL values along both the $q_z$ and the $q_y$ directions ($\text{CCL}_{q_z}$ and $\text{CCL}_{q_y}$) are listed in Table S1 in the Supporting Information. The pristine film had a $\text{CCL}_{q_z}$ around 2.09 nm and $\text{CCL}_{q_y}$ around 1.81 nm indicating that the face-on stacking was the dominant structure as CCL calculated from overall integrate intensity $I(q)$ is about 2.02 nm. These values are larger than the results (around 1.4 nm) reported by Palumbiny et al. for films prepared by the slot-die coating method. Generally, for each solvent, PT samples showed larger CCL values than AD samples which can well explain the trend in the electrical conductivity. Generally, the smaller the $\pi-\pi$ stacking $d$-spacing, the larger the CCL is. The highest $\text{CCL}_{q_z}$ values were found for the DMSO-PT,

---

**Figure 1.** Electrical conductivity of PEDOT:PSS thin films processed with different solvents and the two investigated processing methods.

**Figure 2.** AFM height images for the PEDOT:PSS films processed using different solvents.
DMSO-AD, and MeOH-PT films (2.26, 2.20, and 2.23 nm, respectively). Surprisingly, Tol-PT film exhibits a relatively high CCL_q values of about 2.13 nm, suggesting that Tol could also promote PEDOT crystallization and can cause a slight increase of the film conductivity. The calculated CCL_q values related to the edge-on packed crystal domains also provide interesting information. The values of MeOH-PT, DMF-PT, DMSO-AD, and DMSO-PT increased to 1.95, 2.04, 1.93, and 2.04 nm, respectively. Here, the relative change with respect to the pristine value of 1.81 nm is higher than the CCL_q. This indicates that edge-on packed nanocrystals in these samples had relatively larger size which is an advantage for conductivity enhancement. 

Interestingly, the CCL_q value for the DMF-AD film is smaller compared to the value of the pristine film, which may indicate a different mechanism for the conductivity increase of DMF with respect to the other solvents.

In Figure 3b, the π–π stacking peak intensity is plotted against the polar angle φ and the relative content of the edge-on and face-on crystallites reflecting the orientation information of each sample is listed in Table S1 in the Supporting Information. The quantity of the edge-on and face-on crystallites was estimated by integrating the areas of the I(φ) profiles versus the polar angle φ in the ranges of 0°–30° and 60°–90°, respectively. The ratio of these two integral values against the overall integral in the φ range 0°–90° gives a proper estimation for the fraction of the crystallites with edge-on and face-on orientation. For the pristine film, we estimated a face-on amount of about 0.46 and an edge-on of 0.15. Similarly, all the other samples also showed a larger amount of face-on crystallites. Among them, IPA-PT, DMF-AD, DMF-PT, DMSO-AD, and DMSO-PT exhibited a clear increase of the face-on amount. This is not in agreement with the idea that edge-on packing is beneficial to the charge transport, as these samples all exhibited a greater conductivity increase. Notably, only MeOH-PT showed a clear increase in the edge-on amount (0.16, highest among all the samples), while its face-on amount varied very little. This is interesting if we compare it with IPA-PT sample. Although IPA and MeOH are both alcohols, their effect on PEDOT:PSS film structure is opposite, making them possible tools for tuning the in-plane and out-of-plane charge transport property of PEDOT for hole transport layer applications.

