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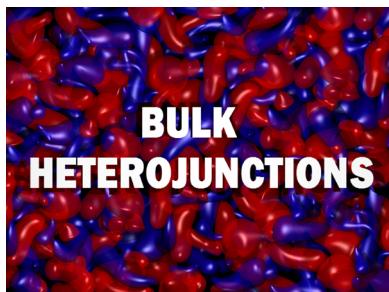
Controlling the Morphology and Performance of Bulk Heterojunctions in Solar Cells. Lessons Learned from the Benchmark Poly(3-hexylthiophene):[6,6]-Phenyl-C₆₁-butyric Acid Methyl Ester System

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1. INTRODUCTION

Photovoltaic cells are an established and increasingly important technology for the production of renewable energy.¹ Despite the expanding use of inorganic semiconductors in photovoltaic cells, molecular semiconductors have a very promising future, and they permit the fabrication of solar modules with several potential advantages, including light weight, flexibility, low-cost production, and the possibility of creating large-area devices.^{2–11}

Since 2000, when Heeger, MacDiarmid, and Shirakawa received the Nobel Prize in Chemistry for discovering and developing conducting polymers,^{12–14} the exploration of new molecular materials with novel electronic properties has become an increasingly exciting area of research. The extraordinary properties of these materials are of both academic and industrial interest. Whereas organic semiconductors of low molecular weight are generally deposited by evaporation under vacuum, films of conjugated polymers are conveniently created from solution using wet processing techniques. For the production of prototypic devices, the commonly used technique of spin coating is effective on the laboratory scale, but it is not suited for large-scale manufacturing because of the attendant waste of material. Alternative techniques for industrial fabrication have been considered, including doctor blading, screen printing, roll-to-roll printing, pad printing, and inkjet printing.^{8,15–24} These techniques for deposition can be performed under ambient conditions and scaled up to large areas with limited loss of material.

Many reviews have been dedicated to the development of molecular photovoltaics.^{11,25–44} Most have focused on general aspects of organic-based solar cells such as operating principles, architectures of devices, materials, and efficiency. In the present review, a special emphasis is placed on the detailed morphology of the active layer as a key factor in the creation of efficient devices. Previous reviews have given an overview of the relationship between morphology and performance, but there is no comprehensive source of information about this topic, and it has not been examined by reviewers with a special interest in molecular organization and supramolecular chemistry. In

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particular, the present review emphasizes the illustrative behavior of blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (Figure 1). This emphasis

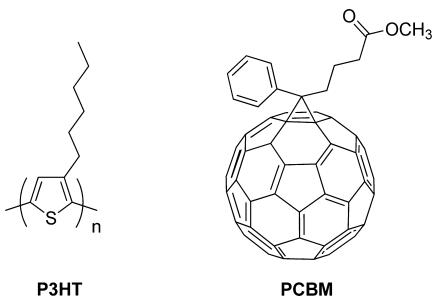


Figure 1. Chemical structures of P3HT and PCBM.

is warranted because P3HT and PCBM have been widely used together in molecular solar cells,⁴⁵ thereby providing a wealth of information that shows how the ultimate performance of cells depends on specific variables involved in the production of the active layers. There is no guarantee that generalizations derived from studying the behavior of P3HT:PCBM blends will prove to be broadly applicable to all other systems. Nevertheless, detailed analysis of the correlation between morphology and performance in a particular system is likely to have a significant heuristic value in the effort to produce improved devices of various types in which complex molecular mixtures are present.

Our review begins with a brief description of the individual properties of P3HT. We then summarize the complex dependence of the electronic properties of P3HT on the conditions under which it is typically processed and on the degree of organization in its structure. Next we outline common parameters and experimental approaches that can be used to help control the molecular organization of mixtures of P3HT:PCBM. In particular, complex metastable nanostructures called bulk heterojunctions can result when the two components are blended. These morphological factors play a critical role in determining the efficiency of the resulting devices. Morphological stability is also addressed, and the review summarizes various strategies that have been devised to overcome the dramatic problem of the eventual separation of two distinct P3HT and PCBM phases that no longer have the desirable properties of more intimate mixtures of the two components. Finally, we show how understanding the P3HT:PCBM system provides a foundation for efforts to increase the efficiency of solar cells made from new components.

2. P3HT

Among semiconducting polymers commonly explored for use in molecular solar cells, P3HT and its close analogues remain among the most interesting candidates. An important issue is the regioregularity of these polymers, which measures the extent to which the sample can be considered to be a single molecular species with a perfect alternation of alkylated and nonalkylated sites on the thiophene rings. In principle, uncontrolled coupling of 3-substituted thiophenes at the 2- and 5-positions can lead to polymers with different degrees of regioregularity due to the formation of head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT) isomers (Figure 2a). This results in four regioisomeric triads in the polymer chain (HT-HT, TT-HT, HT-HH, and TT-HH), as shown in Figure 2b.^{46–49}

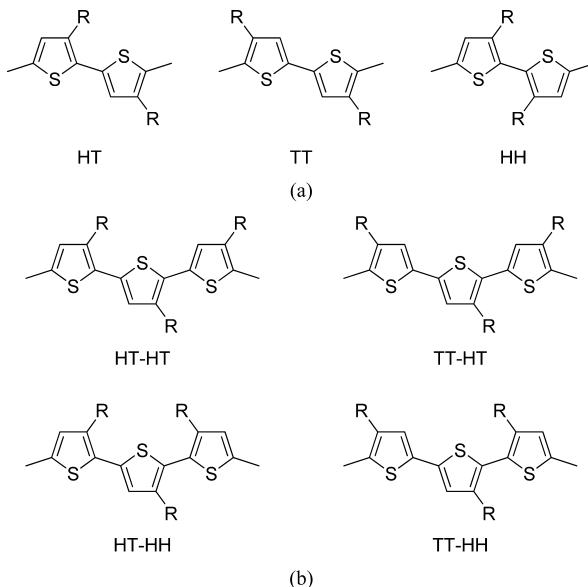


Figure 2. (a) Diad linkages of 3-substituted dithiophenes. (b) Isomeric triads.

The degree of head-to-tail regioregularity is defined as the percentage of thiophene units in the polymer that adopt a head-to-tail orientation. An important advance in the synthesis of poly(thiophene)s was made in 1992, when highly regioregular HT-P3HT was first prepared by Rieke⁴⁹ and McCullough.^{46,50} The degree of regioregularity has a significant effect on the properties of substituted poly(thiophene)s that help determine their behavior in molecular devices. For example, highly regioregular HT-P3HT has high hole mobility in the regular undoped state ($\mu_h = 0.1\text{--}0.3 \text{ cm}^2/\text{V s}$),^{51–55} high crystallinity, and an extended range of absorption up to 650 nm, giving a band gap of about 1.9–2.0 eV. These data show that regioregular HT-P3HT has more extended conjugation than regiorandom P3HT. The HT orientation facilitates coplanarity of adjacent thiophene rings. Indeed, the regioregular HT polymer has a nearly planar conformation with efficient packing and better intra- and intermolecular overlap, whereas the regiorandom polymer has a twisted conformation, which leads to limited conjugation, poor packing, and low crystallinity.

2.1. P3HT: Orientation and Charge Transport

Regioregular HT-P3HT (RR-HT-P3HT) tends to adopt a layered structure in which laterally packed thiophene main chains are separated by alkyl side chains.^{48,50,56,57} Related structures have been observed in thin layers deposited on surfaces. For example, in 1995 Fell et al. dissolved P3HT in chloroform, deposited the polymer by spin coating on glass slides, and detected for the first time an arrangement in which the polymers were oriented with their side chains parallel to the substrate.⁵⁸ In 1999, Sirringhaus et al. used grazing-incidence X-ray diffraction to identify two different orientations of microcrystalline P3HT domains deposited on field-effect transistor (FET) substrates, as shown in Figure 3.⁵⁶ Polymers with high HT regioregularity (RR = 96%) but low molecular weight ($M_w = 28 \text{ kg/mol}$), when deposited by spin coating from chloroform, were found to adopt an “edge-on” arrangement in which the side chains are normal to the substrate surface. In contrast, polymers with low regioregularity (RR = 81%) but high molecular weight ($M_w = 175 \text{ kg/mol}$) were shown to favor a “plane-on” orientation in which the side chains are parallel to the substrate. Yamamoto et al.

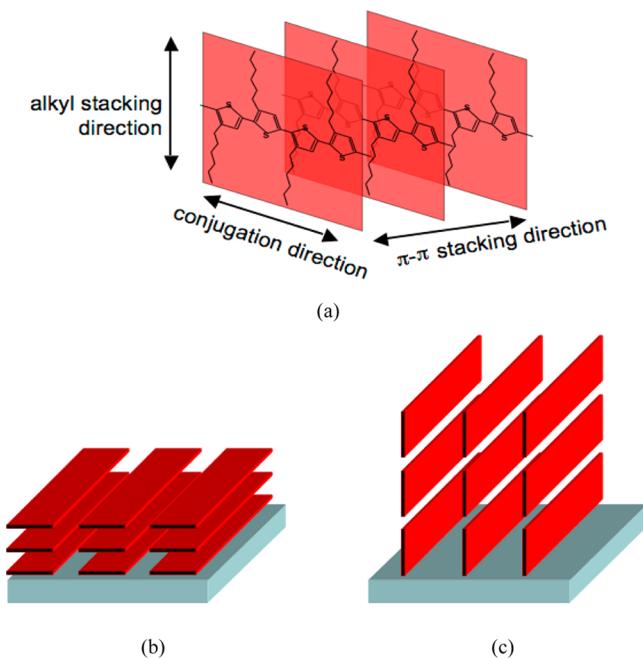


Figure 3. (a) Schematic structure showing the preferred arrangement of adjacent chains of regioregular HT-P3HT. (b) Plane-on orientation of P3HT with respect to an underlying surface. (c) Alternative edge-on arrangement. Reprinted with permission from ref 60. Copyright 2006 Elsevier Ltd.

controlled the orientation and the alignment of the polymer by tuning the surface properties of the substrate.⁵⁹ For example, molecules of P3HT drop-cast on thin films of cross-linked poly(4-vinylphenol) are preferentially oriented edge-on, whereas monolayers of P3HT on Au(111) adopt a plane-on orientation.

A small number of papers have explored the relationship between charge transport in layers of P3HT and the orientation of P3HT within the layers. Sirringhaus et al. showed that the highest hole mobility in molecular field-effect transistors (OFETs) is achieved in P3HT films with an edge-on orientation.⁵⁶ DeLongchamp et al. suggested that the orientation of P3HT relative to the surface is related to the rate of evaporation of solvent, which depends in turn on the speed of rotation used in spin coating.⁶¹ In truth, edge-on orientations appear to be favored by slower rotation and slower evaporation during deposition. Charge transport is fastest in the direction of conjugation. When chains pack, the preferred supramolecular ordering places the π -orbitals of different polymer chains in cofacial stacks. This partial overlap between π -orbitals assists charge transfer between chains, leading to good mobility in two orthogonal directions. In the third direction, however, the insulating alkyl chains impede charge transport, making mobility in this direction inherently low. As a result, films containing more edge-on crystalline phase have higher mobility, as measured in the configuration used to evaluate OFETs. Together, these data suggest that high crystallinity in deposited layers of P3HT can be promoted by properties of the individual molecules, particularly by their regioregularity and molecular weight, as well as by the conditions used for deposition, such as the speed of spinning and the substrate used.

2.2. Casting Techniques: Spin Coating, Dip Coating, and Drop Casting

P3HT tends to assume fibrillar shapes when solutions are evaporated, but the detailed organization depends strongly on

the technique of deposition. Spin coating normally incites a fast evaporation of solvent, leading to less ordered structures than those produced by dip coating or drop casting. These latter methods allow slower evaporation of solvent and thereby promote more ordered arrangements.

Extensive data have demonstrated the influence of the casting method on the orientation of P3HT crystallites. For instance, Sirringhaus et al. obtained an edge-on orientation with a high-molecular-weight polymer ($M_w = 175$ kg/mol, RR = 81%) by drop casting, whereas they observed a plane-on arrangement by spin coating.⁵⁶ In contrast, only an edge-on orientation was obtained with low-molecular-weight P3HT ($M_w = 28$ kg/mol, RR = 96%), regardless of the casting method used. Intermediate cases are also reported in the work of Aasmundtveit,⁶² who obtained two different orientations from stereoregular P3HT (RR > 98%) by spin coating from chloroform. Studies using X-ray diffraction revealed that a mixture of orientations (plane-on and edge-on) is formed in spin-cast films. Sethuraman et al. obtained the same edge-on orientation for films of P3HT ($M_w = 87$ kg/mol, RR = 98.6%) fabricated by drop coating using three different solvents (chloroform, toluene, and 1,2,4-trichlorobenzene).⁶³

In conclusion, the slower evaporation of solvent that occurs in drop casting or dip casting appears to facilitate slower growth of films, leading to a higher degree of order in the structure of P3HT. Under these conditions, P3HT preferentially adopts an edge-on orientation with respect to the underlying surface, whatever solvent is used. In spin casting, self-organization is inhibited by fast drying, and the arrangement of the polymer depends on numerous other parameters such as the regioregularity and molecular weight, the speed of spinning, and the solvent.

2.3. Relationship between Polymer Morphology and Charge Mobility

For a given solvent, the casting method influences the rate of evaporation and therefore the degree of crystallization of P3HT. A beautiful example is provided by the work of Verilhac et al. (Figure 4),⁶⁴ who reported atomic force microscopy (AFM) images that show highly variable surface states according to the method of deposition and the molecular weight of P3HT. Dip coating induces the formation of a morphology that can be described as nanorods, whatever molecular weight is used. In contrast, spin coating results in a clear rodlike morphology only for the fraction of lowest molecular weight.

Molecular weight strongly affects the charge-carrier mobility of layers of P3HT.^{64–72} Methods of deposition that retard evaporation of solvent (dip coating and drop casting) give layers with high charge-carrier mobility. This tendency is also reported in the studies of Wang^{52,73} and Heil,⁷⁴ who reported the transistor mobility of films of P3HT deposited by spin coating and drop casting from chloroform. The mobility obtained from a drop-cast film is higher than that obtained by spin casting, possibly because of higher ordering resulting from the slower rate of evaporation of solvent. Although Bao et al. reported higher mobility for a spin-cast film than for a drop-cast film,⁷⁵ the opposite was again observed when chloroform was used as the solvent. Using P3HT of low molecular weight, Kline et al. obtained higher hole mobility for a film drop-cast from chloroform than from a film made by spin coating.⁶⁸

In summary, when time is allowed for P3HT to crystallize, either by using casting techniques with slow evaporation of solvent or by using solvents with high boiling points, charge

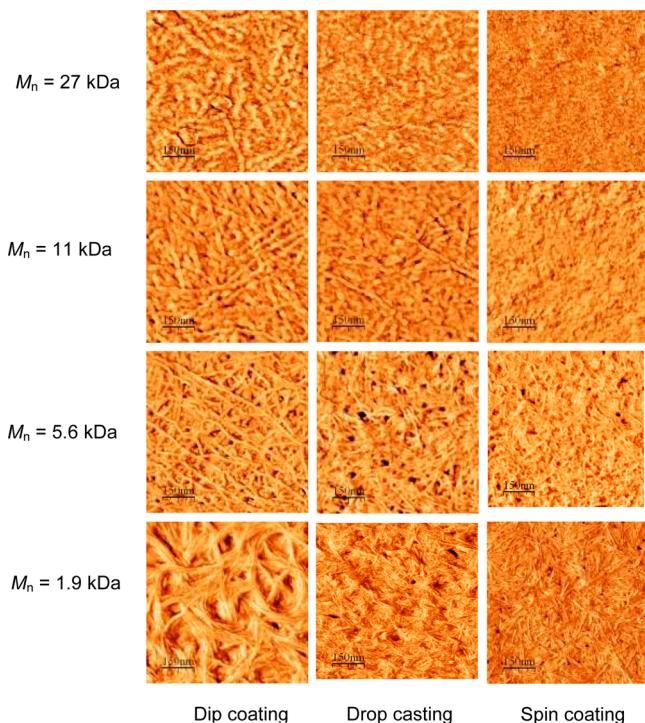


Figure 4. Tapping-mode AFM images of the surface of films of P3HT of different molecular weights, deposited on SiO_2 using various techniques. Reprinted with permission from ref 64. Copyright 2006 Elsevier B.V.

mobility in the resulting films is typically improved. Surin et al. measured high charge-carrier mobility in films of P3HT cast from a high-boiling solvent, 1,2,4-trichlorobenzene (TCB), but only when spin coating was used to deposit the film.⁷⁶ Other techniques may produce films with residual TCB, which may solvate the polymer chains and interfere with charge transport by preventing effective stacking. Cheng et al. also observed that residual solvents can alter the electrical properties of RR-P3HT.⁷⁷ To summarize the plentiful literature related to this subject, various results are gathered in Table 1.

Many research groups have investigated the effect of thermal annealing on hole mobility in thin films of P3HT.^{53,66,81–85} In some cases, heating has been shown to increase mobility,^{53,66,81,84} possibly because annealing can help remove residual solvent, thereby facilitating the ordering and packing of flattened chains. In other cases, however, only modest changes in mobility have resulted from annealing.^{82,85,86} The diverse observations presumably reflect differences in the properties of P3HT⁶⁶ and in the conditions of processing,⁸³ including solvent, source/drain electrodes for OFET devices,⁸³ and treatment of the substrate.⁸²

Together, these data show that the nanostructure of thin films composed of P3HT depends on the intrinsic properties of the polymer (such as regioregularity and molecular weight) and on the conditions of processing (such as the casting technique, solvent, and surface of the underlying support).

