

# Development of Low Band Gap Polymers for Roll-to-Roll Coated Polymer Solar Cell Modules

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**Abstract** Organic photovoltaics (OPV) have the potential for low production cost. Additionally, there has been an increase in both efficiency and stability of small-area OPV devices prepared in research laboratories worldwide and, consequently, attention on OPVs has increased tremendously. In this chapter we describe the challenges of OPVs and give suggestions on how these can be overcome. Design and synthesis of a new group of materials and low band gap polymers are described. Problems and possible solutions of OPV stability are shortly discussed. Furthermore, the latest technology to manufacture large-area OPV modules is described along with production of large-area modules by roll-to-roll printing of a low band gap polymer.

## 1 Introduction

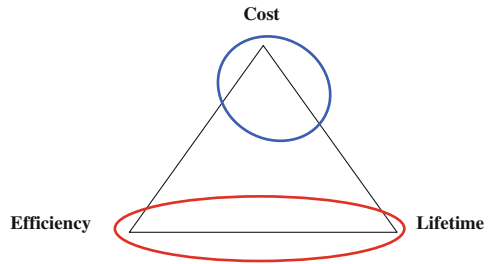
### 1.1 Organic Photovoltaics

In the past, there has been a tremendous focus on renewable energy sources, such as wind, hydro, biomass, geothermal and solar. This is mainly to find alternative energy sources that are CO<sub>2</sub> neutral since United Nations have decided that a 20% reduction in the CO<sub>2</sub> emissions by 2020 is necessary [1, 2]. Furthermore, due to the growth of human population on Earth and its increasing demand for energy, it is

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**Fig. 1** Brabec triangle [4]: red represents inorganic PV and blue represents OPV



**Fig. 2** Illustration of OPV devices, normal structure (*left*) and inverted (*right*)

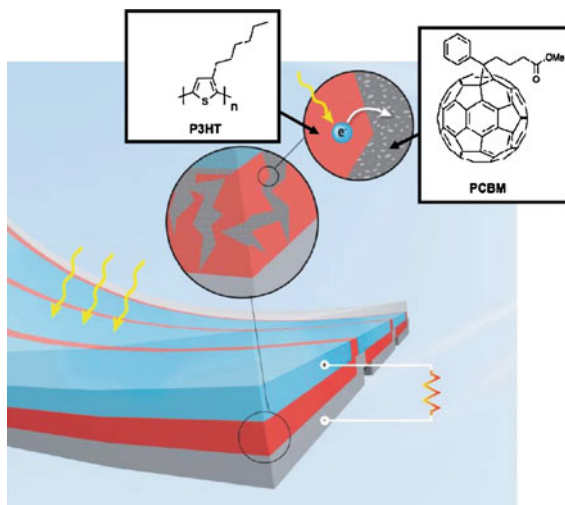
likely that fossil fuels (which are the primary energy sources we depend on today) will be exhausted within the next 30–50 years.

The sun delivers more energy to the Earth's surface than we can consume and thus this renewable energy source is impossible to ignore. To harvest the energy from the sun and turn it into electricity, photovoltaics (PV) are used. There are three generations of photovoltaics. In the first generation, referred to as inorganic PV, the active material is crystalline silicon. In the second generation, referred to as thin film PV, the active layer is typically based on CdS or CuIn(Ga)Se<sub>2</sub> type materials. Finally the third generation, referred to as organic PV or OPV, the active layer is based on polymers or other organic molecules. There are advantages and disadvantages for all three generations. Inorganic PVs are relatively expensive to produce, mostly due to high temperatures and the need for very clean conditions; however, they have a very high efficiency and are very stable [3]. Thin film PVs frequently involve toxic materials and, even though they have demonstrated very high efficiencies and a potentially low cost of production, the controlled fabrication is still a challenge [3]. Polymer-based PVs currently have a low efficiency and poor stability. However, they have a low production cost and can be printed or coated using roll-to-roll (R2R) methods. Thus, a simple comparison shows that the inorganic photovoltaics dominate the areas of efficiency and stability, whereas organic photovoltaics can take the lead in production cost (Fig. 1) [4].

Within the last 5 years the stability and efficiency of small-area organic photovoltaic (OPV) prepared in research laboratories have increased and they now live fully up to the role as a competitor to inorganic PV and thin film PV at the laboratory level. In this chapter we will therefore focus on this type of PV. For further information on OPV (see [4–11]).

Illustrations of two typical OPVs are shown in Fig. 2. The structure is a bulk heterojunction, where the polymer is mixed with a soluble fullerene,

**Fig. 3** Processes in OPV: from sunlight to electricity



e.g., [6,6]-phenyl- $C_{61}$ -butyric acid methyl ester (PCBM), sandwiched between a transparent electrode, typically indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), and a back electrode, Al. Recently, an inverted structure for the OPV device was developed, where the transparent electrode is ITO and ZnO and the back electrode is Ag. The device structure is referred to as inverted due to the inversion of the way the current flows in the cell [12].

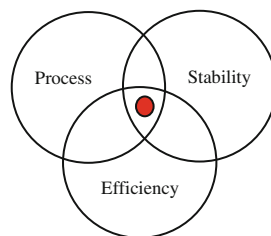
The typical processes in a bulk heterojunction OPV is demonstrated in Fig. 3. The polymer absorbs a photon and an exciton (electron-hole pair) is created. This exciton diffuses to the donor/acceptor interface (i.e., the polymer/PCBM interface), where an electron is transferred from the donor to the acceptor (i.e., from polymer to PCBM). Dissociation of the exciton into free carriers, transport of the free carriers to the electrodes and charge collection at the electrodes complete the working cycle of the OPV. These processes determine how efficient the cell operates, i.e., losses in these processes by charge recombination or non-absorbed photons will result in a decrease in current and, hence, the efficiency will be lower.

## 1.2 Challenges of OPV

In the field of OPV, there are three focus areas within research groups worldwide. Those are: efficiency, stability and production.

So far, power conversion efficiency (PCE) has received the most attention. The literature shows a focus on device structure and device optimization to improve efficiencies mostly for OPV devices based on poly(3-hexyl-thiophene) (P3HT) and PCBM. Since the limit in efficiency for P3HT has been reached, the focus has shifted during the past few years toward designing polymers with a lower band gap

**Fig. 4** Unification challenge of organic photovoltaic [17]



for potential improvement of the PCE. Low band gap polymers are expected to enable a significant increase in the efficiency of the solar cell due to increased absorption in the visible spectrum [13–16]. These types of polymers will be described in detail in the next section.

The focus on stability is increasing and more research groups are carrying out lifetime studies either by long time studies or accelerated studies. The stability can be increased by encapsulating the OPV with layers that protects the cell from water/moisture and oxygen or by design of the polymer [17]. In the third part of this chapter we briefly describe the problems and possible solutions for prolonging the stability of flexible R2R coated OPV modules.

