# 1
# Synthetic Methods for Semiconducting Polymers

*Alberto Bolognesi and Maria Cecilia Pasini*

## 1.1
## Introduction and Overview

Since the discovery of the metallic conductivity in polyacetylene (PA; see Fig. 1.1) [1] it has been clear that the great potential in the development of organic semiconductors was related to the ability of macromolecular chemists to synthesize new structures having a conjugated backbone.
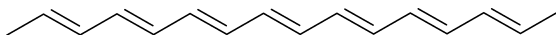


**Fig. 1.1** Structure of polyacetylene in the trans form.

Just after the first work on synthetic method for production of polyacetylene film [2], several approaches were reported for preparing new PAs. The main goals of those synthetic procedures were to overcome PA's drawbacks: its insolubility and its unprocessability [3]. Many new synthetic procedures were developed in those years; some of them represented innovative strategies in macromolecular synthesis and were responsible for the chemical evolution of the semiconducting polymer field.

The dream of conducting PA wires which at the end of the 1970s and the beginning of the 1980s was the driving force of many research groups, soon vanished because the easy oxidation of PA results in dramatic decreases in conductivity and in mechanical properties.

Even though in the middle of the 1980s Narmaan's group [4] was able to produce highly conducting PA ($\sigma$ as high as 100 000 S cm$^{-1}$) by using silicon oil as the solvent for catalyst preparation, the search for new organic semiconductors involved a large number of research teams all over the world. New polymers such as polypyrrole (PPy), polythiophene (PT), polyparaphenylene (PPP), polyphenylenevinylene (PPV) were soon introduced and their chemical modifications were developed even faster, showing in only a few years, by the beginning of the 1990s, that control of the structures induces changes in very important physical parameters such

as solubility and 3D arrangement. The main results of these chemical efforts, however, were related to the "tailoring" of the electronic properties. By a proper choice of the monomer, of the side chains' lengths and/or of their steric hindrances, a fine-tuning of the electrooptical properties can be achieved i.e., full control of the band gap of the system is in the hand of the macromolecular chemists.

What the inorganic chemists obtain by playing with elements of the periodic table such as silicon, indium, gallium, phosphorus, and sulfur can be obtained in the glass reactors of a macromolecular chemistry laboratory without the need of sophisticated machines for coevaporating different elements [5].

Moreover, the tuning of the electronic and optical properties of these new materials can be extended to a very fine level just by controlling the interaction among the chains [6].

We are now at the beginning of the new millennium: Heeger, MacDiarmid and Shirakawa were Nobel laureates in 2000 for their pioneering work on PA. In this new millennium we are entering the area of functional materials: the material is planned and prepared in view of its specific electronic applications. A simple example may better explain this idea.

Organic field effect transistors (FETs) are devices where the $\pi$–$\pi$ interactions (Fig. 1.2) are extremely important in governing the mobility of the carrier, one of the main factors in the working mechanism of these devices [7].

So, if the aim is to fabricate a good FET, it is necessary to optimize the overlap among the $\pi$ backbones of the macromolecules, and usually a crystalline order is the best way to obtain that. A material able to crystallize forming large surface area crystallites is highly desirable.

On the other hand, for the preparation of highly efficient light emitting diodes (LEDs), strong interchain interactions should be avoided because they are responsible for a decrease in the electroluminescence (EL) efficiency, so highly amorphous materials with high interchain distances are necessary [8].

Only after experimenting in the synthesis and application of semiconducting materials it is possible to plan the synthetic pathways such as to control most of the parameters.
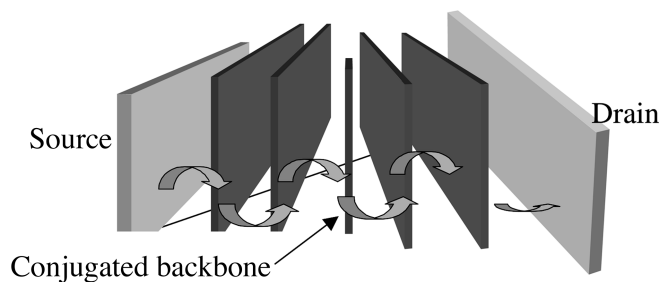


**Fig. 1.2** Example of high packing in a field effect transistor (FET) improving the mobility: the arrows indicate the charges which are transported perpendicularly to the plane of the $\pi$ system between the source and drain. The conjugated $\pi$ system is shown in the dark grey plane of the figure.

