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Multi-level Aggregation of Conjugated Polymers in Solution: Advances and Challenges

Since the discovery of conductive polyacetylene, conjugated polymers have attracted considerable attention in the past decades for their applications in optoelectronic devices, such as organic field-effect transistors (OFETs), light-emitting diodes (OLEDs), and photovoltaics (OPVs). The intrinsic mechanical flexibility of conjugated polymers endows them as promising candidates for flexible and wearable electronics. Through iterative molecular design refinement and processing technique optimization, significant improvements in device performance have been made. The mobility has reached over 10 $cm^2 \cdot V^{-1} \cdot s^{-1}$, exceeding the benchmark of 1 $cm^2 \cdot V^{-1} \cdot s^{-1}$ set by their amorphous silicon counterparts. The conductivity of N-type polymer, poly(benzodifurandione) (PBFDO), exhibited a breakthrough over 2000 $S \cdot cm^{-1}$, making it an ideal conductor with excellent stability and solution-processability. The power conversion efficiency (PCE) of conjugated polymer-based solar cells hits 19%, comparable to the commercial polycrystalline silicon solar cells with 14%–19% PCE. Furthermore, conjugated polymers also show extinguished and promising performance in energy storage and biomedical applications.

The field has progressed structurally from polyacetylene, the first-generation material, to a proper focus on soluble and processible polymers and copolymers. The soluble poly(alkylthiophenes) and the soluble poly(*para*-phenylene vinylene)s (PPVs) are perhaps the most crucial outstanding examples of the second-generation semiconducting polymers. The structure modification focusing on conformation control and side-chain engineering altered the electronic states and facilitated the material processing, which therefore significantly boosted the performance and promoted the establishment of the primary structure-property relationships. Apart from chemical structures, subsequent studies identified the critical effects of the multi-level microstructures of conjugated polymers on their optoelectronic properties. For instance, polythiophenes with high regioregularity resulted in three orders of magnitude higher carrier mobility than that of regiorandom polythiophenes, illustrating that higher crystallinity and long-range order benefit better performance. The molecular structures of the third-generation semiconducting polymers are more complex and contain more atoms in the repeat unit. Most recently, examples with excellent performance including the highly ordered and crystalline poly(2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophene) (PDTTT) and the ever-growing class of donor-acceptor copolymers have emerged. However, further studies demonstrated that some polymers with limited long-range order, such as indacenodithiophene-*co*-benzothiadiazole copolymer (IDTBT) and thiophene-fused benzodifurandione-based PPV derivative (TBDPPV), also exhibited efficient charge transport without high crystallinity. This is mainly attributed to the ordered intrachain conformation and sufficient interchain short contacts. Nowadays, with the progress of characterization and in-depth research, more factors affecting the microscopic morphology beyond crystallinity have been discovered, such as crystal order and defects, grain boundaries, grain size and orientation, phase separation, domain size, connectivity between adjacent domains, and so on. Though great effort has been made, the complex solid-state microstructures of conjugated polymers are still challenging to characterize and control. A comprehensive understanding of molecular and hierarchical structure-related properties is crucial to promote the rational design and processing of high-performance conjugated polymers.

Conjugated polymers are normally fabricated through solution-processed techniques. Due to the complex intermolecular interactions, such as π-π interactions, dispersion interactions, chain entanglement, and so on, polymer chains tend to form aggregates even in dilute solution. The aggregates and the chains will further assemble and grow during the solidification process. Thus, the aggregates and assembly process in the solution will incorporate and affect the solid-state hierarchical microstructures. Regulating the assembly process of a conjugated polymer solution is an effective strategy for manipulating the solid-state hierarchical microstructures. Pei and co-workers proposed the multi-level assembly of conjugated polymers several years ago. More precisely, the one-dimensional polymer chain structures are regarded as primary structures; assembly structures formed from single polymer chains through interactions such as π-π stacking and chain entanglement are considered as secondary structures. Tertiary structures such as crystalline and amorphous regions result from different phase behaviors, while quaternary structures mainly originate in multi-component interactions and phase separation. Changes in aggregation structures at different length scales could determine the ultimate device performance. The factors affecting the aggregation of conjugated polymers in solutions can be summarized as chemical structures, molecular weight, concentration, temperature, aggregation kinetics, solution quality, *etc*. The chemical structures of repeat segments in conjugated polymers will introduce various intra- and intermolecular interactions, such as π-π interaction and hydrogen bond, which will affect the torsion angle