Processing is a rather new topic, since most research has been carried out on small-area devices, e.g.,  $<0.1 \text{ cm}^2$ . However, the OPVs have the advantage that they can be printed on flexible substrates, making the processing of modules both faster and lower in cost compared to inorganic photovoltaics. There are several methods and techniques that need to be studied and in the last part of this chapter, we describe in detail the methods and the preparation of modules based on a low band gap polymer. The overall challenge for scientists working in the field of organic solar cells is to unite their knowledge into a single material such that the resulting device structure yields efficient and stable OPV modules that are easy to produce at a low cost (Fig. 4).

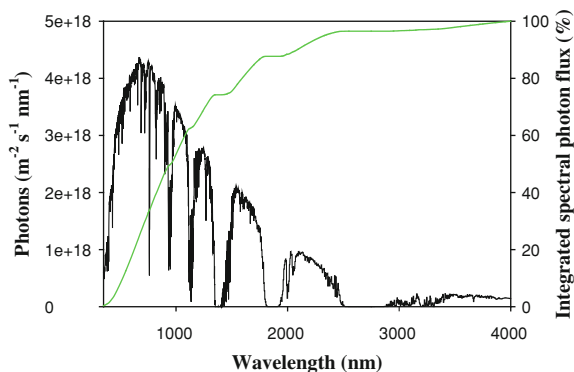
In the following three parts of this chapter, we look upon the challenges separately. We discuss in detail (1) the low band gap materials, the type of polymer that is believed to increase the efficiency of OPV, (2) stability issues, with a focus on thermocleavable side chains and (3) the processing of large area OPV modules and the different techniques that have been developed over the past years.

## 2 Low Band Gap Polymers

### 2.1 What and Why?

Within the past few years the focus within OPV research has been drifting more and more toward low band gap polymers. But what are these polymers and why are they so interesting?

**Fig. 5** Solar spectrum (AM1.5G) shown as number of photons (*black*) and integrated photon flux (*green*)

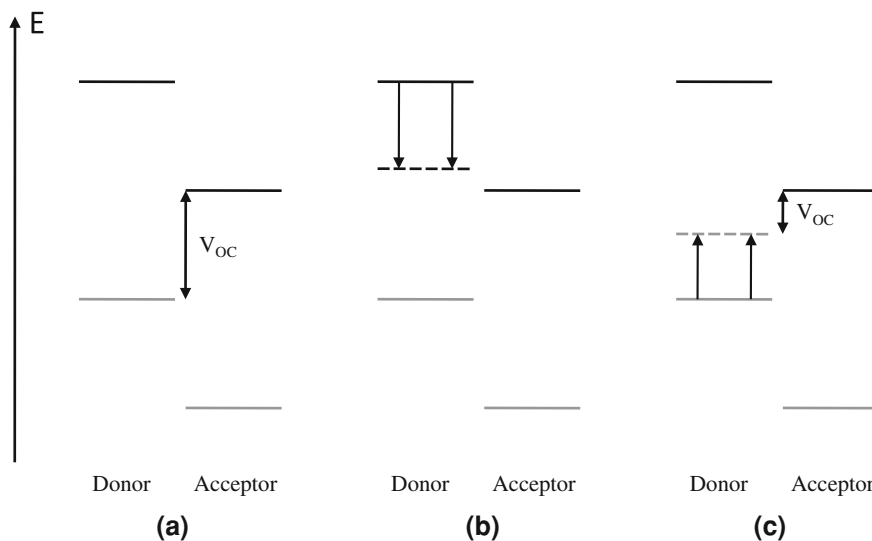


Low band gap polymers are loosely defined as polymers that absorb light with wavelengths longer than 600 nm, i.e. they have a band gap below 2 eV. Low band gap polymers are believed to have the ability to increase the efficiency of OPV devices since they have the ability to harvest more photons from the sun than the classes of polymers developed previously (e.g., MEHPPV, MDMOPPV and P3HT) [13, 15, 16].

In Fig. 5, the solar spectrum (AM1.5G) is shown as number of photons together with the integrated photon flux. This indicates that regular P3HT, which absorbs light up to  $\sim 700$  nm can absorb at most 27.6% of incident photons. If all photons are harvested and converted into electrons this corresponds to a maximum current of  $17.6 \text{ mA cm}^{-2}$ . However, a low band gap polymer that absorbs light to 900 nm, for example, the portion of photons that can be absorbed increases to 46.7%, corresponding to a maximum current of  $29.8 \text{ mA cm}^{-2}$  [15]. These examples highlight the importance of low band gap polymers; however, in practice it is far more complicated than just lowering the band gap. When the band gap is lowered several parameters may change.

In Fig. 6, one can see that if the band gap is decreased by shifting the position of the lowest unoccupied molecular orbital (LUMO) of the polymer to lower energies, it approaches the LUMO of the acceptor (PCBM) and, as a result, it may not be energetically favored for the electron to transfer from the donor to the acceptor, meaning that recombination of electron and hole is favored instead (scenario B) [13, 15]. Furthermore, the open circuit voltage ( $V_{OC}$ ) is reduced if the band gap is lowered by increasing the energy of the highest occupied molecular orbital (HOMO) of the polymer, since the  $V_{OC}$  is determined by the difference between the HOMO of the donor and LUMO of the acceptor in a simple pn-junction (scenario C) [13, 15]. This shows the importance of both designing the polymer and choosing an appropriate acceptor (e.g., PCBM or PC<sub>70</sub>PM) so the energy levels of HOMO and LUMO are aligned optimally.

The different acceptors that are often used in OPV devices are shown in Fig. 7, along with an energy diagram showing their relative energy levels. The energy level alignment can, in principle, also be optimized by addition of another polymer instead of the fullerene based acceptor, i.e., combining a low band gap donor