Even though this field is new, applications of semiconducting polymers are already on the market. There are producers of conjugated polymers (American Dye Sources, Covion/Merck [9]) and producers of devices having a semiconducting polymer as active layer. This does not mean that the research effort has finished, however.

The need for new multifunctional materials, able to combine properties such as self-organization and semiconduction, has induced material scientists to explore new strategies for the preparation of molecules exhibiting a certain complexity. Different chemical functions have to be incorporated in the same molecule to achieve multifunctionality, and this requires a strong and precise planning of the molecules.

High specific functions require a hierarchical organization of matter starting from the basic molecule to the final arrangement of an object at the nano–microscale dimension [10].

Polymer chemistry has recently shown that macromolecules can be considered as starting point for the preparation of specific materials [11]. Long chain macromolecules can bear different functions on the same backbone [12, 13].

Polymers have recently contributed to the development of highly innovative technologies: the new polymeric structures introduced can be applied in the area of micro- [14] and nanoelectronics [15], microbiology [16], nano- and micro-engineering [17] and microfluids [18]. In view of this, a number of different properties such as solubility, electrical conductivity, biological activity, reactivity, photoluminescence (PL), optical absorption, order in the solid state, etc. have to be combined for optimizing the application of the material.

The chemical approach for the realization of these highly advanced materials can also take advantage of recent developments in the area of polymer synthesis. The block copolymer (BC) approach offers a great tool for preparation of materials with different functions that can be organized at different degree of complexity. The recent literature in this area offers a great number of examples supporting this hypothesis [19].

In this chapter, we would also like to give some synthetic guidelines for the developing of BCs suitable for applications mainly in the area of electronics.

We do not discuss in details the electronic properties of the structure presented. The reader may refer to the specific literature of this field reported in Refs. [20, 21].

## 1.2
## Synthetic Pathways for PA

### 1.2.1
### Classical Synthesis for PA

Acetylene was firstly polymerized by Natta and coworkers in 1958 [22]. What was obtained at that time was a powdered, black, intractable compound. The synthetic procedure is very similar to the synthesis of polyethylene using tita-

nium catalysts. In fact Ti (OProp)$_4$ easily reacts with Al(Et)$_3$ to give a Ti–C bond; the polymer chains grow upon insertion of the monomers in the created Ti–C bonds. The work of Shirakawa [1, 23] followed the procedure by Natta, but the catalyst concentration was much higher so that a highly viscous catalytic "soup" remained on the wall of the reaction flask. The diffusion of acetylene in the system, under vacuum, led to the formation of a shiny freestanding film which had to be washed several times in order to remove the catalyst residues. There are several variations to this synthetic approach and the readers may refer to the following reviews for details [24, 25].

As mentioned in the Introduction the main drawbacks to PA are related to its insolubility and to the impossibility of treating the polymer after synthesis: once it is polymerized the polymer must be taken as it is. Attempts to solubilize PA were performed by different groups with two main approaches: the precursor route and grafting.

### 1.2.2
### The Precursor Route

This approach was developed by J. Feast at the beginning of 1980 [26]. The idea was to form a soluble precursor of PA, which upon elimination of some molecular fragments, in a controlled way, may develop the conjugated form of PA. The advantage of this synthetic procedure is in the possibility of obtaining a material that can be dissolved in organic solvents, thus giving a film that upon thermal treatment is transformed into the shiny-metal-like PA. The steps of this synthetic approach are reported in Scheme 1.1.

The first step is obtained by ring-opening metathesis polymerization (ROMP) catalyzed by WCl$_6$. In the second step, the film is thermally treated so that PA is obtained. The disadvantage of this approach is in the synthesis of the monomer to be polymerized and in the possibility that elimination of CF$_3$ groups is not complete and some of them remain in the backbone.

The precursor route is an original and unconventional way for producing a polymer. It was also used, with a different and cheaper monomer, to produce
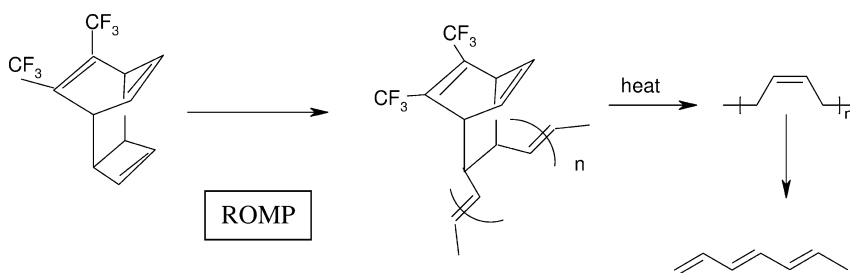


**Scheme 1.1** Durham route to polyacetylene (PA). ROMP = ring opening metathesis polymerization.

polyparaphenylenevinylene (PPV) as will be discussed in Section 1.3.5. Grubbs also obtained soluble and highly conjugated PAs by means of the ROMP of monosubstituted cyclooctatetraene [27].