3. CONTROLLING THE MORPHOLOGY OF BULK HETEROJUNCTIONS

Free holes and electrons cannot be created directly in molecular semiconductors when light is absorbed because excitons have a large binding energy (0.2–1.4 eV).^{87–101} Instead, absorption of light induces the formation of Frenkel-like excitons, which correspond to a neutral mobile excited state.^{102,103} To produce electricity, excitons must subsequently be split apart to generate

free electrons. Excitons are dissociated efficiently at interfaces formed by two molecular semiconductors only when they have an appropriate difference in electron affinity and ionization potential (donor:acceptor interface).^{104,105} The primary mechanism for excitons to reach such interfaces is diffusion. Unfortunately, the typical diffusion length of excitons in relevant conjugated polymers is confined approximately to 4–20 nm.^{102,106–116} To be productive, excitons must be able to reach a suitable interface within this distance before undergoing recombination.

To overcome this hurdle, the concept of intimately blended bulk heterojunctions has been developed. The finding that such structures can be created by simply mixing electron-donating and electron-accepting materials (D:A) under suitable conditions constitutes an early breakthrough in molecular photovoltaics.^{117,118} The high yield of photocurrent in bulk heterojunction devices is attributed to efficient dissociation of excitons at the dispersed interface between the domains. However, if the donor and acceptor are too finely intermixed on the molecular scale, dissociation of excitons will be enhanced due to the large interfacial area, but charge transport will be strongly inhibited due to a large number of bottlenecks and a low density of pathways for charge percolation. Heterojunctions that are too finely intermixed also show increased recombination of excitons. This phenomenon results in decreased efficiency of photovoltaic conversion. In contrast, a full separation of the two components, as in a bilayer structure, will enhance the collection of charge at the electrodes, but the dissociation of excitons will be decreased. This inevitable trade-off makes nanoscale control of the morphology of the active layer a difficult challenge that must be met to produce efficient solar cells. For organic photovoltaic devices, proper morphology of the active layer is primordial and governs the physics of photovoltaic processes.

Kroto, Curl, and Smalley received the 1996 Nobel Prize in Chemistry for discovering a third allotrope of carbon in which the atoms are bonded to form soccer-ball-shaped cages, known as fullerenes or buckminsterfullerenes.^{119–122} The lowest unoccupied molecular orbital (LUMO) of fullerenes is known to be energetically low-lying,¹²³ giving the molecules a high electron affinity and allowing them to accept electrons from numerous polymeric donors such as poly(phenylvinylene), poly(thiophene), and poly(carbazole) under suitable conditions. Furthermore, blends of conjugated polymers with fullerenes show ultrafast photoinduced charge transfer.^{124–127} The prototypic fullerene, C_{60} , has a high electron mobility in thin-film OFETS.^{128–130} However, the typically poor solubility of C_{60} in common solvents and its high tendency to crystallize make achieving desirable morphologies difficult. To overcome this problem, solubilizing substituents have been introduced into fullerenes. Successful examples of this practice are methanofullerenes such as PCBM,^{131,132} the most widely used electron acceptor in composite polymeric devices.^{45,133}

When PCBM is blended with P3HT, the presence of the polymer helps ensure the formation of thin films and contributes to the final properties of the active layer; however, the two components tend to eventually form separated phases. Various strategies have been used to attempt to optimize the morphology of the blend, including control of regioregularity, molecular weight, solvent, and film treatment (such as thermal annealing or solvent annealing). In the following paragraphs, we discuss the effect of all these factors when PCBM is present as a component of mixtures with P3HT.

Table 1. OFET Mobility of P3HT as a Function of the Solvent and Method of Deposition^a

solvent	mobility [cm ² /(V s)]			ref
	dip coating	drop casting	spin coating	
CHCl ₃ (61)		4.5 × 10 ⁻³	9.2 × 10 ⁻³	75
tetrahydrofuran (66)		6.2 × 10 ⁻⁴		
toluene (110)		3.6 × 10 ⁻³	3.2 × 10 ⁻³	
1,1,2,2-tetrachloroethylene (121)		6.8 × 10 ⁻³		
chlorobenzene (132)		4.7 × 10 ⁻³	6.9 × 10 ⁻⁴	
p-xylene (138)		1.9 × 10 ⁻³	1.9 × 10 ⁻⁵	
1,1,2,2-tetrachloroethane (146)		2.4 × 10 ⁻²		
CHCl ₃ (61)		6.18 × 10 ⁻⁴	1.78 × 10 ⁻⁴	74
CHCl ₃ (61)	8.50 × 10 ⁻²		3.80 × 10 ⁻²	73
CHCl ₃ (61)			0.76 × 10 ⁻²	54
thiophene (84)			3.00 × 10 ⁻²	
xylene (138)			4.10 × 10 ⁻²	
cyclohexylbenzene (239)			4.90 × 10 ⁻²	
1,2,4-trichlorobenzene (214)			6.30 × 10 ⁻²	
CH ₂ Cl ₂ (40)		~1 × 10 ⁻³		78
CHCl ₃ (61)		~10 × 10 ⁻³		
tetrahydrofuran (66)		~8 × 10 ⁻³		
toluene (110)		~2 × 10 ⁻³		
chlorobenzene (132)			4.80 × 10 ⁻⁴	79
p-xylene (138)			2.90 × 10 ⁻³	
CHCl ₃ (61)	(8.5 ± 2.0) × 10 ⁻²	(2.1 ± 0.3) × 10 ⁻²	(1.1 ± 0.3) × 10 ⁻³	76
p-xylene (138)	(1.5 ± 0.4) × 10 ⁻²	(1.4 ± 0.5) × 10 ⁻³	(1.5 ± 0.2) × 10 ⁻²	
1,2,4-trichlorobenzene (214)	(2.4 ± 0.7) × 10 ⁻³	(1.5 ± 1.0) × 10 ⁻⁴	(2.3 ± 0.2) × 10 ⁻²	
CH ₂ Cl ₂ (40)			(12 ± 3) × 10 ⁻³	80
CHCl ₃ (61)			3 × 10 ⁻³	
CHCl ₃ (61)		4 × 10 ⁻²	4 × 10 ⁻⁴	59
CHCl ₃ (61)		8.4 ± 0.6 × 10 ⁻²		63
toluene (110)		4.3 ± 0.5 × 10 ⁻²		
1,2,4-trichlorobenzene (214)		7.3 ± 0.6 × 10 ⁻²		
CHCl ₃ (61)			2 × 10 ⁻²	77
1,2,4-trichlorobenzene (214)			12 × 10 ⁻²	

^aThe boiling points of each solvent (°C) are given in parentheses after the name of the solvent.

3.1. Regioregularity of P3HT and Photovoltaic Performance

In pure samples of P3HT, high RR is considered to be beneficial for electronic applications, but it is important to reexamine the effect of RR on photovoltaic performance when PCBM is present simultaneously. Regioregularity affects charge transport and absorption in thin films of P3HT, so increased RR might be expected to lead to enhanced performance in photovoltaic devices composed of P3HT and PCBM. In 2006, Kim et al. obtained devices of the highest efficiency when P3HT with the highest RR (95.4%) was used,¹³⁴ which was attributed to better optical absorption and charge transport resulting from the more ordered chain packing of P3HT. However, it should be noted that the polymer used had a smaller value of molecular weight than samples of lower RR. Indeed, the molecular weight of P3HT

also has a significant effect on the performance of devices because it can alter absorption and transport. In fact, Mauer et al. obtained similar power-conversion efficiencies for samples of P3HT with different values of RR (98% and 94%),¹³⁵ presumably because the materials also differed in molecular weight (25 and 60 kg/mol, respectively). A similar trend was observed by Ebadian et al., who showed that the regioregularity of P3HT could be carefully selected to yield photovoltaic devices with high performance and stability over time.¹³⁶ Highly regioregular P3HT (RR > 98%, $M_w = 64$ kg/mol) provided a better initial power-conversion efficiency due to higher optical density and hole mobility, but its efficiency dropped over time because of the segregation of islands of PCBM. In contrast, devices prepared from P3HT with lower regioregularity (RR = 94%, $M_w = 50$ kg/mol) remained more stable, due to limited separation of PCBM. In this case, the

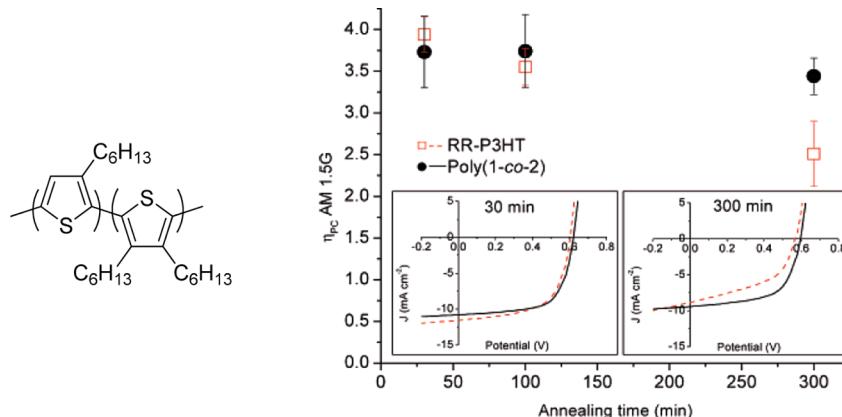


Figure 5. Performance of photovoltaic devices fabricated with standard regioregular P3HT and with a copolymer incorporating 3,4-dihexylthiophene units (structure on the left). The chart on the right gives the average power-conversion efficiency (η) as a function of the annealing time at 150 °C, as well as typical J – V behavior (insets) observed after 30 and 300 min of annealing. The two materials have visibly different properties. The error bars represent the 95% confidence interval of the average values. Reprinted from ref 137. Copyright 2006 American Chemical Society.

combination of higher RR and higher M_w of P3HT did not lead to higher performance.

These observations suggest that high RR is not always the best choice for achieving high photovoltaic performance when all factors are taken into account. For example, P3HT with high RR may offer better performance after appropriate thermal treatment, but lower RR may provide better thermal stability, as demonstrated by Fréchet et al.^{137,138} In 2006, Sivula et al. altered the effective RR of P3HT by introducing 3,4-dihexylthiophene units into the polymer chain.¹³⁷ The lower effective RR of the resulting polymer led to devices with improved thermal stability (Figure 5).

Woo et al. have shown the deleterious segregation of PCBM that occurs when highly regioregular P3HT (96%) is subjected to long thermal treatments.¹³⁸ Indeed, thermal annealing induces crystallization of highly regioregular P3HT and of PCBM within the active layer, resulting in extensive phase segregation of the two components (Figure 6). Consequently, the formation of

crystalline needles of PCBM leads to a decreased interfacial area for charge transfer and thus to lower efficiencies. These studies suggest that the highest degrees of regioregularity are not necessarily beneficial.

Another disadvantage of highly regioregular P3HT lies in the difficulty of making thin films by standard printing techniques. For example, Hoth et al. found that highly regioregular P3HT (RR = 98.5%, M_w = 37 kg/mol, PD = 1.76) is not suitable for inkjet printing using solutions in either tetrahydronaphthalene (THN) or 1,2-dichlorobenzene/mesitylene.^{20,139} The shelf life of the ink was shortened by the formation of inhomogeneous aggregates with dimensions up to 75 nm.

Together, these observations suggest that values of power-conversion efficiency can initially be increased by using blends prepared from highly regioregular P3HT, but enhanced thermal stability can be achieved with polymers of lower RR, with implications for long-term performance.

3.2. Molecular Weight of P3HT and Photovoltaic Performance

The molecular weight of P3HT strongly affects the conformation and packing of the polymer backbone.⁶⁹ Schilinsky et al. varied the molecular weight of P3HT from 2.2 to 11.3 kg/mol and found that higher molecular weight improves the performance of P3HT:PCBM-based solar cells.¹⁴⁰ The observed behavior is consistent with the well-established correlation that links high molecular weight with high charge-carrier mobility and UV-vis absorption. Hiorns et al. observed variations in the power-conversion efficiency as a function of molecular weight (in the range of 4.5–280 kg/mol),¹⁴¹ and they found that the highest efficiency was achieved for devices prepared from P3HT with M_n = 14.8 kg/mol, followed by annealing at 120 °C. Similarly, Ballantyne et al. studied the effect of the molecular weight of P3HT (M_n = 13–121 kg/mol) on charge mobility in thin films made from pristine P3HT and from P3HT:PCBM blends using a highly regioregular polymer.⁷² Polymers with molecular weights in the range of 13–34 kg/mol showed the best charge transport and thus photovoltaic performance. Morana et al. obtained better efficiencies in cells prepared from P3HT with higher molecular weight,¹⁴² using films prepared from solutions in chlorobenzene. Nevertheless, when solutions in *o*-xylene were used to make the films, followed by annealing at 130 °C for 5 min, solar cells prepared from P3HT of lower molecular weight showed better performance. Nicolet et al. have recently used an analysis of

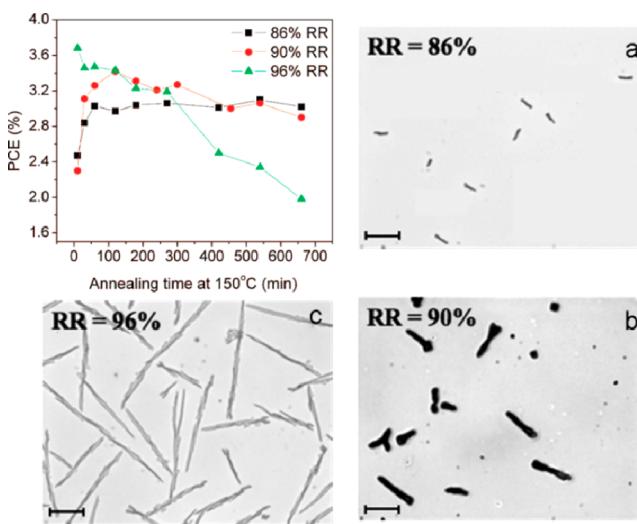


Figure 6. Average efficiencies of bulk heterojunction devices made from 86%, 90%, and 96% RR-P3HT:PCBM annealed at 150 °C for different times. Optical microscopy images of (a) 86%, (b) 90%, and (c) 96% RR-P3HT:PCBM blends at a 55:45 weight ratio after 3 h of annealing at 150 °C. Dark areas are PCBM-rich regions. The scale bar represents 50 μ m. Reprinted from ref 138. Copyright 2008 American Chemical Society.

