

Nanostructuring of Semi-conducting Block Copolymers: Optimized Synthesis and Processing for Efficient Optoelectronic Devices

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Introduction

Research on "synthetic metals" evolved from a rather esoteric occupation to a lively field of activity ever since the discovery, in 1977, of electrical conductivity in the simple hydrocarbon polymer polyacetylene upon oxidation or reduction (doping).^{1,2} Conjugated polymers, though are not the only class of materials known today as "synthetic metals", now form the most widely investigated group. The dramatic development of this field took off in 1990, after the discovery of electroluminescence in a non-doped conjugated polymer thin film sandwiched between electrodes.³ As a result, during the 1990s, research in this highly interdisciplinary area has focused on semiconductor rather than conductor properties. Derivatives of polythiophene (PT), poly(*p*-phenylene) (PPP), poly(*p*-phenylene vinylene) (PPV) and poly(fluorene) (PF) are the major candidates for use as the active material in field-effect transistors, light-emitting diodes, photodetectors, photovoltaic cells, sensors, and lasers in solution and solid state.^{4,5} Besides their semiconductor properties, polymers also provide a way to obtain patterned structures by means of inexpensive techniques such as spin casting, photolithography, ink jet printing, soft lithography, screen printing and micromolding onto almost any type of substrate, including flexible ones.^{4,6} Some applications have already been commercialized (LEDs), while others are certainly technically feasible (plastic solar cells, electronic circuitry). There is good reason to expect that conjugated polymers will play their role in the emerging communication and information technologies, which are based on the use of optical signals for data transfer.

The main advantage offered by polymers over the traditional semiconductor materials is the versatility of processing methods, which allows a polymer to be obtained in virtually any desired shape and in composite form with many other materials. Deposition as a thin film over a macroscopically large area is particularly attractive. Where classical polymer processing could be used, the processing cost would be low. For this to become a reality, the parent conjugated polymers, which are highly intractable because of their conjugated, inflexible backbone, have to be derivatized without degrading their optoelectronic properties. With clever synthetic chemistry, impressive progress has already been made on this point.⁷ An appropriate and well-defined chemical structure is a prerequisite for the control of ultimate properties, but it does not end there. The properties of polymer materials depend sensitively on the details of their processing history, and each step has to be carefully carried out so as to achieve the desired result.

The present presentation focuses on polymers for application in photovoltaic cells, which are either light sensor (photodetector) or energy conversion (solar cell) devices. Our emphasis will be on the latter application; in that arena, a well-performing organic material would have to compete with amorphous silicon with regard to energy conversion efficiency and fabrication costs. The potential of the polymer clearly lies in the promise of large-area, mechanically flexible, active coatings fabricated by inexpensive processing techniques.

The requirements and design of polymer photovoltaic materials

A basic requirement for a photovoltaic material is photoconductivity, i.e., that charges are generated upon illumination. Subsequently then, these charges must drift (move in an electric field) towards electrodes for collection. In an organic molecular material, photoexcitation does not directly yield free charge carriers. Due to the

low dielectric constant of organics, an electron in the excited state is bound to its vacancy (hole) quite strongly, the binding energy being several tenths of an electronvolt.² This bound electron-hole pair is called an exciton. Escape from the Coulomb attraction is promoted by offering an energetically favorable pathway to an electron-accepting molecule. This is the donor-acceptor (D-A) concept, which is commonly applied to organic photovoltaic materials.^{8,9} Dissociation of the exciton, via rapid electron transfer (< 200 fs), leaves a positively charged donor molecule and a negatively charged acceptor molecule. These are cation and anion species, respectively, stabilized by charge delocalization within their conjugated systems and by polarization of their environment. Exciton dissociation occurs at the interface between donor and acceptor species. Although it is not a priori evident what the nature of this interface should be in terms of scale and geometry, optimization within the D-A concept is likely to imply that this interface be made large and easily accessible for the excitons generated. Since excitons have a finite lifetime, they have a finite diffusion range as well. Hence, the requirement of accessibility naturally leads to constraints for the geometry of the interface. A spatially distributed interface with a correlation length of 10 nm would be compatible with the evolution of the exciton: the exciton would have a higher probability of reaching the interface and dissociate than to decay in another way, e.g., radiatively. After dissociation, the charges must be further separated and transported each through its own phase so as to avoid recombination before the electrode is reached. This D-A concept has been recently implemented by using interpenetrating polymer blends of donor and acceptor homopolymers sandwiched between two asymmetric contacts (two metals with different workfunction) for photovoltaic devices.^{9,10} This bi-continuous network of donor-acceptor heterojunctions facilitates simultaneously the efficient exciton dissociation and a balanced bipolar charge transport throughout the whole volume of the device.

