Effect and Mechanism of Solvent Properties on Solution Behavior and Films Condensed State Structure for the Semi-rigid Conjugated Polymers

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Abstract Solvents have an essential association with polymer solution behavior. However, few researches have been deeply done on this respect. In recent years, our research group focus on the study on effect of solvent properties on solution behavior and film condensed state structure for semi-rigid conjugated polymer up till to apply for optoelectronic device. Herein, influence of solvent properties including solubility of solvent, aromaticity, polarity and hydrogen bonds on semi-rigid polymer chain solution behavior, i.e. single chain conformation, chain shape, size and chains aggregated density were studied by means of static/dynamic laser light scattering (DLS/SLS) and exponential law etc. Effect of solvent properties on condensed state structure of the semi-rigid conjugated polymer film was studied by UV absorption spectroscopy, PL spectroscopy and electron microscopy etc. The essential reasons for the influence were discovered and the mechanism was revealed. It was found that solution behavior with different solvent properties had an essential physical relationship with chains condensed state structure of the semi-rigid conjugated polymers. More importantly, there was a quantitative structure-activity relationship between solution and film. The key to this relationship depended on the interaction between solvent molecules and the semi-rigid conjugated polymer chains. This interaction could also affect optoelectronic devices performance. This study is of great significance to effectively control the condensed state structure of the semi-rigid conjugated polymers in the process of dynamic evolution from solutions to films. It not only enriches the knowledge and understanding of both semi-rigid conjugated polymer solution behaviors and film condensed state physics based on polymer physics, but also is meaningful to practical application for conjugated polymer and other traditional polymer systems.

Keywords Semi-rigid conjugated polymer; Solution behavior; Solvents; Condensed state structure; Optoelectronic performance

INTRODUCTION

From the early 20th century with introducing macromolecules concept by Staudinger to the present, the research on polymer materials has been advancing unprecedentedly with polymers annual output hundreds of millions of tons in the world. In this process, basic research on polymer, such as polymer chain dynamic transformation, polymer solution behaviors etc. have got lots of attention.[1−7] The "Observation of the Sources of Global Urban Science and Technology Innovation" released in 2019 analyzed the TOP 1% highly-cited documents from 2017 to 2018,[8] and the non-fullerene solar cells were listed as one of the important research directions. And in this research direction, besides the basic synthesis of non-fullerene acceptors, recent research emphasis is focusing on optimizing the active layer morphology by selecting solvents or improving processing techniques.[9−12] This research is just dedicated to exploring some basic scientific questions about solvents. For example, whether different solvents have intrinsically physical association with the condensed state structure of both conjugated polymer solution and film? What are the key factors of determining this association? And how to use this correlation to control the film condensed state structure and optoelectronic devices efficiency of the conjugated polymer? This research aims to reveal the effect, law and mechanism of solvent properties on both solution behavior of semi-rigid conjugated polymers and the condensed state structure of films based on our research work in recent years. Firstly, it is quite necessary to understand the correlation among solvent properties, solution behavior and condensed state structure for the semi-rigid conjugated polymer.

The Relationship between Polymer Solution Behavior and Its Solvent Properties

Polymer solution is defined as a thermodynamically stable binary or multi-system formed by dissolving polymer in solvent.[13] The essence on polymer solution research is just to polymer solvents research. The research on polymer solutions is of great theoretical and practical significance for the
development and application for polymer materials.\cite{14-17} For example, under specific polymer solution conditions (such as $\theta$ temperature or $\theta$ solvent), the molecular chains in the solution can be unperturbed, which is very important for the study of basic scientific problems on the polymer chain behavior; usually, polymer polymerization is carried out in solution state, and naturally, the polymerized polymer is also in a solution state; extended to optoelectronic devices fabrication of semi-rigid conjugated polymer, it is also a process of solution processing by spin-coating the solution into the film. However, the dissolution behavior of conjugated polymers is obviously different from that of traditional ones because of their semi-rigid backbones. This also provides new opportunity, challenge and research direction for the scholars to be devoted to the semi-rigid conjugated polymer.

The dissolution process of traditional polymers is usually divided into two stages as swelling and dissolution.\cite{18} Swelling usually means that a relatively small amount of the solvent molecules enter the tangled polymer chains, driven by chemical potential when polymer solvent just contacts with the polymer. Due to the strong interaction between the polymer chains, it is difficult for molecular chains to be dissolved directly in solvent alone in the form of a whole chain. Therefore, in the initial stage of dissolution, the solvent molecules diffuse into the polymer, which makes the interaction between polymer chains lower, and the spacing of molecular chain increases and the volume of the polymer swells, so it is called swelling. If the polymer is a linear polymer, the molecular chain will be unentangled, diffused and dissolved from a high concentration to a low concentration under the action of diffusion after swelling, thereby obtaining a homogeneous polymer solution; if the polymer is in a cross-linked state, it can be unperturbed, which is very important for the study of polymerized polymer as shown in Eq. (1). The cohesive energy density mainly reflects the interaction strength between each group in the condensate. If the cohesive energy density has a little difference between polymer and solvent, it is easy to produce interaction and form uniform solution. The square root of the cohesive energy density is defined as the solubility parameter, which can also be used for the selection of appropriate solvent.\cite{19}

$$CED = \frac{\Delta F}{V} = \frac{\Delta H_M - RT}{V}$$  \hspace{1cm} (1)

The principle of solvation often refers to a certain electrophilic-nucleophilic interaction between solute and solvent, which will enhance the interactional strength between polymer and solvent and improve solubility. The principle of similar polarity refers primarily to the good solubility under the condition of similar polarity between polymer and solvent. In addition, the external environmental factors, such as temperature, electric field and other external fields can also affect final solubility of the solvents in the process of dissolution. From the thermodynamic point of view, the mixture free energy under the condition of constant temperature and pressure in the dissolution process can be changed as Eq. (2).\cite{20}

$$\Delta G_M = \Delta H_M - T\Delta S_M$$  \hspace{1cm} (2)

where $\Delta H_M$ and $\Delta S_M$ are mixing enthalpy and mixing entropy, respectively. When $\Delta G_M < 0$, the solute can be dissolved spontaneously. The chaos always increases in the dissolution process, that is, $\Delta S_M > 0$. Therefore, whether the dissolution process can proceed spontaneously, it will depend on the mixing enthalpy and system temperature. Furthermore, applying external electric field can induce polymers molecular orientation in the process of polar solvent dissolution, which will also ultimately affect solution behavior of the polymers.