Table 2. Optimal Polymer:Fullerene Ratios for Use in Solar Cells

polymer	fullerene	optimal ratio	ref
MEH-PPV	PC ₆₀ BB	1:32	145
MEH-PPV	PC ₆₀ BM	1:5	146
MDMO-PPV	PC ₆₀ BM	1:4	147–149
PDDTV	PC ₆₀ BM	1:10	150
PF- <i>co</i> -DTB	PC ₆₀ BM	1:4	151
TDOX	PC ₆₀ BM	1:4	152
PBT _{TTT}	PC ₆₀ BM	1:4	153
	PC ₇₀ BM	1:4	
PCDTBT	PC ₆₀ BM	1:2 and 1:4	154
	PC ₇₀ BM	1:2	
	PC ₇₀ BM	1:4	155
PCPDTBT	PC ₇₀ BM	1:2 to 1:3	156
PF10TBT	PC ₆₀ BM	1:4	157
APFO-green 9	PC ₇₀ BM	1:3	158
APFO-green 9	PC ₆₀ BM	1:3 and 1:4	159
F8T2	PC ₆₀ BM	1:1.5	160
	PC ₇₀ BM	1:2.5	
MEH-PThE ₁ -PPV ₂	PC ₆₀ BM	1:3	161
P3TPQ	PC ₇₀ BM	1:3	162
PTB7	PC ₇₀ BM	1:1.5	163
PBTTbT	PC ₇₀ BM	1:3	164
PBDTTTZ	PC ₇₀ BM	1:3	165
PNDT-DTPyT	PC ₆₀ BM	1:1	166
PDTTTPD	PC ₆₀ BM	1:1	167
PTI-1	PC ₇₀ BM	1:2	168
PBDPTT-C	PC ₇₀ BM	1:2	169
PCPDTBT	PC ₇₀ BM	1:3.5	170
EWC	PC ₇₀ BM	1:2 to 1:3	171
PCPDT-PDPP	PC ₆₀ BM	1:3	172
PDT _P -PDPP		1:1	
PBDTTPT	PC ₇₀ BM	1:1	173
PFV-HBT	PC ₆₀ BM	1:4	174
PPV-HBT		1:4	
PTV-HBT		1:4	
PDTPTPD	PC ₆₀ BM	1:1	175
MEH-PPV	poly[2-methoxy-5-[(2'-ethylhexyl)oxy]-1,4-phenylenevinylene]		
MDMO-PPV	poly[2-methoxy-5-[(3',7'-dimethyloctyl)oxy]-1,4-phenylenevinylene]		
PC ₆₀ BB	[6,6]-phenyl-C ₆₁ -butyric acid butyl ester		
PDDTV	poly(3-dodecyl-2,5-thienylenevinylene)		
TDOX	DPAFL-TDOX-DPAFL = (diphenylamino)fluorenyl-capped thiadiazoloquinoxaline(6,7-dimethyl-4,9-bis[5-(9,9-dioctyl-7-(diphenylamino)fluoren-2-yl)-4-hexylthien-2-yl][1,2,5]thiadiazolo[3,4-g]quinoxaline		
PF- <i>co</i> -DTB	poly[(9,9-dioctylfluorene)-2,7-diyl- <i>alt</i> [4,7-bis(3-(decyloxy)thien-2-yl)-2,1,3-benzothiadiazole]-5',5"-diyl]		
PBT _{TT}	poly[2,5-bis(3-tetradeccylthiophene-2-yl)thieno[3,2- <i>b</i>]thiophene]		
PCDTBT	poly[N-9"-heptadecyl-2,7-carbazole- <i>alt</i> -5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]		
PCPDTBT	poly[2,6-(4,4-dialkyl-4 <i>H</i> -cyclopenta[2,1- <i>b</i> :3,4- <i>b</i> ']dithiophene)- <i>alt</i> -4,7-(2,1,3-benzothiadiazole)] ¹⁵⁶		
PF10TBT	poly[2,7-(9,9-didecylfluorene)- <i>alt</i> -5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]		
APFO-green 9	poly[2,7-(9,9-dioctylfluorene)- <i>alt</i> -5,5-(2,3,6,7-tetraphenyl-9,10-dithien-2-yl)pyrazino[2,3- <i>g</i>]quinoxaline]		
F8T2	poly[(9,9-dioctylfluorene)-2,7-diyl- <i>alt</i> [4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2,2-diyl]		
MEH-PThE ₁ -PPV ₂	poly[1,4-[5-(2-ethylhexyl)oxy]-2-methoxy]phenyleneethynylene-2,5-thiophenylenevinylene-1,4-[5-(2-ethylhexyl)oxy]-2-methoxy]phenylenevinylene]		
P3TPQ	ref 162		
PTB7	ref 163		
PBTTbT	poly(benzothiadiazolethiophene- <i>co</i> -bithiophene) ¹⁶⁴		
PBDTTTZ	BDT = 2-alkylthiophene-substituted benzo[1,2- <i>b</i> :4,5- <i>b</i> ']dithiophene TTZ = thiazolo[5,4- <i>d</i>]thiazole ¹⁶⁵		
PNDT-DTPyT	PNDT = naphtho[2,1- <i>b</i> :3,4- <i>b</i> ']dithiophene DTPyT = 4,7-bis(4-alkyl-2-thienyl)thiadiazolo[3,4- <i>c</i>]pyridine ¹⁶⁶		
PDTTTPD	DTT = 2,5-bis(thiophene-2-yl)thieno[3,2- <i>b</i>]thiophene TPD = thieno[3,4- <i>c</i>]pyrrole-4,6-dione ¹⁶⁷		
PTI-1	ref 168		
PBDPTT-C	poly[(4,5-bis(3,7-dimethyloctyl)benzo[2,1- <i>b</i> :3,4- <i>b</i> ']dithiophene-2,7-diyl)- <i>alt</i> -(2-(2-ethylhexanoyl)thieno[3,4- <i>b</i>]thiophene-4,5-diyl)]		

Table 2. continued

PCPDTBT	poly[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene-2,6-diyl- <i>alt</i> -2,1,3-benzothiadiazole-4,7-diyl] ¹⁷⁰
EWC	ref 171
PCPDT-PDPP	poly[(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene-2,6-diyl)]- <i>alt</i> -[3,6-diphenyl-4-yl-2,5-bis(2-ethylhexyl)[3,4- <i>c</i>]pyrrole-1,4-dione-4',4"-diyl] ¹⁷¹
PDTP-PDPP	poly[N-(2-ethylhexyl)dithieno[3,2- <i>b</i> :2',3'- <i>d</i>]pyrrole]-2,6-diyl]- <i>alt</i> -[3,6-diphenyl-4-yl-2,5-dihexyl[3,4- <i>c</i>]pyrrole-1,4-dione-4',4"-diyl] ¹⁷²
PBDTTPT	BDT = benzo[1,2- <i>b</i> :4,5- <i>b'</i>]dithiophene TPT = bis thiophenedioxopyrrolo thiophene ¹⁷³
PFV-HBT	poly(fluorenevinylene- <i>alt</i> -4,7-dithien-2-yl-2,1,3-benzothiadiazole)
PPV-HBT	poly(phenylenevinylene- <i>alt</i> -4,7-dithien-2-yl-2,1,3-benzothiadiazole)
PTV-HBT	poly(thiophenevinylene- <i>alt</i> -4,7-dithien-2-yl-2,1,3-benzothiadiazole)
PDTPTPD	DTP = N-(2-ethylhexyl)-2,6-bis(trimethylstannylyl)dithieno[3,2- <i>b</i> :2',3'- <i>d</i>]pyrrole TPD = 1,3-dibromo-N-(2-ethylhexyl)thieno[3,4- <i>c</i>]pyrrole-4,6-dione ¹⁷⁵

Table 3. Optimal Ratios for Mixtures of PQT-12:PCBM Used in Reported Organic Photovoltaic Cells

PQT-12		fullerene	solvent	optimal ratio	ref
M _w (kg/mol)	M _n (kg/mol)				
11.2	9.5	PC ₆₀ BM	chlorobenzene	1:4	177
	39		1,2-dichlorobenzene	3:7	
23.293	13.160	PC ₆₀ BM	1,2-dichlorobenzene	1:3	178
		PC ₇₀ BM	chlorobenzene	1:2	
		PC ₆₀ BM	1,2-dichlorobenzene	3:17	

P3HT:PCBM phase diagrams to show that the optimal molecular weight of P3HT is related to the formation of eutectic compositions.¹⁴³ In this case, the higher the molecular weight of P3HT, the higher the fraction of PCBM required to achieve optimal performance. Together, these observations demonstrate persuasively that the optimal molecular weight depends on the conditions of processing.

Ma et al. varied solar cells by using a blend of two samples of P3HT with different molecular weights and found an optimal ratio (4:1) between the components of high molecular weight ($M_n = 62.5$ kg/mol) and low molecular weight ($M_n = 13$ kg/mol).¹⁴⁴ They suggested that the corresponding “ideal morphology” contained highly crystalline domains formed by P3HT of low molecular weight, embedded in an interconnecting matrix consisting primarily of P3HT of high molecular weight.

In summary, high-molecular-weight P3HT leads to higher performance up to a certain point, under fixed conditions of processing and treatment. However, chains of high molecular weight have an increased tendency to tangle, causing twisting and distortion of the polymer backbone.¹⁴¹ This can lead to decreased intrachain charge transport and also to reduced interchain transport because of lower overlap within potentially conjugated segments. In addition, more highly crystalline phases of P3HT were obtained with samples of high regioregularity, but the long-term stability appears to be reduced.^{136–138} We can thus conclude that the crystallinity of P3HT has the important beneficial effect of facilitating charge transport and absorption, thereby leading to improved solar cell performance, at least initially.

3.3. P3HT:PCBM Ratio in Blends

The performance of photovoltaic devices fabricated from blends of donor (D) and acceptor (A) depends strongly on the relative amounts of the components. The optimal D:A ratio depends on the materials used (Table 2) and varies somewhat from laboratory to laboratory, typically because of variables in fabrication. This observation demonstrates that changing one component (either polymer or fullerene) in polymer:fullerene blends affects the morphology in subtle ways.

The concentration of acceptor should be high enough to ensure efficient transport of charge carriers toward the electrodes by establishing pathways for percolation and by creating conducting networks of PCBM within the blend. For PPV:PCBM-based solar cells, fullerenes tend to be incorporated effectively within the amorphous polymers.¹⁷⁶ Therefore, a fullerene content of 80% (by weight) yielded the best performance due to proper nanoscale phase separation and efficient charge transport.^{147–149} Also, for PCDTBT:PC₇₀BM-based solar cells, the optimal ratio also involved high concentrations of the fullerene, such as 1:2 as seen by Wakim et al.¹⁵⁴ and 1:4 as observed by Park et al.¹⁵⁵ The differences in ratio may originate from the solvents used, which were chloroform¹⁵⁴ and 1,2-dichlorobenzene,¹⁵⁵ respectively. As evident in the case of poly(3,3'-didodecylquaterthiophene), a relative of P3HT known as PQT-12, the optimal ratio depends also on the molecular weight of the polymer (Table 3). For example, Moulé et al. found an optimal ratio of 3:7 for a polymer of high molecular weight, whereas more PCBM is required for a polymer of low molecular weight.¹⁷⁷

For blends of P3HT and PCBM, less fullerene is required for making efficient cells than in the case of devices containing PPV or PCDTBT. Müller et al. have proposed a simple rationale for choosing the optimal composition (c_{opt}) of P3H:PCBM blends.¹⁸¹ By using differential scanning calorimetry to construct the phase diagram, they found that this binary system shows eutectic phase behavior, and the D:A ratio that yields devices with the best performance is slightly hypoeutectic. For mixtures consisting of P3HT ($M_n = 14$ kg/mol, $M_w = 22$ kg/mol, RR = 96%) and PCBM, they established that the eutectic point corresponds to a composition c_e of approximately 35% PCBM (Figure 7a). Photovoltaic devices displayed a maximum short-circuit photocurrent J_{sc} at $c \approx c_e$ (Figure 7b). After thermal treatment at 140 °C for 45 min, the short-circuit photocurrent was maximized for blended films in the composition range $c_{opt} \approx 40\text{--}50$ wt % PCBM, which corresponds to slightly hypoeutectic mixtures. It is important to note that many optimal P3HT:PCBM ratios reported in the literature are close to these values,⁴⁵ as shown in Table 4.

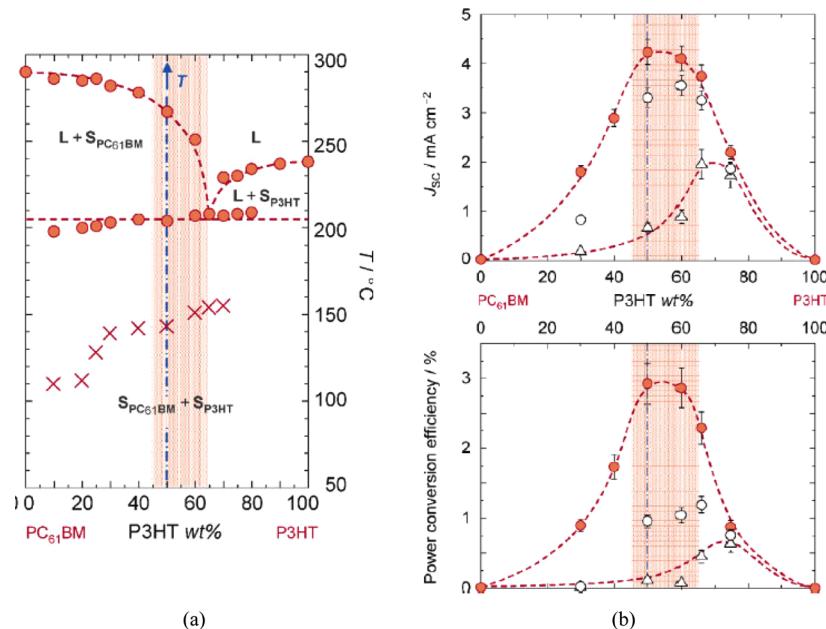


Figure 7. (a) Phase diagram for the P3HT:PCBM system, featuring simple eutectic behavior (peak eutectic temperature $T_e = 205$ °C, eutectic composition $c_e = 65$ wt % P3HT). Liquidus lines were constructed with end-melting and end-dissolution temperatures of neat components and excess component, respectively. Times signs represent the onset of crystallization; highlighted areas in this and the following figures indicate the range of composition corresponding to optimal performance of devices. (b) Dependence of short-circuit current density J_{sc} (top panel) and power-conversion efficiency (bottom panel) on P3HT:PCBM ratios for devices thermally treated at 140 °C after spin casting (filled circles), subsequently melt-quenched from 290 °C (open triangles), and then further annealed at 140 °C (open circles). In accordance with previous reports, J_{sc} is optimized after compositions comprising 50–60 wt % of the polymer are annealed. Error bars represent the estimated percentage error based on comparison of similar devices. Reprinted with permission from ref 181. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

Table 4. Examples of Optimal P3HT:PCBM Ratios in Blends Used in Organic Solar Cells

P3HT			fullerene	solvent	annealing T (°C), t (min)	optimal ratio	ref
M_w (kg/mol)	M_n (kg/mol)	RR (%)					
20.4	7.55	77	PCBM	CHCl ₃	130, 1/3	1:1	182
			PCBM	1,2-dichlorobenzene		1:1	183
		99	PCBM	CHCl ₃		7:3	184
			PCBM	1,2-dichlorobenzene		1:0.66	185
20.6	17.2	99	PCBM	1,2-dichlorobenzene		1:3	186
			PCBM	1,2-dichlorobenzene/CHCl ₃	slow drying	1:0.8	187
35			PCBM	chlorobenzene	150, 15	1:0.8	188
			PCBM	chlorobenzene	150, 10	1:1	189
50		95	PCBM	chlorobenzene	150, 30	1:0.8	190
			PCBM	chlorobenzene	150, 30	1:1	191

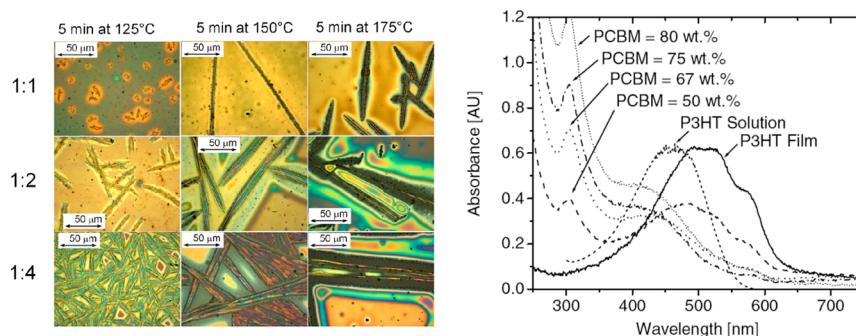


Figure 8. (a, left) Optical microscope images of P3HT:PCBM mixtures. Ratios were varied from 1:1 to 1:4 by weight, and the annealing time was kept constant at 5 min at temperatures of 125, 150, and 175 °C. Reprinted with permission from ref 193. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA. (b, right) UV-vis absorption spectra for P3HT (measured in films and solution) and for composite films of P3HT:PCBM containing different amounts of PCBM. Reprinted with permission from ref 183. Copyright 2005 Elsevier B.V.

Table 5. Solvents Used in the Literature for Studies of Solar Cells (\diamond) and Transistors (Δ), as Well as for Related Work (\S) Involving Systems with a Single Active Molecular Component

Solvents	Methylene chloride	Chloroform	Tetrahydrofuran	Thiophene	Toluene	Tetrachloroethylene	Chlorobenzene	Xylene	1,1,2,2-Tetrachloroethane	Cyclohexanone	1,2-Dichlorobenzene	1,2,4-Trichlorobenzene	Cyclohexylbenzene	Ref.
Boiling Point (°C)	39	61	66	84	112	121	132	138	146	161	183	218	239	
P3HT	x	x		x	x	x	x	x			x	x		75 Δ
	x		x				x				x	x		54 Δ
	x						x							68 Δ
	x	x	x	x							x			78 Δ
	x						x			x		x		76 Δ
	x				x					x		x		63 Δ
	x									x		x		199 Δ
	x	x												80 Δ
							x		x		x			142 Δ
	x			x	x	x	x			x		x		200 \S
	x			x		x	x			x		x		77 Δ
P3AOPT	x									x				201 \S
PCPDTBT	x			x						x				202 Δ
MEH-PPV	x	x				x	x		x	x				203 \S
MDMO-PPV					x	x								204 Δ
PCBM					x	x								205 \S
P3AOPT		Poly[3-(4-alkoxyphenyl)thiophene] Poly[(S)-3-[4-[3,7-dimethyl]octyloxy]phenyl]thiophene]												
PCPDTBT		Poly[2,6-(4,4-dialkyl-4 <i>H</i> -cyclopenta[2,1- <i>b</i> ;3,4- <i>b'</i>]dithiophene)- <i>alt</i> -4,7-(2,1,3-benzothiadiazole)]												
MEH-PPV		Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]												
MDMO-PPV		Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]												

Molecules of PCBM appear to disrupt the crystallization of P3HT during the process of forming films. This effect is demonstrated by measurements using X-ray diffraction, which show a strong decrease in the crystallinity of P3HT as the concentration of PCBM increases.^{188,192} High concentrations of fullerene favor the segregation of PCBM and hence alter the morphology of blends. High temperatures and/or long treatment times can induce the formation of large and sometimes detrimental crystallites of PCBM. This phenomenon was observed by Swinnen et al.¹⁹³ by using optical microscopy, which showed that crystallites of PCBM appeared increasingly at higher temperatures (Figure 8a), especially at higher concentrations.