To better visualize the relationship between the electric conductivity and the PEDOT structural parameters, the electrical conductivity is plotted against the π–π stacking distance and the relative crystallinity (RC) in Figure 4a,b. The RC is calculated according to the literature. Moreover, we also explored in Figure 4c the correlation between the conductivity and the average number of packed PEDOT molecules in the nanocrystal (N_{avg}), as calculated from the CCL and π–π stacking distance (more detailed information are provided in the Supporting Information). According to Figure 4a,c, we can distinguish two main groups: Group A includes DMSO-AD, DMSO-PT,
DMF-AD, DMF-PT, and MeOH-PT with $\sigma$ in the range of 300–800 S cm$^{-1}$, and Group B that includes MeOH-AD, Tol-AD, Tol-PT, IPA-AD, and IPA-PT with $\sigma < 30$ S cm$^{-1}$. As we can see in Figure 4, the two groups show a clear separation along the $x$-axis. Threshold values around $d = 3.5$ Å and $N_{\text{avg}} = 5.8$ were observed. More extended PEDOT crystallites (higher $N_{\text{avg}}$) with chains better packed along the $\pi$-direction (smaller $d$) lead to improved electrical conductivity. In Figure 4b, Group A all have an RC higher than 1.3. However, no critical value was observed as samples from Group B also exhibited quite high RC. For example, the IPA-PT film showed a large RC, but because its $\pi-\pi$ stacking distance was too large (i.e., low $\pi$ orbital overlap) and the $N_{\text{avg}}$ was also not big enough, its conductivity is not comparable to the Group A that exhibits $\sigma > 10^2$ S cm$^{-1}$. It thus seems clear that the statement “the more crystalline, the better” is not entirely true, but the quality of the crystalline packing (expressed here by the $N_{\text{avg}}$ parameter) is a more important diagnostic structural parameter with profound effect on the film conductivity.

In the following, we now concentrate on the mechanism behind the two studied processing methods. In particular, we aim to clarify some interesting and nonintuitive results, such as the large difference between the structures and hence the conductivity of the DMF-AD and the DMF-PT films, and what is the origin of the different morphology of PEDOT:PSS when processed from DMF and from DMSO. In order to study the structuring mechanism induced by the different solvents, in situ GIWAXS was performed (see Figure 5a and Figure S3, Supporting Information). Drop-casting process was monitored in real time starting from the different water/solvent PEDOT:PSS solutions. Obviously, with the increase of solvent boiling point, more time is needed to reach the dry film state. When the added solvent has a boiling point lower than water (MeOH or IPA), the onset of crystallization does not vary too much as after a first quick co-evaporation, the remaining solvent will be mainly water in both cases. Beside the duration of the crystallization process, no special differences were observed in the evolution of the GIWAXS patterns of the MeOH-AD, IPA-AD, and Tol-AD samples. In contrast, DMF-AD and DMSO-AD exhibited a distinct behavior upon drying. For DMSO-AD, a clear solvated precursor state can be observed before the crystallization started (highlighted by the white dashed circle in Figure 5a). The time window where this solvated precursor exists is about 400 s and after 1000 s evolved into free-PSS gradually (Figure 5a and Figure S4, Supporting Information). This is a direct evidence of the existence of PSSH-DMSO component in the DMSO-AD solution as shown in Figure 5b, in agreement with what simulated by Yildirim et al.\cite{17} At the same time, PEDOT crystallization occurs, which is believed to be the reason for the phase separation.\cite{27} Interestingly, the DMF-AD sample exhibits a completely different mechanism, although the boiling points and dielectric constants of DMF and DMSO are quite close. There is no obvious PSSH-DMF solvated precursor state, contrary to the DMSO-AD sample. As highlighted in Figure 5, the added DMF seems to interact with both the PEDOT and PSS polymers, without any preferential interaction with PEDOT or PSS. In the DMF-AD sample, a very broad peak located around 10–18 nm$^{-1}$ is observed before PEDOT crystallization, which subsequently evolves into free-PSS and crystalline PEDOT. Referring to the zwitterion nature of DMF,\cite{31} when the positively charged $[\text{N}(\text{CH}_3)_2]^+$ stuck to the negatively charged $-\text{SO}_3^-$ in PSS, the negative part of DMF was also interacting with the positively charged thiophene ring in PEDOT; thus we can infer the existence of a disordered PEDOT-DMF-PSSH..
precursor formed in the solution as shown in Figure 5c. Evolving from this disordered complex, the crystallization of semiconductive PEDOT domains and the insulated free-PSS matrix start at the same time, so that phase separation becomes no longer feasible, thus no fibrous structures are formed. This is in agreement with what we have observed in the AFM images and well explains the mechanism behind. These results indicate that the solvent processing has different structuring mechanisms depending on the solvent nature. This finding is crucial for modifying the PEDOT:PSS film’s properties for various applications, like transparent hole transport layer in the field of solar cells,[32–34] neuromorphic functional materials,[35,36] and bio-sensing.[37,38]

