



# Significant Mobility Enhancement by Semicrystalline Polymers Additive for Crystallization and Charge Transport in Organic Field-effect Transistor

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## Abstract

The incorporation of semi-crystalline polymers as additives with small-molecule organic semiconductors has emerged as a pioneering method for the alteration of crystallization processes, thin film morphologies, and charge carrier mobility within organic semiconductor matrices. In this paper, we utilize the intrinsic attributes of polyethylene oxide (PEO), acting as a semi-crystalline polymer additive, to modulate the crystallization, phase segregation and charge transport of 6,13-bis(triisopropylsilyl) pentacene (TIPS pentacene). To understand the synergistic effects between varying molecular weights (8, 100, 300 and 900 K) of PEO and the crystallization behavior of TIPS pentacene, we conducted a quantitative analysis of the films' relative crystallinity and crystallographic morphology employing X-ray diffraction (XRD) and optical microscopy. Our findings indicate that higher molecular weight PEOs (300K and 900K) exhibit reduced molecular chain activity, resulting in lower crystallinity at increased doping ratios. Furthermore, attributes such as a high dielectric constant and a substantial melting point, combined with favorable thermoplastic properties, predispose these films to a more susceptible phase separation within the crystalline matrix. Conversely, films with lower molecular weight PEOs (8 and 100 K) showed lesser impact from molecular chain dynamics, leading to enhanced crystal morphology, higher crystallinity, and improved charge carrier mobility by up to 11 times. This substantial enhancement underscores the potential of employing low molecular weight semi-crystalline polymers as additive agents in the development of advanced organic semiconductor devices.

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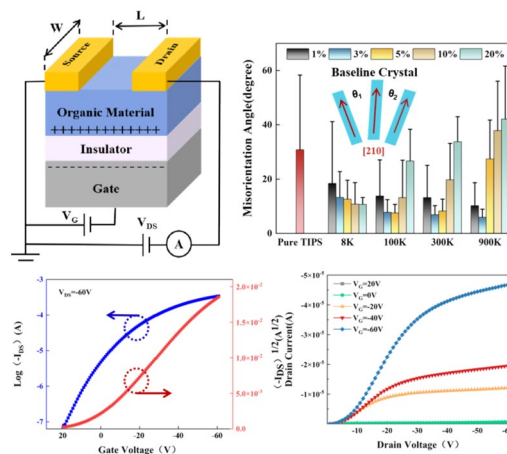
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## Graphical Abstract



**Keywords** Small molecule organic semiconductor · Semi-crystalline polymers · Molecular weight · Film morphology · Relative crystallinity

Recent advancements in the research of organic thin-film transistors (OTFTs) have been substantial, particularly in the development of various solution-processing techniques [1–13]. However, the random orientation of crystals and variations in carrier mobility have created a huge challenge for the application in organic electronics [14–22]. To address these issues, researchers have been focusing on optimizing the molecular design and deposition techniques to enhance the performance and consistency of these materials. Therefore, TIPS pentacene, as a *p*-type organic semiconductor, has become a benchmark semiconductor [23–29] for a large number of related studies. For example, Knepe et al. [24] selected 6,13-bis(triisopropylsilyl) pentacene (TIPS pentacene), which is adapted to a low-temperature, low-cost solution-processing mode, as the preferred choice for the preparation of ultrashort-channel transistors. Not only that, Jousselin-Oba et al. [30] utilized TIPS pentacene's excellent compatibility between stability and solubility to prepare two surrounding synthetic materials, tetracenotetracene (TT) and pentacenopentacene (PP), for modifying the  $\pi$ -topology of molecular organic semiconductors.

The molecular structure of TIPS pentacene is shown in Fig. S1a. Due to its acene unit and substrate side-pair arrangement, the bulky side groups on both sides disrupt the edge-to-face interactions of the aromatic ring [31–37], and further destroy the herringbone packing motifs, which makes TIPS pentacene more resistant to oxidation and degradation [38–41]. Meanwhile, the carbon–carbon triple bond keeps bulky side group substitution at a distance from the aromatic ring [42–44]. This makes  $\pi$ - $\pi$  stacking

between TIPS pentacene molecules possible, and results in improved  $\pi$ -orbital coupling and charge carrier mobility. Due to these great potentials, TIPS pentacene has been showcased in various high performance organic electronic applications [45–51]. For instance, Ajayan et al. [52] utilized TIPS pentacene for flexible/wearable electronics applications in view of the fact that it provides good air stability and high hole mobility in OTFTs. Wang et al. [53] employed the strong charge transport capability inherent in TIPS pentacene as a high-quality crystalline thin film for fabricating an ultrasensitive NO<sub>2</sub> sensor. Additionally, Singh et al. [54] prepared a low-cost heterojunction photodiode by utilizing the high carrier mobility and air stability of TIPS pentacene for application in UV photodetectors.

However, better crystal morphology as well as higher charge transport is usually obtained when TIPS pentacene is mixed and crystallized with polymers, primarily due to the following reasons. Firstly, the polymer additive improves the morphological homogeneity of the organic semiconductor crystals, resulting in an increase in the consistency of the transistor's performance [55, 56]. Secondly, organic semiconductors with polymer additives, such as poly ( $\alpha$ -methylstyrene) (P $\alpha$ MS) and polystyrene (PS), have the potential to initiate and promote vertical phase separation [57–59]. For example, Ohe et al. [60] investigated the phase separation dependent electrical performance of OTFTs in relation to the different molecular weights of P $\alpha$ MS as polymer additives. It was concluded that the driving force of phase separation could be explained by the Flory-Huggins theory. Chae et al. [61] also reported a significant vertical phase separation with the addition of P $\alpha$ MS to TIPS

pentacene, which enhanced the field-effect mobility of the OTFTs while further reducing its electrical hysteresis. As for the polymer additive PS, Bharti et al. [62] reported phase separation induced high carrier mobility and demonstrated electrically stable OTFTs by blending TIPS pentacene with PS. Coincidentally, the OTFTs prepared by Rahi et al. [63] using PS as a polymer additive blended with TIPS pentacene also produced phase separation, and the devices also possessed high electrical stability at different temperatures. These phase separation phenomena occur because the stability of OTFTs in air is improved when the polymer separation leads to the formation of an encapsulation layer at the air interface, separating the semiconductor crystal layer from oxygen and water [64, 65]. In addition, the phase separation also enriches a large number of organic semiconductors at the charge-transfer interface, which further improves the performance of semiconductor devices [66].

Compared to amorphous polymers, relatively few studies have been conducted on blending semicrystalline polymers as additives for the preparation of OTFTs. Semicrystalline polymers compete with organic semiconductors for crystallization when they are blended together, thus providing in-situ crystallization regulation that amorphous polymers cannot provide. In addition, the use of non-conjugated semi-crystalline polymers avoids polymer-induced  $\pi$ - $\pi$  interactions during the crystallization process [67].