In polymers such as P3HT, the extent of conjugation affects the energy of the $\pi-\pi^*$ transition, which corresponds to the absorption of longest wavelength in these materials. The electronic spectra of P3HT therefore provide a measure of the extent of conjugation and the structure of the polymer. As expected, adding PCBM alters the spectra in informative ways. The evolution of the absorption spectra of thin films as a function of the concentration of PCBM is reported in Figure 8b.¹⁸³ It is immediately clear that absorption in the range of 450–600 nm decreases drastically as the concentration of PCBM increases. This means that the active layer in a solar cell must be thicker to have an equivalent absorption. Another noteworthy feature is the

shifted λ_{\max} in the spectral region corresponding to P3HT. Indeed, λ_{\max} is strongly blue-shifted when the concentration of PCBM increases, until it reaches λ_{\max} of P3HT in solution. This shift is attributed to reduced interchain interaction caused by the presence of PCBM. Molecules of PCBM appear to surround chains of P3HT and isolate them from their neighbors.

In essence, the D:A ratio has an important impact on the electronic properties of blends. The relationship between charge transport and the composition of blends has been studied by several groups.^{184,192,194,195} Devices containing only P3HT are ambipolar, which means that the polymer can transport both electrons and holes.^{195,196} Nevertheless, hole transport dominates the conduction process in P3HT. P3HT:PCBM mixtures also show ambipolar behavior, but the more PCBM present, the more the hole mobility decreases because of the less ordered arrangement of P3HT. An opposite tendency is observed for electrons, and the electron mobility increases with the quantity of PCBM.^{188,197} For solar cells, balanced transport is required, and the carrier mobilities of holes and electrons have to be similar.^{188,198} The optimal composition for P3HT:PCBM mixtures will vary according to the molecular weight of P3HT, its regioregularity, and the details of processing. Huang et al. observed a comparable mobility of holes and electrons for a weight ratio of 1:1.¹⁹⁴ Nakamura et al. obtained balanced transport at a PCBM loading of 30%,¹⁸⁴ whereas von Hauff et al.

Table 6. Solvents Used in the Literature in Studies of Donor:Acceptor Blends for Use in Solar Cells (\diamond) and Transistors (Δ), as Well as in Related Work (\$)

Solvents	Chloroform	Tetrahydrofuran	Thiophene	Toluene	Pyridine	Chlorobenzene	Xylene	1,2-Dichlorobenzene	1,2,4-Trichlorobenzene	Ref.
Boiling Point (°C)	61	66	84	112	115	132	138	183	218	
P3HT:T5OHM	x		x		x					206 \$
P3HT:CdSe	x	x						x		207 \diamond
P3HT:ZnO	x						x			208 \diamond
MEH-PPV:C ₆₀	x	x			x	x	x			209 \diamond
MEH-PPV:PC ₆₀ BM			x		x		x			146 \diamond
MEH-PPV:CdS			x	x						210 \diamond
MDMO-PPV:PC ₆₀ BM			x		x					211 \$, 147,212,213 \diamond
				x	x	x				214 \diamond
MDMO-PPV:PC ₇₀ BM				x	x	x				215 \diamond
MDMO-PPV:PC ₇₀ BM				x		x				
MDMO-PPV:PC ₇₀ BP				x		x				216 \diamond
MDMO-PPV:PC ₇₀ PP				x		x				
MDMO-PPV:CdSe	x						x			217 \diamond
PTV:PC ₆₀ BM	x			x						218 \diamond
TDOX:PC ₆₀ BM			x			x				152 \diamond
PM50:PC ₇₀ BM			x		x					219 \diamond

T5OHM	3"-methyl-4"-hexyl-2,2':5':2":5",2"":5""-quinquethiophene-1',1'-dioxide
PC ₇₀ BP	Phenyl-C ₇₁ -propionic acid butyl ester
PC ₇₀ PP	Phenyl-C ₇₁ -propionic acid propyl ester
PTV	Poly(thiénylenevinylen)
TDOX	DPAFL-TDOX-DPAFL: Diphenylaminofluorenyl-capped thiadiazoloquinoxaline(6,7-dimethyl-4,9-di[5-(9,9-dioctyl-7-diphenylaminofluorene-2-yl)-4-hexylthien-2-yl][1,2,5]thiadiazolo[3,4-g]quinoxaline
PM50	Poly[4,8-(didodecyloxy)benzo[1,2- <i>b</i> ;3,4- <i>b</i>]dithiophene- <i>alt</i> -2-[2,6-bis[(E)-2-(5-bromo-3,4-dihexylthiophen-2-yl)vinylyl]-4 <i>H</i> -pyran-4-ylidene]malononitrile[2,1,3]benzothiadiazole (50:50)]

found the electron and hole mobilities to be balanced at a PCBM fraction of 67%.⁸¹ Baumann et al. obtained a balanced transport for a weight ratio of 1:10,¹⁹⁵ and they found that the mobility of holes was $7.3 \times 10^{-3} \text{ cm}^2/(\text{V s})$ and that of electrons was $2.3 \times 10^{-2} \text{ cm}^2/(\text{V s})$. Chiu et al. obtained the lowest μ_e/μ_h ratio (2.2) and consequently the highest power-conversion efficiency at a ratio of 1:0.8.¹⁸⁸ These differences presumably originate from variations in processing and in the properties of the polymers, such as molecular weight and regioregularity.

In conclusion, when the ratio of PCBM to P3HT is low, the interfacial area between P3HT and PCBM becomes small, and electrons cannot easily move through molecules of PCBM to the cathode because the molecules are relatively isolated. Therefore, an exciton formed on P3HT cannot dissociate completely at the interface between P3HT and PCBM, and electrons cannot move to the anode. The best value of the P3HT:PCBM ratio will reflect a balance between efficient dissociation of excitons and effective charge transport. These processes depend on the properties of P3HT (regioregularity and molecular weight), as well as on the conditions of processing.

3.4. Choice of Solvent and Use of "Solvent Annealing"

The rate of evaporation of solvent in the deposition of thin layers depends on the nature of the solvent and the method of deposition. In various ways, the choice of solvent has a significant effect on the morphology of the active layer. Tables 5–7 summarize numerous investigations of organic thin-layer devices carried out using solvents with different boiling points and different photoactive materials.

For devices composed of pure P3HT, numerous solvents have been used. These studies have correlated crystallization of the polymer with electronic properties of the layers, such as mobility of charge. In contrast, for polymer:fullerene-based devices, the number of solvents examined is small because of the typically poor solubility of fullerenes (Table 6). The poor solubility of fullerenes strongly influences the phase segregation of the two components.

In 2001, Shaheen et al. obtained photovoltaic devices of higher efficiency (2.5%) when films of MDMO-PPV:PCBM blends were deposited from chlorobenzene than from toluene.²¹² Studies using composites of PPV and PCBM were generally conducted with a weight ratio of 1:4, which corresponds to a high concentration of fullerene. As a result, segregation of the fullerene in large domains is favorable. The size of the clusters of

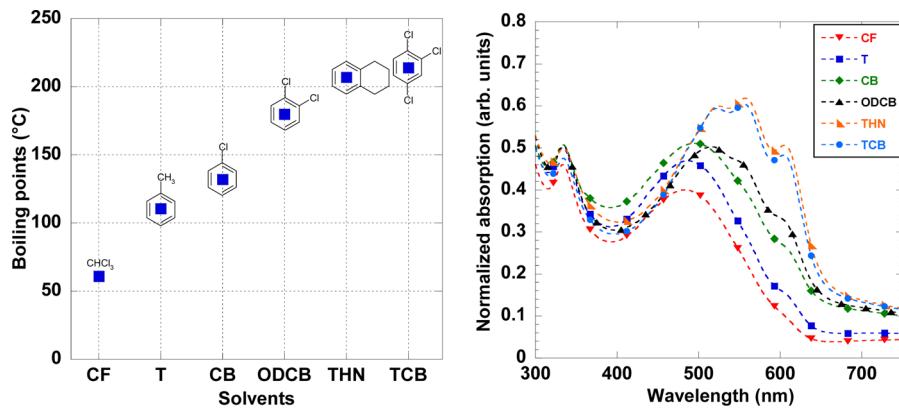


Figure 9. Boiling points of selected solvents and solid-state absorption spectra of thin films of P3HT:PCBM created by spin casting from these solvents. Reprinted with permission from ref 220. Copyright 2011 Elsevier B.V.

Table 7. Solvents Used in the Literature for the Fabrication of Solar Cells (⊗), Transistors (Δ), and Other Systems (§) Containing Films Derived from Pure P3HT and from P3HT:PCBM Blends

Solvents	CHCl ₃	T	CB	Xylene	ODCB	THN	TCB	THN + CB	CHCl ₃ + ODCB	CHCl ₃ + 1-dodecanol	CHCl ₃ + hexane	T + 1-octanethiol	CB + nitrobenzene	Anisole + CB	ODCB + CB	ODCB + Cl-naph	ODCB + mésitylene	ODCB+1,8-octanedithiol	ODCB + DEGDE	ODCB + NMP	Ref.	
Boiling Point (°C)	61	112	132	138	183	204	218															
P3HT	⊗	⊗	⊗					⊗														225 Δ
	⊗								⊗													226 §
	⊗	⊗																				227,228 ☼
		⊗	⊗																			229,230 ☼
	⊗		⊗																			231 ☼
		⊗																				232 ☼
	⊗	⊗																				233 Δ, ☼
		⊗	⊗																			234 Δ
	⊗	⊗	⊗																			235§, 19 ☼
	⊗	⊗	⊗																			236 §
	⊗	⊗	⊗	⊗	⊗	⊗	⊗															220 ☼
P3HT:PC ₆₀ BM								⊗							⊗							20,139,222 ☼
									⊗						⊗							187 ☼
										⊗					⊗							237 Δ, 238 ☼
										⊗												223 ☼
											⊗					⊗						239 ☼
											⊗						⊗					240 ☼
												⊗						⊗				241 ☼
													⊗					⊗				242 ☼
														⊗					⊗			224 ☼
															⊗					⊗		243 ☼
																⊗						244 ☼

T	Toluene
CB	Chlorobenzene
ODCB	1,2-Dichlorobenzene
TCB	1,2,4-Trichlorobenzene
THN	1,2,3,4-Tetrahydronaphthalene
Cl-Naph	1-Chloronaphthalene
DEGDE	Di(ethylene glycol) diethyl ether
NMP	N-Methyl-2-pyrrolidinone

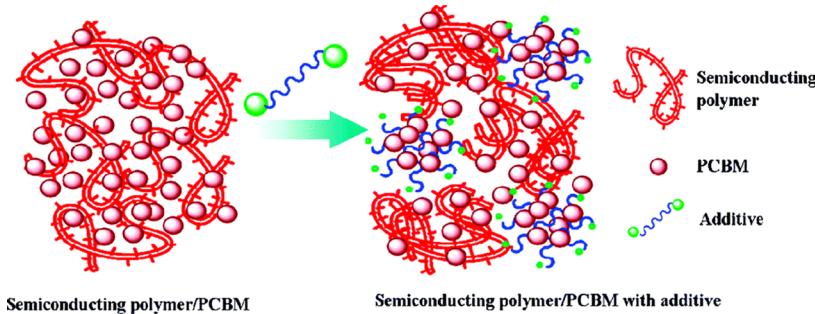


Figure 10. Schematic depiction of the possible role of solvent additives in the formation of bulk heterojunctions derived from PCPDTBT and PCBM. Reprinted from ref 245. Copyright 2008 American Chemical Society.

PCBM within the resulting thin films depends on the choice of solvent.^{147,211,212} For example, Yang et al. observed that the average size of the clusters of PCBM varied from 80 nm for chlorobenzene to 600 nm for toluene.²¹¹ These noteworthy observations reflect the differential solubility of PCBM. Indeed, the solubility of both MDMO-PPV and PCBM in toluene is less than in chlorobenzene. Sun et al. fabricated solar cells from blends of MDMO-PPV:CdSe,²¹⁷ and they demonstrated that the use of 1,2,4-trichlorobenzene (bp 214 °C) led to better photovoltaic performance than in devices prepared from chloroform (bp 61 °C). Liu et al. fabricated devices incorporating MEH-PPV:C₆₀ blends (of the same thickness),²⁰⁹ and they obtained higher yields of photocurrent using spin-cast films deposited from chlorobenzene, 1,2-dichlorobenzene, and xylene than from films made using tetrahydrofuran and chloroform. The authors argue that the aromatic solvents induce better contacts between molecules of C₆₀ and the polymer. It should be noted that these solvents also have different boiling points. Indeed, tetrahydrofuran and chloroform have rather low boiling points (66 and 61 °C, respectively). In addition, the solubility of C₆₀ in chloroform is low and is even smaller in THF. As a result, it is clear that solvent can profoundly affect the tendency of polymer:fullerene blends to form separate phases, by determining both the solubility and the rate of evaporation during the formation of thin films.

The influence of solvent on the performance of devices produced from low-band-gap polymers has been investigated by Park et al.,¹⁵⁵ who reported an efficiency of 6.1% (5.96% certified by the National Renewable Energy Laboratory) for PCDTBT:PC₇₀BM-based cells. These researchers observed higher performance in devices prepared from 1,2-dichlorobenzene than in those made from chloroform or chlorobenzene, presumably because 1,2-dichlorobenzene favors an optimal separation of phases.

In the case of PPV:PCBM-based devices, a large excess of PCBM is required to ensure efficient transfer of charge. For P3HT:PCBM-based cells, the ratios typically used are close to 1:1. Solutions used to make films of these photoactive materials are thereby more diluted in PCBM, and the solubility of the fullerene is thus less critical.

Measurements by UV-vis spectroscopy can demonstrate the effect of solvent on the nanomorphology of active layers. For example, the solid-state absorption of untreated layers of P3HT:PCBM deposited from various solvents with different boiling points is shown in Figure 9.²²⁰ Absorption below 400 nm, which is attributed to molecules of PCBM, does not depend on the solvent used. In contrast, the absorption of P3HT strongly depends on the solvent used, and the differences in the appearance of spectra presumably reflect the different degrees

of chain ordering of P3HT. Self-organization of P3HT occurs while solvent evaporates during spin coating. The use of solvents with low boiling points results in rapid evaporation and poor crystallization of P3HT, leading to less structured spectra. Solvents with high boiling points, such as tetrahydronaphthalene and 1,2,4-trichlorobenzene, evaporate more slowly and promote a higher degree of organization in the structure of P3HT because crystallization can occur. Features in the absorption spectra of P3HT are therefore most structured under these conditions.

Blending of two solvents has been shown to be an attractive way to help control the morphology of active layers containing polymers (Table 7 and Tables S1 and S2, Supporting Information). This approach was pioneered by the Inganäs group,²²¹ who modified the morphology of the active layer fabricated from a blend of PCBM and poly[(9,9-diethylfluorene-2,7-diyl)-co-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]. Devices prepared from CHCl₃ containing a small amount of chlorobenzene (CHCl₃:chlorobenzene = 80:1 by volume) were found to show a significantly improved density of photocurrent, compared with samples prepared from CHCl₃ alone. Since this observation was made, similar approaches have been used to create films of P3HT:PCBM, and the method seems promising for large-scale manufacturing by inkjet printing,^{20,139,222,223} doctor blading,¹³⁹ and spray coating.²²⁴

The use of blends composed of a common solvent and a specialized cosolvent such as alkanethiols or related components constitutes a breakthrough in the production of efficient solar cells (see Table S2, Supporting Information). Studies of the addition of alkanethiols to standard solutions used for fabricating devices were reported first by the Bazan group.^{156,237} They showed that the photoconductivity and charge mobility of P3HT:PCBM-based films are increased when the components are dissolved in a solution of octanethiol (5% by volume) in toluene.²³⁷ Alkanethiols are also effective for achieving highly efficient photovoltaic cells prepared from polymers with low band gaps. In 2007, Peet et al. studied the addition of various 1,*n*-alkanedithiols (alkane = propane, butane, hexane, octane) in chlorobenzene to produce devices containing PCPDTBT and PC₇₀BM.¹⁵⁶ They reported a significantly higher power-conversion efficiency (5.5%) for cells fabricated from mixtures of 1,8-octanedithiol (2.5% by volume) and chlorobenzene than for cells made using solutions in pure chlorobenzene (2.8%). Later, the same group conducted a systematic investigation of the addition of X(CH₂)₈X (X = SH, Cl, Br, I, CN, and COOCH₃) to chlorobenzene to prepare solutions for fabricating PCPDTBT:PC₇₀BM-based solar cells.²⁴⁵ With 1,8-diiodooctane as the cosolvent, the efficiency of solar cells was enhanced from 3.4% to 5.1%. These added solvents have very high boiling points (relative to chlorobenzene) and offer good solubilization of

PCBM. The morphology of thin films prepared under these conditions proved to consist of multiple phases, including fullerene–X(CH₂)₈X phases, polymeric aggregates, and polymer:fullerene mixtures (Figure 10). Aggregation of this type is a plausible outcome of partial separation of the components, on the basis of their mutual affinities. Similar enhancements were observed in thin films of P3HT:PCBM prepared after addition of octanethiol to toluene,²³⁸ as well as after addition of 1,8-octanedithiol to 1,2-dichlorobenzene.²⁴² Many other groups have tuned the morphology of blends fabricated from new conjugated polymers by using various specialized cosolvents.^{163–165,167–170,173,244,246–257}

“Solvent annealing”, which involves keeping prepared films in relatively long contact with solvents or their vapors, is an effective way to alter the morphology of active layers. In 1994, the Inganás group exposed films of poly[3-(4-octylphenyl)thiophene] to vapors of chloroform and obtained more ordered films.²⁵⁸ Since then, the technique has been used to fabricate devices by many other groups.^{198,231,259–270} As normally used, solvent annealing produces highly ordered thin films of polymer by slow evaporation of solvent in a partially closed container such as a Petri dish. Applied to blends, this procedure allows the controlled separation of phases and crystallization of the components. Basically, solvent annealing slows the rate of evaporation during the preparation of the active layer, often with beneficial effects on the performance of the resulting devices. For example, Mihaleitchi et al. found that hole mobility in the P3HT phase of the P3HT:PCBM blend was improved by 30-fold,²³¹ and Shrotriya et al. also reported an enhanced rate of exciton generation and an increased probability of dissociation.²⁶¹ Despite improvements in morphology induced by solvent annealing alone, in some cases additional thermal treatment may be necessary to obtain high efficiency.^{198,262,265,271}

In summary, numerous studies of the effects of solvents have been carried out in attempts to control the morphology of active layers. There is now an extensive range of solvents for fabricating solar cells based on bulk heterojunctions of donor and acceptor. Solvents with higher boiling points allow P3HT to crystallize more extensively. Slowing the evaporation of solvent can be achieved by solvent annealing. Although research has shown that solvent annealing by itself can lead to films with improved performance, additional treatments such as thermal annealing may also be beneficial to optimize the efficiency of solar cells. A particularly promising way to promote productive separation of phases is the addition of α,ω -alkanedithiols and related compounds.