The Correlation Among Polymer Solution Concentration and its Condensed State Structure as well as Dynamic Evolution of Molecular Chain Motion

According to the viewpoint of modern condensed matter physics of polymer, the polymer solution concentration can be attributed to the following five ranges: extremely dilute solution, dilute solution, sub-concentrated solution, concentrated solution and extremely concentrated solution.\cite{18} The solution concentration varies from extremely dilute solution to concentrated solution, corresponding to the different motion states of polymer chains in the solution. In an extremely dilute solution, the polymer chains are isolated single chains, and there is no interaction between polymer chains, when the concentration increases to dynamic contact concentration $C_r$, although it is still in the dilute solution range, the polymer chains in the solution is still in an isolated single chain. Actually, interactions with other molecular chains have arisen due to the molecular chain thermal motion, such as translational motion, rotational motion, or uneven solvation. When the solution concentration is further increased up till the contact concentration $C_t$ which is already in the range of sub-concentrated solution, at this juncture, the polymer single chains in the solution already start to contact, overlap and fill in

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**DOI:** [10.1007/s10118-021-2555-6](https://doi.org/10.1007/s10118-021-2555-6)
the whole solution system. But in fact, some multi-chain aggregations have been formed in the solution due to the interaction between some molecular chains, continuing to increase the solution concentration up till entanglement concentration \( C_e \). At this time, the solution is in the range of concentrated solution, and molecular chains overlap and entanglement is further increased, and an entanglement network is formed with relatively uniform chain distribution. By now there are still solvent molecules in the system, so a certain solvation effect still exists, when the solution concentration is continuously increased up till solvent ratio disappears, it is called as extremely concentrated solution. At this point, effects of both solvation and excluded volume disappear in the solution, and the molecular chain is in Gaussian distribution. 

For polymer solution research, each concentration range is of its unique existence and research value: extremely dilute solution and dilute solution are quite suitable for studying polymer single-chain crystal;\(^{[19]}\) sub-concentrated solution is suitable for studying different interactions between polymer chains;\(^{[20]}\) concentrated solution and extremely concentrated solution are suitable for scaling research.\(^{[21,22]}\) In the practical application for polymer materials, their application direction and field are also very different due to the changed concentration ranges of polymer solution. For example, the applications for polymer material polymerization, coatings, film-forming for optoelectronic devices are all in the range of dilute solution or sub-concentrated solution, while applications for electrospinning and rubber are all in the range of concentrated solution or extremely concentrated solution.\(^{[16,17]}\)

**Research and Challenge for Semi-rigid Conjugated Polymer Physics**

Classical polymer is a large class of polymer materials with random coil molecular chain conformation. According to its application, it can be classified as rubber, fiber, plastic, polymer adhesive, polymer coating and polymer-based composite materials etc. Semi-rigid conjugated polymers refer to a polymer material with semi-rigid chain conformation. They are mainly used in optoelectronic fields, such as polymer light emitting diodes (PLED), polymer solar cells, organic field effect transistors and organic electric pumping lasers.\(^{[9−12,23−26]}\) These semi-rigid conjugated polymers not only exhibit optoelectronic functions through the delocalized \( n \) electrons on the molecular chain, but also are of the inherent ductility and processability. At present, the main research directions of semi-rigid conjugated polymers include the synthesis for high performance optoelectrical polymer materials,\(^{[22,24]}\) surface and interface properties of donor-acceptor conjugated polymer blends,\(^{[25,26]}\) optoelectronic polymers film-forming way and the device structure optimization.\(^{[27]}\) As we know, semi-rigid conjugated polymer with optoelectronic functions needs to undergo three main processes from material synthesis to device fabrication: solvent dissolution, solution processing to film and device fabrication. Among them, the two processes of solution processing to film and device fabrication mainly involve macroscopic operations and research, and the results are easy to be observed and tested, so they have been widely studied.\(^{[23−27]}\) However, the research on solvent dissolution and solution behavior for the semi-rigid conjugated polymer is usually limited by research methods and tool, and therefore it was rarely reported so far. At present, although researchers have realized that the solution behavior (single-chain conformation, single-chain shape and size, aggregation shape, size, chain packing density of the aggregation, etc.) has a very important relationship with the condensed state structure of the thin film, a quantitative research to reveal the structure-activity relationship between solution and film and mechanism from the physical essence are quite scarce no matter from basic theory or experiment. Therefore, this research is of theoretical and practical significance, not only to understand the interaction between solvent and solute, solution behavior as well as condensed state structure formation and mechanism, but also to realize the physical essence of improving optoelectronic performance, regulating the condensed state structure of semi-rigid conjugated polymers to fabricate highly efficient, highly stable optoelectronic devices. The research is also instructive for other classical polymer systems.

In this research, we focus on the influence and mechanism of solvent properties on solution behavior and film condensed state structure for the semi-rigid conjugated polymers. The research comes from the different perspectives, such as solvent solubility, aromaticity, polarity and hydrogen bonding to explore solution behavior of the semi-rigid conjugated polymer by using static/dynamic laser light scattering and spectroscopy, structure and morphology characterization methods etc. The correlation between solvent and solution behavior as well as the structure-activity relationship between solution behavior and film condensed state structure were systematically studied, the solution behavior of semi-rigid conjugated polymer and the condensed state structure formation as well as the dynamic evolution process were explored, and their characteristics, laws and related mechanisms were revealed. Besides, some methods and conclusions were obtained, which laid a solid theoretical and experimental foundation for enriching the understanding of semi-rigid conjugated polymer solution behavior and condensed matter physics of conjugated polymers.

**EFFECT AND MECHANISM OF SOLVENT PROPERTIES**

**Influence of Solvent Solubility on the Condensed State Structure of Semi-rigid Conjugated Polymer**

In order to investigate the influence of different solvents on the condensed state structure of semi-rigid conjugated polymer, the research firstly start with the most common solvent property, i.e., solubility, which is the most commonly used for evaluating solvents. Poly(9,9-diocrylfluorene (PFO), the most representative polyfluorene polymer, was selected as the research system, and its structural formula is shown in Scheme 1. As a classic blue-light conjugated polymer material, PFO not only has a simple structure and a variety of chain conformations, but also is a model of hair-rod-shaped conjugated polymer, so it has been widely concerned by academic community.\(^{[34−37]}\) PFO chains conformation in solution can be transformed from a conformation with the main chain torsion angle of 135° to the more coplanar \( \beta \) conformation with the main chain torsion angle of 165° under special external conditions (as shown in Fig. 1). The \( \beta \) conformation can significantly improve the PFO
molecular chain’s orderliness, stability and carrier mobility of optoelectronic device. Current studies have shown that lowering solution temperature or adding poor solvent can lead to the transformation from α conformation to β conformation. And β conformation will show a unique absorption peak in the UV-Vis absorption spectrum, which is beneficial to explore influence of different solvents on PFO condensed state structure.[28]

Scheme 1 Structure of poly(9,9)dioctylfluorene (PFO). [28]