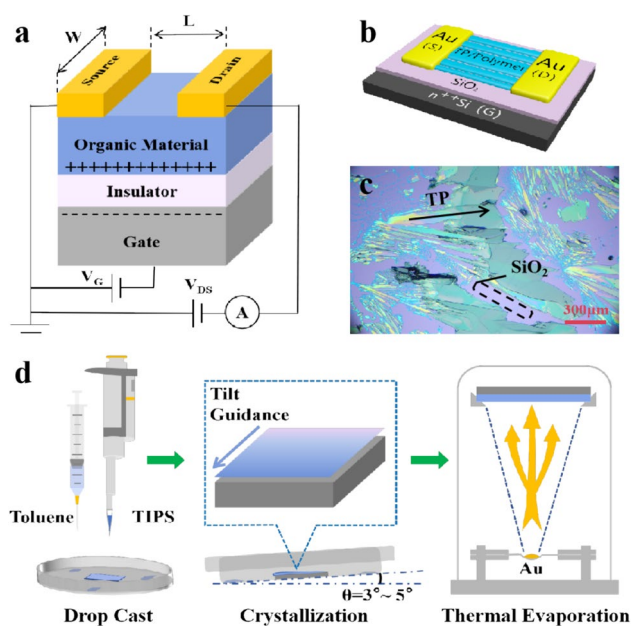
Herein, semi-crystalline polymers, poly(ethylene oxide) (PEO), a non-conjugated semi-crystalline polymer (molecular structure shown in Figure S1b), is chosen to manufacture and is available in a wide range of molecular weights. Moreover, PEO has extensive applications in construction materials, pharmaceutical production, lightweight textiles, and oil and mining industries [68]. PEO as a semicrystalline polymer is mixed with organic semiconductor TIPS pentacene as an additive, which allowed effective control of the semiconductor crystallization and charge transport. In particular, four molecular weights of PEO, each with five different mixing ratios, were studied for their effect on the crystallinity, crystal morphology and charge carrier mobility of TIPS pentacene mixing.

The polymer material PEO was purchased from Sigma Aldrich. The small molecule organic semiconductor TIPS pentacene was purchased from Tokyo Chemical Industry (TCI). A total of four different molecular weights of PEO, including 8K, 100K, 300K and 900K, were used in this work. Firstly, two separate solutions with a concentration of 3 mg/mL were prepared using toluene as the solvent and TIPS pentacene and PEO as solutes, respectively. The solution of TIPS pentacene was stirred for 30 min at ambient temperature, while the solution of PEO was heated and stirred for 30 min at 70 °C to ensure that all PEO was

dissolved. Next, to find the optimal weight ratio of PEO, PEO was added to TIPS pentacene at different ratios, including 1, 3, 5, 10 and 20%. The mixed solution was stirred at a room temperature for an additional 30 min. Finally, the solutions with different ratios were drop-cast onto a silicon substrate with a 300 nm thick silica dielectric layer. In particular, in order to reduce the thickness of the crystallized layer, 20  $\mu$ l of the mixed solution was deposited onto a substrate with a size of approximately 1.3 cm<sup>2</sup>. The substrate was placed at an angle (3°~5°) to facilitate crystallization, and the crystal growth took place in a solvent rich environment [69–72].

Upon the completion of crystallization, to minimize the effect of metal electrodes on the crystalline films, we placed the samples in an X-ray diffractometer (XRD) to test the wide-angle physical phases in a bulk sample to obtain source data for XRD. To prepare the metal electrodes, we fabricated OTFTs by thermally evaporating 50 nm gold deposited on the crystals as source and drain. The evaporation rate is 1 Å/s at a pressure of 10<sup>-7</sup> Torr. The process of drop cast, crystallization and thermal evaporation is illustrated in Fig. 1d.

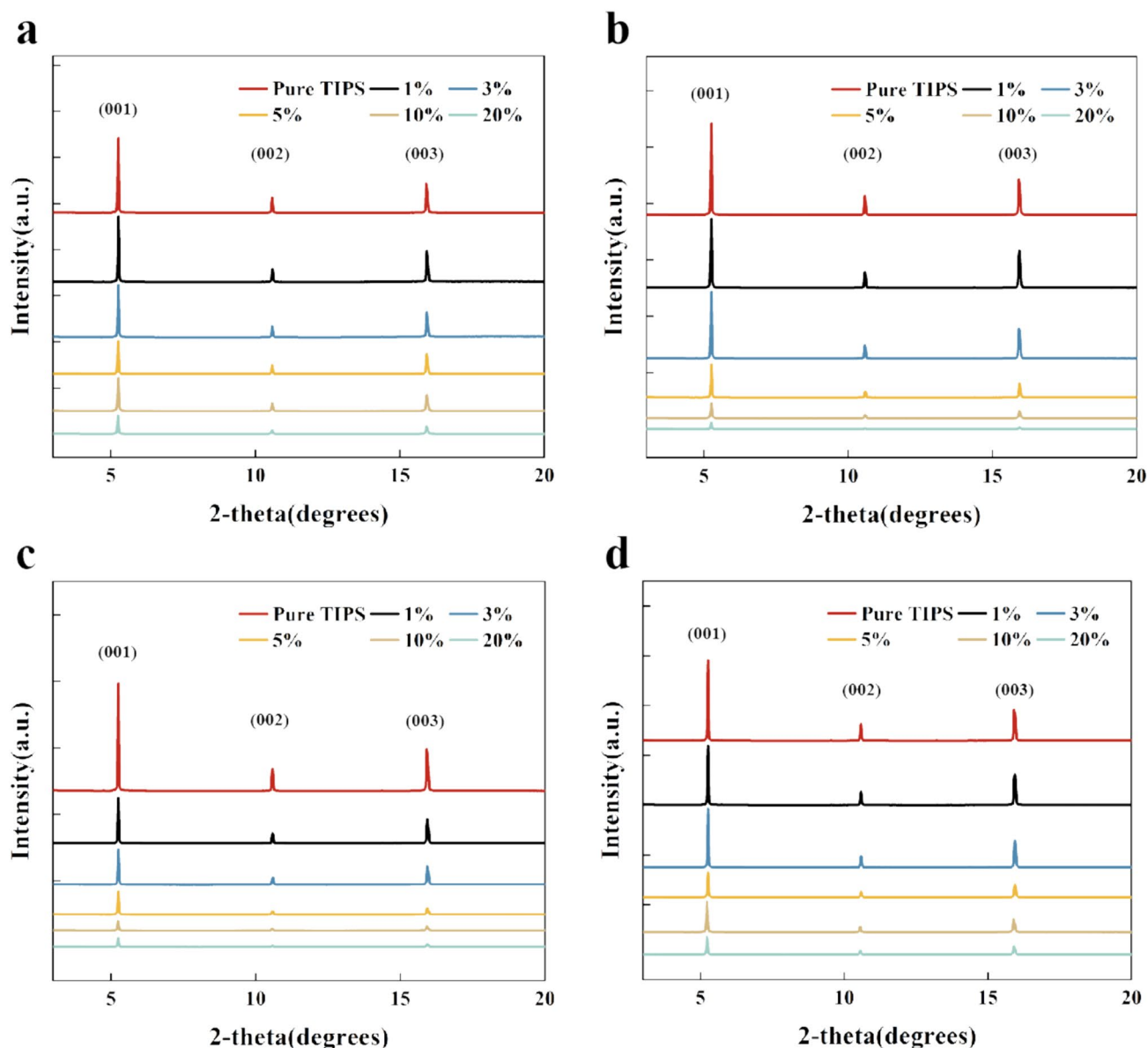
Polarized light microscopy captured images of the organic crystals. The electrical properties were characterized by measuring the output curves ( $I_{DS}$ - $V_{DS}$ ) and transfer curves ( $I_{DS}$ - $V_{GS}$ ), with a Keithley 2636B Source Meter at room temperature.