3.5. Thermal Annealing

Thermal treatment has proven successful for controlling the nanomorphology of active layers. In 2000, Dittmer et al. observed an enhanced external quantum efficiency in devices fabricated from P3HT blended with *N,N'*-bis(1-ethylpropyl)-3,4,9,10-perylenebis(tetracarboxyl diimide) after 60 min of annealing at 80 °C.²⁷² The observed improvement presumably arose from increased crystallinity of P3HT induced by thermal annealing,^{272,273} which resulted in increased charge transport in the layers. The effect of annealing on P3HT:fullerene-based devices was studied productively by Camaioni et al.^{274,275} and by Padinger et al.²⁷⁶ Camaioni et al. investigated the effect of mild thermal treatment (50–60 °C) on the performance of P3HT:fulleropyrrolidine-based solar cells.^{274,275} The authors observed a 3–4-fold increase in power-conversion efficiency after annealing. In 2003, Padinger et al. reported that treatment of

completed P3HT:PCBM devices (after deposition of the electrode) gave devices with an efficiency of 3.5%,²⁷⁶ setting a record at the time for cells fabricated from a blend of polymer and fullerene. Since then, extensive studies have been carried out to exploit thermal annealing as an effective way to control the morphology of the active layer and enhance its performance in devices.

The beneficial effect of thermal annealing on the nanostructure and performance of devices is well documented. Thermal treatment induces phase separation of the two components. Studies using transmission electron microscopy by Yang et al. revealed that thermal treatment induced more extensive crystallization and the formation of interconnected fibrils of P3HT.²⁷⁷ In addition, this tendency was confirmed by measurements using X-ray diffraction, which clearly showed increased crystallinity of P3HT within annealed P3HT:PCBM samples.²⁷⁸ Higher degrees of crystallization of P3HT lead to increased absorption. After thermal treatment, thin films composed of pure P3HT show an increased hole mobility because of enhanced crystallinity.^{53,70,82,279} For as-cast films, the mobility of blend-based films is lower than that of pure P3HT-based films, because molecules of PCBM disrupt the crystalline network of P3HT. However, charge mobility in films prepared from the blends can be improved by annealing.^{84,86,142,280–282} Thermal annealing under appropriate conditions of temperature and time can thereby lead to enhanced performance of photovoltaic cells. Improved efficiency may originate from increased absorption of light, enhanced charge transport, or improved efficiency of carrier collection, which can all result from the creation of crystalline domains that have attained an optimal size. It is noteworthy that thermal annealing has also been shown to be effective for productively restructuring active layers composed of polymers other than P3HT^{164,283–291} and acceptors other than PCBM.^{164,244,292–295} For example, devices fabricated from blends of PCPDTBT with PCBM have shown higher efficiency after thermal annealing.²⁹⁶

Before annealing, the active layer generally consists of different phases, which may range from amorphous to semicrystalline. This initial state depends on such factors as the regioregularity of the polymeric components, the solvents used, and the method of evaporation. Typically, polymers with high regioregularity produce more fully crystalline phases. P3HT:PCBM films, when spin-coated from solvents of relatively low volatility, again favor a higher degree of crystallinity. Furthermore, enhanced crystallinity can also be induced by additives and by solvent annealing of unheated films. Thermal treatment has a more profound effect on films in which the components are largely amorphous, and it has a relatively minor influence on films in which the components have already achieved a high degree of crystallinity. This tendency can be demonstrated by changes in the absorption spectra of films of P3HT (Figure 11), which reveal important information about the degree of order before and after treatment.²²⁰ In the case of films spin-coated from CHCl₃ and toluene, the region above 400 nm is affected by annealing, and the region of strongest absorption of P3HT is red-shifted. Moreover, shoulders at 545 and 600 nm become more pronounced. Spectral changes in films of P3HT:PCBM resulting from annealing can be attributed to an increased degree of crystallinity of P3HT within the films. This tendency is also observed, although to a lesser degree, in films deposited from chlorobenzene and 1,2-dichlorobenzene. For devices prepared from THN and TCB, the principal structures of the spectra are the same, indicating that the organization of the components of

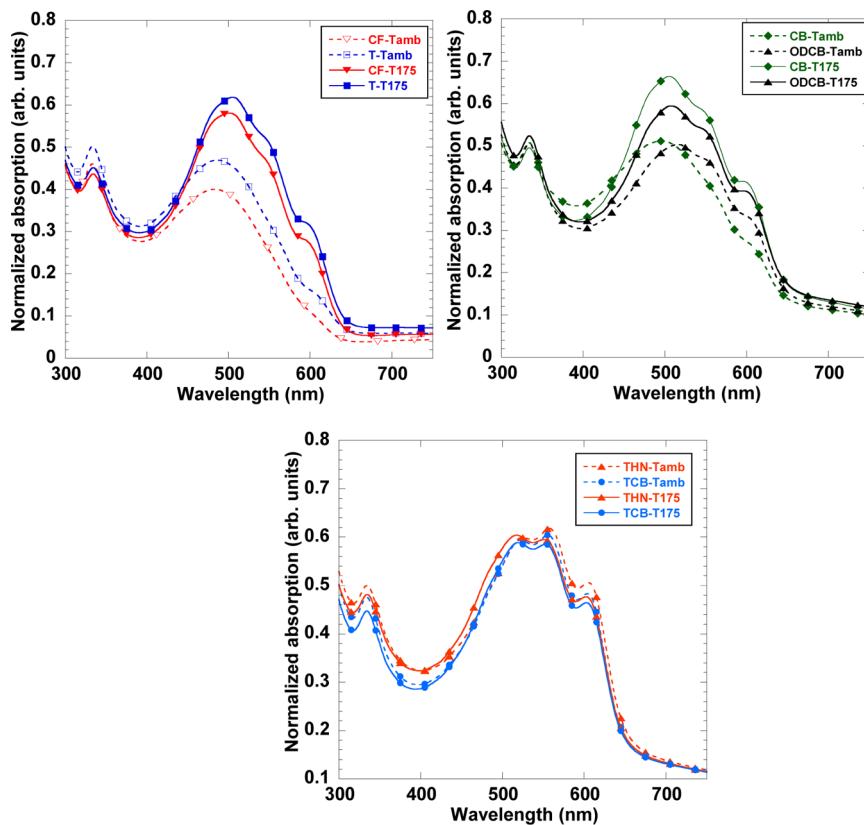


Figure 11. Absorption spectra of thin films of P3HT:PCBM spin-cast from different solvents before thermal annealing (T_{amb}) and after thermal annealing at 175 °C for 5 min (T_{175}). Reprinted with permission from ref 220. Copyright 2011 Elsevier B.V.

the films is essentially unchanged after annealing at 175 °C for 5 min.

Similar observations have been made by Kim et al.¹³⁴ P3HT of higher regioregularity offers better performance in both untreated and annealed devices (annealing at 140 °C for 2 h). However, we note that the improved efficiency is more pronounced when devices are fabricated from P3HT of lower regioregularity (with RR = 93%, the efficiency rose from 1.3% to 1.8%, an increase of 38.5%), and it is less pronounced in devices fabricated from highly regioregular P3HT (when RR = 95.2%, the efficiency rose from 2.1% to 2.4%, an increase of only 12.5%).

Thermal annealing can be performed either before (pre-production) or after (postproduction) the deposition of electrodes. Better efficiency is attained when devices are treated after the electrodes are deposited.^{297–303} Researchers have suggested that covalent C–Al and C–O–Al bonds may be formed between deposited aluminum and polymers during heating.^{304,305} This process could lead to increased contact between the active layer and the electrode³⁰¹ and may decrease the potential barrier between the electrode and the active layer. Many groups have performed annealing twice, both before and after deposition of electrodes, to fabricate efficient solar cells.^{306–312}

Thermal treatment allows the separation of phases within the active layers to be controlled by properly tuning the temperature or/and duration of annealing. Indeed, thermal treatment requires very careful consideration of time and temperature. To shed light on this topic, Table 8 summarizes the conditions of annealing that have been used to produce P3HT:PCBM-based solar cells. The table specifies key conditions of processing, including the regioregularity and molecular weight of P3HT, the solvent used,

and the P3HT:PCBM ratio by weight. Table 8 reveals that a wide range of temperatures and times have been used to make P3HT:PCBM-based solar cells; in addition, the optimal conditions of treatment differ from laboratory to laboratory. These discrepancies presumably result from variations in the properties of the materials used, the compositions of the blends, and the solvents selected. For example, Woo et al. noted that the optimal time of annealing was different for films of P3HT with different values of regioregularity.¹³⁸ When devices were heated at 150 °C, those fabricated from P3HT with regioregularity of 96% required the shortest annealing time (30 min) to achieve the highest efficiency, whereas devices prepared from P3HT of lower regioregularity (RR = 90% and 86%) needed longer annealing times (60 and 120 min, respectively). Roger et al. observed that optimal annealing temperatures increased with the molecular weight of P3HT.¹⁴¹ Thermal annealing alters the conducting networks of P3HT and PCBM within bulk heterojunction devices. Indeed, prolonged thermal treatment induces the formation of large aggregates of PCBM in the films. This extensive phase segregation leads to decreased dissociation of excitons and thus to decreased performance.

The rate of cooling after thermal annealing also influences the performance of polymer solar cells,^{84,320,326} although this point is not discussed extensively in the literature. Dante et al. observed the formation of large crystalline needles of PCBM (with dimensions up to 200 μm long and several micrometers wide) within films of P3HT:PCBM (1:0.8 by weight, deposited from toluene),⁸⁴ which had been annealed at 150 °C for 15 min and slowly cooled to room temperature at a rate of 2 °C/min. Removing annealed films from the hot plate immediately did not induce any phase segregation, presumably due to the shorter

Table 8. Optimal Conditions (*) for Annealing P3HT:PCBM-Based Solar Cells^a

structure	P3HT				D:A ratio	solvent	annealing			η (%)			
	M_w	M_n	DP	RR			pre/post	temp	time	as-	ann-	P_{in}	area
glass/ITO/HTL/ P3HT:PCBM/Ca/Al				RR	1:1	ODCB	pre	110*	20*		2.8	100	11
glass/ITO/HTL/ P3HT:PCBM/Al	44	28		96	1:1	CB	post	110*	10*		3.2		
glass/ITO/HTL/ P3HT:PCBM/Al	50			RR	1:0.8	CB	pre/post	50/140*	30/4		1.4	100	4.5
glass/ITO/HTL/ P3HT:PCBM/LiF/Al		14.8*	2.1	~ 100	1:1	CB	post	120*	30	0.60	3.6	100	28
glass/ITO/HTL/ P3HT:PCBM/LiF/Al	37.7	25.5		98.5	1:2	CHCl ₃	post	140*	5*	0.42	2.55	100	
glass/ITO/HTL/ P3HT:PCBM/Ca/Ag				98.5	3:2	CB/NtB	post	180*	30	3.94	4.3	100	7.85
glass/ITO/HTL/ P3HT:PCBM/Al	59.75		1.5	96	1:0.8	CB	pre	140	30*	1.06	3.85	100	
glass/ITO/HTL/ P3HT:PCBM/Al	71		1.5	99	1:0.8	CB (ANN)	post	140	30*	1.04	2.31	100	
glass/ITO/HTL/ P3HT:PCBM/Al	44.7		1.53	RR	1:1	CB/1,3,5- TCB	pre	150*	30		1.67	100	18
glass/ITO/HTL/ P3HT:PCBM/Al	12			96	1:1	CB	post	140	120*		~4.5	85	
glass/ITO/HTL/ P3HT:PCBM/Al	87			RR	1:0.8	CB	post	100*	10	2.2	3.96	80	
glass/ITO/HTL/ P3HT:PCBM/TiO _x /Al	87.5				5:3	CB	pre	140*	10		3.09	100	?
glass/ITO/HTL/ P3HT:PCBM/Al	21.1	11.6		>96	1:1	CB	post	140*	15		3.0	100	4.5
glass/ITO/HTL/ P3HT:PCBM/Al		25.7	1.5	86	11:9	ODCB	post	150	120*	<1	3.9	100	3
		18.0	1.4	90				150	60*		3.8		
		28.6	1.5	96				150	30*		3.8		
glass/ITO/HTL/ P3HT:PCBM/LiF/Al	11.6			96	1:1	CB	pre	140	120*		3.2	85	9
glass/ITO/HTL/ P3HT:PCBM/Al	50–60				1:0.65	CB	post	140	3*		3.0		
							pre	150	30	0.5	1.60	100	
glass/ITO/HTL/ P3HT:PCBM/Al	11.6			96	1:1	CB	post	150	30		3.00		
glass/ITO/HTL/ P3HT:PCBM/Al	50			94	1:1	ODCB (ANN)	pre/post	50/110*	15/15		2.16	85	9
		64		98			pre/post	40/140	10/30	2.3	2.2 ^A	100	10.4
glass/ITO/HTL/ P3HT:PCBM/LiF/Al		10.5	1.2	98	1:1	ODCB	post	40/140	10/30	2.5	1.9 ^A		
glass/ITO/HTL/ P3HT:PCBM/Ca/Al					1:1	CB/CHN	pre	150	15*		3.05	100	4
glass/ITO/HTL/ P3HT:PCBM/LiF/Al					5:3	CB	post	150	5	0.79	3.15		
glass/ITO/HTL/ P3HT:PCBM/Al	42.4	21		96.8	1:1	CB	pre	150	5–10*		2.8	100	
							post	150	30	0.61	1.10	100	6
											3.37		
ITO						indium tin oxide							
HTL						hole-transporting layer (poly[3,4-(ethylenedioxy)thiophene]:poly(styrenesulfonate) (PEDOT:PSS))							
T						toluene							
CB						chlorobenzene							
ODCB						1,2-dichlorobenzene							
1,3,5-TCB						1,3,5-trichlorobenzene							
TCB						1,2,4-trichlorobenzene							
NtB						nitrobenzene							
THN						1,2,3,4-tetrahydronaphthalene							
CHN						cyclohexanone							

^aThe hole-transporting layer is PEDOT:PSS. Units: M_n , kg/mol; M_w , kg/mol; RR, %; temp, °C; time, min; P_{in} , mW/cm²; area, mm². The terms “as-” and “ann-” refer to before and after annealing, respectively.

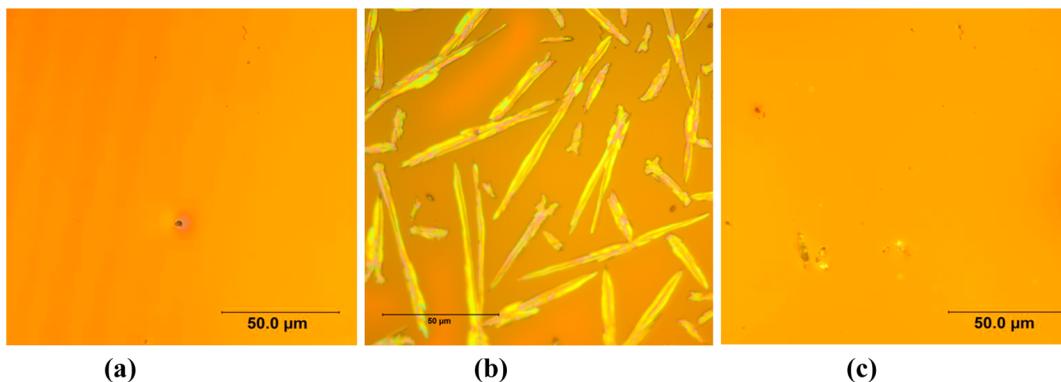


Figure 12. (a) Optical micrograph of the untreated P3HT:PCBM film. (b) Image obtained after annealing on a hot plate at 150 °C for 15 min and slow cooling at a rate of 2 °C/min (scale bar 20 μm). (c) Image produced after cooling by immediate removal from the hot plate. Reprinted from ref 84. Copyright 2008 American Chemical Society.