### 1.2.3
### The Grafting Approach

The rigidity of the  backbone is a limit to the solubility of a polymer. By taking into account the equation:

$$\Delta G_s = \Delta H_s - T \Delta S_s$$

(the subscript "s" indicates that the thermodynamic functions are considered for the solubilization process), solubilization occurs when $\Delta G_s$ is negative. However, while $\Delta H_s$ can be negative because of the good interactions between the solvent and the polymer chains, the $\Delta S_s$ value is not positive because of the limited conformational freedom of the polymer backbone in solution with respect to the solid state, due to the stiffness of the macromolecules. So the thermodynamics indicates a great difficulty in solvating the polymer. To overcome this difficulty, some groups tried to solubilize PA by grafting it onto a flexible polymeric chain exhibiting a high conformational freedom so that the overall value of $\Delta S$ is positive. A simple summary of the route developed is reported in Scheme 1.2.
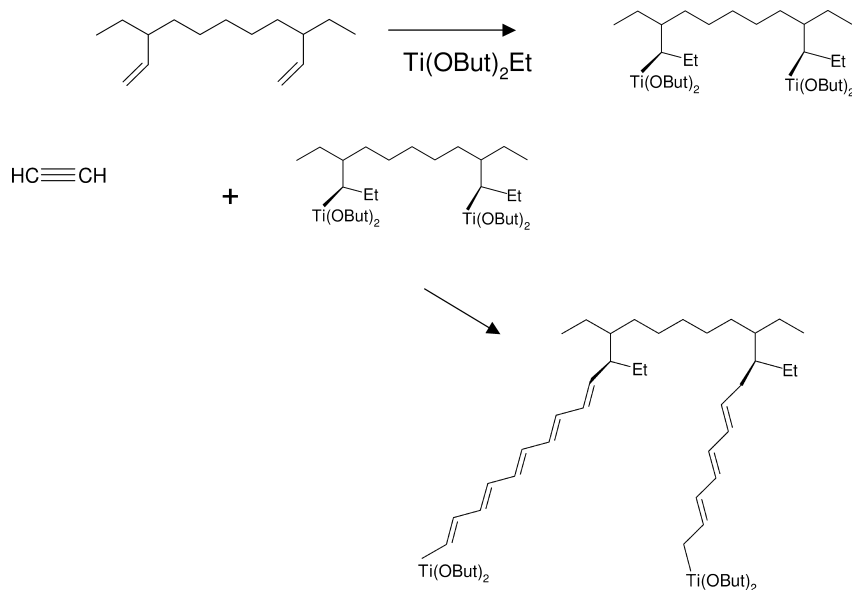


**Scheme 1.2** Grafting of PA onto soluble substrate.

This procedure [28] is based on the mechanism of the ZieglerNatta $\alpha$-olefin polymerization. During this process, the reaction between Ti(OBut)$_4$ catalyst and AlEt$_3$ leads to the formation of a Ti–C bond. Polymerization of the monomers (ethylene, propylene, etc.) occurs by insertion into the Ti–C bond. If the activated catalyst reacts with a polymer containing vinyl double bonds (for example a vinyl group of 1,4-*cis* polybutadiene containing 1,2 units) these will act as an olefin inserting in the Ti–C bond. At this step, the bubbling of acetylene in the solution makes possible the growth of a PA chain directly from the soluble polymeric backbone. A control of the ratio between Ti and the 1,2 units of the polymer allows control of the relative amount of PA with respect to polybutadiene. Even though a bluish solution is obtained, it was found that a certain degree of aggregation is present, probably due to the strong interchain interactions among the PA chains.