**Fig. 1** a Principle of operation of *p*-type OTFTs. b Bottom-gate, top-contact device architecture for OTFTs with *p*-type semiconductor. c An optical image of pure TIPS pentacene (TP) film. d Fabrication process of OTFTs, which is consisted of drop casting the solution, crystallization, and thermal evaporation of gold as source and drain contact electrodes

Bottom gate, top contact configuration was chosen as the transistor structure type, as shown in Fig. 1b. As illustrated in Fig. 1a, the organic semiconductor layer separates the source and drain. This layout requires that charge carriers, once injected from the electrodes, pass through the organic semiconductor layer to reach the conducting channel. The top-contact electrode, on the other hand, ensures that the organic semiconductor layer, when thin, has a large contact area, thereby reducing contact resistance and simplifying the fabrication process. As pure TIPS pentacene crystallizes, the crystals are randomly oriented and have lower coverage, as shown in Fig. 1c. According to a previous study by Ebagninin et al. [73] PEO with different molecular weights

shows significant differences in their rheological properties caused by the entanglement of light and heavy chains when dissolved in solution, which obviously has a great influence on the crystallinity as well as the crystal morphology of TIPS pentacene. In order to further systematically investigate the effect of PEO as a polymer additive on TIPS pentacene, pure TIPS pentacene crystals were set as the control group, while organic crystals with different PEO molecular weights and weight ratios were studied as the experimental group. The optimal molecular weights and optimal weight ratios of PEO were explored and determined based on both crystallinity and crystal morphology.



**Fig. 2** XRD diffractograms of pure TIPS pentacene and the blended crystals with PEO with different molecular weights including **a** 8K, **b** 100K, **c** 300K and **d** 900K

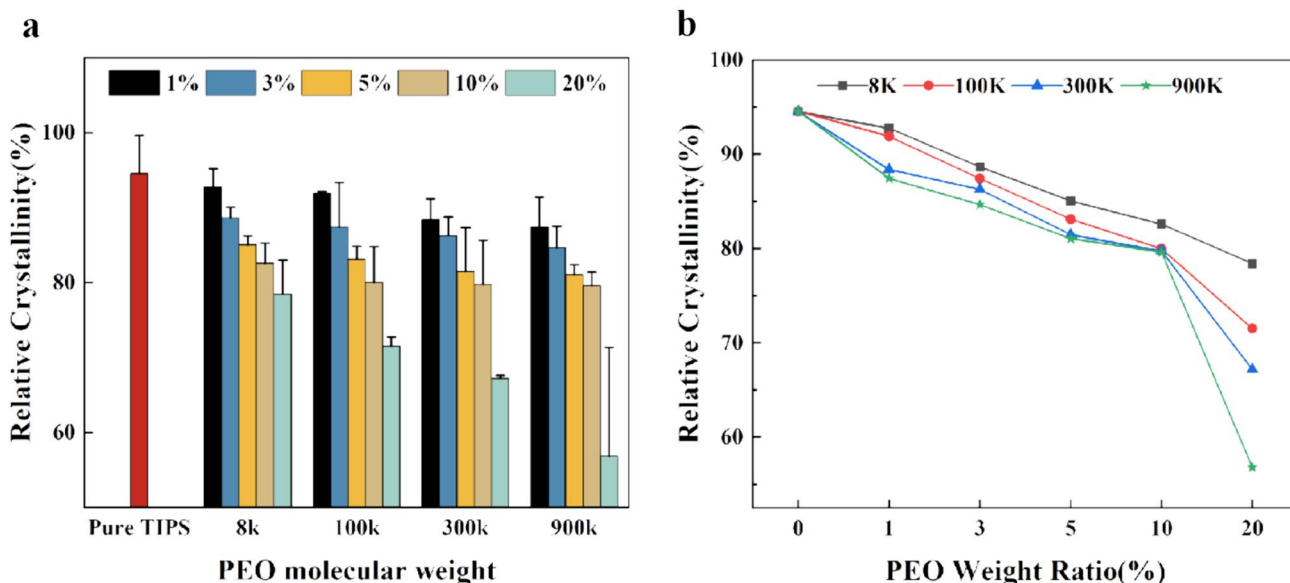
X-ray diffraction tests were performed on all substrates and obtained 21 sets of X-ray diffractograms. The data curves obtained after testing are shown in Fig. 2a–d. In order to compare the crystallinity, we fitted the curves by using the software MDI Jade 6, measured the relative crystallinity of each set of data, and compared each set of crystallinity data as shown in Fig. 3a–b. Crystallinity is the degree of integrity of the crystal structure in a material, which reflects the percentage of perfect lattices in the crystal [74]. Without considering other influencing factors, a higher relative crystallinity undoubtedly provides OTFTs a stronger charge transport capability.

The relative crystallinity of the pure TIPS pentacene crystals in Fig. 3a is  $94.5 \pm 5.07\%$ . It was also found from the histograms that the relative crystallinity of the mixed crystals decreases as the weight ratio of PEO in the mixed solution continues to increase. It is noted that the 100K molecular weight PEO at a 1% doping ratio shows a small error in relative crystallinity, indicating stable and reproducible measurements, likely due to uniform film formation and consistent crystallization processes. Conversely, at a 3% doping ratio, the error significantly increases, suggesting greater variability in crystallinity. This larger error may arise from inhomogeneous film formation, increased disorder due to polymer chain entanglement, and higher sensitivity of the X-ray diffraction technique to variations in sample thickness or density at higher concentrations. These factors introduce complexities that amplify measurement inconsistencies, leading to the observed larger error. Therefore, for the OTFTs of TIPS pentacene/PEO mixtures, a lower weight ratio of mixing is favorable for obtaining a higher

crystallinity and charge carrier mobility, if the molecular weight of PEO remains unchanged.