Table 9. Additives Used To Modify Binary Donor:Acceptor Solar Cells (⊗) and Related Thin-Film Devices (§)

active blend	additives	ref	active blend	additives	ref
P3OT:C ₆₀	Au, Ag (nanoparticles)	329*	P3HT:PC ₆₀ BM	BT4T	346*
MEH-PPV:PC ₆₀ BM	Cu(CN)4P	330*		BT4T-12	
P3HT:PC ₆₀ BB	Ag (nanoparticles)	331*		MDMO-PPV	322*
P3HT:PC ₇₀ BM	Au (nanoparticles)	332*		F8BT	347*
PCDTBT:PC ₇₀ BM				Ra-P3HT	348*
Si-PCDTBT:PC ₇₀ BM				poly(1)-block-poly(2)	349*
P3HT:PC ₆₀ BM	Pt (nanoparticles)	333*		DHPT3	350* ^Δ
	Au (nanoparticles)	334*		P3HT- <i>b</i> -P(S _x A _y)-C ₆₀	351*
	MWCNTs	335*		P3HT- <i>b</i> -C ₆₀	323*
	SWCNTs	335–337*		P3HT-C ₆₀	352*
	TiO ₂	325*		PTPA-P3HT-PTPA	353*
	OA-Fe ₃ O ₄ (nanoparticles)	338*		FLC8	354*
	P3MEET-CuBr	339*		HDPE	355*
	Cu(CN)4P	340, 341 [§]		i-PS	
	DPA	342*		a-PS	
	PSP	343*		PCBSD	356*
	coumarin 6 dye	344 [§]		PCBPEG	357*
	3HT	345*			
OA	oleic acid				
PCBB	[6,6]-phenyl-C ₆₁ -butyric acid butyl ester				
Cu(CN)4P	[2,3,12,13-tetracyano-5,10,15,20-tetrakis(3,5-di- <i>tert</i> -butylphenyl)porphyrinato]copper(II)				
P3MEET-Cu ⁺	Cu ⁺ -chelated poly(alkoxythiophene)				
	<i>rr</i> -poly[3-[2-(2-methoxyethoxy)ethoxy]thiophene]				
DPA	9,10-diphenylanthracene				
PSP	ionomer (partially sulfonated polystyrene)				
MWCNTs	multiwalled carbon nanotubes				
SWCNTs	single-walled carbon nanotubes				
3HT	3-hexylthiophene				
BT4T	oligo(benzothiadiazole- <i>alt</i> -3,3''-dihexyl-2,2':5',2":5",2''-quaterthiophene)				
BT4T-12	oligo(benzothiadiazole- <i>alt</i> -3,3''-didodecyl-2,2':5',2":5",2''-quaterthiophene)				
F8BT	poly(9,9'-diethylfluorene- <i>co</i> -benzothiadiazole)				
DHPT ³	thieno[3,2- <i>b</i>]thiophene- <i>alt</i> -pentathiophene				
FLC8	poly[2,3-bis(thiophene-2-yl)acrylonitrile-9,9'-diethylfluorene]				
P3HT- <i>b</i> -P(S _x A _y)-C ₆₀	P3HT = poly(3-hexylthiophene), S = styrene, A = acrylate				
PTPA-P3HT-PTPA	poly(4-vinyltriphenylamine)- <i>b</i> -poly(3-hexylthiophene)- <i>b</i> -poly(4-vinyltriphenylamine)				
HDPE	high-density polyethylene				
i-PS	isotactic polystyrene				
a-PS	amorphous atactic polystyrene				

overall time of heating (Figure 12). However, Xue et al. observed that slow cooling after annealing at 140 °C for 4 min resulted in higher efficiency in films of P3HT:PCBM (1:1 by weight) prepared from CHCl₃.³²⁶ The differences observed in these two

reports presumably result from variations in experimental parameters such as the nature of the polymer, solvent, weight ratio, and annealing conditions. In truth, the conditions of

cooling may deserve as much attention as the conditions of initial annealing in determining the properties of the resulting devices.

Microwave irradiation has been recently explored as an alternative method of treatment to enhance the performance of polymeric solar cells.^{327,328} Studies of the resulting films by X-ray diffraction revealed that microwave annealing induces crystallization of P3HT within P3HT:PCBM active layers, leading to changes that are similar to those observed during the course of thermal annealing.³²⁷ Improved performance has been demonstrated for P3HT:PCBM devices after microwave treatment. For example, by irradiating devices with microwaves at 2.45 GHz and 600 W, Ko et al. obtained an efficiency of 3.6% (AM1.5).³²⁷ Such treatments could be useful for large-scale manufacturing.

3.6. Role of Nonsolvent Additives: Ternary Blends

In the previous section summarizing the effect of solvents on the morphology and performance of active layers, the notion of solvent additives was introduced to refer to substantial quantities of components of lower volatility that are added to the standard solvents used in preparing thin layers. These added solvents have higher boiling points than the principal solvents, thereby retarding evaporation from the active layer. In addition, the added solvents alter the relative solubility of the components of the layer. P3HT:PCBM and analogues have also been modified by the incorporation of various compounds that are designed to remain in the active layer as a third component added to the D:A blend. The presence of such additives can introduce potentially beneficial optoelectronic properties and productively alter the morphology of the active layer. Additives that have been tested include metals, oxides, carbon nanotubes, small molecules, and polymers, as summarized in Table 9. The chemical structures of certain additives are presented in Figure 13.

Adding suitable quantities of Ag,^{329,331} Pt,³³³ and Au^{329,334} as metallic nanoparticles to bulk heterojunctions of donor and acceptor can lead to an increase in photocurrent. Kim et al. reported that the incorporation of highly conducting Au and Ag nanoparticles increases electrical conductivity.³²⁹ Indeed, they obtained improved efficiency in bulk heterojunction solar cells composed of P3OT:C₆₀ by doping with nanoparticulate Au or Ag (1.7 or 1.4 wt %, respectively). Naidu et al. enhanced the power-conversion efficiency by incorporating 4.5 wt % Ag nanoparticles in solar cells fabricated from blends of P3HT and PCBB.³³¹ After adding a small amount (0.04 wt %) of Pt nanoparticles to P3HT:PCBM active layers, Chang et al. obtained a power-conversion efficiency of 4.8%, a 55% improvement relative to that of unmodified thin films.³³³ In contrast, however, Topp et al. concluded that particles of Au with an average size of 14.9 ± 0.2 nm were not suitable for improving P3HT:PCBM-based solar cells,³³⁴ using metal loading varying from 3 to 16 wt %. According to these authors, particles of Au perturbed the organization of the polymer phase, resulting in decreased hole mobility. The main difficulty of this additive appears to be the agglomeration of nanoparticles. Recently, the influence of Au nanoparticles with a truncated octahedral structure on the active layer in donor-acceptor polymer bulk heterojunction solar cells (P3HT:PC₇₀BM, PCDTBT:PC₇₀BM, Si-PCPDTBT:PC₇₀BM) was investigated by Wang et al.³³² Particles of Au with an average diameter of approximately 70 nm were synthesized by a solution-based method.³⁵⁸ Their incorporation at an optimized concentration (5%) led to increased J_{sc} , FF, and IPCE, possibly resulting from improved absorption of light caused by nanoparticle-induced scattering in the active layer.

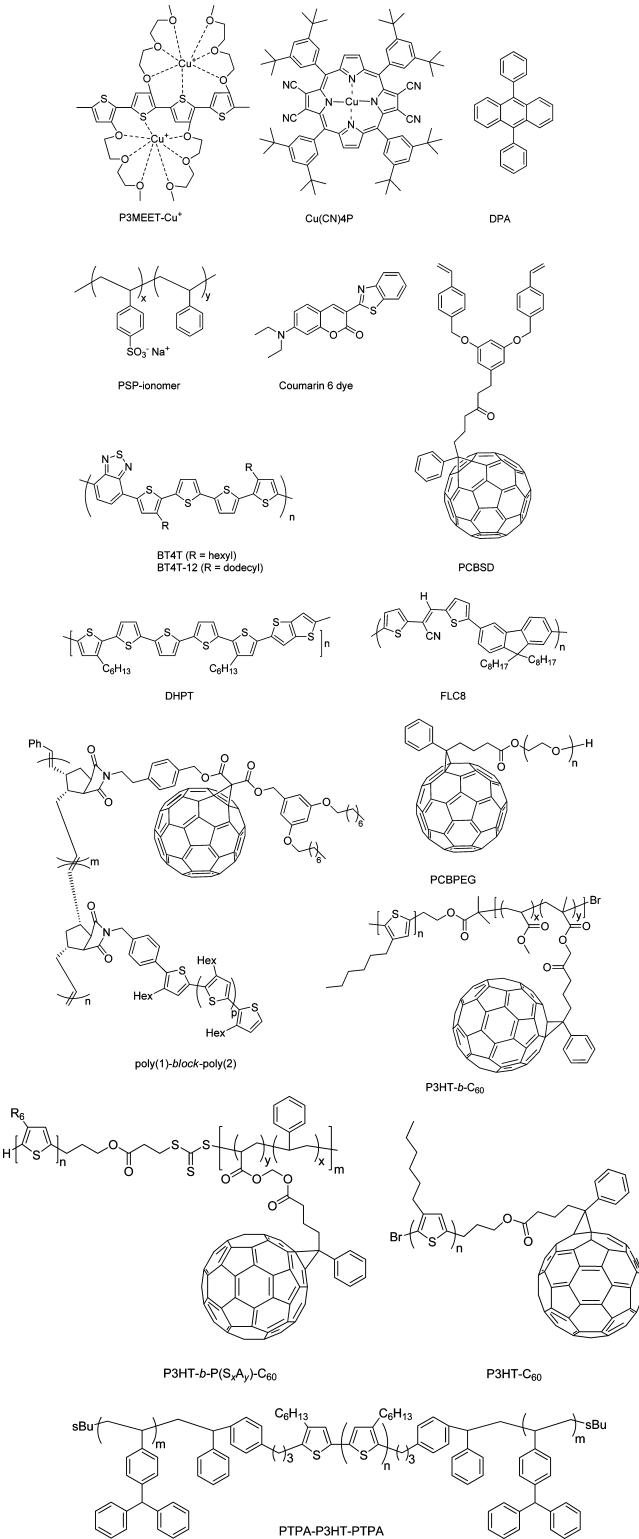


Figure 13. Structures of reported additives.

Carbon nanotubes have also been widely tested as additives.^{335–337,359} Carbon nanotubes have high electron mobility and have been successfully integrated in molecular photovoltaic devices both as electron acceptors^{360,361} and as transparent electrodes.^{359,362,363} However, the efficiency of these devices is distinctly lower than in fullerene-based counterparts, mainly because of the presence of metallic nanotubes, which significantly suppress the effective hole mobility and facilitate

recombination.³⁶¹ Moreover, the dispersion of large amounts of nanotubes in matrixes of polymer is not possible, and the length of the carbon nanotubes is typically similar to the thickness of the photoactive layers, thereby causing short circuits. Nevertheless, the introduction of nanotubes at low concentrations may facilitate the dissociation of excitons at the polymer/nanotube or polymer/fullerene interfaces, and it may also enhance electron transport through the nanotubes. Berson et al. incorporated carbon nanotubes into P3HT:PCBM-based cells,³³⁵ and they demonstrated that 1 wt % did not disrupt crystallization of P3HT. According to these authors, nanotubes improve the extraction of charge within the active layer.

Small molecules such as the porphyrin Cu(CN)4P,^{340,341} 9,10-diphenylanthracene,³⁴² and coumarin 6 dye³⁴⁴ (see Figure 13 for the structures) have also been added to mixtures of P3HT and PCBM. For example, the Dastoor group used Cu(CN)4P as a photosensitizer to absorb light outside the spectral range of usual polymer:fullerene devices.^{330,340,341} Further exploration is needed to better establish the potential of small molecules as additives for altering the morphology of active layers or improving their performance in various ways.

An interesting way to modify and optimize morphology is by incorporating additional polymers or copolymers in P3HT-based solar cells.^{323,349–354} Bechara et al. used the copolymer DHPT3 as an agent for nucleating crystallization in P3HT:PCBM active layers.³⁵⁰ They argued that its addition to the active layers induces a remarkable structural ordering of the poly(thiophene) phase. The resulting order enhances charge transport and widens the range of absorption. As a consequence, the efficiency of the untreated device was doubled by the addition of 5% DHPT3 to the active layer. Similarly, Yang et al. showed that adding 5% donor:acceptor diblock copolymer based on P3HT containing C₆₀ (P3HT-*b*-P(S_xA_y)-C₆₀) led to 35% higher efficiency,³⁵¹ compared with that of P3HT:PCBM solar cells without the additive.

Adding polymers or copolymers to mixtures of P3HT and PCBM is an attractive way to tune morphology and to stabilize devices against destructive thermal phase segregation.^{323,349,352,353} Sivula et al. controlled the morphology of P3HT:PCBM mixtures by adding a selected diblock copolymer.³⁴⁹ Adding 17% to the active layer prevented macroscopic separation of phases, even after annealing at 140 °C for 10 h. Lee et al. introduced the diblock copolymer P3HT-*b*-C₆₀ in P3HT:PCBM blends, and they showed that its presence enhances the crystallinity of P3HT in films, leading to improved transport of holes to the electrode.³²³ More interestingly, the addition of small amounts of P3HT-*b*-C₆₀ suppressed nanophasse separation during long periods of thermal annealing, due to the preferential location of the diblock copolymer at the P3HT:PCBM interface. The same group also modified P3HT:PCBM blends by incorporating P3HT end-capped with C₆₀ in an effort to improve the long-term thermal stability of devices.³⁵² Recently, Tsai et al. introduced a triblock copolymer donor containing segments of poly(3-hexylthiophene) and poly(4-vinyltriphenylamine) to alter the separation of phases of PCBM and P3HT.³⁵³ This triblock additive can suppress large-scale phase separation and segregation of PCBM during thermal annealing.

Adding fullerene derivatives to mixtures of polymer and PCBM is another promising way to adjust morphology and to stabilize devices against destructive thermal phase segregation.^{356,357,364} For example, Cheng et al. introduced PCBSD,³⁵⁶ a styryl-functionalized [6,6]-phenyl-C₆₁-butyric acid dendron

ester (see Figure 13 for the structure), into a blend of P3HT and PCBM in an effort to create active ternary blends. In situ polymerization of the styryl group was performed by heating. Photovoltaic devices prepared from the blend P3HT:PCBM:PCBSD (6:5:1 by weight) showed enhanced resistance to the effects of heating at 150 °C for 25 h. Molecules of PCBSD appear to suppress large-scale phase separation and segregation of PCBM during thermal annealing. More recently, Tai et al. have used fullerene end-capped polyethylene glycol (PCBPEG) as an additive to control the morphology of P3HT:PCBM active layers.³⁵⁷ Adding suitable concentrations of PCBPEG led to increased power-conversion efficiency and long-term stability. The presence of PCBPEG was found to inhibit the aggregation of PCBM, possibly because nucleation centers are immobilized by the long polymeric chains of incorporated molecules of PCBPEG.

In summary, various additives can be incorporated into basic donor:acceptor mixtures such as P3HT:PCBM to modify properties of the active layers, including morphology and optoelectronic performance. The effectiveness of the additive depends in part on its concentration in the layers. The studies summarized demonstrate the potentially beneficial effects of this method under suitably chosen conditions.

4. MORPHOLOGICAL STABILITY

Devices that contain active layers consisting of multiple molecular components have a major drawback: they are prone to structural instability resulting from phase segregation of the components. As discussed above, optimal morphology for high efficiency in solar cells can be achieved by controlling the segregation and crystallization of the components through careful adjustment of numerous parameters involved in fabrication, including the nature of the P3HT used (regioregularity and molecular weight), the solvents, the ratio of the components, thermal annealing, and other factors. However, the optimized morphological structure is often inherently unstable because the components of the active layer can still diffuse over time, especially at elevated temperatures, to form structures with more extensive separation of phases. The resulting change in the nano/microstructure will reduce the interfacial area of the donor:acceptor blend, thereby increasing the efficiency of exciton dissociation and leading to lower photocurrent. In this way, the performance of devices can degrade.

