Donor-acceptor block copolymers
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Abstract
A brief historical overview is given of the progress made concerning plastic photonic and in particular photovoltaic devices. The D–A semiconducting block copolymer concept is introduced as a way to control the active layer morphology of organic solar cells. Principles of block copolymer microphase separation are presented and the requirements for the materials finding applications in organic electronic devices are outlined. After an overview of previous work, the aim and outline of this thesis are presented.
1.1 Introduction

Over the last couple of decades people have become increasingly aware of the fact that the excessive use of fossil fuels could lead to several problems in the future. First, the earth’s fossil fuel reserve is limited and since they are not only used as a fuel, but are also the source for the production of the many different (chemical) substances that we rely on in our present-day life, we need to preserve this reserve as long as possible. Another disadvantage of fossil fuels is that the waste products produced during combustion have huge negative effects on public health and the environment. The so-called ‘greenhouse effect’ is the origin of a global temperature change induced by gases such CO₂, NOₓ etc. and was first described by Fourier almost 200 years ago.¹ The temperature increase caused by these naturally abundant gases was calculated by Nobel laureate Arrhenius to be 35 K (from 253 to 288 K), making life on earth possible.² Arrhenius also calculated that a two-fold increase of the amount of CO₂ would lead to a worldwide increase in temperature of 5-6°C. Since the discovery of the internal combustion engine, the extra emission of greenhouse gases (mainly CO₂) has already leaded to an increase of the global temperature by several degrees. This change in temperature, although small, could cause big climate changes, melting of the (polar) ice-caps, a rising of the sea level world-wide and many other yet unforeseen effects, which would have dramatic effects for life on earth.

In order to diminish the use of fossil fuels, alternatives were sought in renewable energy sources. One of the biggest energy sources on earth, one that exceeds the current worldly energy demand by several thousand times, is sunlight.³ There are several ways to make use of the energy from solar radiation and a very elegant one is the direct conversion of solar energy into electrical energy by photovoltaic devices. Many research groups are currently investigating this field intensively and promising results towards cheap ‘plastic’ solar cells have been reported.⁴-⁶ Before the large scale production of this type of solar cell can take place a deeper understanding of the different processes involved is indispensable.

1.2 History

In the late 1970’s an important discovery was made by Heeger, MacDiarmid and Shirakawa,⁷, ⁸ which resulted in a new, completely unexplored and fascinating area of multidisciplinary research.⁹ Their discovery of enhanced conductivity (up to 10³ S) in trans-polyacetylene films upon oxidative doping, was therefore awarded with the 2000 Nobel Prize in Chemistry.¹⁰-¹² Until the discovery of this unique behavior, polymers used
to be associated with electrically insulating properties, which makes them useful for insulating electrical wires.

Polyacetylene is the simplest example of a conjugated polymer, characterized by alternation of single and double bonds. This conjugated structure leads to an extensive delocalization of the $\pi$-electrons along the backbone, resulting in a strong optical absorbance and (semi)conductive behavior. Charges created or pumped into these materials are mobile, with electron and hole mobilities being approximately equal. In diodes, however, the electron current is considerably lower than the hole current, which can be attributed to traps. The origin of this low electron mobility lies in the fact that they are more easily oxidized than reduced and therefore hole injection is easier than electron injection.

In 1990 the first electroluminescent (EL) properties, the emission of light upon excitation by the flow of an electric current, were reported by Burroughes et al. For poly($p$-phenylene vinylene) (PPV). By sandwiching this conjugated polymer between two electrodes (of which at least one is transparent), a light-emitting diode (LED) can be fabricated. Two years later the inverse (photovoltaic) process was reported by Saraciftci et al. In the years following these discoveries many photonic applications based on optoelectronic and semiconducting polymers have been introduced. A few of these devices are field-effect transistors (FETs), photovoltaic devices, photodetectors, sensors, polymeric light-emitting diodes (PLEDs), and solution and solid state lasers. Mainly the field of PLEDs has expanded rapidly and at present full color flexible displays and white light emitting PLEDs for back-lighting have been described. The first commercial full-color active matrix displays based on PLED technology was introduced in 2002 by Philips.