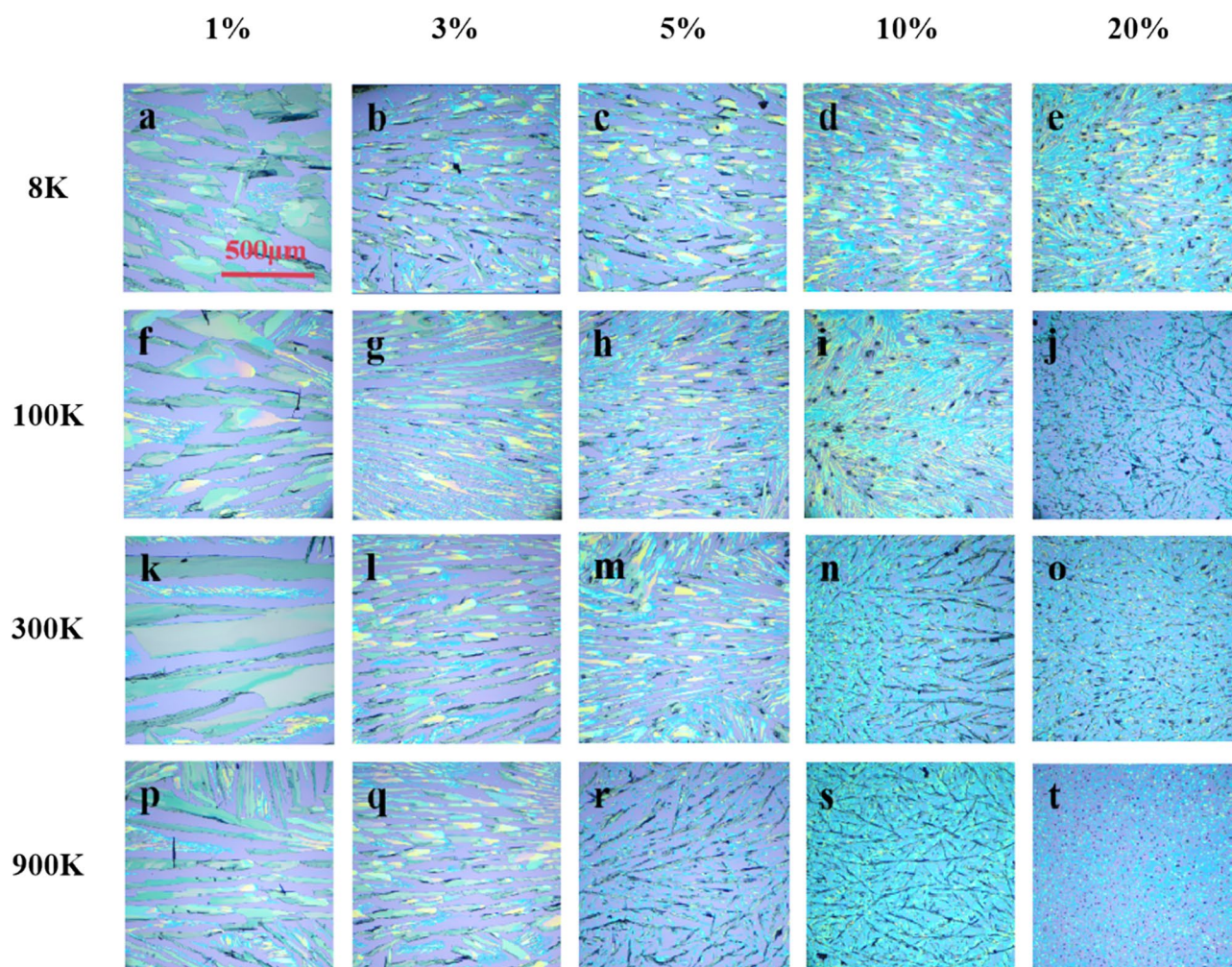
As seen in Fig. 3b, when the mixing weight ratio of PEO is constant, PEO with 8K and 100K molecular weights exhibits higher relative crystallinity compared to the counterpart with 300K and 900K molecular weights. It is well known that the molecular weight of a polymer is a quantitative parameter of the molecular chain length. In a previous study by Bunn et al. [75] the molecular chain activity of a polymer was found to decrease if the repeated length of the molecular chain increases (higher molecular weight). This slows down the crystallization of the polymer in solution at any given temperature, leading to decreased crystallinity. Thus, as the molecular weight of a polymer additive increases, the ability decreases of the molecular chains to arrange themselves into single crystals at low concentrations or into dendrites at high concentrations, which reduces the overall crystallinity of organic semiconductor crystals incorporating this polymer additive. It can be seen that the crystals formed when low molecular weight PEO is added as semi-crystalline polymer to TIPS pentacene at lower weight ratios have better relative crystallinity. For example, when 8K PEO was added to TIPS pentacene at 1, 3 and 5% by weight, the relative crystallinity was  $92.77 \pm 2.46\%$ ,  $88.66 \pm 1.36\%$ , and  $85.05 \pm 1.19\%$ , respectively. In comparison, the relative crystallinity of TIPS pentacene with 900K molecular weight PEO at 20% by weight was only  $56.81 \pm 14.53\%$ . Due to the large amount of data, see Table S1 in the Supporting Information for details.

In addition to the relative crystallinity, the crystal morphology also plays a very important role in charge transport. Figure 4 contains the crystal morphology of



**Fig. 3** Relative crystallinity statistics of pure TIPS pentacene crystals and TIPS pentacene/PEO blend crystals, as illustrated in **a** histogram and **b** line graphs