## 1.3
### Conjugated Polymers by Step-Growth Polymerizations

There are several different step-growth polymerizations allowing the preparation of conjugated polymers. Most of them use monomers containing reactive groups that can be specifically created in order to make the polymerization possible. Specific catalytic systems must be used for each kind of reactive group. An example of the mechanism for this kind of polymerization is reported in Scheme 1.3 for the Yamamoto polymerization [29] catalyzed by Ni derivatives; R is an aromatic molecule (benzene, thiophene).
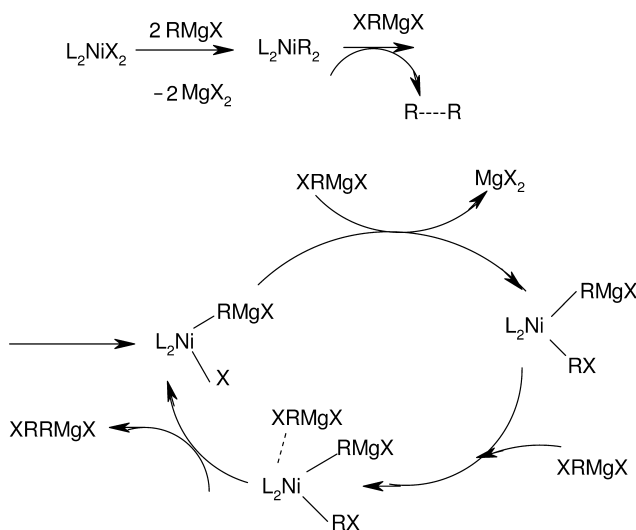


**Scheme 1.3** Catalytic cycle of the Ni-catalyzed polymerization.

## 1.3.1
## Poly(3-Alkylthiophenes)

With the synthetic approach reported above, many polymeric structures can be obtained. The most widespread application of the Yamamoto synthesis is the preparation of poly(3-alkylthiophenes) (PATs). The route for polymer synthesis starting from the monomer is reported in Scheme 1.4.

With this procedure, a head-to-tail connection in the range of 90% can be reached as determined from ^{1}H-NMR analysis of the polymer [30]. Since 3-alkyl-thiophene is an asymmetric monomer, different kinds of microstructures can be achieved in the polymerization process depending on the ratio between the thiophene ring bearing a Grignard reagent in positions 2 and 5.

In fact in the last step of Scheme 1.4 the reaction of Mg with 2,5-diiodo-3-alkylthiophene may give two isomers according to Scheme 1.5. Polymerization occurring only with monomers **2** or monomers **3** leads to a regioregular polymer with a head-to-tail conversion of 100%. But as monomers **2** and **3** are present in the reaction mixture irregularities in the microstructure are generally observed.

In Scheme 1.5, it is shown how different microstructures in the polymer chain can be formed due to the presence of the two isomers **2** and **3**. The microstructure can be controlled through ^{1}H-NMR as reported in the literature [30].
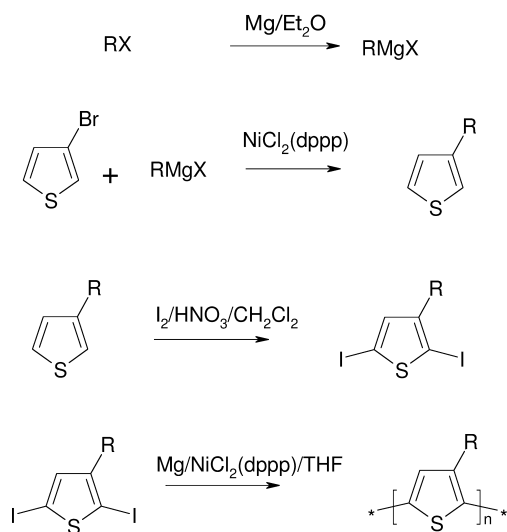