1.3 Organic Solar Cells

Over the last couple of decades there has been an increasing demand for inexpensive renewable energy sources that can compete with fossil fuel-based energy sources. A good candidate is the photovoltaic device (PVD), which directly converts the solar energy in electrical energy by producing a current in reverse bias upon illumination. The currently used single crystalline silicon-based photovoltaic (PV) cells have a rather high efficiency (25%), but they are very expensive due to their relative thickness (~150 µm) and the high costs of production. An alternative is the so-called ‘plastic’ or organic solar cell, based on organic materials such as conjugated polymers. This type of PV device is not only cheaper, but also mechanically flexible and the great know-how
in industry concerning processing provides the possibility of low cost large area thin film fabrication. Only thin layers of active material are necessary and it is thus possible to apply these solar cells onto virtually any substrate, including curved or flexible ones. Another advantage is the versatility of the organic synthesis, allowing for several properties (e.g. energy levels, solubility and thin film forming properties) to be adjusted. Currently only relatively low efficiencies of around 4-5% are reached in optimized devices. Besides these completely organic cells, exist the hybrid cells, incorporating both organic and inorganic materials, such as the Grätzel cell, which show quite good performances with maximum efficiencies around 10%.

**Figure 1.1** A schematic representation of the device structure of a simple (bilayer) photovoltaic device, with an electron donating layer (right) and an electron accepting layer (left). The processes that occur upon illumination: (a) excitation (exciton formation), (b) exciton diffusion, (c) charge separation and (d) hole and electron transport.

An organic solar cell generally consists of an active layer sandwiched between two electrodes with a different work-function or electron affinity, where at least one of these electrodes should obviously be transparent, as shown in figure 1.1 for a simple bilayer device. Often ITO on a glass or plastic substrate is used as anode and a low work function metal (e.g. aluminum (Al) or calcium (Ca)) as cathode. Upon illumination several
processes take place consecutively. First, an exciton (bound hole–electron pair) is created by promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of an electron donor (D). This exciton needs to be dissociated in separate charges, but this so-called photo-induced charge generation can only take place efficiently in the presence of an electron acceptor (A). This donor–acceptor device concept, known since 1958, should replace the p and n functions present in inorganic PVDs. In order for an electron to be transferred from donor to acceptor, the gain in energy upon moving an electron from the LUMO of the donor to the LUMO of the acceptor, which is given by the difference in energy between the ionization potential of the donor ($I_D$) and the electron affinity of the acceptor ($E_A$), should exceed the Coulombic energy of the exciton ($U_C$):

$$I_D - E_A \geq U_C$$

After the charge separation, the charges should be collected at the electrodes, by making use of the built-in potential between the two dissimilar electrodes. The electron donor will generally act as hole transporting material and the electron acceptor as electron transporting material. For the creation of a photocurrent, separate continuous pathways towards both electrodes are a necessity. If continuous pathway is present, charges may accumulate and eventually charge recombination will take place, reducing the efficiency of the device.

1.3.1 Active layer morphology

An exciton has a finite lifetime and it therefore also has a limited diffusion range, the exciton diffusion length, which is on the order of several nanometers. Only at the interface between donor and acceptor material the exciton will be actually dissociated. Excitons that are not able to reach the electron acceptor will return to their ground state under the emission of light or heat. It is therefore of crucial importance that this interface is as large as possible and that the donor phase has a size comparable to the exciton diffusion range. For a balanced bipolar charge transport towards the electrodes, it is necessary that both materials form a continuous pathway towards the appropriate electrodes. These two factors make that the morphology of the active layer holds the key to an efficient device. In the ideal case the active layer would consist of an interpenetrating bicontinuous network of the two materials on the length scale of the exciton diffusion length.
The most efficient organic PV device known up to today is based on slowly dried P3HT (poly(3-hexyl thiophene)). In the last decade, however, a large amount of attention was given to the so-called bulk heterojunction device based on a blend of MDMO-PPV and PCBM, with efficiency exceeding 3%. The MDMO-PPV (poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)-p-phenylene vinylene]) acts as an electron donor and the PCBM ([6,6]phenyl C_{61} butyric acid methyl ester) is a material based on fullerene[60] (or C_{60}), which acts as an electron acceptor. C_{60} can accept up to six electrons and is known for its excellent fast kinetics (electron transfer from PPV to C_{60} takes place in ~40 fs.) and electron transport properties. An interpenetrating network of acceptor rich and poor phases is formed upon spin-casting from a chlorobenzene solution, but this morphology depends strongly on the type of solvent and the casting and annealing conditions used. The active layer consists of fullerene crystallites in a matrix of blended compounds and optimization revealed that best device performances were obtained for percentages of PCBM of 80 wt.-%. This rather large amount of PCBM is necessary to ensure a good charge transport. Besides directly enhancing electron transport, the high level of PCBM also increases hole mobility of the PPV and the dielectric constant of the blend, which in turn facilitates the dissociation of electron-hole pairs. When one would be able to control the active layer morphology, it should be possible to reduce the amount of this non light-absorbing material and thus further optimize the device performance.