For PT-processed films, no obvious peak shift was observed during the drying of solvent drop, which means that either the solvent did not influence the intermolecular stacking distances or the distances were decided before the start of the X-ray acquisition (about 100 s later after the start of the solvent evaporation). It should be noted that a significant shift of the peak position and peak width was not observed in the in situ AD experiments, beside for the shift in the free-PSS distance for the DMF-AD and DMSO-AD experiment (see Figure S4, Supporting Information). However, it is obvious that the peak intensity changes dramatically during drying. As shown in Figure S5a in the Supporting Information, the evolution of the main GIWAXS peaks exhibited different behaviors for MeOH-PT, DMF-PT, and DMSO-PT samples (Figure S5b–d, Supporting Information). All the GIWAXS signals exhibited an increase during the drying process for the DMF-PT and DMSO-PT samples, but the relative increase is higher for DMF-PT than DMSO-PT, which well explains the higher RC calculated from the ex situ data of the DMF-PT sample. Interestingly, the 100 peaks of MeOH-PT showed a slight decrease over time. This indicates that MeOH has a great affinity for the system and can even penetrate into the PEDOT:PSS layered domains, altering the molecular packing along the 100 direction. This is also evidenced by the fact that the 100 peak (and the 200 peak as well) of MeOH-PT are shifted to smaller q-values if compared to the ones of DMF-PT and DMSO-PT. At the same time, the π–π stacking and free-PSS peaks of the MeOH-PT sample change with time similarly to what observed for DMSO-PT (see Figure S5c,d, Supporting Information).

The effect of the different solvents onto the PEDOT:PSS structure can also be rationalized looking at the polymer–solvent affinity. The Flory–Huggins χ parameter can be used as a measure of the interaction between the different solvents and polymers. Namely, the lower the χ parameter, the higher the polymer–solvent affinity is.[39,40] The Flory–Huggins χ interaction parameter for all the solvents and PSS was calculated and is listed in Table 1 following the equation

$$\chi = \frac{V_s}{RT} \left(\delta_s - \delta_p\right)^2 + 0.34$$  \hspace{1cm} (1)

where $V_s$ is the molar volume of solvents, $\delta_s$ is the solubility parameter of solvents, and $\delta_p$ is the solubility parameter of polymer. MeOH exhibits the highest interaction among all the solvents used, with a χ parameter of 2.4, followed by DMSO ($\chi = 4.9$) and DMF ($\chi = 6.7$). These values confirm the increase in conductivity and the structural changes observed for these
Table 1. Solvent–PSS interaction parameters calculated for the films processed via the PT method.\(^{41,42}\) Note: The \(T\) values listed here are the drying temperatures for each sample (namely, 35, 41, 56, 130, and 140 °C for MeOH, IPA, Tol, DMF, and DMSO, respectively).

| Solvents | Polarity | \(V_s\) [cm\(^3\) mol\(^{-1}\)] | \(T\) [K] | \(\delta_1\) [MPa\(^{0.5}\)] | \(\delta_2\) [MPa\(^{0.5}\)] | \(\chi\) |
|----------|----------|------------------|---------|-----------------|-----------------|-----|
| Tol      | 2.4      | 105.9            | 329     | 18.3            | 41.3            | 20.8|
| IPA      | 17.9     | 76.4             | 314     | 23.6            | 41.3            | 9.5 |
| MeOH     | 32.7     | 40.4             | 308     | 29.7            | 41.3            | 2.4 |
| DMF      | 36.7     | 77.1             | 403     | 24.7            | 41.3            | 6.7 |
| DMSO     | 46.7     | 71.0             | 413     | 26.4            | 41.3            | 4.9 |