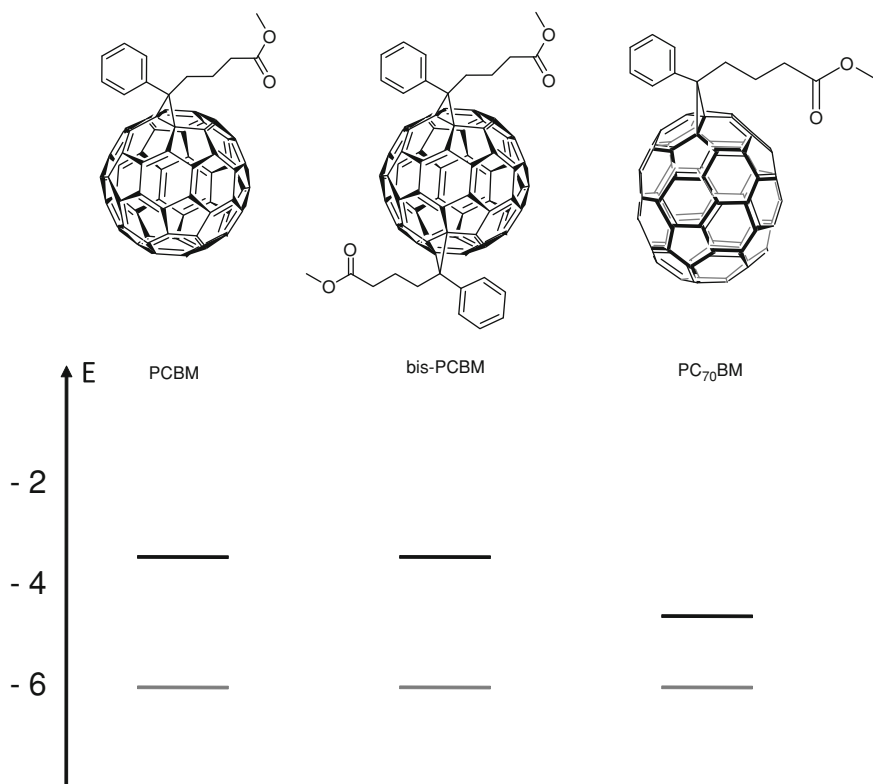


**Fig. 6** Consequences of lowering the band gap of the donor. Gray lines denote the LUMO and black lines represent the HOMO levels

polymer with an acceptor polymer in a polymer–polymer OPV device [18]. This approach has not been pursued by many.

The band gap of a polymer is affected by several factors, such as donor–acceptor units, intramolecular interactions and molecular weight. The band gap is affected by the molecular weight ( $M_w$ ) of the polymer, since an increase in  $M_w$  decreases the band gap due to a longer conjugation length [13].

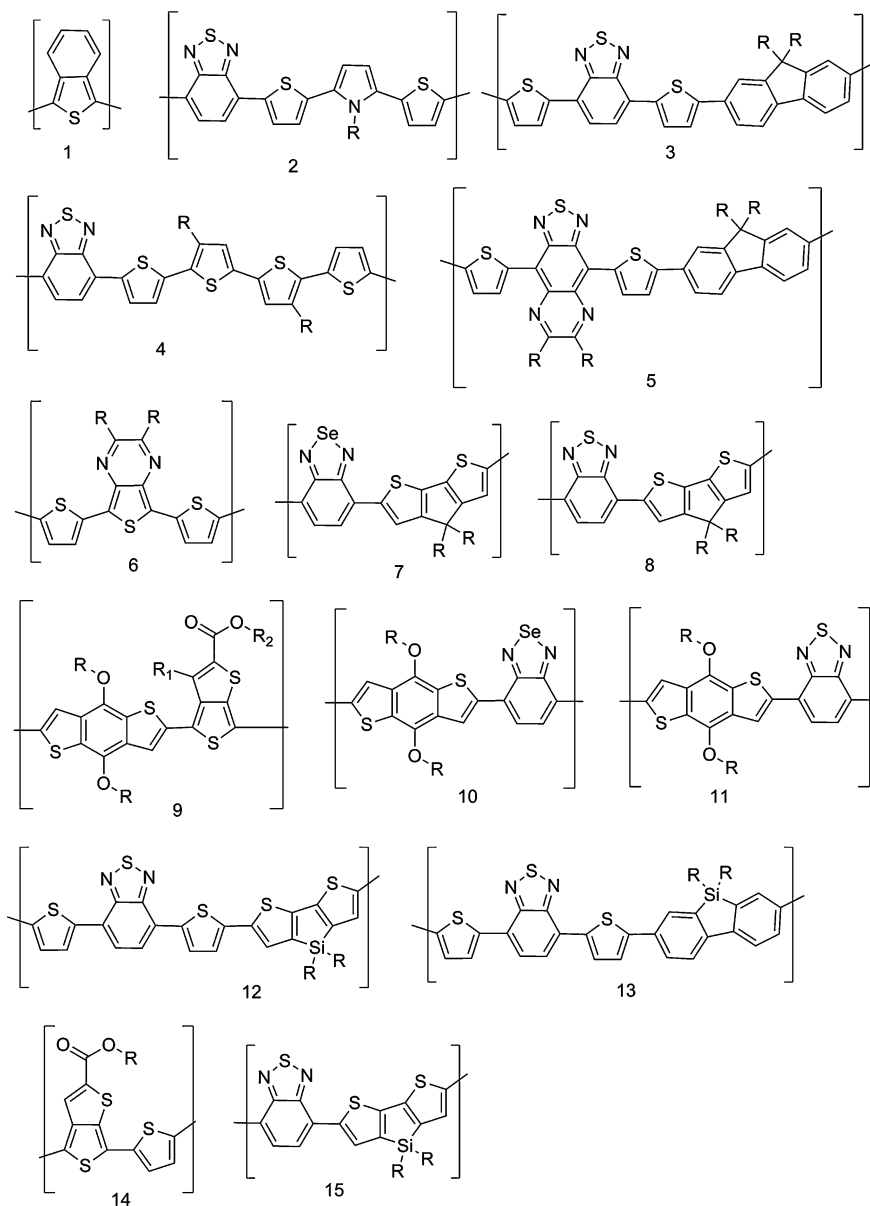
Conjugated polymers with an alternating single double bond structure normally have two resonance structures: the aromatic and the quinoid forms. The aromatic form is normally lower in energy than the quinoid form and, hence, it is the dominating form in the polymer backbone. The band gap of the polymer is lowered if the energy difference between the two is decreased, i.e., the difference between double and single bond length is decreased [13]. An example of a polymer where the quinoid form is more stable than the aromatic is poly(isot-hianaphtalene) (PITN). Here the thiophene ring loses its aromaticity when going to the quinoid form, however, the benzene ring gains aromaticity and stabilizes the quinoid structure. Another way to lower the band gap of the polymer is to use donor–acceptor alternation, which increases the double bond character between the units, thereby stabilizing the quinoid form of the polymer back bone [13, 15]. The donor unit, often thiophene, is electron-rich and therefore increases the electron density between the units or donating electrons to the acceptor, which is electron poor. Copolymers with donor and acceptor alternating units are the most dominating low band gap polymers, as seen in Fig. 8. There are a few details one needs to keep in mind when designing these types of polymers. The energy levels of the acceptor should fit those of the donor. An example of optimizing the



**Fig. 7** Different acceptors used in OPV devices along with their corresponding energy diagram [19–22]. For other examples of fullerenes see [15]

polymer and lowering its band gap was shown for copolymers of benzothiadiazole and thiophenes, where the number of thiophenes was varied from 1 to 4. It was found that the band gap decreased with an increasing number of thiophenes [23]. And using benzo-bis-thiadiazole as the acceptor unit decreased the band gap to 0.6 eV [23]. Furthermore, when the band gap of the polymer is lowered, the energy level alignment with the acceptor in OPV device should be taken into account as described above.