In the process of exploring molecular chain conformation change and condensed state structure dynamics evolution in PFO solution state, the research first begins from the difference of solvation caused by the solubility of different solvents. Adding different volume ratios of ethanol (poor solvent) to the chloroform (good solvent) in PFO solution reduced the solubility of the mixed solution and caused PFO molecular chains to aggregate.[28] Fig. 2(a) shows the UV absorption spectra of PFO solution with different ratios of chloroform/ethanol. The absorption peak at 437 nm is the characteristic peak of β conformation; and Fig. 2(b) shows the content of β conformation in solutions with different ethanol ratios. It was obviously shown in Fig. 2(b) that the content of β conformation increased with the ratios of ethanol, and rapidly increasing to 40% firstly and then stabilizing at 40% with almost no change, while at the same time, the main peak of the absorption spectrum was red-shifted. According to the occurrence of β conformation, we define the molecular chain aggregates as mesoscopic aggregates when the ethanol ratio is less than 30% in the solution; and define the chain aggregation as macroscopic aggregation when the ratios of ethanol is more than 40% in the solution. In order to further explore their differences, characteristics and laws of these two kinds of aggregates, we inspected the two kinds of aggregation through the filtration experiments, and carried out the filtration experiments with chloroform/ethanol mixed ratios of both 5:1 and 4:6, respectively. Figs. 3(a) and 3(b) show the changes in the UV absorption spectra before and after the filter experiment. In Fig. 3(a), the ratio of chloroform/ethanol was 5:1 (at this time, the chain aggregation was attributed to mesoscopic aggregation), and it can be clearly observed that the characteristic peak of β conformation disappeared after the filtration experiment, while the characteristic peak of α conformation did not change obviously; in Fig. 3(b) the ratio of chloroform/ethanol was 4:6 (macro-aggregation occurred at this time), and it was found that both α and β conformations disappeared after the filtration experiments. Therefore, a conclusion could be drawn that the mesoscopic aggregation was mainly composed of β conformation, while the macroscopic aggregation was composed of both α and β conformation. The dynamic formation mechanism of the two aggregations is shown in Fig. 4. With the gradual increase in the ratio of ethanol (poor solvent), mesoscopic aggregation was firstly formed in the PFO solution; continuing to increase the poor solvent content, a greater degree of macro-aggregation was formed on the basis of mesoscopic aggregation. In macro-aggregation, the β conformation of PFO chains was arranged orderly while the α conformation was arranged randomly and played a binding role to the ordered β conformation; it made the β conformation more tight and stabilized in the poor solvent ethanol, so β conformation content remained un-

https://doi.org/10.1007/s10118-021-2555-6
changed after adding 40% ration of poor solvent ethanol. This research reveals that the $\beta$ conformation formation requires the mesoscopic aggregation as a transition state, thus further to form macro aggregation with both high $\beta$ conformation content and stability. This research also reveals that the difference of solvent solubility directly affects molecular chains condensed state structure in the PFO solution, and finally affects the carrier mobility and efficiency of the optoelectronic devices.

Building on this work, we further explored the dynamic evolution process and mechanism of the PFO $\beta$ conformation formation. The research was first started from the mutual transformation between $\alpha$ and $\beta$ conformations, and influence of different solvents on the dynamic process of PFO $\beta$ conformation formation was deeply studied. Similarly, the addition of a poor solvent was used to induce the transformation from $\alpha$ conformation to $\beta$ conformation. The UV absorption spectra of PFO solutions with different toluene (good solvent)/ethanol (poor solvent) mixed ratios are shown in Fig. 5. It was found that the $\beta$ conformation appeared only when the ethanol content reached 40% in the solution. In order to explore the dynamic process of $\beta$ conformation formation, we used static/dynamic laser scattering (DLS/SLS) to study the changes of single chain to aggregation in PFO solutions with different ethanol ratios. $R_g$, $R_h$ and $R_g/R_h$ are the root mean square radius of gyration, hydrodynamic radius and shape parameters, respectively, which can reflect single chain changes in the size, shape and aggregation. In solutions with different ethanol ratios, the above parameters are shown in Table 1. From the Table 1, $R_g$ and $R_g/R_h$ decreased gradually with the increase of ethanol ratio, which indicated that the single chain in the solution gradually collapses from the rigid extended chain to coil as poor solvent increase. DLS was used for exploring chains condensed state change in PFO solution with different ethanol ratios as shown in Figs. 6(a) and 6(b). Fig. 6(a) shows the relationship between correlation function and the relaxation time. It could be seen that the correlation function curve moved toward the direction of relaxation time increase as the solubility of the mixed solution decrease (i.e., ratio of ethanol increase), indicating that the PFO volume increases and undergoes a process of single chains gradual aggregation; Fig. 6(b) shows the distribution of hydrodynamic radius $R_h$ obtained by the correlation function fitting. It could be seen that the aggregated size

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**Fig. 3** Normalized UV-Vis absorption spectra of the solution with the ratio of (a) chloroform:ethanol=5:1 and (b) chloroform:ethanol=4:6 before and after filtration. (Reprinted with permission from Ref. [28]; Copyright (2012) American Chemical Society).

**Fig. 4** Schematic diagram of the formation mechanism of PFO mesoscopic aggregation and macroscopic aggregation. (Reprinted with permission from Ref. [28]; Copyright (2012) American Chemical Society).
of single chains gradually increases with the decrease of solubility of the mixed solution (i.e., the ratios of ethanol increase) in the solution so that micron-sized chains aggregation was formed when the ethanol content reached 30%. To sum up, influence mechanism of different solvent solubility in the transformation process from \( \alpha \) to \( \beta \) conformation in PFO solution was revealed as shown in Fig. 7. In a good solvent, PFO existed in a semi-rigid and stretched \( \alpha \) conformation. When the ratios of ethanol gradually increased in the range of 0% to 40% in a poor solvent, the PFO molecular chain became gradually curled and formed aggregation due to the increase of intermolecular force. However, at this time, the \( \beta \) conformation was not formed yet. When the ethanol content reaches 40%, the intramolecular/intermolecular force increased so that the aggregated molecular chains could overcome the transitional barrier from \( \alpha \) conformation to \( \beta \) conformation, and both the conformation planarity and orderliness were increased. Finally, the conformational transition from \( \alpha \) conformation to \( \beta \) conformation occurred.

As we know, fabricating conjugated polymer optoelectronic devices must go through the process from solution to thin film by spin-coating and then to devices. Therefore, optoelectronic performance of semi-rigid conjugated polymer film is essentially determined by solution behavior in precursor solution, which has been approved by more and more experts and scholars. However, most of the current researches still focus on materials synthesis and device construction to improve optoelectronic efficiency, and research of aiming at molecular chains dynamic evolution process from precursor solution to film formation is quite rarely reported due to the limitation of solution research methods and means. At present, only a few research results infer that the polymer chain structure remains unchanged in the process from solution to film, but it lacks the support from theoretical and quantitative data. The purpose of the research is to start from solution behavior of semi-rigid conjugated polymer to achieve effective control to both solution processing and film condensation state structure in order to fundamentally carry out the establishment of quantitative structure-activity relationship between solution and film.