three solvents when the PT processing method was used. Moreover, the greater affinity of DMSO toward PSS with respect to DMF-PSS confirms the different behavior observed in the in situ results of the AD-processed sample, where demixing between a PSS-DMSO phase and PEDOT crystallites was observed. In addition, when we compare the \(\chi\) value of MeOH with IPA, it becomes easy to explain the obvious orientation difference between them as it is shown in Table S1 in the Supporting Information. The much lower value for the PSS/Methanol \(\chi\) parameter (reflecting the higher polarity of MeOH with respect to IPA) suggests a stronger interaction of PSS with the MeOH, leading to a profound restructuring of the system toward a more phase-separated structure with highly crystalline and ordered PEDOT domains. All these factors have beneficial effect on the electron conductivity.

### 3. Conclusions

In summary, a systematic and fundamental study was performed on the effects that different organic solvents have on the PEDOT:PSS structure and electrical conductivity when they are used as additive to the starting solution or as post-treatment media. Ex situ GIWAXS together with AFM have been employed to unveil the structure–property relationship of drop-coated PEDOT:PSS films. Based on our observation, high conductivity is not necessarily related to the overall sample crystallinity, but rather to a shortened \(\pi\)-\(\pi\) stacking distance (i.e., higher \(\pi\)-\(\pi\) stacking peak \(q\) value in GIWAXS) and to a higher number of PEDOT chains coherently packed in the crystalline domains (\(N_{coh}\)), indicating the importance of the quality and size of the nanocrystals rather than only the quantity of them. In addition, a larger phase separation observed by AFM also helps to increase the electrical conductivity by improving the coherence of the charge transportation among the PEDOT domains, which suggests a good distribution of PEDOT in PSS to improve the conductivity property. The mechanism of crystal formation was also elucidated by using in situ GIWAXS. Different kinds of precursors were observed before the PEDOT crystallization sets in. In particular, two different structuring mechanisms were observed when DMF and DMSO are added to the PEDOT:PSS:water solution. PEDOT crystals and free-PSS developed simultaneously from the supersaturated solution when DMF in water was used. On the contrary, in the presence of DMSO, a PSS-DMSO precursor phase was observed which resulted in a greater phase separation between the PEDOT domains and PSS matrix. The preference of the DMSO for the PSS phase promotes crystallization of PEDOT into crystalline domains of better quality than the ones observed for DMF, allowing for better film electrical conductivity. We hope that this contribution may be an inspiration for researchers to pave the way toward more efficient strategies to optimize the structural properties of conductive polymers in various application fields, such as flexible electronics, sensors, and organic photovoltaics.

### 4. Experimental Section

**Materials:** PEDOT:PSS (Clevios PH1000) was purchased from Heraeus. DMSO, DMF, toluene, IPA, and MeOH were purchased from Sigma Aldrich. All the chemicals were used as received.

**Film Preparation:** For AD processing, a volume fraction of 5% solvents was added into the pristine PEDOT:PSS solution. Before drop casting, boro-glass (17.8 mm × 13.8 mm × 0.7 mm) substrates used for electrical conductivity measurement and bare Si wafer substrates used for morphology characterization were washed successively with detergent, ethanol, acetone, and i-propanol. After a further 10 min UV–ozone treatment, 80 µL of the solution was dropped onto the substrates and was left to dry overnight. After drop casting, the PEDOT:PSS films were annealed at 130 °C for 20 min and then homogenous films were acquired. For PT processing, 60 µL of solvent was dropped onto the prepared pristine films and then the films were left drying at 35, 41, 56, 130, and 140 °C for MeOH, IPA, Tol, DMF, and DMSO, respectively.