Recently, several strategies have been developed to improve the thermal and morphological stability of polymer:fullerene bulk heterojunction cells. For example, modifying poly(thiophene)s so that they have a controlled amount of disorder in their backbone can suppress crystallization and disfavor the separation of phases containing polymer and fullerene during thermal annealing.¹³⁷ Introducing polymers or copolymers as additives in blends of P3HT and PCBM can also stabilize the morphological structure of devices against destructive segregation of phases in thermal treatment.^{323,349,352,353} Analogously, adding fullerene derivatives to blends of polymer and PCBM is a promising way to alter morphology and to stabilize devices against destructive thermal phase segregation.^{356,357,364}

To suppress the aggregation of PCBM, Zhang et al. synthesized two fullerene derivatives functionalized with triphenylamine or 9,9-dimethylfluorene (Figure 14) for use as new acceptors in polymeric solar cells.³⁶⁵ These compounds showed electron mobility similar to that observed in OFETs composed of PCBM, as well as high power-conversion efficiency (~4%) in solar cells. Moreover, aggregation of the fullerene

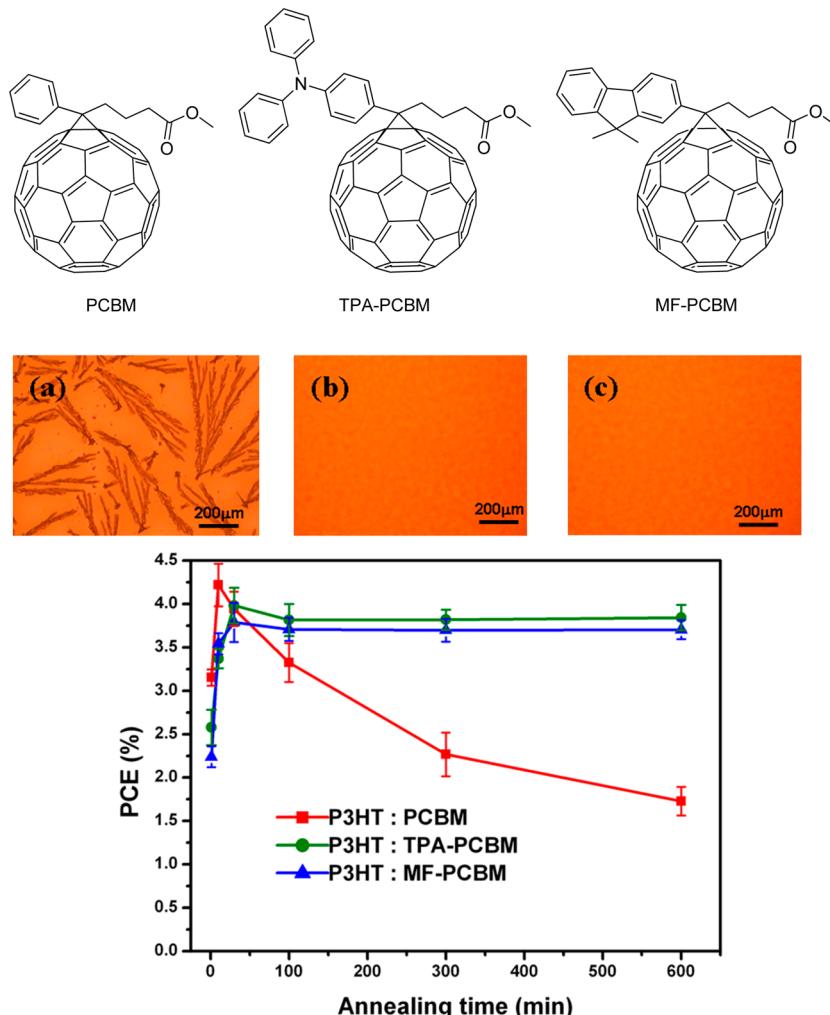


Figure 14. Structures of derivatives of PCBM functionalized with triphenylamine (TPA-PCBM) and dimethylfluorene (MF-PCBM) and their behavior as components of devices (top row). Optical images of films annealed at 150 °C for 10 h: (a) P3HT:PCBM, (b) P3HT:TPA-PCBM, and (c) P3HT:MF-PCBM. Power-conversion efficiency as a function of the annealing time for devices containing PCBM, TPA-PCBM, and MF-PCBM (bottom row). All devices were treated at 150 °C. Reprinted from ref 365. Copyright 2009 American Chemical Society.

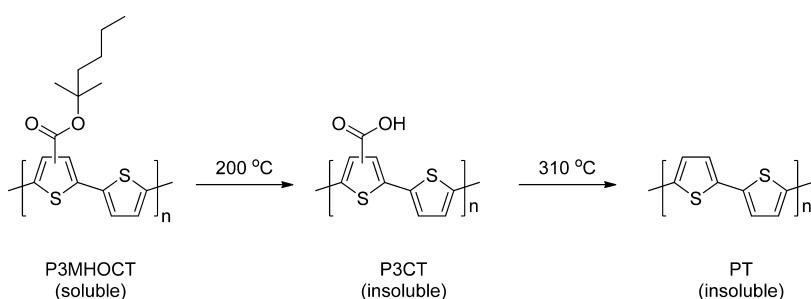


Figure 15. Thermal cleavage of a poly(thiophene).^{366,367}

derivatives during thermal annealing was suppressed, resulting in high morphological stability of devices made from these compounds (Figure 14). The authors attributed this observation to the amorphous nature and high glass-transition temperature of the new PCBMs.

The morphology of the active layer can also be stabilized by using thermocleavable materials.^{366–370} For example, Krebs et al. showed that enhanced stability in photovoltaic devices can be achieved by thermal annealing of a thermocleaved poly-thiophene substituted with carboxylic acid moieties,^{366,367} as

shown in Figure 15. Heating poly[(-(2-methylhexan-2-yl)oxy)carbonyl]dithiophene] (P3MHOCT), which incorporates multiple thermally cleavable ester groups, cleaves the alkyl chains and eventually leads to decarboxylation, thereby producing an unsubstituted poly(thiophene) (PT) with limited solubility. A device composed of a PT:PC₇₀BM heterojunction with an active area of 3 cm² showed the best efficiency (1.5%, 100 mW/cm², AM1.5G, 70 °C), as well as a slow decay of the performance over 500 h of continuous illumination in a nitrogen atmosphere (330 mW/cm², AM1.5G, 25 °C).

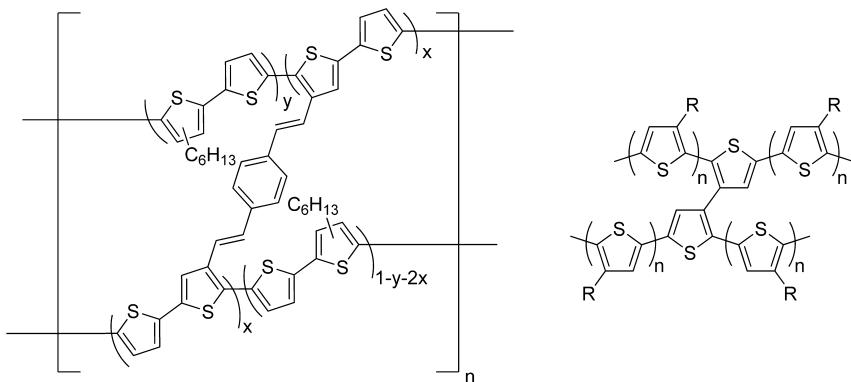


Figure 16. Molecular structures of bridged poly(thiophene)s³⁷² and branched B-P3HT copolymers.³⁷³

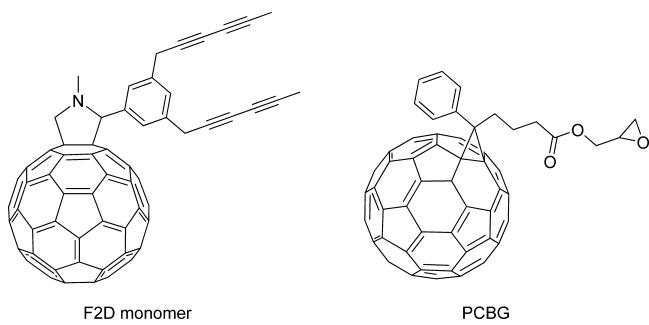


Figure 17. Cross-linkable derivatives of fullerenes of potential use as components of the active layers of solar cells.

Bertho et al. reported the effect of prolonged storage at elevated temperatures on both the morphology and the photovoltaic performance of solar cells containing PCBM and high- T_g PPV,³⁷¹ which is characterized by a glass transition temperature of 138 °C. This high- T_g material leads to firmer matrixes of polymer, thereby limiting the possible migration and segregation of PCBM. In contrast, active layers composed of MDMO-PPV:PCBM showed rapid formation of clusters of PCBM after annealing.

Other groups have used bridged poly(thiophene)s to produce molecular solar cells. For example, Zhou et al. showed that photovoltaic performance can be improved by using cross-linked polymers with a proper content of conjugated bridges (Figure

16).³⁷² Tu et al. used interchain branches in P3HT for preparing photovoltaic devices.³⁷³ In their case, however, increasing the degree of branching overly suppressed the formation of ordered P3HT domains, leading to a decreased mobility of holes and a reduced photovoltaic performance. This approach may be ineffective because cross-linking is already present in the polymer, before it is blended with PCBM to obtain a mixture of donor and acceptor. Moreover, cross-linking may distort the main chain of the polymer and lead to poor solubility. Nevertheless, these results demonstrate once again the importance of appropriate packing in the solid state as a determinant of optimal charge transport and performance.

Cross-linking the components of active layers is an appealing way to prevent segregation of phases. In 2005, the Hummelen group synthesized fullerene derivatives with diacetylene substituents (Figure 17),¹¹⁴ which can be cross-linked thermally. However, no solar cell has been realized with this compound. Morphological stabilization of bulk heterojunction solar cells has been achieved by using an epoxide-functionalized PCBM as demonstrated by Drees et al.,³⁷⁴ who exploited a cross-linkable fullerene, C₆₁-butyric acid glycidol ester (PCBG), shown in Figure 17. Polymerization was induced by an initiator or by heating, resulting in networks of fullerene. As a consequence, the diffusion of molecules of fullerene was restricted.

Miyanishi et al. reported a new cross-linkable regioregular poly[3-(5-hexenyl)thiophene] (P3HNT) for use in photovoltaic devices to improve thermal and morphological stability.³⁷⁵ This

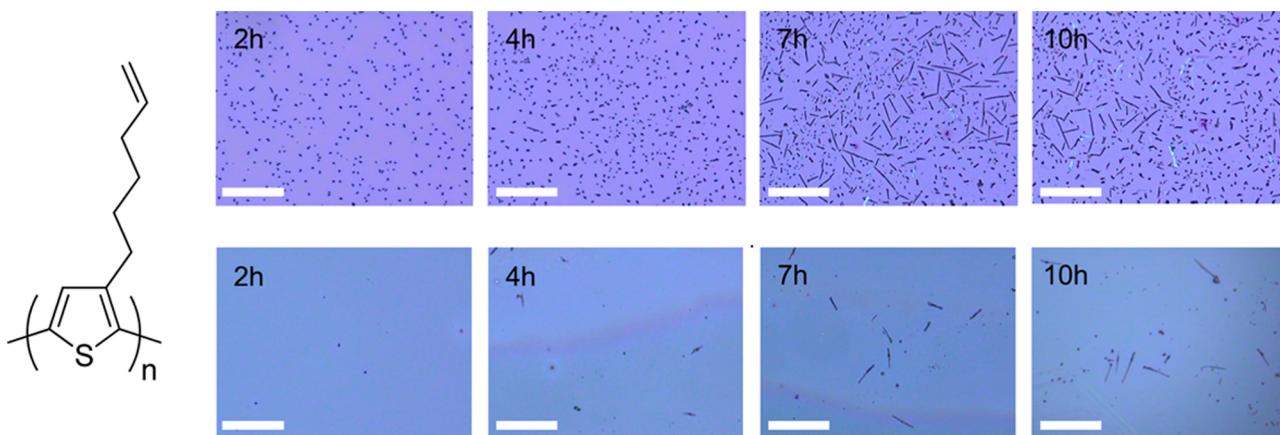


Figure 18. Cross-linkable regioregular poly[3-(5-hexenyl)thiophene] (P3HNT) and its behavior in thin films containing PCBM. Optical microscope images of films of P3HT:PCBM (top row) and P3HNT:PCBM (bottom row) after thermal annealing at 150 °C. Annealing times are presented in the images, and the scale bars correspond to 200 μm. Reprinted from ref 375. Copyright 2009 American Chemical Society.

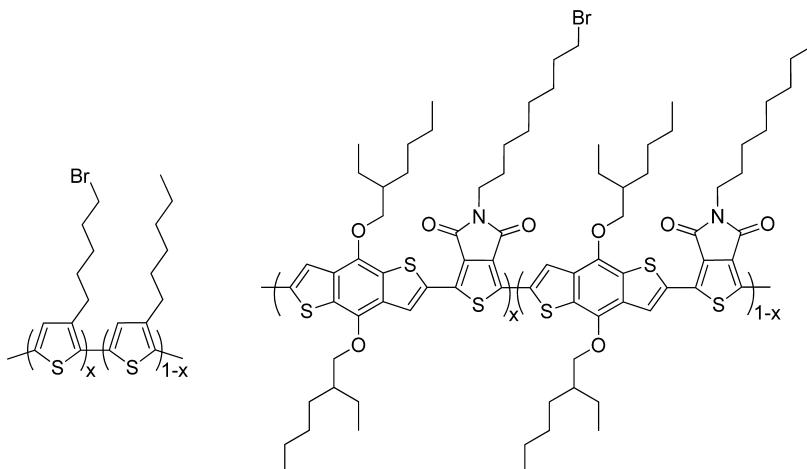


Figure 19. Photo-cross-linkable bromine-functionalized poly(3-hexylthiophene) (P3HT-Br)³⁷⁶ and thieno[3,4-*c*]pyrrole-4,6-dione-based polymer.³⁷⁷

polymer undergoes cross-linking of the vinyl groups of the side chains upon thermal treatment, as confirmed by the insolubility of films in organic solvents and by their thermal behavior. After prolonged thermal treatment, the formation of large aggregates of PCBM was suppressed by cross-linking of the polymer, leading to greater stability of devices created from P3HT compared with those containing P3HT (Figure 18).

The use of cross-linkable molecules was also explored by Fréchet and collaborators.^{376,377} Photo-cross-linkable bromine-functionalized poly(3-hexylthiophene) (P3HT-Br) copolymers (Figure 19) have been developed for application in solution-processed molecular photovoltaics.³⁷⁶ Unlike devices prepared from blends of either P3HT:PCBM or P3HT-Br:PCBM without UV treatment, those made from photo-cross-linked P3HT-Br:PCBM proved to be stable even when annealed for two days at the elevated temperature of 150 °C. This indicates that the separated nanophase inside the bulk heterojunction blend is stabilized. In the same manner, the Fréchet group reported the first photo-cross-linkable donor:acceptor conjugated polymer for application in bulk heterojunction solar cells.³⁷⁷ The polymer contains units of thieno[3,4-*c*]pyrrole-4,6-dione (TPD) with a terminal primary bromide functionality allowing for photo-cross-linking of the polymer in devices (Figure 19). The resulting TPD-based polymers, blended with PC₇₀BM, provided photovoltaic devices that remained stable during 72 h of thermal annealing at 150 °C, showing that photo-cross-linking maintains a productive morphology of the active layer throughout the thermal treatment.

In summary, a variety of materials have shown promise in attaining high efficiency in solar cells and especially in achieving acceptable stability. These new materials appear to restrict the migration and segregation of components of the active layer, including relatively small molecules such as PCBM.

5. EFFICIENCY OF POLYMERIC SOLAR CELLS

Bulk heterojunction solar cells based on blends of P3HT:PCBM typically show efficiencies in the range of 2–4%.⁴⁵ Efficiencies exceeding 4% have been achieved by multistep morphological optimization in which various parameters are adjusted.^{20,134,177,187,319,324,378–381} In addition, it should be noted that the efficiency of cells can be enhanced by using buffer layers, a subject reviewed by Po et al.³⁸² The buffer materials are selected according to their properties of energetics and transport, so that charge carriers can be collected and transported but those of the

opposite sign are blocked. In this way, efficiencies higher than 4% can be achieved by using hole-extraction layers or electron-extraction layers such as those containing metal oxides (TiO_x ,^{307,383} NiO_x ,³⁸⁴ ZnO_x ,^{385,386} V_2O_5 ,³⁸⁷ WO_3 ,³⁸⁷ and CuO_x ,³⁸⁸), carbon nanotubes,³⁵⁹ polymers (improved poly[3,4-(ethylenedioxy)thiophene]:poly(styrenesulfonate) (PEDOT:PSS),^{389–391} poly(aniline) (PANI),³⁹² PASS-*g*-PANI,³⁹³ improved PEDOT,³⁹⁴ sulfonated poly(diphenylamine),³⁹⁵ P3HT,³⁹⁶ and poly(thiophene)³⁹⁷), and various small molecules (CuPc ,³⁹⁸ PCBM,³⁹⁹ and 2,7-bis(diphenylphosphoryl)spiro[fluorene-7,11'-benzofluorene]⁴⁰⁰). For example, Irwin et al. reported a power-conversion efficiency of 5.2% resulting from insertion of NiO as a hole-transporting layer.³⁸⁴ In addition, PEDOT:PSS has been widely used as a hole-transporting layer in molecular photovoltaic devices.⁴⁰¹ The use of PEDOT:PSS with high conductivity, as a result of doping by solvent, has led to particularly high performance.³⁸⁹

A factor that limits photovoltaic performance is a relatively low current density, which is partially due to a poor spectral match between the absorption of the photoactive layer and solar emission. Most conjugated polymers have a band gap of ≥ 1.9 eV and consequently absorb light only at wavelengths of < 650 nm.⁴⁰² Fullerenes also have very low absorption coefficients outside the UV region.⁴⁰³ To improve utilization of solar light, new polymers with low band gaps need to be developed. Efficiencies of 4–7% can be attained in devices containing suitable low-band-gap polymers, as shown in Table 10. It should be noted that small amounts of specialized additives are sometimes required to reach high efficiency, presumably by favoring an optimal morphology.^{136,163,169,245,247,255,404–406}

There are often important differences in the reported efficiency from laboratory to laboratory, even for the benchmark P3HT:PCBM system. In part, the variability is presumably due to different materials and conditions of processing (including the nature of the polymer, donor:acceptor ratio, solvent, and conditions of annealing). In addition, it should be noted that determining power-conversion efficiencies accurately is not trivial. These measurements require a solar simulator, which is a standard light source that provides an indoor source of calibrated solar irradiation. The simulator must contain adequate filters to meet the specifications of an air-mass coefficient of 1.5 (AM1.5G for global solar irradiation and AM1.5D for direct and circumsolar irradiation). Solar simulators are generally based on xenon arc lamps, but some incorporate lamps of tungsten,