Therefore, the influence of solvent solubility on the condensed state structure of semi-rigid conjugated polymer film was studied systematically. By adding different ratios of PFO poor solvent to induce chains conformation to change, we have carried out the quantitative theoretical calculation on \( \beta \)-conformation content in the same concentration of PFO solution and its spin-coated film, as shown in Table 2. From the Table 2, it was surprisingly found that the \( \beta \)-conformation content in the PFO solution was almost the same as that in the film under the same solution concentration, that is, the PFO \( \beta \)-conformation content could be quantitatively inherited from the solution to the film. This is the first time to report that the molecular chain conformation can be quantitatively inherited from solution to film. In order to further ex-
To explore the quantitative relationship between the chain conformation in the semi-rigid conjugated polymer solution and device performance, we used the photo-CELIV transient current curve to calculate the hole mobility of the PFO field effect device, as shown in Fig. 8(c), it was amazingly found that PFO $\beta$ conformation could significantly prompt the hole mobility by an order of magnitude for the PFO field effect device. To sum up, the conclusion that chain conformation in the semi-rigid conjugated polymer solution could be quantitatively inherited into the film clarified an important and long unresolved issue on molecular chains structure-activity relationship between solution and film for academic community, and well proved the quantitative conformation heredity. More importantly the structure-property relationship between solution and film could directly bring about an order of magnitude enhancement in device carrier mobility, which not only revealed that film condensed state structure could be directly controlled by starting from the solution behavior, but also laid a solid theoretical and experimental foundation for the practical application of conjugated polymers and other classical polymers in the future.

### Influence of Solvent Aromaticity on Chain Solution Behavior and Film Condensed State Structure for the Semi-rigid Conjugated Polymer

In solution, the interaction of semi-rigid conjugated polymer is mainly showed the interaction of $\pi$-$\pi$ and van der Waals force by

### Table 2

| Ethanol ratios | $\beta$-Conformation contents (in solution) | $\beta$-Phase contents (in films) |
|---------------|------------------------------------------|----------------------------------|
| 0%            | 0% 10% 20% 30% 40%                      | 0% 0% 5.5% 9.1% 36.1%            |

Fig. 7 Schematic diagram of the formation mechanism of chain condensed state structure in the PFO solution as ratios of ethanol increase. (Reprinted with permission from Ref. [29]; Copyright (2016) Elsevier).

Fig. 8 Photo-CELIV transients at varying light intensity under holes with (a) 0% $\beta$ phase content, (b) 5.4% $\beta$ phase content, (c) dependence of hole mobility on the density of light with different $\beta$ phase contents. (Reprinted with permission from Ref. [30]; Copyright (2016) American Chemical Society).
itself or with solvent molecules. We believe that aromatic solvent molecules can also form π-π interactions with the semi-rigid conjugated polymers. In order to systematically explore the influence and mechanism of solvent properties on solution behavior and film condensed state structure for the semi-rigid conjugated polymers, we researched the influence of solvent aromaticity on the condensed state structure.\cite{31} we first explored the effect of solvent aromaticity on the PFO chain solution behavior. Chlorobenzene (CB) and toluene (Tol) were selected as aromatic solvents, respectively, and tetrahydrofuran (THF) and chloroform (CF) as non-aromatic solvents, respectively. Although in a dilute solution, the interaction between polymer chains was neglected and polymer was evenly dispersed in the solution as a single chain, the shape of the single chain was still affected by the interaction between polymer chains and solvent molecules. The polymer single chains properties could be obtained with SLS method. In sub-concentrated solutions, polymer chains were entangled, interpenetrated and self-assembled due to mutual contact and various complex intermolecular interactions, so the chain segments motion will slow down. In concentrated solutions, polymer chains undergo a condensed process inevitably because of stronger intermolecular interactions. Therefore, the polymer chain structure with different concentrations corresponded to a different chain motion relaxation mode in the solution. The DLS method can be used to explore the chain motion relaxation process and dynamic evolution behavior under the state of polymer solution in a wider concentration range.\cite{38} By DLS and SLS, the shape of a polymer single chain can be described by the shape parameter $\rho$ ($R_d/R_h$). For a flexible chain, the $\rho$ value is 1.78 in a good solvent. The bigger the $\rho$, the more extended the chain conformation and the stronger the chain rigidity.\cite{39,40} Table 3 shows the shape parameter $\rho$ of PFO single chains in different solvents. It was found that the $R_h$ value of the PFO chain was about 10 nm in four selected solvents, indicating that the PFO chain was indeed dissolved as a single chain in these four solvents. In addition, the $\rho$ values of all PFO chains were much higher than 1.78, which meant that PFO single chains adopted a more extended chain conformation. However, it was easy to see that the $\rho$ value of PFO single chain in the aromatic solvents CB and Tol was significantly bigger than that in the non-aromatic solvents THF and CF, which indicated that the rigidity of PFO single chain was significantly stronger in the aromatic solvents CB and Tol than that in non-aromatic solvents THF and CF. And this conclusion is just contrary to the fact that polymer chain rigidity is stronger in good solvent than that in neutral solvent according to Hildebrandt parameter rule. Therefore, we believe that the aromatic solution does have a strong π-π interaction with the main chain of PFO in the solution, which is much stronger than the solubility.

In the above four solvents (shown in Fig. 9), it was found that the $R_h$ values of PFO chains were mainly distributed in the range of 10 nm corresponding to single chains; they were also distributed in the range of 10–100 nm and 100–1000 nm, corresponding to chain aggregation. As the solution concentration increases, PFO chains were easier to form aggregation, and when the solution concentration was 5 mg/mL, $\beta$ conformation could be formed in the above four solvents.\cite{31} Therefore, DLS was used to explore the effect of solvent aromaticity on the PFO chain condensed state structure (including the size of chain aggregation and chain packing density). Chain packing density can be represented by the fractal dimension $d_f$. The higher the $d_f$ value, the looser the molecular chain packing, and the smaller the $d_f$ value, the tighter the molecular chain packing.\cite{34,35} From Figs. 9 and 10, it could be found that the aggregate size was bigger up till about 100 nm in the aromatic solvents CB and Tol than that in the non-aromatic solvents THF and CF (Fig. 10b). In Fig. 11 and Table 4, the $d_f$ value was opposite to the above results at a concentration of 5 mg/mL: the $d_f$ values in the aromatic solvents CB and Tol were smaller than those in the non-aromatic solvents. When the solution concentration was in 3 mg/mL, the $d_f$ value was of the same trend. It indicated that the $d_f$ value was always lower in the aromatic solvents CB and

**Table 3**  PFO single chain behavior in solution state with concentration 5 mg/mL with different solvents.\cite{31}

| Solvents | $R_h$ (nm) | $R_f$ (nm) | $\rho$ ($R_d/R_h$) |
|----------|------------|------------|-------------------|
| CB       | 32.1       | 12.2       | 2.63              |
| Tol      | 28.1       | 10.9       | 2.58              |
| THF      | 20.8       | 10.5       | 1.98              |
| CF       | 22.7       | 9.9        | 2.30              |

![Fig. 9](https://doi.org/10.1007/s10118-021-2555-6) (a) Normalized intensity correlation function of PFO solutions; (b) Corresponding $R_h$ distribution of PFO aggregations in different solvents. PFO solution concentrations were all 1.0 mg/mL. (Reprinted with permission from Ref. [31]; Copyright (2019) Elsevier.)
Tol than those in THF and CF with the non-aromatic solvents, showing that PFO molecular chains were stacked more denser in non-aromatic solvents THF and CF than in the aromatic solvents CB and Tol.