**Film Characterization:** The electrical conductivity of the films was measured with four-point probe system (Ossila). The film thicknesses were measured by profilometer (Veeco, Dektak 6M). The results of DMSO-AD and DMSO-PT as two examples are shown in Figure S6 in the Supporting Information, and a table of the result of all the samples is also provided. AFM measurements were carried out on a Veeco Dimension V scanning probe microscope (Plainview, NY, USA). Veeco RTESPw tips (resonant frequency 267–294 kHz, spring constant 20–80 N m\(^{-1}\)) were used in the tapping mode. Software WxSM (Version 4.0 Beta 9.1, Madrid, Spain) was used to analyze the obtained AFM images.[43]

GIWAXS measurements were carried out at the Dutch-Belgium Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, particularly optimized for polymer investigation.[44–46] The sample-to-detector distance was about 121 mm and an X-ray wavelength \(\lambda = 1.033\) Å was used. The incident angle was set as 2°. All images were recorded using a Frelon detector with pixel size 47 µm × 47 µm. The scattering angle scale was calibrated using the known peak position from a standard Silver Behenate sample. GIWAXS images during the ex situ observation were acquired using a 30 s per frame temporal resolution. The duration was 20 min for MeOH-AD, IPA-AD, Tol-AD, and all the PT process, and was 30 min for DMF-AD and DMSO-AD. Static images were acquired at the end of each spin-coating experiment with an exposure of 60 s. The experiment was repeated for three different times using identical spin-coating parameters and reproducible results were obtained. The beam center position and the angular range were calibrated using a silver behenate standard sample. GIWAXS patterns and intensities were reduced using a home-made MATLAB-based code. The GIWAXS patterns were corrected for the so-called missing wedge correction and were presented as a function of the vertical \(q_y\) and parallel \(q_z\) scattering vectors, and the scattering vector coordinates for the GIWAXS geometry are given by

\[
\begin{align*}
q_y &= \frac{2\pi}{\lambda} \left[ \cos(2\theta_f) \cos(\alpha_f) - \cos(\alpha_i) \right] \\
q_z &= \frac{2\pi}{\lambda} \left[ \sin(2\theta_f) \cos(\alpha_f) \right] \\
q_x &= \frac{2\pi}{\lambda} \left[ \sin(\alpha_i) + \sin(\alpha_f) \right]
\end{align*}
\]
where $2\theta$ is the scattering angle in the horizontal direction and $q_z$ is the exit angle in the vertical direction. The parallel component of the scattering vector is thus calculated as $q_y = \sqrt{q_x^2 + q_z^2}$. $I(q)$ is integrated over the $\pi$-$\pi$ stacking peak center, and the width of it is set to ±0.1 Å⁻¹. The average number of packed PEDOT chains in the nanocrystal discussed in the main text was calculated as

$$N_{avg} = \frac{CCL_{-q_y} \times \%}{d} + \frac{CCL_{+q_y} \times \%}{d}$$

where CCL$q_y$ and CCL$q_z$ represent the in-plane and out-of-plane correlation length of the crystal, and $\%$ represent the edge-on and face-on fraction in the film, and $d$ represents the $\pi$-$\pi$ distance of the packed PEDOT chains.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors declare no conflict of interest.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

film formation mechanism, in situ GIWAXS, PEDOT:PSS, polar solvent processing, structure–property relationship