Table 10. Examples of High Power-Conversion Efficiencies (PCEs) of Photovoltaic Devices Prepared from New Polymers

device structure	ratio	solvent	surface (mm ²)	PCE (%)	ref
glass/ITO/PEDOT:PSS/pBBTDPP2:PC ₇₀ BM/LiF/Al	1:2	ODCB	9	4.0	407
glass/ITO/PEDOT:PSS/PCDTBT:PC ₇₀ BM/TiO _x /Al	1:4	CB/ODCB	12	6.9	408
glass/ITO/PEDOT:PSS/P3:PC ₆₀ BM/Ca/Al	1:1.5	CB	3	6.4	256
glass/ITO/PEDOT:PSS/TQ1:PC ₇₀ BM/LiF/Al	1:2–1:4	ODCB	4–6	5.7–6.0	409
glass/ITO/PEDOT:PSS/BisDMO-PFDTBT:PC ₇₀ BM/Ca/Al	1:3	ODCB	12	4.0	410
glass/ITO/PEDOT:PSS/PDPP-BDP:PC ₇₀ BM/Ca/Al	1:2	ODCB	9.5	4.45	411
glass/ITO/PEDOT:PSS/PBDTTT-E:PC ₇₀ BM/Ca/Al	1:1 and 1:1.5	CB/DIO	10	5.15	412
glass/ITO/PEDOT:PSS/PBDTTT-CF:PC ₇₀ BM/Ca/Al				7.73	
glass/ITO/PEDOT:PSS/PBDTTT-C:PC ₇₀ BM/Ca/Al				6.58	
glass/ITO/PEDOT:PSS/PSBTBT:PC ₇₀ BM/Ca/Al	1:1	ODCB	12	5.1	413
glass/ITO/PEDOT:PSS/P4H:PC ₇₀ BM/Al	1:2.5	ODCB	10.2	4.05	414
glass/ITO/PEDOT:PSS/POD2T-DTBT:PC ₇₀ BM/Al	1:1	ODCB	9	6.26	415
ITO/PEDOT:PSS/PBSTDGBT:PC ₇₀ BM/Ca/Al	1:3	ODCB	16	3.64	416
ITO/PEDOT:PSS/PBGBTBT:PC ₇₀ BM/Ca/Al	1:3			3.47	
ITO/TiO _x /Si-PCPDTBT:PC ₆₀ BM/PEDOT:PSS/Ag	1:1.5	ODCB	NI	5	417
ITO/TiO _x /Si-PCPDTBT:bis-PC ₆₀ BM/PEDOT:PSS/Ag				4	
glass/ITO/PEDOT:PSS/PTPTPTDPP13:PC ₇₀ BM/Ca/Al	1:3	ODCB	4	4.1	418
glass/ITO/PEDOT:PSS/PTPTPTDPP12:PC ₇₀ BM/Ca/Al	1:4			4.3	
glass/ITO/ZnO/C-PCBSD/PTPTPTDPP13:PC ₇₀ BM/PEDOT:PSS/Ag	1:3			4.6	
glass/ITO/ZnO/C-PCBSD/PTPTPTDPP12:PC ₇₀ BM/PEDOT:PSS/Ag	1:4			5.1	
glass/ITO/PEDOT:PSS/PBnDT-HTAZ:PC ₆₀ BM/Ca/Al	1:2	TCB	12	4.36	419
glass/ITO/PEDOT:PSS/PBnDT-HTAZ:PC ₆₀ BM/Ca/Al				7.10	
glass/ITO/PEDOT:PSS/N-P7:PC ₇₀ BM/Al	1:4	CB	25	4.86	420
glass/ITO/PEDOT:PSS/PDTS-BTD:PC ₇₀ BM/LiF/Al	1:1.5	CB	4	4.42	421
glass/ITO/MoO ₃ /PDTS-BTD:PC ₇₀ BM/LiF/Al				4.91	
glass/ITO/ZnO/PDTS-BTD:PC ₇₀ BM/MoO ₃ /Ag				5.51	
ITO/PEDOT:PSS/PGeTPBTBT:PC ₇₀ BM/Ca/Al	1:4	ODCB	4.5	5.02	422
glass/ITO/PEDOT:PSS/EI-PFDTBT:PC ₇₀ BM/Ca/Al	1:2	1,2,4-TCB	10	5.07	423
glass/ITO/PEDOT:PSS/pBCN:PC ₆₀ BM/Ca/Al	1:1	CB	NI	4.20	424
glass/ITO/PEDOT:PSS/pBCN:PC ₇₀ BM/Ca/Al	1:1	CB		4.88	
glass/ITO/PEDOT:PSS/PBDFDTBT:PC ₇₀ BM/Ca/Al	1:1.5	ODCB	NI	4.66	425
ITO/PEDOT:PSS/HXS-1:PC ₇₀ BM/LiF/Al	1:2.5	ODCB/DIO	3.6	5.4	406
glass/ITO/PEDOT:PSS/PCPDTBT:PC ₇₀ BM/Al	1:2 to 1:3	CB/DOT	17	5.2–5.5	156
glass/ITO/PEDOT:PSS/PCPDTBT:PC ₇₀ BM	1:3.6	CB/DIO		5.12	245
ITO/PEDOT:PSS/PTTBBDT-C8:PC ₇₀ BM/BCP/LiF/Al	1:2	CHCl ₃ /DIO	49	4.83	247
glass/ITO/PEDOT:PSS/PBDPTT-C:PC ₇₀ BM/Ca/Al	1:2	ODCB/DIO	NI	5.21	169
glass/ITO/PEDOT:PSS/PBDTTTZ:PC ₇₀ BM/Ca/Al	1:2 to 1:3	ODCB/DIO	NI	~ 5.2	165
glass/ITO/PEDOT:PSS/PBTTPD:PC ₇₀ BM/Al	1:1.5	CHCl ₃ /DIH	NI	7.3	255
glass/ITO/PEDOT:PSS/PCPDTBT:PC ₇₀ BM/Ca/Al	1:3	CB/DIO	16	~ 4.5	404
glass/ITO/PEDOT:PSS/PBDTTT-C:PC ₇₀ BM/Ca/Al	1:1.5	ODCB/DIO	10	6.58	405
glass/ITO/PEDOT:PSS/PTB7:PC ₇₀ BM/Ca/Al	1:1.5	CB/DIO	10	7.40	163
		ODCB/DIO		7.18	
pBBTDPP2	poly[3,6-bis(4'-dodecyl[2,2']bithiophene-5-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4]pyrrole-1,4-dione]				
PCDTBT	poly[N-9'-heptadecyl-2,7-carbazole- <i>alt</i> -5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]				
P3	ref 256				
TQ1	poly[2,3-bis(3-octyloxy)phenyl]quinoxaline-5,8-diyl- <i>alt</i> -thiophene-2,5-diyl]				
BisDMO-PFDTBT	poly[2,7-(9,9-bis(3,7-dimethyloctyl)fluorene)]- <i>alt</i> -[5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)]				
PDPP-BDP	poly{2,7'-(4,5-bis(2-ethylhexyl)benzo[2,1-b:3,4-b']dithiophene)- <i>alt</i> -5-(diethylhexyl)-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione}				
PSBTBT	dithieno[3,2-b;2,3'-d]silole polymer, poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl- <i>alt</i> -(2,1,3-benzothiadiazole)-4,7-diyl]				
PBDTTT	poly[4,8-bis-substituted benzo[1,2-b:4,5-b']dithiophene-2,6-diyl- <i>alt</i> -4-substituted thieno[3,4-b]thiophene-2,6-diyl]				
P4H	poly[2,7-((3,6-dioctyloxy)-9,9-dihexylsilafluorene)- <i>alt</i> -5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]				
POD2T-DTBT	poly[(benzo-2,1,3-thiadiazole-4,7-diyl)- <i>alt</i> -(3',4"-bis(2-octyldodecyl)-2,2';5',2";5",2"-quaterthiophene-5,5"-diyl)]				
PBDTTT-E	ref 412				
PBDTTT-CF					
PBDTTT-C					
PBSTDGBT	ref 416				
PBGBTBT					
Si-PCPDTBT	poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl- <i>alt</i> -(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl]				
PTPTPTDPP	thienylphenylenethiylenephenylenethiényl (TPTPT) dibromodithienylketopyrrolypyrrole (DPP)				
PBnDT-HTAZ	BnDT = benzodithiophene				
PBnDT-HTAZ	TAZ = 2-alkylbenzo[d][1,2,3]triazole				
N-P7	poly[2,7-(9,9-dioctylfluorene)- <i>alt</i> -5,5-(5',8'-di-2-thienyl-2',3'-diphenylquinoxaline)]				

Table 10. continued

PDT5-BTD	poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2- <i>b</i> :2',3'- <i>d</i>]silole)-2,6-diyl- <i>alt</i> -(2,1,3-benzothiadiazole)-4,7-diyl]
PGeTPTBT	ref 422
EI-PFDTBT	ref 423
BCN	benzodithiophenethiophenecyanovinylene
PBDFDTBT	BDF = benzo[1,2- <i>b</i> :4,5- <i>b</i> ']difuran DTBT = 4,7-dithienyl-2,1,3-benzothiadiazole
HXS-1	poly[2-(5-(S,6-bis(octyloxy)-4-(thiophene-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-yl)-9-octyl-9H-carbazole]
PTTBDT-C8	ref 247
PBDPTT-C	poly[(4,5-bis(3,7-dimethyloctyl)benzo[2,1- <i>b</i> :3,4- <i>b</i> ']dithiophene-2,7-diyl)- <i>alt</i> -(2-(2-ethylhexanoyl)thieno[3,4- <i>b</i>]thiophene-4,5-diyl)]
PBDTTTZ	benzo[1,2- <i>b</i> :4,5- <i>b</i> ']dithiophene (BDT) thiazolo[5,4- <i>d</i>]thiazole (TTZ)
PBTPPD	poly[didodecylthiophenethieno[3,4- <i>c</i>]pyrrole-4,6-dione]
PTB7	ref 163

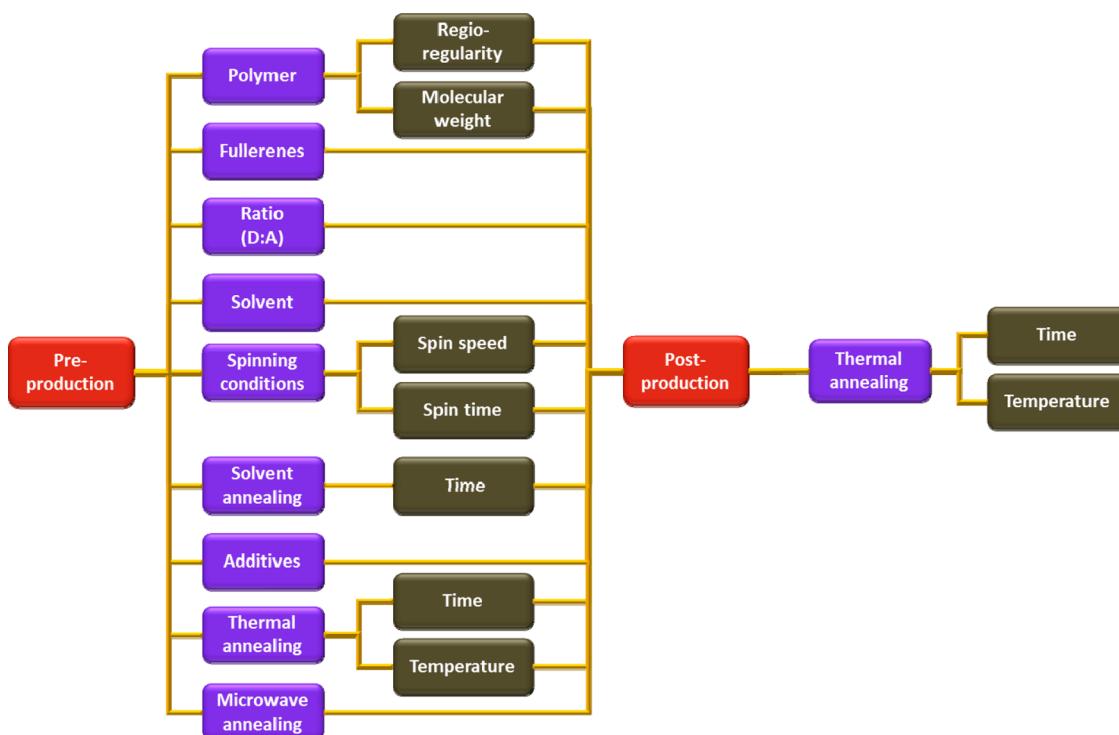


Figure 20. Panorama of variables that can be adjusted to help control the nanomorphology of P3HT:PCBM blends.

mercury, or metal halide. The filters are used to minimize the mismatch between the spectra of the simulator and the sun itself. As a consequence, all solar simulators do not necessarily yield identical spectra. Moreover, lamps age and the incident-light power must therefore be monitored and controlled carefully. Various irradiance meters are available, such as bolometric detectors, thermopile detectors, and calibrated photodiodes. Generally, the standard light-input power used is 100 mW/cm². To help standardize methods and results, researchers should consult recent references related to measuring and reporting solar cell efficiencies.^{426,427}

Another potential source of variability arises because the geometry of the active surface area and the shape of the photovoltaic cell can influence performance, sometimes dramatically.^{4,428–430} The method of irradiation must also be considered. It has been demonstrated that the use of a shadow mask with an aperture smaller than or equal to the active area of the cell avoids overestimation of the current density.⁴²⁸

Ultimately, the best way to avoid mistakes in determining the power-conversion efficiency of photovoltaic cells is to have the

results confirmed in another laboratory. In particular, devices can be sent to institutes able to certify performance, such as the National Renewable Energy Laboratory (NREL).^{9,198,431–433}

6. CONCLUSIONS

During the past decade, the field of polymeric photovoltaics has seen extensive advances, both in the efficiency of devices and in understanding of the basic physical processes. An important part of the progress has resulted from studies related to controlling the nanomorphology of the active layer. The present review has outlined how the morphology of the active layer can affect the performance of devices, using the benchmark behavior of P3HT:PCBM blends to illustrate key principles. Diverse strategies for controlling the nanomorphology of P3HT:PCBM blends are recapitulated in Figure 20. The morphology of photoactive polymer:fullerene blends can be controlled by adjusting various parameters, either during the formation of films or during subsequent treatments. Experimentally, the following parameters have been identified as most significant for their influence on the nanoscale morphology of polymer:fullerene

blends before film deposition: the molecular weight and regioregularity of P3HT, the P3HT:fullerene ratio, the identity of solvents used, and the presence of additives. Key parameters after film formation include annealing by exposure to heat, solvents, and microwave irradiation. Optimizing cells is complicated by the fact that all these various parameters are interrelated, and the choice of one parameter depends on the others. When new polymers are present, or even when established polymers such as P3HT with new properties of regioregularity or molecular weight are used, new optimizations must be carried out step by step. As a result, the present review cannot provide a formulaic solution to the problem of selecting the components of the active layers of solar cells and optimizing their performance; instead, the goal of the review is to underscore the importance of morphology, identify key parameters that can help control molecular organization in the active layer, and serve as a guide for researchers in their efforts to create optimal architectures.

ASSOCIATED CONTENT

Supporting Information

Tables of solvents and cosolvents used in the fabrication of bulk heterojunctions in thin-film solar cells and other devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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Biographies



Minh Trung Dang obtained his master's degree in chemistry from the Université du Maine (Le Mans, France) in 2006. He then completed his Ph.D. in 2009 at the Université Bordeaux 1, where he studied molecular photovoltaic cells under the joint supervision of Lionel Hirsh and Guillaume Wantz. He is currently a postdoctoral fellow at the Université de Montréal, where he is working with Jim Wuest to develop bulk heterojunction cells containing novel polymeric compounds and small molecules.



Lionel Hirsch obtained his master's degree in electrical engineering at Université Bordeaux 1 in 1992, and he received his Ph.D. in materials science from Université Bordeaux 1 in 1996. In 1998, he was appointed Research Scientist at CNRS, where he worked on white and blue GaN-based LEDs and helped develop a technique based on ion beam-induced charges to map the collection efficiency of UV detectors. He is currently interested in organic electronics, with a focus on the mechanisms of the transport and recombination of charges. He directs the French organic electronics network, which brings together more than 40 laboratories (www.gdr-electronique-organique.fr).



Originally from northern France, Guillaume Wantz obtained his master's degree for work carried out at the Graduate School of Chemistry and Physics of Bordeaux in 2001 and at Philips Research (Eindhoven, The Netherlands). In 2004, he received his Ph.D. in electronic engineering from Université Bordeaux 1, where he studied polymeric light-emitting diodes. As Assistant Professor at Université Bordeaux 1, he worked on organic field-effect transistors, and he was appointed to a tenured position as Associate Professor at the Institut Polytechnique de Bordeaux (IPB) in 2006. He is broadly interested in organic electronics with a focus on solar cells.



James D. Wuest received his A.B. in 1969 from Cornell University and his Ph.D. in 1973 from Harvard University, where he was a student of R. B. Woodward. After serving as an assistant professor of chemistry at Harvard, he moved to the Université de Montréal in 1981. His work uses tools from a wide range of disciplines, including synthesis, structural chemistry, surface science, and computation, to develop guidelines for controlling molecular organization in materials.

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