A disadvantage of blends is that they always give a dynamic structure, far from its completely phase separated equilibrium structure. The morphology of such blends is hard to control and can change during the operation of the device due to the high operating temperatures, influencing their performance. It was actually shown that the performance of these devices decreases quite dramatically upon illumination, which is partly caused by photodegradation and partly by a change in active layer morphology. It is of vital importance that we gain a real control over the active layer morphology of the device to get a better understanding of the device itself and to be able to improve its performance.

Several different concepts have been applied in order to gain control over the active layer morphology, often via structural self-organization. Among these were the exploitation of self-assembled monolayers (SAM), the preparation of oriented ultra-thin films via self-assembly based on the charge transfer interaction, an approach based on nanoparticles to control the phase separation in photovoltaic devices and the self-organization through hydrogen bonding. One of the most promising concepts was introduced by Müllen et al. They have made use of the columnar self-organization of discotic liquid crystals. The hexaphenyl-substituted hexabenzocoronene (HBC-PhC_{12}) self-organizes into columnar phases and an electron acceptor (perylene) is trapped
between these columns, thus forming an interpenetrating network. Our group\textsuperscript{95-103} and, more recently also several other groups,\textsuperscript{104-107} have used the microphase separation of block copolymers in order to gain control over the morphology of the active layer in photovoltaic devices on the nanometric scale.

### 1.4 Structural self-organization of block copolymers

Diblock copolymers are known for their microphase separation,\textsuperscript{108-112} a self-structuring into highly ordered lattices on the lengthscale of the radius of gyration of the two blocks, which is usually on the order of several tens of nanometers and is therefore comparable to the exciton diffusion length. For a flexible and non-crystallizing (coil-coil) diblock copolymer the type of microphase separation (e.g. spheres, cylinders, gyroids and lamellae) depends on three major factors: the Flory-Huggins segment-segment interaction parameter ($\chi$) between the two blocks, the total degree of polymerization ($N$) and the composition in volume fractions ($f_A$ and $f_B$) of the two blocks.\textsuperscript{110} The value of $\chi$ is an indicator for the incompatibility of the two blocks, the value increases for more incompatible blocks, and depends mainly on the chosen monomers. Microphase separation only takes place when the product $\chi N$ exceeds a critical value, the order-disorder transition (ODT). When increasing this $\chi N$ value even further, it passes from weak segregation – where the type of morphology at a certain composition depends strongly on $\chi N$ – via intermediate segregation to strong segregation – where the type of morphology is practically independent of $\chi N$. For a certain type of block copolymer (in the strong segregation limit) the type of morphology depends mainly on the volume fractions of the two blocks.

These interesting self-organizational properties can be used to gain control over the morphology of the active layer of an organic solar cell by synthesizing a diblock copolymer containing both an electron donating and an electron accepting block. One block should thus consist of either a conjugated polymer, that absorbs light, donates electrons and transports holes, or a polymer with pendant light absorbing moieties. The second block could again consist of a conjugated polymer with lower-lying HOMO and LUMO levels, or it should contain an electron acceptor and transporter such as C\textsubscript{60}. To optimize the type of morphology so that it meets the requirements of an efficient solar cell device, the volume fraction of the two blocks should be adjustable.

Usually conjugated polymers are not flexible, but form a rigid rod and some of them even possess liquid crystalline properties.\textsuperscript{113} A so-called ‘rod-coil’ block copolymer, with one rigid block, shows completely different phase separation behavior than the more
classical coil-coil type block copolymer.\textsuperscript{114-116} The $\pi-\pi$-stacking of the conjugated part of such block copolymers can induce self-organization not only through incompatibility of the two blocks, but also through attraction of similar blocks. Even in solution this type of substance could aggregate into organized structures. Only in recent years some advances have been made on the elucidation of the self-organizational properties of the type of block copolymers containing a conjugated segment. It is generally accepted that the $\chi$ parameter for such block copolymers is much larger than for coil-coil block copolymers\textsuperscript{112, 117, 118} and therefore the microphase separation can take place at much lower degrees of polymerization (lower molecular weights). Also the type of morphology found, such as arrowheads, wavy and zigzag lamellae or arrow-head structures,\textsuperscript{114, 119} could be very different from the conventional types. Often some type of fibrillar structures are observed, where the conjugated segments aggregate to form a ribbon, surrounded by the coil block.\textsuperscript{120, 121} It must be noted here that the type of morphology depends on the volume fractions, which are much larger for rigid rods than for coils of the same weight. Also the radius of gyration, and therefore the length-scale at which phase separation takes place, is much larger for the rigid rods. Energy minimization studies could give an idea of the lengthscale of phase separation that can be expected for such block copolymers.