Other design methods to decrease the band gap of a polymer are retention of backbone planarity, thereby keeping the conjugation length as long as possible. Thus, the torsion angle between units should be kept to a minimum by decreasing the steric hindrance in the molecule, e.g., using smaller side chains. [13]. Side groups can have another effect on the band gap of the polymer. When an electron donating group (e.g., alkoxy or alkyl) is attached to a ring, it pushes electrons into the aromatic system, making it easier to remove an electron from the HOMO due to a raise in the energy level. When an electron accepting group (e.g., fluorine or carbonyl) is attached, it pulls electrons away from the aromatic system, lowering the LUMO of the polymer and, therefore, the band gap [13].



**Fig. 8** Examples of low band gap polymers reported in the literature. Their band gap and photovoltaic data is reported in Table 1 along with references

Substituents can also influence the band gap by intermolecular effects. For P3HT the hexyl side chains ensure the polymer orders in a lamellar structure in film. This is clearly seen in UV-vis spectrum of a solution and film of P3HT; the band gap is decreased for the film [15].



**Table 1** Band gap and photovoltaic data for the low band gap polymers shown in Fig. 8. The data for P3HT are given at the end of the table as a reference

Polymer	Band gap (eV)	I <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF (%)	Efficiency (%)	Reference
1	1.00	0.05	0.55	30	0.008	[16,24–27]
2	1.60	3.10	0.72	37	1.0	[28–31]
3	1.78	4.66	1.04	46	2.2	[32, 33]
4	1.65	3.59	0.61	46	1.0	[23, 34]
5	1.27	3.40	0.58	35	0.7	[35–39]
6	1.20	3.50	0.56	58	1.1	[40]
7	1.30	5.00	0.52	34	0.9	[41]
8	1.73	16.2	0.62	55	5.5	[42–44]
9A	1.61	14.7	0.70	64	6.6	[45]
9B	1.63	9.20	0.76	45	3.1	[21]
10	1.52	1.05	0.55	32	0.2	[46]
11	1.70	2.97	0.68	44	0.9	[46]
12	1.51	10.7	0.62	52	3.4	[47]
13	1.82	9.50	0.90	51	3.4	[48]
14	1.30	–	–	–	1.0	[20]
15	1.45	12.7	0.68	55	5.1	[49]
P3HT	1.99	10.6	0.61	67	4.4	[50–52]

Design of the polymer is thus of great importance to control the band gap and one should bare the following in mind during the design process:

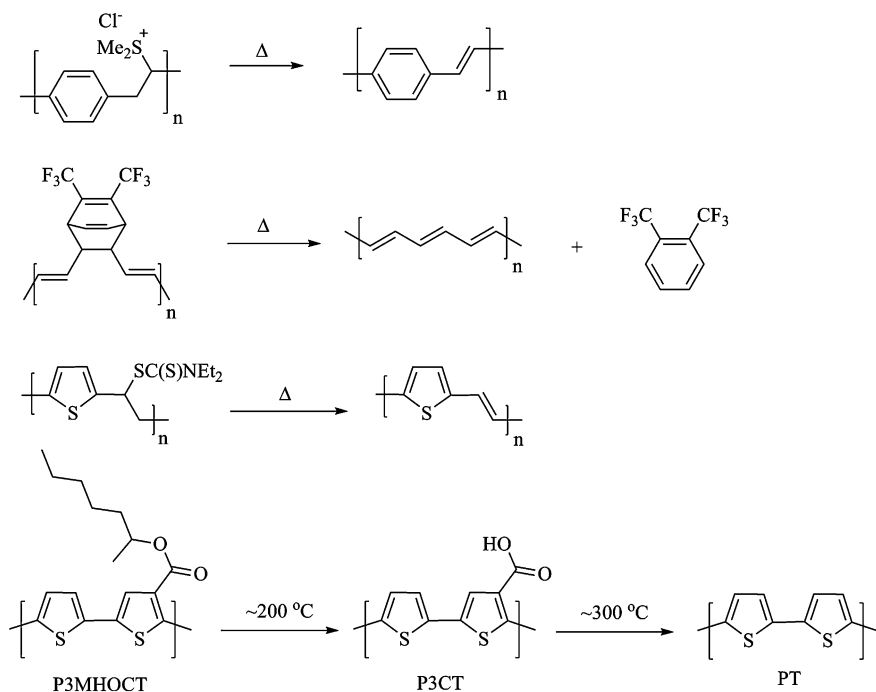
- Donor and acceptor units should be chosen to “fit” each other
- Choice of side chains (solubility, electron donating/accepting, steric hindrance and intermolecular interactions)
- Synthesis of polymers that ensures high molecular weight

Examples of low band gap polymers reported in the literature are given in Fig. 8. In Table 1, the corresponding band gap and photovoltaic data is summarized.

### 3 Stability and Degradation of OPV

#### 3.1 Degradation of OPV

Stability of OPV devices is a relatively new research topic in the field of OPV. The lifetime of a device has gone from minutes to years with in the past decade. This is largely due to a better understanding of the degradations paths that an OPV device can follow. The types of degradation include, but are not limited, to the following [16]:



**Fig. 9** Thermocleaving of polymers

- Reaction with either water or oxygen (all layers)
- Degradation of electrodes and PEDOT:PSS, e.g., diffusion of Al electrode into the active layer
- Photooxidation, this is especially for polymers with an alkoxy side chain
- Impurities in the polymer, e.g., Pd particles from the catalyst used in the synthesis of the polymer
- Morphology

This indicates that the stability of OPV devices can be improved with careful considerations to design of both the polymer and the device. However, other ways to increase the stability of the devices have also been reported, e.g., encapsulation layers such as PET or glass [53, 54].

### 3.2 Materials to Ensure Higher Stability

There have been reports on polymers with increased stability by way of thermocleavable side chains [55]. Historically conjugated polymers were prepared by thermal routes, as shown in Fig. 9. PPVs and polyacetylenes were prepared by the Wessling [56–59] and Durham [60–62] routes. Recently, the dithiocarbamate route

was developed [63–67]. Common to these three approaches, the conjugated polymer backbone is formed in the last thermal step. A different route employs tertiary ester groups that are cleaved upon heating to form the acid and further heating results in decarboxylation and formation of the rigid polymer backbone as shown in Fig. 9. The advantage of the latter technique is that the conjugated backbone is present throughout the whole process and device films are active in photovoltaic devices before and after thermocleavage.