The morphological structure of a polymer is just the aggregation structure formed by polymer chains arrangement and packing. In order to investigate the influence of solvent aromaticity on the condensed state structure of the film, the film morphology structure was researched. The height diagram and the phase graph were obtained simultaneously by atomic force microscope (AFM, shown in Fig. 12). It was obviously found from Fig. 12 that the morphology of PFO films prepared from different solutions with different solvents showed obvious individual differences: PFO chains were assembled into fibrous structures in aromatic solvents CB and Tol shown in Figs. 12(b) and 12(d) (phase diagram), respectively. However, a morphological structure as a circular sheet was observed in Fig. 12(f) (phase diagram) in the film from the non-aromatic solvent THF. In Fig. 12(h) (phase diagram), the short rod-like morphology was observed in the film from CF solvent. According to the literature, the polymer film morphology is independent of the film thickness, but is only connected with stacking mode and packing structure of the conjugated polymer chain.\[31\] In addition, the fibrous structure is more likely to be formed in the film-forming precursor solution with a good solvent when the polymer film is prepared by solvent annealing, and it is helpful to improve the carrier mobility of optoelectronic film. Therefore, compared with non-aromatic solvents THF and CF, aromatic solvents CB and Tol are more conducive to enhancing the efficiency of PFO optoelectronic devices.

The optoelectronic film formation is a self-assembly dynamic evolution process from a single chain in a solution to two-dimensional film. In this process, the solvents and solution concentrations play an important role. In addition, polymer chains entanglement, penetration and certain flexibility are also the premise of carrying out the molecular chain self-assembly. PFO is a wormlike semi-rigid conjugated polymer with both extended conjugated main chain backbone and

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**Table 4** PFO fractal dimension \(d_f\) in different solution concentrations with different solvents\[^{[31]}\]

| Solvents | Fractal dimension \(d_f\) |
|----------|--------------------------|
|          | 3 mg/mL                  | 5 mg/mL                  |
| CB       | 1.75                     | 1.82                     |
| Tol      | 1.75                     | 1.80                     |
| THF      | 1.86                     | 1.96                     |
| CF       | 1.90                     | 1.91                     |

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**Fig. 10** (a) Normalized intensity correlation function of PFO solutions; (b) Corresponding \(R_h\) distribution of PFO aggregations in different solvents. PFO solution concentrations were all in 5.0 mg/mL. (Reprinted with permission from Ref. [31]; Copyright (2019) Elsevier).

**Fig. 11** Plot of \(\log(q)\) versus \(\log q\) for the aggregation. (a) PFO solution concentrations were all in 3.0 mg/mL; (b) PFO solution concentrations were all in 5.0 mg/mL. (Reprinted with permission from Ref. [31]; Copyright (2019) Elsevier).
flexible side chain. Based on the above research results, PFO self-assembly process from single chain to aggregation in solution and the mechanism was inferred, as shown in Fig. 13. In the dilute solution, the PFO single chain had a more planar geometry and longer effective conjugation length in CB and Tol solvents than in the non-aromatic solvents THF and CF due to the strong \( \pi-\pi \) interaction between PFO conjugated main chain and the aromatic solvent molecules. Therefore, the PFO chain could firstly form the \( \beta \) conformation in the aromatic solvents CB and Tol. With the increase of solution concentration, PFO single chains began to self-assemble to form chain aggregation and the rigid PFO single chains were easier to be oriented to form fibrous structures and big-sized aggregation since aromatic solvent molecules adhered to the PFO chains and were of a bigger excluded volume, but the PFO chains could not be closely packed. However, the interaction between PFO molecular chains and solvent molecules was weakened in the non-aromatic solvents THF and CF, but their interchain interaction was enhanced. So, the PFO chains could self-assemble into an amorphous structure with small-sized aggregation and close packing.

In conclusion, this study revealed the influence of solvent aromaticity on PFO chain solution behavior and film condensed state structure. It was declared that solution behavior of PFO chains was intrinsically linked to aromaticity of the solvent. In the dilute solution, the PFO single chain adopted a more rigid chain conformation in the aromatic solvents CB and Tol due to the strong \( n-n \) interaction between PFO conjugated main chain and the aromatic solvent molecules. With the increase of the solution concentration, although big size PFO chain aggregation appeared, the PFO chains packing density decreased due to the bigger excluded volume of PFO chains. At the same time, an ordered fiber structure was observed in the film fabricated from aromatic CB and Tol solvents, which is very beneficial to improving the carrier mobility of optoelectronic devices. Differently, in the non-aromatic solvents THF and CF, circular flakes and short rod-like morphology with an amorphous structure were observed in the film, respectively. It showed that the aromaticity of solvent affected not only the chain solution behavior, but also the condensed state structure of the film as well as the carrier mobility of the optoelectronic device. Therefore, by simply selecting the solvents, the influence, characteristics, laws and mechanism of the solvent on the chain solution behavior and film condensed state structure, and even the optoelectronic performance were revealed. It is significant to deeply understand the physical essence to fabricate optoelectronic devices with high carrier mobility, high efficiency and high stability.

**Influence of Hydrogen Bonds in the Solvents on the Condensed State Structure from Solution to Film for the Semi-rigid Conjugated Polymers**

As a strong intermolecular force, hydrogen bond is one of the strong driving forces for supramolecular materials self-assembly. In this part, we are dedicated to exploring the influence of hydrogen bonding in the solvents on the condensed state structure from solution to film for the semi-rigid conjugated polymers. \(^{[32]}\) Firstly, we chose a polyfluorene derivative poly-(9-hydroxy-9-(4-octyloxy)phenyl) fluorene (PFFOH) as research system, which can form the intramolecular/intermolecular hydrogen bonds since it has a hydroxyl at the 9th position (as shown in Scheme 2). Otherwise, it can also form PFFOH-solvent hydrogen bonds in different solvents. \(^{[46,47]}\) Until now there still are few reports on the hydrogen bond interaction between semi-rigid conjugated polymers and solvents. Therefore, this research is of great significance not only to understand the relationship between solvents, solution behavior and film condensed state structure, but also to reveal the physical essence of film condensed state structure formation.