**Scheme 1.4** Yamamoto route to poly(3-alkylthiophenes). R=alkyl chain; with a number of C atoms>4 the polymer is soluble X=bromine; dppp=diphenylphosphinepropane.
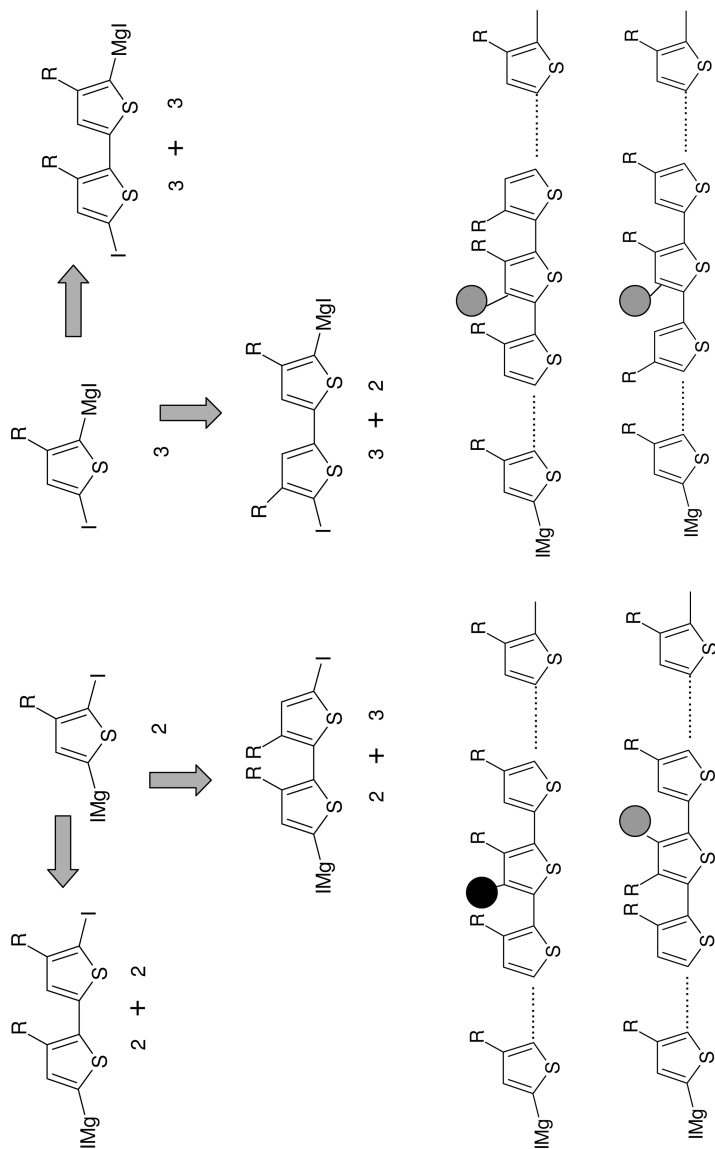
**Scheme 1.5** Representation of the possible microstructures in a poly(3-alkylthiophene) chain. The black point indicates an aromatic proton in a regioregular enchainment; the grey points indicate aromatic protons in irregular connections.

Chemists' ability to control the ratio between monomers **2** and **3** makes it possible to control to some extent the electrooptical properties of the polymers. In fact when the linking between two monomers is the one indicated as **2+3** (head-to-head connection) the adjacent monomers being out of plane interrupt the conjugation length. On the other hand, with the connection shown as **2+2** (Scheme 1.3, head-to-tail) the planarity of the backbone is maintained and a conjugation length higher than the one obtained for the **2+3** situation is reached.

Higher conjugation length shifts the absorption towards higher wavelengths, while shorter conjugation length gives rise to polymers with a blue shift in the absorption. Thus, a fine-tuning of the optical properties can be reached by a proper control of the defects introduced in the polymer backbone.

As the ratio between the two monomers **2** and **3** influences the microstructure of the polymers, synthetic procedures attempting to obtain only one of the two possible monomers have been proposed. McCullough and Lowe in 1992 [31] reported a synthetic procedure to form the Grignard compound only in the 5 position of a 2,5-dihalogenated 3-alkylthiophene. A description of this synthesis is reported in Scheme 1.6.
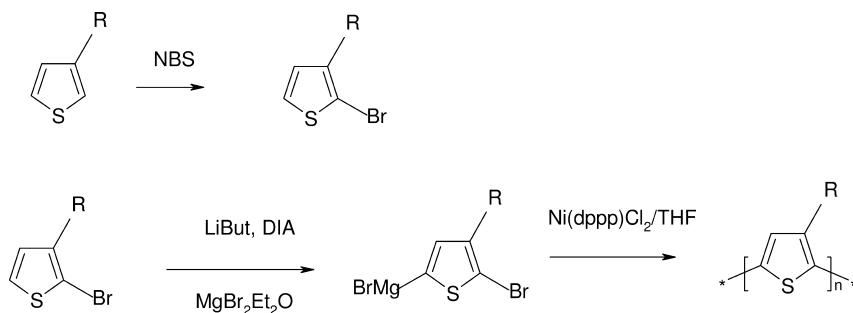


**Scheme 1.6** McCullough's route to regioregular poly(3-alkylthiophenes) (PATs). DIA=diisopropylamine.

In subsequent years, other synthetic routes were reported describing new methods for obtaining highly regioregular PATs. It was found [32, 33] that with a ratio between monomer **2** and **3** near to 4 the polymer remaining as residue to hot acetone extraction has an almost 100% head-to-tail connection. The optimal ratio between the two monomers can be reached by following the procedure of Scheme 1.7. A detailed explanation on this matter is reported in Ref. [34].