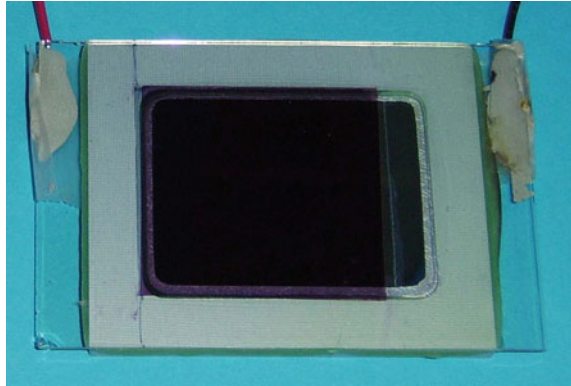
The thermocleavable side chains have also been studied on low band gap polymers where a dithienylthienopyrazine was coupled with different donor groups to produce polymers with band gaps between 1.17 and 1.37 eV. Photovoltaic performance was carried out and the highest efficiency was measured to be 1.21%. However, with a material loss upon heating to 200°C where the alkyl chain of the ester was removed, the performance decreased and no further thermocleaving was observed before decomposition at 400°C. The decrease in performance was ascribed to phase segregation in the active layer upon heating [68]. However, in a similar study where the donor was thiophene it was found that the decay in device stability was similar for both oxygen and inert atmospheres, indicating stability toward oxygen when aluminium electrodes are used [69].

## 4 Manufacture of Large Area OPV Modules

### 4.1 Production Methods

The typical laboratory polymer solar cell is prepared by spin-coating solutions of the materials onto a rigid glass substrate covered by a layer of ITO. The standard device employs a spincoated layer of the hole conducting PEDOT:PSS from an aqueous dispersion followed by spincoating of the active materials from an organic solvent such as chlorobenzene. The metallic electron collecting back electrode is applied by evaporation in a high vacuum. This approach has proven highly successful for materials screening, testing and development of the polymer solar cell technology in academia, requiring a relatively small investment in equipment (metal evaporator and a source meter). It should be noted that the device geometry with ITO/PEDOT:PSS as the transparent hole collecting front electrode requires that the evaporated back electrode is the electron collector, implying that it must be a low work function metal, such as aluminium or calcium. This is problematic in terms of device stability and, as a result, most academic device work is performed in an inert glovebox environment with very low humidity and oxygen content. In order to take those devices outside the laboratory there are strict requirements for the encapsulation that often requires active getter materials that remove oxygen and water from the enclosed compartment. An example of an encapsulated device is shown in Fig. 10, where a device prepared on glass is sealed with a glass fiber-filled, thermosetting epoxy against a milled aluminium back plate [53].

**Fig. 10** A rigid encapsulation of a 10 cm<sup>2</sup> low band gap laboratory device prepared on a glass substrate with a milled aluminum back plate. The sealing of the device was achieved with a glass fiber-filled, thermosetting epoxy



An additional problem with the devices prepared on rigid glass substrates and evaporated metal electrodes is the relatively slow batch process with which they are prepared. In the typical laboratory experiment, a batch in the order of 10 devices is prepared over the course of several hours including cleaning the substrates, spin-coating, masking and removal of unwanted material, evaporation and encapsulation and an optimistic production time for such a device is around an hour. While this is clearly not prohibitive for laboratory work and development, it is impossible to implement this as a cost-effective method in a competitive solar cell market. While it is possible to envisage the scaling of device production on rigid glass substrates, the poor performance and stability makes it unlikely to be successful and a different approach must be sought to create a financially viable manufacturing process for polymer solar cells.

## 4.2 Other Film Forming Techniques

The most favored academic film forming technique, spin-coating, described above, is limited by the fact that it provides no control of the pattern of the formed film (zero-dimensional). Spin-coating is, however, very successful because it enables very good control over the film thickness, allows for preparation of very thin films and is highly reproducible. An additional reason for the success of spin-coating is that it is a non-equilibrium film forming technique, which allows the experimenter to prepare films in cases where wetting is not possible in an equilibrium situation. In many cases experiments have been successful without the experimenter ever knowing what peril (s)he faced! There are many other film forming techniques [70] available, some of which are suited for particular purposes while others are less suitable for polymer solar cells. The most well-known film forming techniques are:

- ink jet printing,
- electro/magnetographic printing,

- offset printing,
- screen printing,
- rotary screen printing,
- gravure printing,
- pad printing,
- flexographic printing,
- slot-die coating,
- curtain coating,
- slide coating,
- spray coating and
- knife coating.

Ink jet and electrographic coating are unique because they employ a digital master and provide full two-dimensional patterning of the printed area. Only ink jet printing has been used successfully in the context of polymer solar cells. Offset printing, screen printing, rotary screen printing, gravure printing, pad printing, flexographic printing all provide full two-dimensional patterning, but require a master plate with the desired layout. The complexity of the master is simplest and lowest in cost for screen printing, mid-range for rotary screen, flexographic and offset printing, and quite expensive for gravure printing, in which an engraved roller is required. They are all contact techniques, meaning that the application of the ink to the substrate is made through physical contact between the master and the substrate. It is currently debated whether this type of method can be used to apply the active layer. They have all been explored in the context of polymer solar cells, but none have been truly successful. Slot-die coating is a non-contact technique that allows for one-dimensional patterning. Curtain coating, slide coating, spray coating and knife coating are all non-contact zero-dimensional techniques, but curtain and slide coating allow for exceptionally high speeds and multilayer formation. In addition to the above techniques, several more exist that are derived from this overall set of printing and coating techniques. There is currently no clear view on which techniques are the most suitable and each is plausible, pending dedicated development of ink systems that suit the requirements of each individual technique. A few facts have, however, been influential on the development of the different techniques in the context of polymer solar cells. The most important factor is scale, as some of these techniques simply cannot be made to work on a small scale. This is possibly also the reason for the success of the few techniques that work on a small scale. The second factor is ink usage because some techniques require enormous amounts of ink before printing can even be started. Flexographic and gravure printing require that the rollers be continuously bathed and this can easily mean that liters of ink are required. Finally, research has focused on film formation of the active layers. It is anticipated that a mature polymer solar cell technology is a fully-printed, multilayer structure and it is likely that several different film forming techniques will enter the final process, with each being chosen because of its particular advantage for a specific layer.

### **4.3 Roll-to-Roll Printed Modules Based on a Low Band Gap Polymer**

A frequently-highlighted attribute of polymer solar cells is their flexibility. While this is true, it is often misunderstood that flexibility is a prerequisite for success in application. While this may be the case in a few instances, it is unlikely that the success of the technology rests on a flexible product. The flexibility is, however, beneficial during manufacture to decrease costs and increase throughput. Many of the film forming techniques mentioned above are R2R compatible and this is viewed as a prerequisite for a printing or coating technique to be valuable. In order to prepare a low band gap polymer solar cell by R2R coating it is necessary to have a device geometry that enables the R2R processing of all layers.

The most successful process described so far is ProcessOne [71] that employs an inverted geometry (see Fig. 2), where ITO-covered PET is employed as the substrate. The ITO is patterned by screen printing and etch resist followed by etching, stripping and washing away the resist. The ITO is converted into the electron collecting electrode by slot-die coating a thin ZnO layer on top of the ITO to give a patterned PET/ITO/ZnO substrate that serves as a platform for testing virtually any active layer materials combination. The active layer material is slot-die coated onto the PET/ITO/ZnO composite electrode. The device is completed by slot-die coating of PEDOT:PSS on top as the hole collecting electrode. The PEDOT:PSS electrode is improved by screen printing a full silver electrode or a silver grid electrode on top depending on the sheet resistivity of the PEDOT:PSS and on whether semi-transparency is required. The complete five-layer device is thus prepared by a combination of screen printing and slot-die coating. Selected steps of the process are shown in Fig. 11. The low band gap polymer yielded semi-transparent modules with a deep blue, semitransparent color.