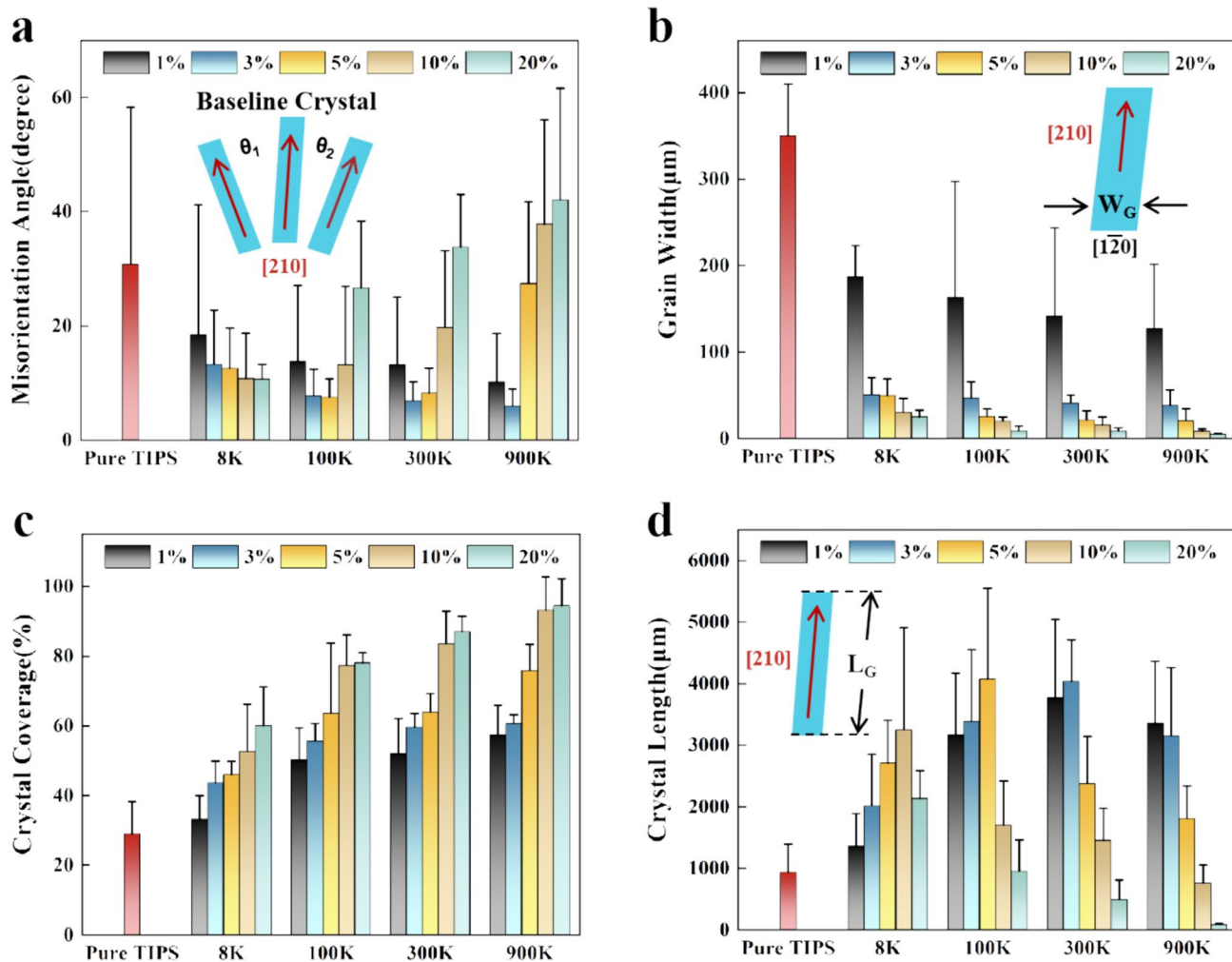


**Fig. 4** Optical images of TIPS pentacene and PEO hybrid crystals. The molecular weights of PEO are **a–e** 8K, **f–j** 100K, **k–o** 300K and **p–t** 900K. Figure **a–t** share a 500  $\mu\text{m}$  scale

TIPS pentacene mixed with different weight ratios of PEO (including four molecular weights of 8, 100, 300 and 900K). Since the solutions in this experiment were prepared by heating the PEOs to dissolve in toluene and then gradually cooling them to crystallize in a toluene-rich environment, the mixed solutions crystallized in a manner whereby the molecular chains formed single crystals or dendritic crystals according to the lamellar crystalline structure of the folded chains. From Fig. 4, it is clearly observed that the grain width of the crystals decreases with the increase of PEO mixing ratio, but the coverage of the crystal film increases gradually. In addition, the long-range ordering of the crystals is greatly improved when the PEO mixing ratio is low.

Next, the morphology of the crystals in terms of orientation angle, crystal length, grain width and crystal film coverage were quantitatively investigated. The crystal misorientation angles as shown as  $\theta_1$  and  $\theta_2$  in the inset of Fig. 5a. These two angles are formed by a pre-selected

baseline crystal with two neighboring crystals on the left and right side, respectively. The mean values of the misorientation angles for the pure TIPS pentacene crystals and the mixture crystals of TIPS pentacene/PEO were obtained based on 10 crystal measurements. For the pure TIPS pentacene crystals without the addition of PEO, the average misorientation angle is  $30.81 \pm 27.50^\circ$ . As PEO with molecular weight of 8K is mixed into TIPS pentacene at different weight ratios, the average orientation angle of the obtained crystal films starts to decrease gradually. When the mixing ratio reaches 20%, the average orientation angle is only  $10.70 \pm 2.52^\circ$ . By coincidence, when 100K, 300K and 900K molecular weight PEO is mixed in the appropriate weight ratio, the decrease of the crystal misorientation angle was also observed. The reduction of misorientation angle due to polymer additive was also previously confirmed by He et al., who reported the addition of the polymer P $\alpha$ MS led to a significant reduction in the crystal misorientation

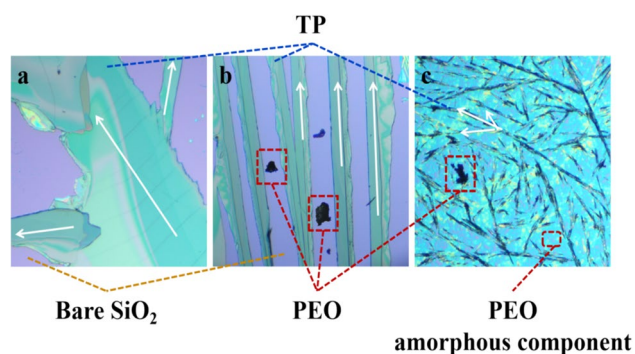


**Fig. 5** In order to compare the morphological differences between the pure TIPS pentacene crystals and the crystals of TIPS pentacene/PEO blends, histograms were plotted based on the PEO molecular weight

and mixing weight ratio, including: **a** misorientation angle ( $\theta$ ), **b** grain width  $W_G$ , **c** crystal coverage, and **d** crystal length of  $L_G$

angle of TIPS pentacene and improved the long-range ordering of the crystal film [76]. However, it is worth noting that the misorientation angle of the crystals increases inversely when the mixing ratio of PEOs of 100K and 300K molecular weights exceeds 10% by weight, and also when the mixing ratio of PEO of 900K molecular weight exceeds 5% by weight. This phenomenon can be attributed to the vertical phase segregation between TIPS pentacene and PEO. It is well known that as a semi-crystalline polymer, its semi-crystalline nature enables PEO to form crystals in a manner similar to TIPS pentacene, while at the same time, its amorphous component plays a very important role in impacting the diffusion coefficient of TIPS pentacene and the surface energy of the faceted evolution in the crystallization process.