Andersson et al. [35] showed that polymerization of thiophenes bearing bulky substituents, does not only influence the band gap, but also has an effect on the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) positions i.e., on the electronic affinity (EA) and ionization potential (IP) of the polymers. These two parameters are extremely important in governing the charge injection in a LED from the two electrodes.

R = ‒(CH$_2$)$_5$OCH$_3$; (CH$_2$)$_6$OCH$_3$; (CH$_2$)$_{10}$OCH$_3$
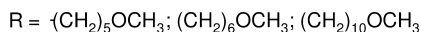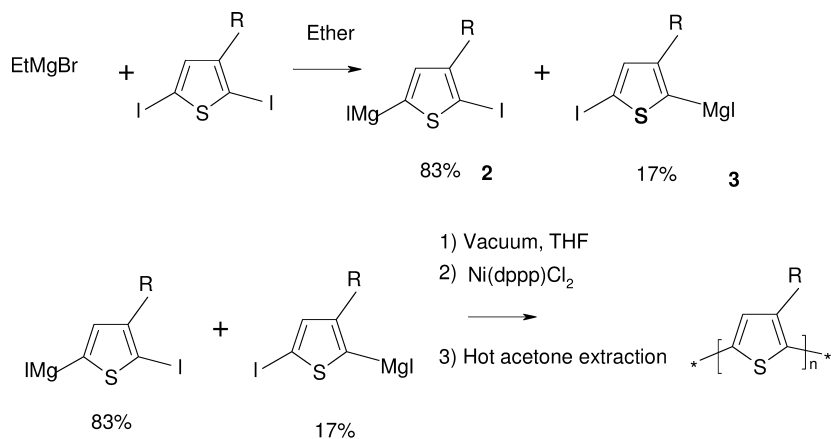
**Scheme 1.7** Easy route to highly regioregular PATs.

Catellani et al. [36] showed that by copolymerizing 3,4-dialkylsubstituted thiophene, together with 3-alkylsubstituted thiophene, the band gap can be continuously varied to obtain copolymers covering all the visible range in absorption.
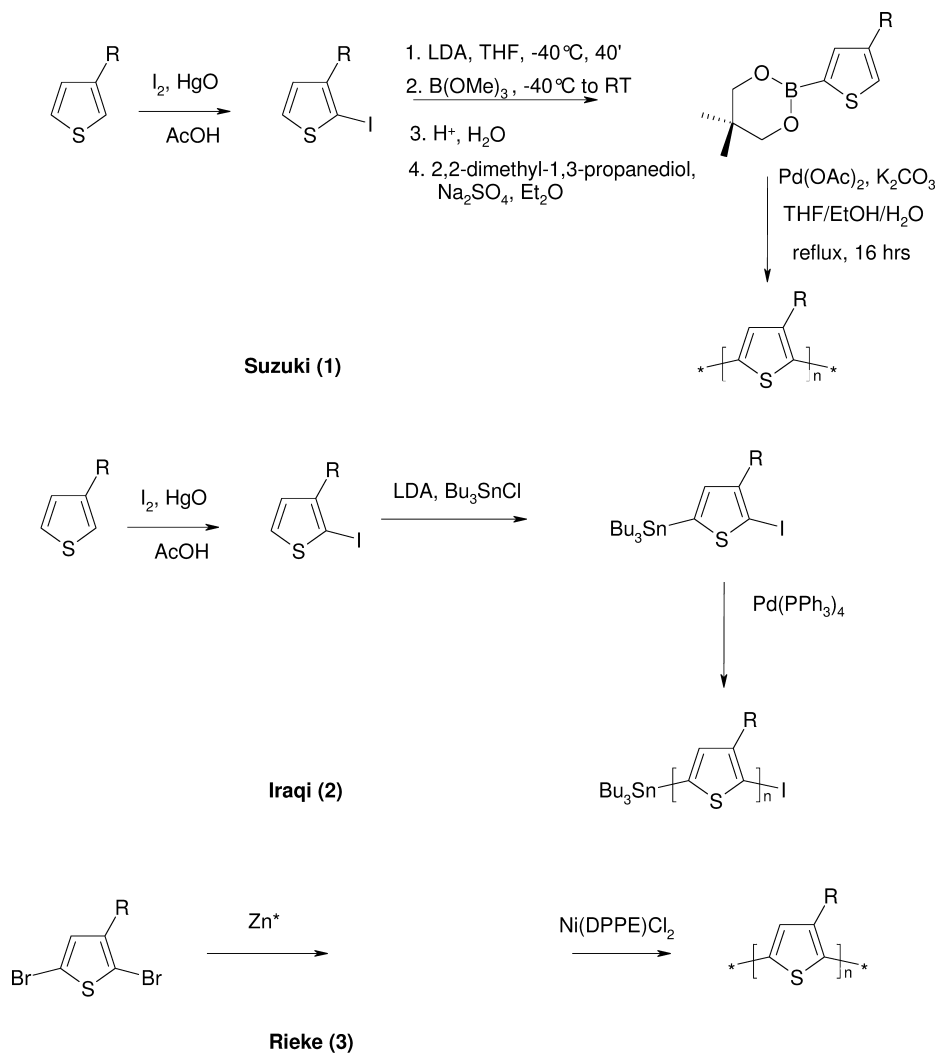
PATs have been extensively studied for their interesting electrooptical properties. Even though they were investigated for the preparation of LEDs, the most promising applications are suggested for the fabrication of photovoltaic cells and for field effect transistors (FETs). The PL quantum yield (QY) in the solid state does not exceed 22% [37] for PATs bearing highly branched substituents, a value which is a factor of 2 lower than the QY of substituted PPV emitting in the same spectral region. Highly regioregular PATs exhibit good charge mobility in the solid state because of good overlap between the $\pi$ systems of adjacent macromolecules and this property can be conveniently used for FETs with high on/off ratios [38].