The performance of this type of device is very sensitive to the morphology of the blend, since exciton dissociation as described above occurs only at the donor-acceptor interface, and charge transport depends on the geometry and composition of the phases. A system of spatially distributed donor-acceptor heterojunctions may contain imperfections that degrade performance, such as fully dispersed domains and cul-de-sac-type discontinuities of the donor and/or acceptor phases. Furthermore, the extended interface area is accompanied by an enlarged phase boundary volume in which donor and acceptor species are molecularly mixed. This is likely to result in increased energy level disorder, causing an increase of the charge trap density and a reduction of the electron and/or hole mobility. Hence, though exciton dissociation may be enhanced, transport is impeded by the circuitous geometry of the interface. For these and other reasons, the overall device performance can be lower than expected. The transport problem is altogether absent in a double-layer structure with a single, planar donor-acceptor heterojunction. Since, however, the exciton diffusion range is typically ca 10 nm and hence shorter than the light absorption depth, a properly dimensioned and structured network of donor-acceptor heterojunctions should be more efficient in terms of the exciton dissociation than the simple double-layer structure. It is not obvious how to impose such a nanometer-size and regularly interpenetrating morphology on a mixture of donor and acceptor homopolymers: they would probably either mix molecularly or phase separate into nearly pure components. This is exactly the point at which block copolymers provide the answer, because of their ability to self-organize. Block copolymers are a well-known class of compounds that can show well-ordered, regular morphologies through microphase separation, which is along the strategy outlined above.¹¹ The composition of the components is fixed due to the synthesis, the morphology of phase-separated films can be controlled (by the interaction parameters, block lengths and ratios), and the dimensions of the domains are in the order of several nanometers. Therefore, this class of materials seems to be destined to yield much higher performances in photovoltaic devices than the homopolymer blend. The simplest molecule would be a photovoltaic diblock copolymer consisting of a block with donor functionality linked to a block with acceptor properties. The electronic functions could be either in the main chain of the blocks or in substituents. Microphase separation would produce a suitable geometry at the proper scale that could be fine-tuned via the lengths of the blocks. In this context, cylindrical and bi-continuous interpenetrating morphologies are the most appropriate ones.

Photovoltaic performance of donor–acceptor block copolymers

Based on the general principles discussed above, we have designed and synthesized a self-structuring block copolymer especially for photovoltaics.¹² It is a diblock copolymer consisting of a semiconducting rod block and a coil block densely functionalized with acceptor moieties (ex. C₆₀). The synthesis of such a rod–coil polymer poses several challenges. To obtain a well-defined material providing a bi-continuous interpenetrated microphase-separated structure throughout its volume, good control over the length of both blocks and their volume ratio is desirable. Furthermore, the incorporation of a sufficient amount of acceptor moieties into one block of the diblock copolymer is necessary for satisfying two requirements for the efficient operation as a photovoltaic material: (i) creating an accessible donor–acceptor interface at which dissociation of excitons into separate charge carriers is promoted, thus reducing the probability of decay along other routes, of which luminescence is one; (ii) providing separate pathways for transport of holes (via the rod block) and electrons (via coil block), thus reducing the recombination probability. A reduction of the photoluminescence lifetime relative to the non-acceptor-functionalized diblock copolymer is a first indication that an effective donor–acceptor interface has been created by incorporating the electron acceptor. In such examples the PL intensity is found to be reduced by three orders of magnitude as a result of the incorporation of the acceptor moieties. Both copolymer films exhibit similar morphologies, which makes the comparison legitimate. These results are taken as evidence for an efficient, very rapid electron transfer from the donor block to the acceptor.¹²