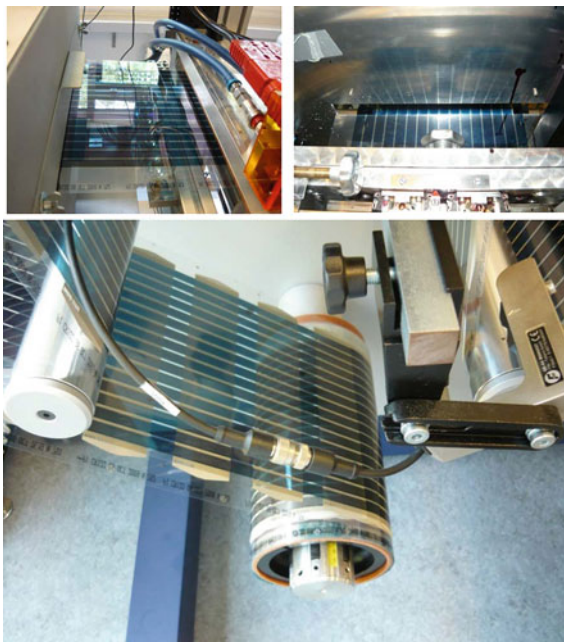
The IV curves of one module of indoor measurements under a solar simulator and outdoor measurements (Fig. 12) are shown in Fig. 13 and the photovoltaic data is summarized in Table 2. It shows a small decrease in current when measured outdoors and, even though the voltage is increased outdoors, the overall efficiency is higher under the simulated sun, which has a higher intensity (1000 versus 915 W m<sup>-2</sup>).

All modules were characterized by a R2R procedure under a solar simulator and the average efficiency of the modules was 0.3%. However, it is clear that after annealing under the sun for about 30 min, the efficiency of the modules increased to 0.5–0.6%. Lifetime studies were carried out at 55 and 85°C and clearly showed the effect temperature has on the stability of the modules, i.e., the stability decreases at higher temperatures (85 versus 55°C).

## **5 Summary and Outlook**

In this chapter, we have described the possible solutions to some challenges in the area of OPV. We have described in detail how the efficiency is believed to increase for low band gap polymers and provided examples from the literature.

**Fig. 11** The slot-die coating of the low band gap polymer onto PET/ITO/ZnO. The wet film is shown immediately after the slot-die coating head (*top right*). The dry film is shown as it exits the oven (*top left*). The completed and laminated devices are shown below where the semitransparent blue color of the devices is visible



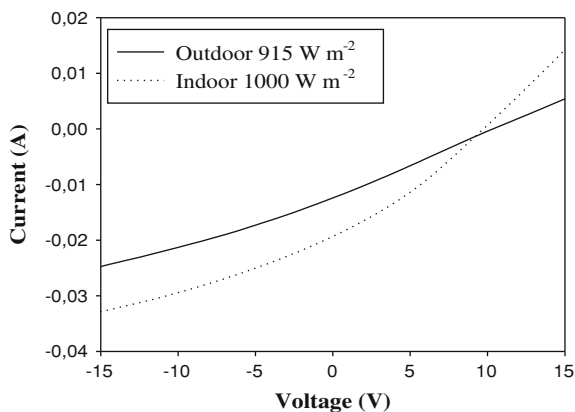
**Fig. 12** Outside testing of one of the completed modules on a solar tracking platform for general testing of OPV modules and panels. The inset shows the low band gap device



Additionally, we have shown that device stability can be improved using thermocleavable side chains. And finally, production methods were described, along with the results of production of large-area modules based on low band gap polymers. The challenge for OPV devices is to combine the efficiency, stability and production into a single material.

Therefore, it is of great importance to design the optimal material. This can be accomplished by using donor and acceptor units that fit together. Another factor one must bear in mind is the choice of side chain, which can have an effect on:

**Fig. 13** IV curves for large area modules based on low band gap polymers measured outdoors and indoors



**Table 2** Photovoltaic data of a module where measurements were performed outdoors and indoors under a sun simulator

	$I_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF (%)	$\eta$ (%)
Indoor	0.20	9.5	29	0.55
Outdoor	0.13	10.3	26	0.38

(1) the band gap, by intermolecular ordering or withdraw/donating groups, (2) the production method, by ensuring solubility and (3) the stability, by thermocleavable ester groups.

It is clear that polymer solar cells hold great potential as a novel type of low-cost photovoltaic technology. There are, however, several developments needed before one can realize polymer solar cells as a competitive photovoltaic technology. The largest cost limitation currently is the transparent ITO electrode and there are currently few performing alternatives. The elimination of ITO is anticipated to enable a cost reduction in the range of 20–35%. The operational stability of the devices must be improved significantly in order for polymer solar cells to reach beyond the crowded thin film photovoltaic market. Finally, the power conversion efficiency is likely to require improvements to the 10–15% range before the technology can become pervasive.

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## References

1. Energy Information Administration (EIA), International Energy Outlook 2006, report # DOE/EIA-0484 (2006)
2. Politiken.dk, <http://politiken.dk/eu/article261249.ece> article in Danish published in 2007