Other synthetic approaches have been introduced for the preparation of PATs: all of them can be considered a development of the synthetic route described above. In Scheme 1.8 the main pathways are reported with their references. It is difficult to establish a criterion for the choice of the reaction to be performed.

A comparison among the polymers resulting from different synthetic approaches is reported in Table 1.1.

For the details on the reactions 1, 2, 3 (Scheme 1.8) see Refs. [39–41] respectively.

One of the most studied and used derivative of PAT is poly(3,4-diethyloxy)-thiophene (PEDOT) which has been recently introduced onto the market for many purposes. It is sold as a blue suspension in water containing the anion of polystyrenesulfonic acid (PSS) as counterion (Fig. 1.3).

**Suzuki (1)**

1. LDA, THF, -40 °C, 40'
2. B(OMe)$_3$, -40 °C to RT
3. H$^+$, H$_2$O
4. 2,2-dimethyl-1,3-propanediol, Na$_2$SO$_4$, Et$_2$O

I$_2$, HgO / AcOH

Pd(OAc)$_2$, K$_2$CO$_3$
THF/EtOH/H$_2$O
reflux, 16 hrs

**Iraqi (2)**

I$_2$, HgO / AcOH

LDA, Bu$_3$SnCl

Pd(PPh$_3$)$_4$

Bu$_3$Sn

**Rieke (3)**

Zn*

Ni(DPPE)Cl$_2$

**Scheme 1.8** Synthetic pathways to regioregular poly(3-alkylthiophenes). LDA = lithium diisopropylamide, DPPE = diphenylphosphineethane.

**Table 1.1** Different synthetic approaches to PATs.

|                | Mw      | Mn      | Mw/Mn | Regioregularity % | Yield % |
|----------------|---------|---------|-------|-------------------|---------|
| Ni             | 15 000  | 13 000  | 1.15  | 98–100            | 35      |
| Suzuki         | 40 000  | 27 000  | 1.5   | 96–97             | 55      |
| Iraqi (Stille) | 16 000  | 11 000  | 1.4   | 96                | 96      |
| Rieke          | 7 000   | 6 100   | 1.15  | 90–94             | 63      |
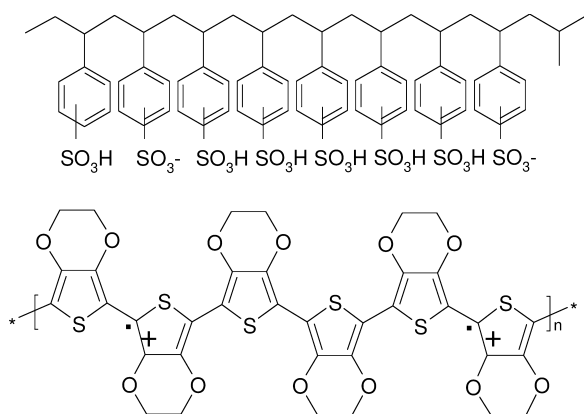
**Fig. 1.3** Poly(3,4-diethyloxy)thiophene (PEDOT)/PSS structure.