In order to explore PFFOH chains condensed state structure in different solutions, we used dynamic/static laser light scattering to characterize the three PFFOH dilute solutions with concentration of 0.1 mg/mL (i.e., pure chloroform solu-

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**Fig. 12** AFM height and phase images of PFO films prepared from different solvents. (a, c, e, g) Height images of PFO films; (b, d, f, h) Phase images of PFO films. (Reprinted with permission from Ref. [31]; Copyright (2019) Elsevier).
tion, chloroform solution mixed with 20% tetrahydrofuran solvent, and pure (100%) tetrahydrofuran solution). The results are shown in Fig. 14 and Table 5. In pure chloroform (CF) solution, PPFOH presented a small and single-sized chains aggregation, and its hydrodynamic radius ($R_h$) was only 42.9 nm, showing a dense chain aggregation with smaller $d_f$; in CF mixed solution with 20% tetrahydrofuran (THF) solvent, the $R_h$ of aggregation was obviously increased to 89.0 nm, which indicated that chains aggregation size became bigger and the chains motion speed became slower than that in pure CF solvent; while the aggregation size ($R_h$) in pure THF solution was increased till 99.0 nm, it is slightly bigger than that in adding 20% THF solvent. It was considered that the essential reason for the size increase depended on whether the hydrogen bond interactions of intramolecular/intermolecular have

**Scheme 2** Chemistry structure of the PPFOH. [32]

**Fig. 13** The self-assembly process of PFO chains from single chains to aggregation in the solutions: (a) aromatic solvents (CB and Tol), (b) without aromatic solvents (THF and CF). (Reprinted with permission from Ref. [31]; Copyright (2019) Elsevier).

**Fig. 14** PPFOH CF/THF mixed dilute solutions with PPFOH concentration in 0.1 mg/mL with different THF ratios. (a) Normalized intensity correlation function. (b) $d_f$ Values for reflecting chain aggregation density from the plot of log$(q)$ versus log$q$. (Reprinted with permission from Ref. [32]; Copyright (2019) American Chemical Society).
been formed between PPFOH and solvent molecules. It could be seen from the correlation function curve of DLS (Fig. 14a) that chains relaxation behavior of PPFOH showed obviously large-scale and slow relaxation mode in the solution with THF solvent, indicating that the molecular chain had formed a large-scale cross-links or clusters. [39] Combined with \( R_d / R_h \) and \( d_l \) results by SLS in Table 5, it can be inferred that there was only strong hydrogen bond interaction and \( \pi-\pi \) conjugate interaction between PPFOH intramolecular/intermolecular in the CF solution, but no hydrogen bond interaction between CF solvent and PPFOH, thereby forming a rigid chains aggregation state structure in the pure chloroform (CF) solution; in the solution mixed with THF concentration of 20%, there were both the intramolecular/intermolecular hydrogen bonding interaction, \( \pi-\pi \) conjugate interaction between PPFOH and the hydrogen bond interaction between PPFOH molecules and THF solvent; however, in pure THF solution, there was only a certain number of hydrogen bonds between THF solvent molecules and PPFOH. Therefore, the original dense chain aggregation in CF solvent was broken after adding 20% THF solvent and 100% (pure) THF solvent, as shown in Table 5, forming a kind of loose structure between vesicle and disorder polymer coils.

In order to explore the influence of different precursor solvents on the electronic state of PPFOH solution and film, UV-Vis absorption and PL emission spectrum research on the solution and film were carried out as shown in Figs. 15(a) and 15(b), respectively. Since there was no hydrogen bond interaction between the CF solvent and PPFOH molecules in the solution with CF solvent, the solution system mainly presented intramolecular/intermolecular hydrogen bond and \( \pi-\pi \) conjugate interaction between PPFOH itself, and thus in the process of spinning coating, the interaction between CF solvent and PPFOH could not be formed. Therefore, no matter in the solution or the film, the shapes of the absorption spectra (Fig. 15a) and emission spectra (Fig. 15b) were unchanged since there was no hydrogen bond interaction between CF solvent and PPFOH molecule. From this result, an important fact was surprisingly found in the solution with CF solvent, that is, PPFOH molecular chain conformation could be transferred from the solution to the film. However, in the solution with THF solvent, PPFOH dissolved more fully due to the hydrogen bond interaction between PPFOH and THF solvent, and thus the interaction between PPFOH molecules was relatively reduced, and the absorption and emission spectra were blue-shifted. [48, 69] However, the intramolecular/intermolecular hydrogen bond interaction between PPFOH could be reformed in film due to the rapid volatilization of THF solvent in the process of film-forming, and therefore the absorption and emission spectra were different, similar to the result of the film of CF as solvent. The fundamental reason was that the solvent evaporates rapidly in the process of spinning film, and the hydrogen bond interaction between PPFOH and THF in the solution disappeared in the film because of the rapid volatilization of THF solvent. Instead, the hydrogen bond interaction between PPFOH intramolecular/intermolecular led to film-forming properties convergence in different precursor solvents.

In order to explore the orderliness of aggregation structure of the PPFOH molecules in different solvents, we adopted TEM to characterize the aggregation state structure morphology of the above three solvents (chloroform solution, chloroform solution mixed with 20% tetrahydrofuran solvent, and 100% tetrahydrofuran solution), and used the high-resolution transmission electron microscopy (HRTEM) and Fourier transform (FET) images to observe the ordered structure of the aggregation state structure, as shown in Fig. 16. Figs. 16(a), 16(b) and 16(c) are the TEM, HRTEM, and FET images of the PPFOH solution with 0% THF solvent (pure CF solution), respectively. It could be seen from Fig. 16(b) that there was a small amount of fine lattice fringes in the CF solvent due to the strong interaction caused by the hydrogen bond between PPFOH backbone and \( \pi-\pi \) conjugate interaction. Fig. 16(c) shows that there were only a few irregular crystals in this area. Figs. 16(d), 16(e) and 16(f) are the TEM, HRTEM and FET images of the PPFOH CF/20% THF mixed solution, respectively. It could be seen from Fig. 16(e) that although the ordered structure area increased in the aggregation, the ordered direction was anisotropic and the lattice

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Table 5  \( R_g, R_h, R_d / R_h \) and \( d_l \) of PPFOH CF/THF mixed solutions with different THF ratios. [32]

| THF ratios | \( R_g \) (nm) | \( R_h \) (nm) | \( R_d / R_h \) | \( d_l \) |
|-----------|----------------|----------------|---------------|--------|
| 0% (CF)   | 42.9           | 100            | 2.30          | 1.02   |
| 20%       | 89.0           | 110            | 1.20          | 1.15   |
| 100%      | 99.0           | 116            | 1.20          | 1.24   |

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Fig. 15  (a) Normalized UV-Vis absorption spectra of PPFOH solutions and films with different solvents. (b) Normalized PL emission spectra of PPFOH solutions and films with different solvents. (Reprinted with permission from Ref. [32]; Copyright (2019) American Chemical Society).

https://doi.org/10.1007/s10118-021-2555-6
fringe spacing was increased. The reason was that there were not only hydrogen bonds and n-π conjugate interactions between PPFOH molecules after adding 20% THF solvent, but also hydrogen bonding interactions between PPFOH chains and THF solvent molecules in the system. The two synergistic interactions resulted in the presentation of lattice image, as shown in Fig. 16(f). Figs. 16(g), 16(h) and 16(i) are TEM, HRTEM and FET images of PPFOH 100% THF solvent, respectively. Obviously, it could be seen that a large number of long-range ordered structures from Fig. 16(h) with further increase of lattice fringe spacing, and Fig. 16(i) shows more obvious lattice structure, which was due to the fact that there was only hydrogen bond interaction between PPFOH chain and THF solvent molecules in the 100% THF solvent, increasing flexibility of the molecular chain and making the chains easier to arrange and packing into an ordered structure. The fact above well proved that in CF solvent, the interaction between PPFOH main chain caused by intermolecular hydrogen bond and n-π conjugate interactions were far more than the hydrogen bond between PPFOH and THF in 20% as well as 100% THF solvents, thus leading to dense chain aggregation in the CF solvent. While the molecular chain could become looser and stretched in a mixed PPFOH solution with 20% and 100% THF solvents, which was more conducive to forming an ordered chain structure.