To visualize the semicrystalline nature of PEO and the role of vertical phase polarization of the amorphous



**Fig. 6** The different types of film morphology. **a** Pure TIPS pentacene (TP) crystals, **b** mixture film crystals formed by 300K molecular weight PEO mixed with 1% by weight into TIPS pentacene, **c** mixture film crystals formed by 900K molecular weight PEO mixed with 10% by weight into TIPS pentacene



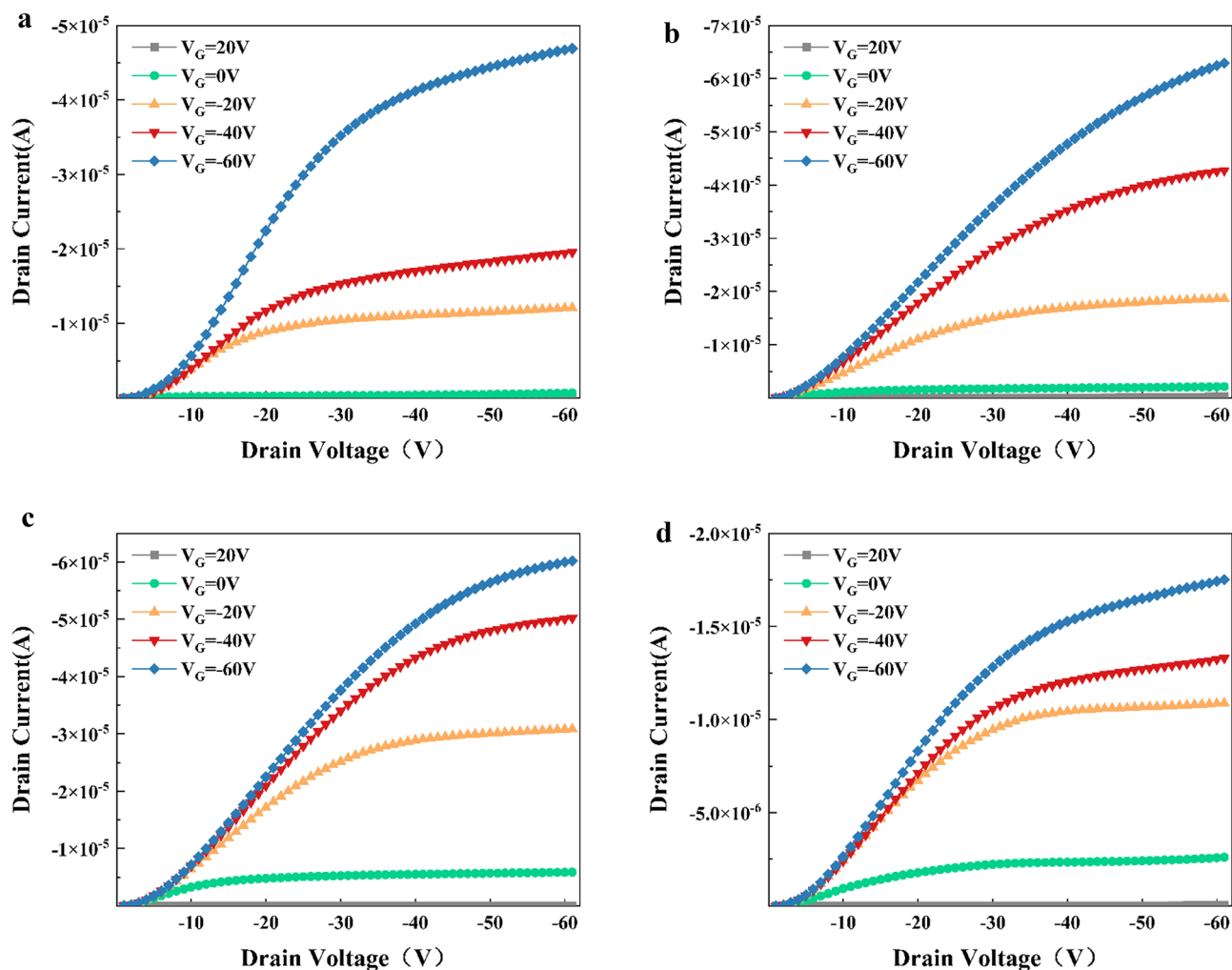
components, three representative experimental groups of thin-film microscope optical images are shown in Fig. 6a–c. When pure TIPS pentacene crystallizes (Fig. 6a), the crystal misorientation angle is large. After the high molecular weight PEO are mixed with TIPS pentacene at lower weight ratios (or low molecular weight PEO were mixed TIPS pentacene at appropriate ratios), the isotropy of the TIPS pentacene is greatly enhanced, and the PEO simultaneously nucleates and crystallizes at the periphery of the TIPS pentacene (as shown in the red boxes in Fig. 6b, c). This phenomenon is related to the physical properties of the PEO itself and the crystallization process of the mixed solution. First of all, from the point of view of physical properties, PEO has a high dielectric constant of about 3.7–3.9, which is a polar substance. The electrostatic attraction between solute molecules and materials with high dielectric constant is greater, which makes them attract each other and easy to condense. This allows PEO to interact more strongly with polar substrates in mixed solutions, thus preferentially forming an underlying structure. By coincidence, Gu et al. found that poly(vinylidene) fluoride (PVDF), a semicrystalline polymer similar to PEO, precipitated out of the solution as a substructure, before forming phase separation due to the high dielectric constant of PVDF and increased crystallinity when mixed with the organic substance dimethylphthalate (DMP) [77]. Secondly, the high molecular weight PEO has good thermoplasticity and a high melting point (about 60°C). PEO is completely dissolved in toluene by heating and then crystallizes on the substrate by dropwise addition, and its good thermoplasticity allows PEO to be uniformly distributed on the substrate surface along with the solution. As the toluene evaporates and cools down, PEO with a high melting point precipitates first out of the solution and forms a stable substrate layer on the substrate (as shown in Fig. 4n, o, s, t), which lays the foundation for the TIPS pentacene crystal growth. These two features of PEO have been previously reported in other literatures. For example, Szymczyk et al. utilized the thermoplasticity of PEO to modify the thermoplastic properties of elastomer. In their study, a series of PTT-b-PEO copolymers with different contents of flexible PEO segments were synthesized by two-step melt polycondensation, which resulted in copolymers with good thermoplastic elastomer properties [78]. In contrast, Yang et al. exploited the high melting point property of PEO to improve device stability in exploring its optical properties and self-assembling nanostructures via solvent annealing. They also created a novel intrinsic bifunctional block copolymer electret and investigated the effect of this design and self-assembly morphology on the storage of phototransistors [79]. Finally, in terms of the

solution crystallization process, the chain mobility of PEO is limited, and the higher molecular weight of PEO determines its weaker mobility and usually a slower crystallization rate at room temperature, which allows the faster-crystallizing TIPS pentacene to crystallize at the top of the amorphous region of PEO [76]. The layering phenomenon makes PEO lose the ability to guide the crystallization and diffusion of TIPS pentacene, resulting in the reverse increment of misorientation angle as observed in the optical images.

Next, average grain width  $W_G$  are determined as shown in the inset in Fig. 5b.  $W_G$  was calculated along the crystal short axis [1 20], based on 10 measurements. After summarizing the data, it is found that compared to the TIPS pentacene/PEO hybrid crystals, the crystals of pure TIPS pentacene have an average grain width of  $350.37 \pm 59.57 \mu\text{m}$ . Regardless of the influence of any molecular weight of PEO, as the weight ratio of PEO increases, the corresponding grain width appears to be reduced to different extent. This is the inevitable result of the competing crystallization between PEO and TIPS pentacene. Kleemann et al. found that when different polymers are added to TIPS pentacene as additives, the decrease in grain width leads to the loss of polycrystalline structure, and the increase in crystal defects makes it easier to trap carriers and reduces the charge-carrier mobility of the OTFTs [80]. Therefore, from the point of view of grain width, larger TIPS pentacene crystals mixed with a low weight ratio of PEO will show larger charge carrier mobility.