The block copolymer morphology in thin films may also differ quite a lot from their bulk properties, and might thus deviate strongly from the normal phase diagram.\textsuperscript{39} The different surface energies play an important role in the self-organization of block copolymers in thin films and can strongly influence the orientation of the phases.\textsuperscript{39} For the application, where charge transport to the electrodes is essential, it is important that the phases are oriented perpendicular to the electrodes.

### 1.5 Controlled free radical polymerization techniques

Well defined products with a relatively low polydispersity are necessary in order to achieve a good phase separation.\textsuperscript{122} There are several living polymerization techniques that can assure such low polydispersities. Well-known techniques of living polymerization, such as cationic and anionic polymerization, have as major drawbacks the limited number of different monomers that can be polymerized (and therefore also functional groups that can be incorporated) and the strictly dry and oxygen-free conditions that are necessary during polymerization.

Recently, new techniques have been developed that combine the robustness of a free radical polymerization with the control of a living polymerization. The four main types of such ‘living’/controlled free radical polymerizations (CRP)\textsuperscript{123-125} are atom
transfer radical polymerization (ATRP), nitroxide-mediated controlled free radical polymerization (NMRP), reversible addition-fragmentation chain transfer (RAFT) and initiator-chain transfer-termination (iniferter). Both ATRP and NMRP are based on the principle of reversible activation-deactivation cycles in which the growing end of the polymer chain is chemically stabilized to give a dormant species. In this way the concentration of free radicals is lowered significantly and the irreversible transfer and termination reactions are inhibited. RAFT is also based on the presence of a dormant species consisting (a dithio-compound), which is formed upon reaction of the growing radical chain with an added chain transfer (thiocarbonylthio) compound. The iniferter technique is based on the formation of a reactive radical, that initiates a polymer chain, and a relatively stable counter radical that will not propagate a radical chain, but undergoes mainly chain transfer and radical termination. The main advantage of NMRP over the other techniques is that no substance (metal or other) has to be added, which may be hard to remove afterwards. This technique is also thought not to interfere with the olefinic double bonds that constitute the conjugated structure of the electron donor. Klaerner et al. used NMRP to synthesize a polyfluorene-based ABA type triblock copolymer.

Coil-coil diblock copolymers can be easily synthesized using NMRP. In most cases the product of an earlier controlled radical polymerization, still containing the nitroxide end-group, is re-employed in a second polymerization with a different monomer. This technique cannot be applied for the synthesis of rod-coil diblock copolymers, since conjugated polymers are usually synthesized via polycondensation. Generally, the synthesis of such block copolymers is performed via the reaction of the (living) end of a coil polymer with a rigid rod, but in that case homopolymer always remains present, since a large excess of one polymer is needed in order to drive the reaction to completion and tedious work-up procedures would be necessary to remove this excess homopolymer. A new strategy should therefore be adopted, where the block copolymer is synthesized by polymerizing the second coil block starting from a macro-initiator for NMRP based on a conjugated polymer rigid rod with a nitroxide end-group. The use of NMRP not only ensures low polydispersities for the second block, but also allows one to adjust the length of the second block, thus enabling the optimization of the active layer morphology of a solar cell through variation of the type of microphase separation.
1.6 Towards semiconducting block copolymers for photovoltaic devices

1.6.1 General synthetic strategy

The general strategy adopted for the synthesis of donor–acceptor (D–A) diblock copolymers is depicted in figure 1.2. The synthesis starts with the polycondensation of a conjugated polymer with solubilizing side-chains to form a ‘hairy’ rod (a). This polymer is then transformed into a macro-initiator for NMRP (b) and subsequently the second coil block, containing a functional comonomer, is polymerized (c). After the grafting of an electron acceptor, such as C$_{60}$ (d), the final product can be used for the fabrication of a photovoltaic device via spin casting.