This research was aimed to influence of hydrogen bonding of the solvents on the condensed state structure from solution to film for the semi-rigid conjugated polymers. It was found that hydrogen bonding played an important role in the formation of the condensed state structure in the dynamic evolution process from solution to film formation. It is also found that the semi-rigid conjugated polymer system with hydrogen bond interactions is of the characteristics of molecular chain conformation heredity in the process of dynamic evolution from solution to film: that is, the chain conformation of the conjugated polymer in solution could be better inherited into the film in the process of film formation when there is no hydrogen bond interaction between solvent and polymer; on the contrary, the chain conformation of the conjugated polymer in solution could not be inherited in the process of film formation. This research clarified the hereditary relationship and mechanism from PPFOH solution to film condensed matter structure. It is of great theoretical and practical significance to deeply understand the dynamic process from solution processing to film-forming and to control pre-solution behavior in order to fabricate high-efficiency and high-stability optoelectronic devices.

**Influence of Solvent Polarity on the Condensed State Structure of Semi-rigid Conjugated Polymer Film**

Different solvent parameters can act on the polymer solution from different views, thereby affecting the condensed state structure of polymer. The solvent polarity can reflect the polarized ability of a substance, so it can be used as a criterion to polymers solubility in the solution. In this research, we introduced an external electric field (EEF) to induce the chains conformation change of the semi-rigid conjugated polymer in the dynamic transition process from solution to film, and explored the influence of solutions with different polar solvents on the condensed state structure of polymer films. We chose poly(9,9-diocetylfluorene) (PFO) as the research system. It is a widely used classic optoelectronic conjugated polymer due to its excellent blue light properties, multiphase structure, as well as its hairy rod-shaped polymer model, physical properties, such as molecular weight, dispersion, and regioregularity etc., which can have a huge impact on its microstructure and charge transport performance, and also is helpful for us to deeply explore the mechanism of its condensed state structure change. Other studies have shown that external electric field can align the polymer chains to form a crystalline structure in the process of annealing or drying for poly(3-hexylthiophene) (P3HT) films, and can make the P3HT carrier transport performance great enhancement. However, how about the effect of external electric field on the non-polar conjugated polymer? So far, it has not been reported yet. Herein, we explored synergistic effect of the external electric field and the different polarity solvent vapor annealing on the molecular chain orientation, film aggregation structure and carrier mobility of the non-polar conjugated polymer PFO. The research aims at understanding the action and mechanism of solvent polarity, so it is of great significance to understand the physical essence of the solvent action based on polymer physics.
In order to fabricate high carrier mobility and high efficiency optoelectronic devices.

In order to explore the influence of solvent polarity on the condensed state structure of polymer films under the induction of an external electric field, we selected a variety of solvents ranging from non-polar to polar, such as methanol, n-hexane, cyclohexane, toluene, chlorobenzene and chloroform. The related solvent parameters are shown in Table 6. A schematic diagram of annealing in different solvent atmospheres under the induction of an external electric field is shown in Fig. 18. The PFO film was quickly blown dry with dry nitrogen after applying solvent vapor and the external electric field, so as to fix the fine-tuned aggregation structure of the film.

In order to study the influence of solvent polarity on the non-polar PFO by external electric field, we selected n-hexane, cyclohexane (Cy), toluene (Tol), chlorobenzene (CB), chloroform (CF) and methanol (MeOH) for the solvent, respectively. Firstly, UV-Vis absorption spectroscopy was used to investigate the changes of PFO films subjected to different solvent vapors annealing and an external electric field. We calculated the content of β phase in the PFO film in order to quantitatively investigate the influence of external electric field and solvent polarity on chain orderliness, and the results are shown in Table 7.

From Table 7, it was found that the β phase content was the lowest at 0.5% in the PFO film with n-hexane steam annealing, and the following was cyclohexane at 0.9%, toluene at 4.5%, and chlorobenzene at 5.0%. Obviously, the β phase content of the chloroform solvent vapor film was the highest up to 16.2%. And the increase of β phase was positively correlated with the increase of solvent polarity, which indicated that PFO orientation has been successfully induced up to form β phase under the synergistic action of the external electric field and strong polar solvent vapor annealing. The results came from the dipolar polarization of the solvent molecules to induce the planarization transformation of PFO molecular chain conformation and then to form the ordered β phase under the action of external electric field. At the same time,
Table 7  β-Phase of PFO films annealed in different solvent vapors with or without EEF. 

| Solvent vapors | β-Phase content (%) | Increase value of β-phase content (%) |
|----------------|---------------------|--------------------------------------|
| n-Hexane       | 16.7±0.2            | 0.5                                  |
| Cy             | 20.3±0.1            | 0.9                                  |
| Tol            | 15.9±0.3            | 4.5                                  |
| CB             | 17.3±0.2            | 5.0                                  |
| CF             | 18.7±0.2            | 16.2                                 |
| MeOH           | 0±0.0               | 0                                    |

PFO film of nonpolar solvent vapor with n-hexane and Cy exhibited a weak β-phase increase after applying external electric field, which also indicated that the external electric field had a weak effect on the PFO chain because of PFO weak polarity, indicating PFO chain itself weak response to external electric field.

In order to explore the synergistic effect of external electric field and solvent polarity on the charge transport properties of PFO films, we chose the representative solvents Cy, Tol and CF, respectively and fabricated their thin film devices. The current density voltage (CV) curve was measured to the PFO thin film devices with and without applying the external electric field treatment in the vapor annealing process, and the hole mobility of the PFO devices were calculated using the space charge limited current (SCLC) method (as shown in Fig. 19), which were shown in Table 8. It could be found that: under the action of an external electric field, the hole mobilities of these three types of PFO devices were all increased, and the hole mobility of the Cy film increased to 7.50×10⁻⁴ cm²·V⁻¹·s⁻¹; the film treated with Tol increased to 5.50×10⁻⁴ cm²·V⁻¹·s⁻¹; however, the film treated with CF increased to 1.12×10⁻³ cm²·V⁻¹·s⁻¹; their growth rates were 16.5%, 93.0% and 187%, respectively. Obviously, the film annealed by CF has a stronger synergistic effect with the external electric field, and shows an order of magnitude enhancement in the carrier mobility. The results provide a new understanding of non-polar conjugated polymers, and it is very conducive to extending application for non-polar conjugated polymer in optoelectronic fields.