Received: April 12, 2020
Revised: June 15, 2020
Published online: July 29, 2020

[1] H. Shi, C. Liu, Q. Jiang, J. Xu, Adv. Electron. Mater. 2015, 1, 1500017.
[2] B. J. Worfolk, S. C. Andrews, S. Park, J. Reinspach, N. Liu, M. F. Toney, S. C. B. Mannsfeld, Z. Bao, Proc. Natl. Acad. Sci. USA 2015, 112, 14138.
[3] Z. Fan, P. Li, D. Du, J. Ouyang, Adv. Energy Mater. 2017, 7, 1602116.
[4] N. Saxena, B. Pretzel, X. Lamprecht, L. Bießmann, D. Yang, N. Li, C. Bilko, S. Bernstorf, P. Müller-Buschbaum, ACS Appl. Mater. Interfaces 2019, 11, 8.
[5] R. Kroon, A. Desalegn, D. Mengistie, J. Kiefer, J. D. Hyynen, Y. Ryan, C. Mu, Chem. Soc. Rev. 2016, 45, 6147.
[6] Y. Honma, K. Itoh, H. Masunaga, A. Fujiwara, T. Nishizaki, S. Iguchi, T. Sasaki, Adv. Electron. Mater. 2018, 4, 1700490.
[7] A. M. Nardes, R. A. J. Janssen, M. Kemerink, Adv. Funct. Mater. 2008, 18, 865.
[8] S. Zhang, Z. Fan, X. Wang, Z. Zhang, J. Ouyang, J. Mater. Chem. A 2018, 6, 7080.
[9] Z. Zhu, C. Liu, F. Jiang, J. Xu, E. Liu, Synth. Met. 2017, 225, 31.
[10] D. T. W. Toolan, A. Isakova, R. Hodgkinson, N. Reeves-McLaren, O. S. Hammond, K. J. Edler, W. H. Briscoe, T. Arnold, T. Gough, P. D. Topham, J. R. Howse, Macromolecules 2016, 49, 4579.
[11] J. Y. Kim, J. H. Jung, D. E. Lee, J. Joo, Synth. Met. 2002, 126, 311.
[12] Y. Wang, L. Yang, X. Shi, X. Shi, L. Chen, M. S. Dargusch, J. Zou, Z. Chen, Adv. Mater. 2019, 31, 1807916.
[13] G.-H. Kim, L. Shao, K. Zhang, K. P. Pipe, Nat. Mater. 2013, 12, 719.
[14] C. M. Palumbini, F. Liu, T. P. Russell, A. Hexemer, C. Wang, P. Müller-Buschbaum, Adv. Mater. 2015, 27, 3391.
[15] J. Liu, L. Qiu, G. Portale, M. Koopmans, G. ten Brink, J. C. Hummelen, L. J. A. Koster, Adv. Mater. 2017, 29, 1701641.
[16] C. J. Takacs, Y. Sun, G. C. Welch, L. Perez, X. Liu, W. Wen, G. C. Bazan, A. J. Heeger, J. Am. Chem. Soc. 2012, 134, 16597.
[17] E. Yildirim, G. Wu, X. Yong, T. L. Tan, Q. Zhu, J. Xu, J. Ouyang, J. S. Wang, S. Wang, J. Mater. Chem. C 2018, 6, 5122.
[18] Q. Jiang, C. Liu, H. Song, H. Shi, Y. Yao, J. Xu, G. Zhang, B. Lu, J. Mater. Sci.: Mater. Electron. 2013, 24, 4240.
[19] T. Horii, Y. Li, Y. Mori, H. Okuzaki, Polym. J. 2015, 47, 695.
[20] D. Alemu, H. Y. Wei, C. K. Ho, C. W. Chu, Energy Environ. Sci. 2012, 5, 9662.
[21] X. Wang, A. K. K. Kyaw, C. Yin, F. Wang, Q. Zhu, T. Tang, P. I. Yee, J. Xu, RSC Adv. 2018, 8, 18334.
[22] J. P. Thomas, L. Zhao, D. McGrillivray, K. T. Leung, J. Mater. Chem. A 2014, 2, 2383.
[23] Q. Wei, M. Mukaida, Y. Naitoh, T. Ishida, Adv. Mater. 2013, 25, 2831.
[24] L. Bießmann, N. Saxena, N. Hohn, M. A. Hossain, J. C. G. Veinot, P. Müller-Buschbaum, Adv. Electron. Mater. 2019, 5, 1800654.
[25] W. Shi, T. Zhao, J. Xi, D. Wang, Z. Shuai, J. Am. Chem. Soc. 2015, 137, 12929.