![Schematic representation of the synthesis of D–A diblock copolymers.](image)

**Figure 1.2** Schematic representation of the synthesis of D–A diblock copolymers.
1.6.2 Previous work

Our group has previously employed the D–A block copolymer design with the objective to enhance control over morphology and opto-electronic properties of PVDs.\textsuperscript{95-98, 100-102, 132-134} The chemical structure of the diblock copolymer poly[(2,5-dioctyloxy)-1,4-phenylene vinylene]-block-poly[styrene-stat-(4-[60]fulleromethylstyrene)] (abbreviated as DOO-PPV\textsubscript{k}-b-P(S-stat-C\textsubscript{60}MS)\textsubscript{x(yz)}) that was employed is shown in figure 1.3 and consists of a rigid-rod like PPV block (donor) and a second styrenic block bearing pendant C\textsubscript{60} as an electron acceptor.

A PPV homopolymer bearing only one aldehyde end-group was synthesized using the Siegrist polycondensation and afterwards transformed into a macro-initiator for NMRP by end-functionalization with TEMPO. The latter is an initiator suitable for the controlled polymerization of styrenic monomers. This macro-initiator was then used for the copolymerization of styrene (S) and 4-chloromethylstyrene (CMS) to yield a diblock copolymer. Fullerenes were subsequently grafted onto this second statistical copolymer block via atom transfer radical addition (ATRA).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Chemical structure of the diblock copolymer DOO-PPV\textsubscript{k}-b-P(S-stat-C\textsubscript{60}MS)\textsubscript{x(yz)}, where k = n+1.}
\end{figure}

Atomic force microscopy (AFM) studies of thin films spin-cast from 1,2-dichlorobenzene (o-DCB) or chloroform showed elongated features with a fairly uniform thickness of approximately 15 nm. on the surface. These features might either indicate
phase separation or the presence of crystal needles at the surface, possibly caused by the presence of a small quantity of homopolymer PPV in the sample.

The fluorescence of the films, compared to a film of the block copolymer without C\(_{60}\), is almost entirely quenched, which is a strong indication for energy or charge transfer from the PPV to the C\(_{60}\). Devices were fabricated in following configuration glass/ITO/PEDOT:PSS/active layer/Al. Device performances were not extremely high, but similar to bulk-heterojunction devices based on MDMO-PPV with a low concentration of PCBM\(^{85}\) However, a comparison between devices made with the block copolymer and devices made with a blend of the two homopolymers (DOO-PPV and P(S-stat-C\(_{60}\)MS)) clearly shows that the block copolymer functions better (see table 1.1). Cross-sectional scanning electron microscopy (SEM) images show, in support of this assumption, that the grain structure for the block copolymer is much finer than the one for the blend.

<table>
<thead>
<tr>
<th></th>
<th>(U_{oc}) (V)</th>
<th>(J_{sc}) (µA·cm(^{-2}))</th>
<th>(S) (mA·W(^{-1}))</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOO-PPV-b-P(S-stat-C(_{60})MS)</td>
<td>0.52</td>
<td>5.8</td>
<td>6.0</td>
<td>0.23</td>
</tr>
<tr>
<td>Blend: DOO-PPV / P(S-stat-C(_{60})MS)</td>
<td>0.40</td>
<td>0.15</td>
<td>0.2</td>
<td>0.28</td>
</tr>
</tbody>
</table>

The block copolymers, when cast from CS\(_2\), showed some very interesting macroscopic ordering on the order of several micrometers. These so-called microporous honeycomb structures consist of well-organized hexagonally packed spherical pores with a diameter of 3-5 µm. The origin of this phenomenon was revealed to be the lowering in temperature of the film during the solvent evaporation and the subsequent formation of water droplets on the surface by condensation. After complete evaporation of the CS\(_2\) the water droplets remain in the solidified polymer solution and after their evaporation their form remains as holes in the film.\(^{135-137}\)
1.9 Outline of this thesis

Some of the very important work performed by De Boer et al. showed that the principles of using block copolymers for photovoltaic devices could be beneficial. A deeper study into the principles and different processes involved is necessary in order to optimize the device performances. In order to get such better understanding, a more controlled and versatile method of synthesis, which allows for good control over the molecular structure, is vital. In such a way, the different structural parameters that govern the phase separation and electronic processes can be varied and finally tuned. It is vital for a better understanding of the influence of the morphology on the device performance, that the molecular structure of the block copolymers is highly controlled. In this thesis the emphasis therefore lies on getting a better control over this molecular structure.