and interchain π-π stacking. Besides, the functional groups and side chains could also influence polymer conformation. A subtle relationship between charge transport and polymer packing should be carefully modulated to maximize the devices' performance. Recently, Segalman and coworkers systematically investigated the chain rigidity of several different high-mobility donor-acceptor conjugated polymers in dilute solution. The persistence lengths measured by small angle neutron scattering (SANS) correlated well with the dihedral distributions from density functional theory (DFT), revealing that the rigid polymer chains arise from planar and collinear conjugated units. The molecular weight of the resulting polymers also plays a crucial role in determining the polymer film's morphology and electric performance, which results from domain connectivity and inherent effects of chain length. Geng and coworkers demonstrated that diketopyrrolopyrrole (DPP)-based polymers displayed increased length of 1D rigid rod-like aggregates with molecular weights increased from 21 kDa to 135 kDa. The further bar-coating process highlighted the significance of morphology and polymer alignment affected by molecular weight. The concentration of polymer solution seriously affects the density of interchain contact sites and the aggregate evolution during solidification. Diao and coworkers confirmed the emergence of concentration-controlled chiral lyotropic liquid crystal mesophases in IID-based polymers by combining *in situ* and *ex situ* optical and electron microscopy and X-ray scattering. Upon the concentration increased beyond the threshold, the overall symmetry breaking of the IID-based polymer nanofibers occurred and was amplified during the multimolecular assembly process. The solution temperature is also one of the most critical parameters in the solution processing of conjugated polymers, which mainly affects solubility and molecular thermal motion. Jackson, Pablo, and their coworkers explored the single-chain conformational properties of conjugated polymers through theoretical calculation, providing a rich temperature-dependent conformational landscape. Besides, Pei and coworkers explored solution temperature's effect on polymer chain conformation. The strong molecular motion at high temperatures would assist the aggregated polymer in overcoming the crystallization energy barrier and in forming orderly packed structures, which provided a simple way to tune the solution-state aggregation of conjugated polymers towards high-crystallinity films with high device performance. The abundant interactions and conformation freedom of conjugated polymers might lead to complex aggregation behaviors in solution. Revealing the kinetics and thermodynamics of polymer aggregation is also crucial for precisely manipulating the solution-state aggregation and solid-state microstructures. Pei and coworkers unraveled the energetic and structural information of naphthalene diimide (NDI)-based polymers during aggregation. They verified that kinetic and thermodynamic stable aggregates originating from different backbone conformations lead to significantly different solid-state microstructures and optoelectronic properties. In addition to the contributors mentioned above, additives blended in polymers could change their morphology and mechanical property. External stimuli such as UV irradiation and the aging process could also significantly regulate interchain aggregation.