3. Kippelen B, Brédas J-L (2009) Organic photovoltaics. *Energy Environ Sci* 2:251–261
4. Brabec CJ (2004) Organic photovoltaics: technology and market. *Sol Mater Energy Sol Cells* 83:273–292
5. Helgesen M, Søndergaard R, Krebs FC (2009) Advanced materials and processes for polymer solar cell devices. *J Mater Chem* 20:36–60
6. Spanggaard H, Krebs FC (2004) A brief history of the development of organic and polymeric photovoltaics. *Sol Mater Energy Sol Cells* 83:125–146
7. Coakly KM, McGehee MD (2004) Conjugated polymer photovoltaic cells. *Chem Mater* 16:4533–4542
8. Hoppe H, Sariciftci NS (2004) Organic solar cells: an overview. *J Mater Res* 19:1924–1945
9. Special issue: (2004) The development of organic and polymer photovoltaics. *Sol Energy Mater Sol Cells* (83):2–3
10. Special issue: (2005) Organic-based photovoltaics. *MRS Bull.* 30(1)
11. Brabec CJ, Sariciftci NS, Hummelen JC (2001) Plastic solar cells. *Adv Funct Mater* 11:15–26
12. Waldauf C, Morana M, Denk P, Schilinsky P, Coakley K, Choulis SA, Brabec CJ (2006) Highly efficient inverted organic photovoltaics using solution based titanium oxide as electron selective contact. *Appl Phys Lett* 89:233517
13. Kroon R, Lenes M, Hummelen JC, Blom PWM, De Boer B (2008) Small bandgap polymers for organic solar cells (polymer material development in the last 5 years). *Pol Rev* 48:531–582
14. Chen J, Cao Y (2009) Development of novel conjugated donor polymers for high-efficiency bulk-heterojunction photovoltaic devices. *Acc Chem Res* 42:1709–1718
15. Bundgaard E, Krebs FC (2007) Low band gap polymers for organic photovoltaics. *Sol Energy Mater Sol Cells* 91:954–985
16. Winder C, Sariciftci NS (2004) Low band gap polymers Low band gap polymers for photon harvesting in bulk heterojunctions solar cells. *J Mater Chem* 14:1077–1086
17. Jørgensen M, Norrman K, Krebs FC (2008) Stability/degradation of polymer solar cells. *Sol Energy Mater Sol Cells* 92:686–714
18. McNeill CR, Abrusci A, Zaumseil J, Wilson R, McKiernan MJ, Burroughes JH, Halls JJM, Greenham NC, Friend RH (2007) Dual electron donor/electron acceptor character of a conjugated polymer in efficient photovoltaic diodes. *Appl Phys Lett* 90(1–3):193506
19. Lenes M, Wetzelaer G-JAH, Kooistra FB, Veenstra SC, Hummelen JC, Blom PWM (2008) Fullerene bisadducts for enhanced open-circuit voltages and efficiencies in polymer solar cells. *Adv Mater* 20:2116–2119
20. Yao Y, Liang Y, Shrotriya V, Xiao S, Yu L, Yang Y (2007) Plastic near-infrared photodetectors utilizing low band gap polymer. *Adv Mater* 19:3979–3983
21. Liang Y, Feng D, Wu Y, Tsai S-T, Li G, Ray C, Yu L (2009) Highly efficient solar cell polymers developed via fine-tuning of structural and electronic properties. *J Am Chem Soc* 131:7792–7799
22. Kim JY, Lee K, Coates NE, Moses D, Nguyen T-Q, Dante M, Heeger AJ (2007) Efficient tandem polymer solar cells fabricated by all-solution processing. *Science* 317:222–225
23. Bundgaard E, Krebs FC (2006) Low band gap conjugated polymers based on thiophene, benzothiadiazole and benzobis(thiadiazole). *Macromolecules* 39:2823–2831
24. Wudl F, Kobayshi M, Heeger AJ (1984) Poly(isothianaphthene). *J Org Chem* 49:3382–3384
25. Cava MP, Lakshminikatham MV (1975) Nonclassical condensed thiophenes. *Acc Chem Res* 8:139–144
26. Kobayshi M, Colerani N, Boysel M, Wudl F, Heeger AJ (1985) The electronic and electrochemical properties of poly(isothianaphthene). *J Chem Phys* 82:5717–5723
27. Henckens A, Knipper M, Polec I, Manca J, Lutsen L, Vanderzande D (2004) Poly(thienylene vinylene) derivatives as low band gap polymers low band gap polymers for photovoltaic applications. *Thin Solid Films* 451–452:572–579
28. Dhanabalan A, van Duren JKJ, van Hal PA, van Dogen JIJ, Janssen RAJ (2001) Synthesis and characterization of a low bandgap conjugated polymer for bulk heterojunction photovoltaic cells. *Adv Funct Mater* 11:255–262

29. van Duren KJ, Dhanabalan A, van Hal PA, Janssen RAJ (2001) Low-bandgap polymer photovoltaic cells. *Synth Mater* 121:1587–1588
30. Brabec CJ, Winder C, Sariciftci NS, Hummelen JC, Dhanabalan A, van Hal PA, Janssen RAJ (2002) A low-bandgap semiconducting polymer for photovoltaic devices and infrared emitting diodes. *Adv Funct Mater* 12:709–712
31. Winder C, Mühlbacher D, Neugebauer H, Sariciftci NS, Brabec C, Janssen RAJ, Hummelen JK (2002) Polymer solar cells and infrared light emitting diodes: dual function low band gap polymer. *Mol Cryst Liq Cryst* 385:[213]93–[220]100
32. Svensson M, Zhang F, Veenstra SC, Verhees WJH, Hummelen JC, Kroon JM, Inganäs O, Andersson MR (2003) High-performance polymer solar cells of an alternating polyfluorene copolymer and a fullerene derivative. *Adv Mater* 15:988–991
33. Shi C, Yao Y, Yang Y, Pei Q (2006) Regioregular copolymers of 3-alkoxythiophene and their photovoltaic application. *J Am Chem Soc* 128:8980–8986
34. Bundgaard E, Shaheen SE, Krebs FC, Ginley D (2007) Bulk heterojunctions based on a low band gap copolymer of thiophene and benzothiadiazole. *Sol Energy Mater Sol Cells* 91:1631–1637
35. Chen M, Perzon E, Andersson MR, Marcinkevicius S, Jönsson SKM, Fahlman M, Berggren M (2004) 1 micron wavelength photo- and electroluminescence from a conjugated polymer. *Appl Phys Lett* 84:3570–3572
36. Wang X, Perzon E, Oswald F, Langa F, Admassie S, Andersson MR, Inganäs O (2005) Enhanced photocurrent spectral responses in low-bandgap polyfluorene and C<sub>70</sub>-derivative-based solar cells. *Adv Funct Mater* 15:1665–1670
37. Perzon E, Wang X, Zhang F, Mammo W, Delgado JL, de la Cruz P, Inganäs O, Langa F, Andersson MR (2005) Design, synthesis and properties of low band gap polyfluorene for photovoltaic devices. *Synth Met* 154:53–56
38. Chen M, Perzon E, Robisson N, Jönsson SKM, Andersson MR, Fahlman M, Berggren M (2004) Low band gap donor-acceptor-donor polymers for infra-red electroluminescence and transistors. *Synth Met* 146:233–236
39. Perzon E, Wang X, Admassie S, Inganäs O, Andersson MR (2006) An alternating low band-gap polyfluorene for optoelectronic devices. *Polymer* 47:4261–4268
40. Wienk MM, Turbiez MGR, Struijk MP, Fonrodona M, Janssen RAJ (2006) Low band gap poly(di-2-thienylthienopyrazine):fullerene solar cells. *Appl Phys Lett* 88(1–3):153511
41. Hou J, Chen TL, Zhang S, Chen H-Y, Yang Y (2009) Poly[4, 4-bis(2-ethylhexyl) cyclopenta[2, 1-b:3, 4-b']dithiophene-2, 6-diyl-alt-2, 1, 3-benzoselenadiazole-4, 7-diyl], a new low band gap polymer in polymer solar cells. *J Phys Chem C* 113:1601–1605
42. Peet J, Kim JY, Coates NE, Ma WL, Moses D, Heeger AJ, Bazan GC (2007) Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols. *Nat Mater* 6:497–500
43. Mühlbacher D, Scharber M, Morana M, Zhu Z, Waller D, Gaudiana R, Brabec C (2006) High photovoltaic performance of a low bandgap polymer. *Adv Mater* 18:2884–2889
44. Mühlbacher D, Scharber M, Morana M, Zhu Z, Waller D, Gaudiana R, Brabec C (2006) High photovoltaic performance of a low bandgap polymer. *Adv Mater* 18:2884–2889 correction
45. Hou J, Chen H-Y, Zhang S, Chen RI, Yang Y, Wu Y, Li G (2009) Synthesis of a low band gap polymer and its application in highly efficient polymer solar cells. *J Am Chem Soc* 131:15586–15587
46. Hou J, Park M-H, Zhang S, Yao Y, Chen L-M, Li J-H, Yang Y (2008) Bandgap and molecular energy level control of conjugated polymer photovoltaic materials based on benzo[1, 2-b:4, 5-b']dithiophene. *Macromolecules* 41:6012–6018
47. Huo L, Chen H-Y, Hou J, Chen TL, Yang Y (2009) Low band gap dithieno[3,2-b:2',3'-d]silole-containing polymers, synthesis, characterization and photovoltaic application. *Chem Comm* (37):5570–5572
48. Wang E, Wang L, Lan L, Luo C, Zhuang W, Peng J, Cao Y (2008) High-performance polymer heterojunction solar cells of a polysilafuorene. *Appl Phys Lett* 92:033307-1–033307-3