One of the factors that influence such control is the relatively low solubility of the macro-initiator based on DOO-PPV. As will be demonstrated in chapter 3, the lack of good solubility of this macro-initiator leads to the formation of aggregates in the monomer solution used for the polymerization of the coil block. This causes a loss of control and unwanted termination, transfer and other side-reactions result in a block copolymer that does not have a well-controlled structure. In order to gain better control over the coil polymerization and a better solubility of the resulting block copolymer, the synthesis of a new PPV derivative with branched octyl side-chains, poly[(2,5-di(2’-ethyl)hexyloxy)-1,4-phenylene vinylene] (DEH-PPV), is described in chapter 2. The influence of several reaction parameters for the polymerization of this polymer on the chain length and the polydispersity is investigated and column chromatography is introduced as a method of purification.

Another major point of concern for most current organic photovoltaic devices, is the fact that the absorption maximum ($\lambda_{\text{max}}$) of PPV lies around 470-480 nm., which is on the blue side of the solar spectrum. In order to improve device performances a different conjugated polymer with a smaller band-gap should be employed, so as to improve the spectral overlap with respect to the solar spectrum. In the second part of chapter 2, the synthesis of a poly(2,5-thylenylene vinylene) (PTV) derivative is described that allows for control over the length of the polymer. This semiconducting polymer has an absorption maximum up to around 600 nm.

In order to improve the phase separation behavior of the block copolymers and allow for a systematic study of the influence of morphology on the photovoltaic device performances, it is probably necessary to introduce different types of block copolymers.
with stronger segregation behavior. As stated before, one of the methods for improving the phase separation is increasing the product $\chi N$. By changing the chemical nature of the second block from polystyrene to for instance polyacrylate one would increase the value of $\chi$. However, TEMPO is not a good initiator for acrylic monomers and this should therefore be replaced by another initiator for NMRP, capable of controlled polymerization of acrylates. This was done in our group by using a macro-initiator based on TIPNO, but only limited research was performed.\(^9\) Benoit \textit{et al}.\(^{138}\) published some results for acrylate copolymerizations with different comonomers, but the presented results were incomplete (see also chapter 3). For several reasons, among which solubility, polymerizations performed with a rigid rod-like macro-initiator are not well comparable to classical living controlled polymerizations. Chapter 3 is therefore dedicated to the (co)polymerizations of acrylic monomers both via ‘normal’ NMRP and NMRP starting from a macro-initiator based on a conjugated polymer.

Besides this advantage, another advantage of polyacrylate compared to polystyrene is the lower glass transition temperature ($T_g$), which greatly improves the mechanical properties. These enhanced mechanical properties will facilitate the handling and fabrication of (flexible) devices through better film-forming properties. The great difference in ‘softness’ between the PPV and acrylate block will enhance contrast in atomic force microscopy (AFM) measurements and staining procedures for scanning and transmission electron microscopy (SEM and TEM) will be easier, thus facilitating morphological characterizations.

In chapter 4 the functionalization of the coil block is presented. As stated in paragraph 1.5, in previous work the method of ATRA was used to graft the C$_{60}$ onto the polymer chain. The disadvantage of this method is, that it yields a great amount of crosslinked product, since every polymer chain contains multiple reactive groups and fullerene can also react up to at least 12 times. In this chapter a different method of functionalization is therefore introduced that yields products that are better soluble and at the same time allows for a good prediction of the amount of C$_{60}$ incorporated in the block copolymer.

Finally, the results of thermal, photophysical and morphological characterizations and of resistivity and mobility measurements and the device performances for the products synthesized in the previous chapters are presented in chapter 5. A study was done on the deposition and annealing techniques that would allow for the phase separation to take place. A part of this chapter is dedicated to the self-organization of these rod-coil
type block copolymers in solution and the influence of partial solvent mixtures on this solution structure.

The stability of organic photovoltaic devices under operating conditions is one of the major problems that has to be solved before the commercialization of such solar cells. It is known that some conjugated polymers such as PPV are very sensitive towards reaction with oxygen. The breakdown of the polymer via oxidation by singlet oxygen ($^1\Delta_g$) is one of the main reasons for the premature failure of organic solar cells and other devices. Chapter 6 contains a study of the singlet oxygen formation by block copolymers in solution and the influence of C$_{60}$ on the stability of PPV. This is the first time such a study has been performed in solution, since this requires the presence of both donor and acceptor functionalities in a single molecular structure.
1.8 References

General Introduction

General Introduction

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Chapter 1