Besides the single-component systems mentioned above, the multi-level aggregation in multi-component systems also plays a critical role in determining optoelectronic properties. For blends of polymers, the microstructure is more complex because additive components may affect the phase and aggregation behaviors of conjugated polymers. Crucial parameters such as phase separation, miscibility, and effective charge transport channels between different components should be clarified. Bao and coworkers blended poly(2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-*c*]pyrrole-1,4-dione-*alt*-thieno[3,2-*b*]thiophen) (DPPT-TT) with elastomer polystyrene-block-poly(ethylene-*ran*-butylene)-block-polystyrene (SEBS). DPPT-TT nanofibers formed from phase separation exhibited reduced crystallinity but still high aggregation, *i.e.*, nanoconfinement effect, which enhanced stretchability without affecting charge transport mobility. This blending method provided a common strategy to realize intrinsically stretchable devices with high performance. In organic solar cells, moderate phase separation is expected because it can boost both the separation of excitons and the transport of free carriers which benefits device performance. DeLongchamp and coworkers found that adding phenyl-C61-butyric acid methyl ester (PCBM) to the P3HT solution could slow polymer solution-state aggregation, which finally tuned the solid-state morphology. Wang and coworkers blended PM6 polymer with different non-fullerene acceptors and promoted ordered interchain interactions of PM6 polymer *via* a cold-aging strategy. Enhanced and balanced hole and electron mobilities improved the filling factor and PCE in solar cell devices. Doping is an effective approach to tuning the carrier density and electronic conductivity in conjugated polymers. However, a system containing conjugated polymers with different charge states, neutral dopants, and dopant count ions produced by doping reactions makes the aggregation process more complicated. Therefore, besides pristine solution-state aggregation, miscibility and disturbed polymer original packing caused by dopants should be taken into consideration equally. Pei and coworkers reported two n-doped polymers with thiophene-fused benzodifurandione-based oligo(*p*-phenylenevinylene) (TBDOPV) backbones. Rigid planar backbones but disordered crystalline structure of TBDPPV and TBDOPV-T feature them excellent structural tolerance and outstanding miscibility with n-dopant *N*-DMBI. Both high concentrations and high mobility of the charge carriers showed their promising application in electrical conductivity and thermoelectric performance. As for ionic–electronic systems, ionic and electronic interactions between conjugated polymers and additives play a more important role in controlling their aggregation. Chen, Liu and coworkers controlled the phase separation between the conductive PEDOT (poly(3,4-ethylenedioxythiophene)) and the insulating PSS (poly(styrene sulfonate)) by anneal-

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ing and subsequent solvent post-treatment which boosted carrier mobility and carrier concentration synergistically *via* the formation of well-crystallized molecular morphology.

Based on the understanding of the multi-level aggregations of conjugated polymers, several aspects and future directions for high-performance organic electronic devices are proposed as follows. (1) The polymer physics of conjugated polymers is unclear, and traditional polymer physics is often difficult to explain conjugated polymers' experimental phenomena. This is mainly because the intrinsic rigid properties of π-conjugated systems differ significantly from those of traditional flexible chains. Besides, complex interactions among rigid backbones, flexible side chains, and solvent should be clarified, because these interactions strongly determine the aggregation behavior. The manipulation of multi-level assembly of conjugated polymers is usually based on trial-and-error approaches. Moreover, advanced computational techniques can be introduced to build databases for designing new structures and optimizing processing parameters. (2) The qualitative or quantitative relationships between the different hierarchical microstructures of conjugated polymers remain obscure. Molecular design can adjust the intrachain structure of conjugated polymers, but the effects of lower-level structures on higher-level ones remain obscure. (3) The ordered and disordered microstructures of conjugated polymers require more precise structural models to build a bridge between the complex microstructures and their corresponding performance. Therefore, charge transport properties and mechanisms in real polymer systems could be appropriately inferred according to given structures. (4) During the solidification process, conjugated polymers' chain conformation and aggregation structures changed dynamically. It is necessary to develop *in situ* characterization techniques and theoretical simulations to directly observe the aggregation and evolution of conjugated polymers from solution to solid state. In this way, we can explore the mechanisms of the assembly process and precisely control the multi-level structures. (5) Intrinsic stretchability is one of the significant merits of employing conjugated polymers in flexible electronic devices. Managing the multi-level assembly process is one of the effective strategies for improving the mechanical properties of the conjugated polymer film. (6) Multi-component blending system is also an effective method to regulate the conjugated polymer assembly process. A clear understanding of the interactions among the multi-components and the quantified influence on the aggregation behavior is helpful in achieving better device performance.

The development of advanced characterization techniques such as high-resolution scanning tunneling microscopy (STM), liquid-phase and cryogenic transmission electron microscopy (TEM) is transforming our understanding of the physical and chemical mechanisms underlying of the dynamic multi-level aggregation and multi-level microstructures of materials. It is believed that with the help of powerful characterizations, the hierarchical structures of conjugated polymers and the structure-property relationships will be unraveled more explicitly, which contributes to further boosting electrical performance in optoelectronic devices.

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