When comparison is made between the D–A block copolymer and the blend of the donor and acceptor homopolymers of the corresponding blocks, an enhancement in photovoltaic performance is observed going from the blend to the block copolymer. This superior response can be seen in measurements of current versus voltage (I – V) on devices from the blend and the block copolymer under monochromatic illumination of 1 mW/cm² at 458 nm. The enhancement is mainly due to the larger D–A interface and the higher continuity of transport pathways for charges in the block copolymer.

Although both blend and block copolymer show almost complete quenching of the fluorescence in the solid state, the obtained collection efficiencies (the ratio of collected electrons and absorbed photons) are significantly smaller than unity. This could be attributed to several processes among which the following two seem to be the most important ones. Firstly, exciton dissociation upon photoexcitation could be neither the only nor the main energy deactivation pathway. Energy transfer could compete with the dissociation, or the charge separation might not be effective.¹³ Secondly, in either system, blend or block copolymer, mixing of donor and acceptor at the molecular scale may introduce increased energy level disorder in both phases, which results in an increase of the charge trap density with a significant increase of the space-charge field and, consequently, in a reduction of the electron and/or hole mobility.¹⁴

The results obtained with a C₆₀-modified PPV-PS block copolymer, which still leave ample room for optimization as far as microstructure is concerned, seem to validate the block copolymer strategy towards self-assembling materials for photovoltaic applications. Other strategies have been recently pursued with success making use of the self-assembling properties of liquid-crystal materials.¹⁵

Conclusions

The record photovoltaic power conversion efficiency in polymer semiconductors is ~5%. This record was achieved by optimizing the network structure of donor and acceptor homopolymer blends via trial and error in the solvent casting of polymer films.¹⁶ The best reported photovoltaic quantum efficiency, 34% at 490 nm, is obtained by judiciously engineering, through a self-assembly approach, the microstructure of liquid-crystal materials and by paying extra attention to the absorption spectrum of the active material.¹⁵ In our opinion, the scientific and technology challenges for highly efficient polymer photovoltaic materials and devices are the following: (i) obtaining chemically ultra-pure polymer materials; (ii) optimizing the light absorption of the active polymer for efficient harvesting of the solar spectrum; (iii) making a judicious choice of donor and acceptor

polymer pairs for the most efficient exciton dissociation and charge transport; (iv) understanding and optimizing the electrode/polymer and donor polymer/acceptor polymer interfaces for better charge extraction/injection; (v) last but not least, optimizing/controlling the nanostructuring of the active material. Most efficiently and elegantly, the nanostructuring can be accomplished through self-organization of matter rather than by manipulation or machining, wherever possible. As is illustrated in this presentation, the idea seems to be highly applicable to block copolymers, which can be chemically fine-tuned to show phase separation at the proper scale and to possess the desired chemical, physical and electronic properties, fulfilling thus all the requirements imposed by the challenges enumerated above. With chemical routes towards conjugated polymers being so different from those employed for conventional polymers and requiring ultra-high chemical purity, synthetic chemists face an enormous challenge in dealing with block copolymer architectures. The success of making a diblock copolymer with each block possessing an electronic function, and having its targeted photovoltaic characteristics confirmed, is the first encouraging step in the pursuit of this strategy for the bottom-up design of optoelectronic materials.¹⁷

Acknowledgments

The following people are gratefully acknowledged for their contribution to the work described: Prof. T. Heiser, Dr. C. Brochon, Dr. G. Schlatter, Dr. K. van de Wetering, Dr. N. Leclerc, Ngov Chheng and Dr M. Brinkman.

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