[26] S. Kee, N. Kim, B. S. Kim, S. Park, Y. H. Jang, S. H. Lee, J. Kim, J. Kim, S. Kwon, K. Lee, Adv. Mater. 2016, 28, 8625.
[27] E. Dauzon, A. E. Mansour, M. R. Niazi, R. Munir, D. M. Smailies, X. Sallenave, C. Plesse, F. Goubard, A. Amassian, ACS Appl. Mater. Interfaces 2019, 11, 17570.
[28] E. J. W. Crossland, K. Trenfel, F. Fischer, K. Rahimi, G. Reiter, U. Steiner, S. Ludwigs, Adv. Mater. 2012, 24, 839.
[29] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. De Leeuw, Nature 1999, 401, 685.
[30] S. M. Kim, C. H. Kim, Y. Kim, N. Kim, W. J. Lee, E. H. Lee, D. Kim, S. Park, K. Lee, J. Rivnay, M. H. Yoon, Nat. Commun. 2018, 9, 3858.
[31] M. B. Shundalau, P. S. Chybirai, A. I. Komyak, A. P. Zazhogin, M. A. Ksenofontov, D. S. Umreiko, J. Appl. Spectrosc. 2011, 78, 326.
[32] X. Fan, W. Song, T. Lei, B. Xu, F. Yan, N. Wang, H. Cui, Z. Ge, Mater. Chem. Front. 2019, 3, 901.
[33] H. Tang, Y. Shang, W. Zhou, Z. Peng, Z. Ning, Sol. RRL 2019, 3, 1800256.
[34] W. C. Lai, H. C. Yu, S. H. Yang, T. F. Guo, P. Chen, L. J. Lin, H. C. Hsu, A. Singh, C. W. Chu, Org. Electron. 2019, 73, 266.
[35] R. Kozma, R. E. Pino, C. G. Pazzienza, Advances in Neuromorphic Memristor Science and Applications, Springer, Netherlands 2012.
[36] P. Gkoupidenis, N. Schafer, B. Garlan, G. C. Malliaris, Adv. Mater. 2015, 27, 7176.
[37] S. Zhang, Y. Chen, H. Liu, Z. Wang, H. Ling, C. Wang, J. Ni, B. C. Saltik, X. Wang, X. Meng, H. Kim, A. Baidya, S. Ahadian, N. Shamsamakhi, M. R. Dokmeci, J. Trava-Sejdic, A. Khademhosseini, Adv. Funct. Mater. 2020, 30, 2070005.
[38] S. Zhang, H. Ling, Y. Chen, Q. Cui, J. Ni, X. Wang, M. C. Hartel, X. Meng, K. J. Lee, J. Lee, W. Sun, H. Lin, S. Emaminejad, S. Ahadian, N. Shamsamakhi, M. R. Dokmeci, A. Khademhosseini, Adv. Funct. Mater. 2020, 30, 1906016.
[39] M. L. Huggins, Br. Polym. J. 1972, 4, 465.
[40] P. J. Flory, J. Chem. Phys. 1942, 10, 51.
[41] M. N. Kobrak, Green Chem. 2008, 10, 80.
[42] W. H. Ferrell, D. I. Kushner, M. A. Hickner, J. Polym. Sci., Part B: Polym. Phys. 2017, 55, 1365.
[43] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, A. M. Baro, Rev. Sci. Instrum. 2007, 78, 013705.
[44] M. Borsboom, W. Bras, I. Cerjak, D. Detollenaere, D. Glastra Van Loon, P. Goedtkindt, M. Konijnenburg, P. Lassing, Y. K. Levine, B. Munneke, M. Oversluizen, R. Van Tol, E. Vlieg, J. Synchrotron Radiat. 1998, 5, 518.
[45] W. Bras, I. P. Dolbnya, D. Detollenaere, R. Van Tol, M. Malfois, G. N. Greaves, A. J. Ryan, E. Heeley, J. Appl. Crystallogr. 2003, 36, 791.
[46] G. Portale, D. Cavallo, G. C. Alfonso, D. Hermida-Merino, M. Van Drongelen, L. Balzano, G. W. M. Peters, J. G. P. Goossens, W. Bras, J. Appl. Crystallogr. 2013, 46, 1681.