49. Hou J, Chen H-Y, Zhang S, Li G, Yang Y (2008) Synthesis, characterization and photovoltaic properties of a low band gap polymer based on silole-containing polythiophenes and 2, 1, 3-benzothiadiazole. *J Am Chem Soc* 130:16144–16145
50. Ma W, Yang C, Gong X, Lee K, Heeger AJ (2005) Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. *Adv Funct Mater* 15:1617–1622
51. Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K, Yang Y (2005) High-efficiency solution-processable polymer photovoltaic cells by self-organization of polymer blends. *Nat Mater* 4:854–868
52. Kim Y, Cook S, Tuladhar SM, Choulis SA, Nelson J, Durrant JR, Bradley DDC, Giles M, McCulloch I, Ha C-S, Ree M (2006) A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene:fullerene solar cells. *Nat Mater* 5:197–203
53. Krebs FC, Alstrup J, Spanggaard H, Larsen K, Kold E (2004) Production of large-area polymer solar cells by industrial silk screen printing, lifetime considerations and lamination with polyethyleneterephthalate. *Sol Energy Mater Sol Cells* 83:293–300
54. Krebs FC (2006) Encapsulation of polymer photovoltaic prototypes. *Sol Energy Mater Sol Cells* 90:3633–3643
55. Krebs FC, Spanggaard H (2005) Significant improvement of polymer solar cell stability. *Chem Mater* 17:5235–5237
56. Gagnon DR, Capistran JD, Karasz FE, Lenz RW, Antoun S (1987) Synthesis, doping, and electrical conductivity of high molecular weight poly(p-phenylene vinylene). *Polymer* 28:567–573
57. Garay RO, Mayer B, Karasz FE, Lenz RW (1995) Synthesis and characterization of poly[2, 5-bis(triethoxy)-1, 4-phenylene vinylene]. *J Polym Sci, Part A: Polym Chem* 33:525–531
58. Lenz RW, Han CC, Stengersmith J, Karasz FE (1988) Preparation of poly(phenylene vinylene) from cycloalkylene sulfonium salt monomers and polymers. *J Polym Sci, Part A: Polym Chem* 26:3241–3249
59. Wessling RA (1985) The polymerization of xylene bisdialkyl sulfonium salts. *J Polym Sci, Polym Symp* 72:55–66
60. Bott DC, Brown CS, Chai CK, Walker NS, Feast WJ, Foot PJS, Calvert PD, Billingham NC, Friend RH (1986) Durham poly acetylene: preparation and properties of the unoriented material. *Synth Met* 14:245–269
61. Feast WJ, Winter JN (1985) An improved synthesis of polyacetylene. *J Chem Soc, Chem Comm* 4:202–203
62. Furlani A, Napoletano C, Russo MV, Feast WJ (1986) Stereoregular polyphenylacetylene. *Polym Bull* 16:311–317
63. Henckens A, Colladet K, Fourier S, Cleij TJ, Lutsen L, Gelan J, Vanderzande D (2005) Synthesis of 3, 4-diphenyl-substituted poly(thienylene vinylene), low band-gap polymers via the dithiocarbamate route. *Macromolecules* 38:19–26
64. Nguyen LH, Gunes S, Neugebauer H, Sariciftci NS, Banishoeib F, Henckens A, Cleij T, Lutsen L, Vanderzande D (2006) Precursor route poly(thienylene vinylene) for organic solar cells: photophysics and photovoltaic performance. *Sol Energy Mater Sol Cells* 90:2815–2828
65. Banishoeib F, Adriaensens P, Berson S, Guillerez S, Douheret O, Manca J, Fourier S, Cleij TJ, Lutsen L, Vanderzande D (2007) The synthesis of region-regular poly(3-alkyl-2, 5-thienylene vinylene) derivatives using lithium bis(trimethylsilyl)amide (LHMDS) in the dithiocarbamate precursor route. *Sol Energy Mater Sol Cells* 91:1026–1034
66. Banishoeib F, Henckens A, Fourier S, Vanhooyland G, Bresselge M, Manca J, Cleij TJ, Lutsen L, Vanderzande D, Nguyen LH, Neugebauer H, Sariciftci NS (2008) Synthesis of poly(2, 5-thienylene vinylene) and its derivatives: low band gap materials for photovoltaics. *Thin Solid Films* 516:3978–3988
67. Giroto C, Cheyns D, Aernouts T, Banishoeib F, Lutsen L, Cleij TJ, Vanderzande D, Genoe J, Poortman J, Heremans P (2008) Bulk heterojunction organic solar cells based on soluble poly(thienylene vinylene) derivatives. *Org Electron* 9:740–746

68. Helgesen M, Krebs FC (2010) Photovoltaic performance of polymers based on dithienylthienopyrazines bearing thermocleavable benzoate esters. *Macromolecules* 43: 1253–1260
69. Helgesen M, Krebs FC (2008) Thermocleavable low band gap polymerslow band gap polymers and solar cells therefrom with remarkable stabilitystability toward oxygen. *Macromolecules* 41:8986–8994
70. Krebs FC (2009) Fabrication and processing of polymer solar cells: A review of printing and coating techniques. *Sol Energy Mater Sol Cells* 93:394–412
71. Krebs FC, Gevorgyan SA, Alstrup J (2009) A roll-to-roll process to flexible polymer solar cells: model studies, manufacture and operational stabilitystability studies. *J Mater Chem* 19:5442–5451