In order to confirm the correlation and physical essence of increasing the mobility and the PFO chain orderliness, we used X-ray diffraction methods to explore effects of different polarity solvents on the orderliness and crystallinity for the semi-rigid conjugated polymer films, as shown in Fig. 20. It could be seen that there was a relatively strong diffraction peak at 2θ=6.8° in all PFO films, which was attributed to (200) crystalline peak of PFO, corresponding to the interplanar spacing of the PFO octyl side chain; at the same time, it was found that there was also a relatively weak diffraction peak at 2θ=14.8° attributed to (040) crystalline peak of PFO, corresponding to the interplanar spacing of the n-r stacking of the PFO chains. According to the (200) and (040) peaks, we de-
scribed the PFO chains crystal arrangement as shown in Fig. 20(d). Among them, the PFO framework adopted π-π stacking with an “edge on” model to parallel to the substrate surface, and then stacked along perpendicular to the substrate surface. This indicated that the external electric field made the PFO chain orientation along the electric field direction. By comparing the peak intensity change of (200) crystallization, PFO ordered structure change along the direction of external electric field could be known after applying an external electric field. Under the induction of an external electric field, the (200) peak intensity of the PFO film annealed by cyclohexane vapor had no obvious change, and the (040) peak intensity had a slight increase, while the (200) and (040) peak intensity had significant increase in toluene and chloroform solvents, indicating that toluene and chloroform solvents were more conducive to the orientation and stacking the PFO chains along the electric field direction after applying external electric field. Therefore, more crystallites were formed in the PFO film, which was quite conducive to reducing grain boundaries and increasing orderliness. In addition, the (200) and (040) peak intensity increments of the film treated with chloroform vapor were significantly higher than those of the film with toluene vapor, indicating the increase of ordered area in the PFO film after using both chloroform vapor annealing and external electric field. At the same time, it was also found that red-shift of the (040) peak increased as solvent polarity increased after applying the external electric field, indicating that the π-π stacking spacing decreased and the molecular chains stacking became closer. Therefore, we conclude that external electric field orientation to non-polar PFO strongly depends strongly on the solvent polarity. The higher the polarity, the more favorable to PFO chains-oriented crystallization and close stacking. The reason is that the strong dipole moment with high polarity molecules is easier to be oriented by external electric field, and thus push PFO chains arrangement along the electric field direction to form oriented crystals and reduce the grain boundary. This is also the reason of the increase of film hole mobility compared with other solvent vapor annealing after chloroform vapor annealing.

In summary, we described the mechanism of non-polar PFO chains orientation and arrangement in the synergistic process of vapor annealing with different polar solvents and external electric field as shown in Fig. 21. The process could be divided into four stages: 1. firstly, the solvent molecules penetrated into the PFO film and caused the film to swell, which increased the free volume of the PFO chain movement.
and reduced the interaction between the chains. At this time, the PFO molecular chain conformation could be fully adjusted and formed a local orderly structure; 2. the solvent small molecules were polarized under the induction of the external electric field and their dipoles were first oriented along the external electric field direction; 3. driven by the polarized solvent molecules, the aromatic ring of PFO molecule began orientation along the external electric field direction by a single bond internal rotation of the molecular chain, that is, the \( \beta \) conformational transition, and the steric hindrance of the PFO side chain was reduced, resulting in the increase of PFO main chain planarity; 4. with the conformational transitions, PFO chains were aligned and formed an extended directional ordered structure. Essentially, the induced solvent molecules by the external electric field played a decisive role in the PFO chains orientation. The higher the polarity of the solvent, the stronger the driving force for the conformational change of the molecular chain. Finally, removing the external electric field and solvent molecules, the ordered structure in the film was retained.

The research has proven that the condensed state structure of PFO film is well controlled and hole mobility of the weakly polar PFO is obviously enhanced by vapor annealing process with different polar solvents under the condition of applying an external electric field. The obtained results can be extended to other conjugated polymer systems for large-area thin film processing. This research reveals the synergistic effect of solvent polarity and external electric field from a new perspective, and enriches the understanding and knowledge of weak polar semi-rigid conjugated polymers, so it is of great theory and practical significance for basic research and practical applications of the conjugated polymers.

CONCLUSIONS AND PERSPECTIVES

This research focused on the effect and mechanism of solvent properties on solution behavior and film condensed state structure for the semi-rigid conjugated polymers from different perspectives, such as the solubility of solvent, aromaticity, hydrogen bonding and polarity. Combined with the application for semi-rigid conjugated polymers in the field of optoelectronics, the influence of solvents on carrier mobility of optoelectronic devices was also studied. When solvent solubility was decreased, the aggregation was formed in the solution of the semi-rigid conjugated polymer PFO, the molecular chain conformation change from \( \alpha \) conformation to \( \beta \) conformation has happened, and the \( \beta \) conformation content in the solution state could be quantitatively inherited into the film. This is the first report on the conjugated polymers chain conformation heredity from solution to film. The research also revealed the influence, characteristics, laws and mechanism of solvent aromaticity on the condensed state structure in the dynamic evolution process from solution to film. In the dilute solution, PFO single chain adopted a more rigid chain conformation in the aromatic solvents CB and Tol. As the solution concentration increase, bigger size PFO chain aggregation but lower chain packing density appeared. At the same time, an ordered fiber structure was observed in the film fabricated from aromatic CB and Tol. In the non-aromatic solvents such as THF and CF, wafer-shaped and short rod-shaped structures with amorphous morphology were observed in both films, respectively. This indicated that solvent aromaticity affected not only the chains solution behavior, but also the condensed state structure of the films. The study also revealed that bigger size and loosely stretched chain aggregation could be obtained in the solution when the hydrogen bonds were formed between solvent and solute, while the hydrogen bond interaction was no longer existent in the process of film-forming process with solvent complete volatilization; at this time, the condensed state structure in the solution was not related to the condensed state structure in the film, and the molecular chain conformation in the solution cannot be inherited into the film. On the contrary, when there is no hydrogen bond interaction between the solvent molecules and the solute, but only the interactions between conjugated polymers, chains aggregation size in the solution state was small and dense, and the chain conformation in the solution could be well inherited to the film. This consequence lay a solid theoretical and experimental

![Fig. 21 Orientation mechanism diagram of PFO chains under the polar solvent vapor annealing and EEF treatment. (Reprinted with permission from Ref. [33]; Copyright (2020) American Chemical Society).](https://doi.org/10.1007/s10118-021-2555-6)
The stronger solvent polarity was, the more solvent vapors annealing and external electric field induction. The oriented crystals under the synergistic effect with both the foundation for establishing the quantitative structure-activity relationship between solution and film. The research also revealed that the PFO film with weak polarity also could form the oriented crystals under the synergistic effect with both solvent vapors annealing and external electric field induction. The stronger solvent polarity was, the more β conformation was formed, which was quite conducive to enhancing the hole mobility of photoelectronic devices.

ACKNOWLEDGMENTS

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