Afterwards, the crystal film coverage and grain length were quantitatively analyzed, as shown in Fig. 5c. Crystals with a certain degree of crystallinity, smaller misalignment angles, and higher crystal film coverage and dimensions (including crystal width and crystal length) can ensure more favorable charge transport properties over a wider range. It can be inferred from Fig. 5c that the crystal film coverage of TIPS pentacene/PEO blended crystal films increases with the increasing weight ratio of PEO mixing, which is influenced by the semicrystalline nature and amorphous components of PEO. When 900K PEO is mixed into TIPS pentacene at 20% weight ratio to form a crystal film, the coverage is as high as  $94.58 \pm 7.67\%$ . This is a significant increase compared to the coverage of  $29.00 \pm 9.28\%$  based on pure TIPS pentacene. Unlike the crystal film coverage, the crystal length of TIPS pentacene is affected by multiple factors such as the crystallization of PEO and the guidance of the amorphous component. The thin film crystals formed after the addition of PEO to TIPS pentacene in the appropriate weight ratio show signs of improvement compared to the pure TIPS pentacene





**Fig. 7** Output curve of OTFTs based on TIPS pentacene/PEO blend film. The molecular weights of PEO are **a** 8K, **b** 100K, **c** 300K and **d**. 900K

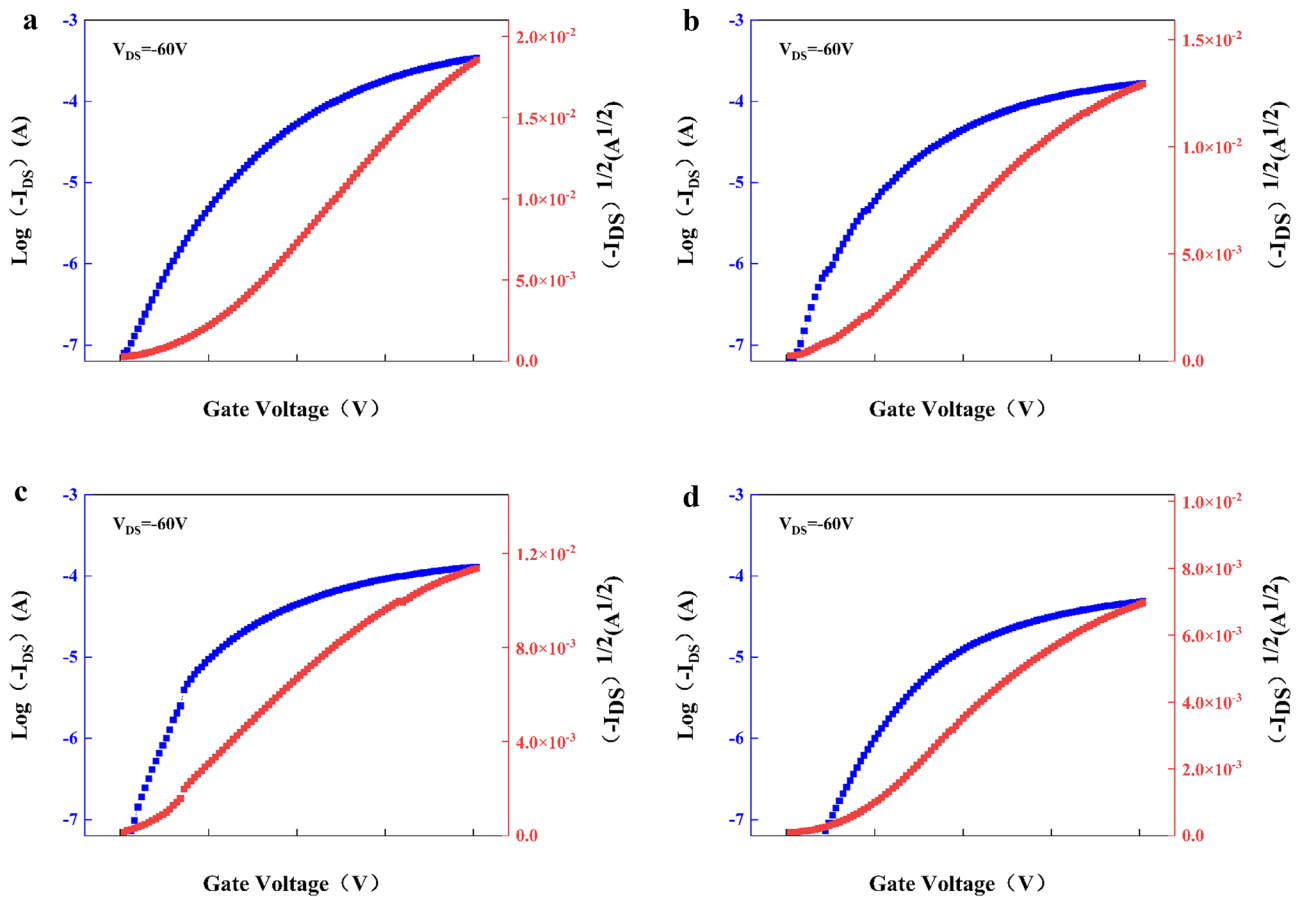
crystalline crystals as shown in Fig. 5d. The mean crystal length  $L_G$  of this study was obtained based on 10 measurements of the crystals along the long axis [210]. The pure TIPS pentacene crystal length was  $938.39 \pm 454.29 \mu\text{m}$ , while the TIPS pentacene/PEO blended thin film crystals with a molecular weight of 100 K and a mixing weight ratio of 5% had a crystal length of  $4074.20 \pm 1474.71 \mu\text{m}$ . Note that due to the long extension of the crystals on the silicon substrate, multiple microscope optical images are required for the measurements.

To measure the electrical properties of OTFTs, the output curves and transfer curves were tested as shown in Figs. 7, 8. From the transfer curve, the hole mobility of the OTFTs can be calculated based on Eq. 1:

$$I_{DS} = \mu C_i \frac{W}{2L} (V_{GS} - V_T)^2 \quad (1)$$

where  $\mu$  is the hole mobility,  $I_{DS}$  is the saturation drain current,  $C_i$  is the capacitance of the gate dielectric layer ( $11.5 \text{ nF/cm}^2$  since the  $\text{SiO}_2$  thickness of the silicon substrate for this study is 300 nm). The length and width of the conductive channel between the gold electrodes are denoted by  $L$  and  $W$ , respectively, as shown in Fig. 1a.  $V_T$  and  $V_{GS}$  denote the threshold voltage and gate source voltage.

At last, the mobility of pure TIPS pentacene film crystals with those incorporating the PEO additive with four different molecular weights were calculated and compared, as shown in Fig. 9a–d. It is found that the hole mobility of OTFTs was enhanced only for 8 and 100K PEO at mixing weight ratios of 3 and 5%. Among them, the highest value of hole mobility of the TIPS pentacene crystals mixed with 8K PEO at 3% by weight reached  $0.73 \text{ cm}^2/\text{Vs}$ . It is worth mentioning that the highest mobility of all four molecular weight PEO was obtained at a weight ratio of 3%. While our experimental results indicate that polymer additives like PEO can sometimes promote nucleation and crystallization of TIPS

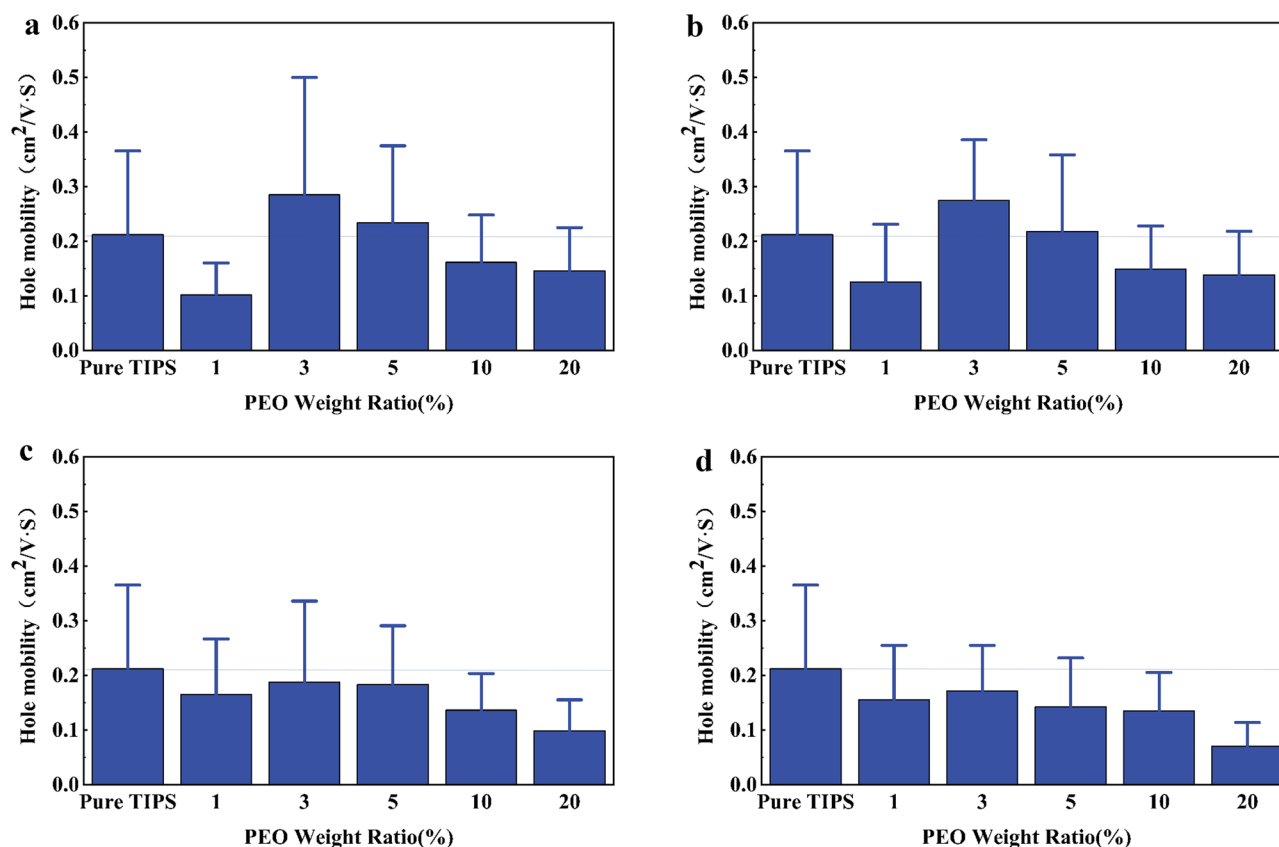


**Fig. 8** Transfer curve of OTFTs based on TIPS pentacene/PEO blend film. The molecular weights of PEO are **a** 8K, **b** 100K, **c** 300K and **d** 900K

pentacene, they can also decrease relative crystallinity, especially at higher concentrations or molecular weights. The semi-crystalline nature of PEO reduces molecular chain mobility, competing with TIPS pentacene for crystallization and thus lowering crystallinity. Even with low molecular weight PEO, crystallinity appears lower than pure TIPS pentacene because PEO introduces additional nucleation sites disrupting the perfect lattice structure. However, an appropriate doping ratio of low molecular weight PEO significantly improves crystal morphology, enhancing charge carrier mobility in OTFTs, making PEO a valuable additive despite a slight reduction in crystallinity. For reference, optical images of pure TIPS pentacene crystalline films are provided in Fig. 1c. Therefore, the improved hole mobility is attributed to the combination of the relatively high crystallinity and more superior morphology of the thin-film crystals. This is a 11 times enhancement as compared to that of the pure TIPS pentacene crystalline films as reported from a previous work [81].

In summary, we report to control the crystallization, morphology, and crystallinity of the organic small-molecule semiconductor TIPS pentacene by varying the molecular

weight and mixing weight ratio of the semicrystalline polymer PEO as an additive. We found that adding low molecular weight PEO (8K or 100K) at a 3% or 5% weight ratio ensured a relatively high relative crystallinity while maintaining a low misorientation angle and a large crystal width of the TIPS pentacene crystals, resulting in a 11-time enhancement of charge carrier mobility of up to  $0.73 \text{ cm}^2/\text{Vs}$ . This is due to that the polymer chains of low molecular weight PEO play an important role in guiding the semiconductor crystallization to form more superior crystal morphologies, while at the same time exerting less influence on the structural integrity of the TIPS pentacene crystals. Unlike the thin film crystals formed by high molecular weight PEO (300K or 900K) as an additive, the low molecular chain activity of high molecular weight PEO leads to a decrease in the crystallinity of the mixed solution. At the same time, when the mixing ratio of PEO increases above a certain percentage, its high dielectric constant, good thermoplasticity, high melting point and other physical properties enable the polymer to preferentially crystallize close to the substrate and vertically phase-separate from the organic semiconductor, eventually forming a two-layer



**Fig. 9** PEO hole mobility of pure TIPS pentacene crystal films and TIPS pentacene/PEO hybrid crystal films at different molecular weights and mixing ratios. PEO molecular weights are **a** 8K, **b** 100K, **c** 300K, **d** 900K

structure. While this increases the coverage of the thin film crystals, the ability of the polymer to control the crystal orientation is gradually weakened, which ultimately reduces the charge transport of the OTFTs. We believe that the present study systematically provides an insight into the laws of how semicrystalline polymers as additives affect the crystallization of organic semiconductors, and also presents a novel pathway for enhancing the charge carrier mobility of organic crystals.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s13391-024-00510-2>.

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## Declarations

**Conflict of interest** The authors declare that there is no conflict of interest or known competing interests associated with this work.

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