This suspension can be used to form a thin conducting layer acting as protecting film on ITO (Indium Tin Oxide) covered glass. LEDs prepared with a protective layer of PEDOT on ITO show better performances and longer lifetimes [42].

PEDOT is obtained through an oxidative coupling using $FeCl_3$ or $Na_2S_2O_8$ as oxidizing agent, starting from 3,4-ethylenedioxythiophene.

This synthetic procedure, an oxidative coupling, is widely used in many polymerizations with aromatic monomers. It has been applied for polymerization of 3-alkylthiophenes [43] and other substituted polythiophenes [44–46]. The advantage of the approach is in the simple procedure for monomer preparation: it is not necessary to introduce halogen atoms onto the rings. However in the case of 3-alkylthiophene polymerization, irregularities in the polymer microstructure are formed: head-to-tail connection reaches values around 70%. Moreover, the polymers formed are in the doped state and a careful removal of the catalyst impurities is necessary. This cleaning procedure is extremely important for all applications in electronics. Traces of metal impurities are undesirable because they act as dopants leading to a quenching of PL and EL and to a relatively high conductivity.

The $FeCl_3$ polymerization is often used to polymerize substituted symmetric dimers and trimers to obtain a polymer with a well-defined microstructure. Inganäs has shown that in the case of nonsymmetric thiophene monomers bearing bulky substituents a regioregularity as high as 90% can be obtained [47]. The following examples (reactions 1, 2, and 3 in Scheme 1.9) are reported to evidence the wide application of this method [48–50].

A recent review concerning all the synthetic approaches to PATs is reported in Ref. [51]. The synthetic procedures outlined for PAT polymerization can be extended with some modifications to obtain other polymers: by applying the same approaches to different monomeric units, polymers exhibiting a wide range of electrooptical properties can be synthesized.
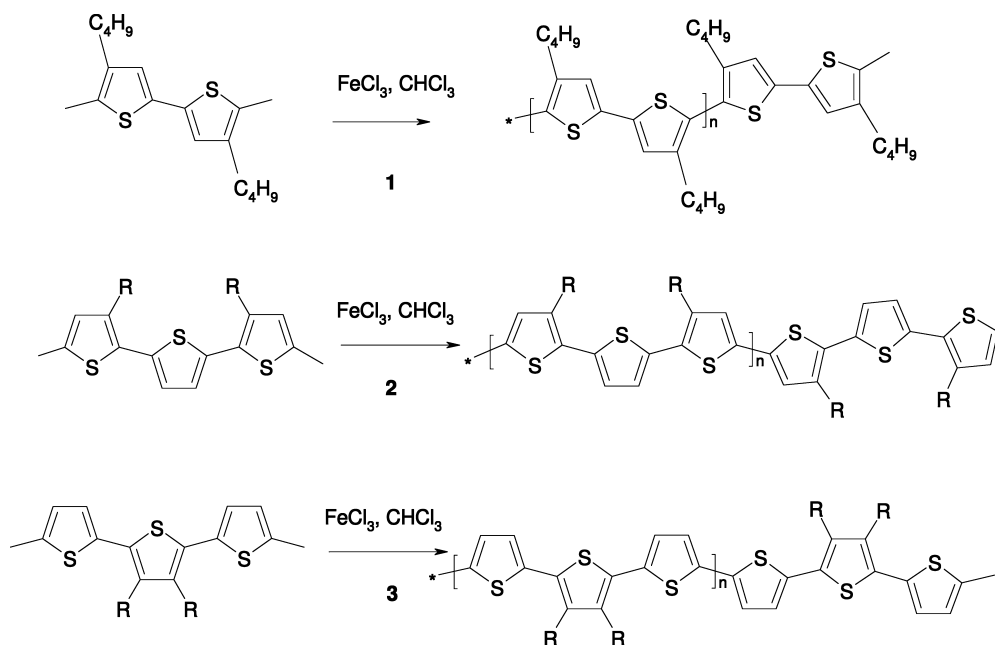
**Scheme 1.9** Polymerization by means of oxidative coupling; for details of reaction 1, 2, 3 see [48–50].

## 1.3.2
**Polyparaphenylenes**

The simple extension of the Yamamoto synthesis to phenylenes produces the polyparaphenylene (PPP) derivatives.

These polymers were synthesized in their insoluble form at the end of the 1970s by Jones et al. [52] and Yamamoto. The Kovacic polymer [52] was a brown, insoluble and amorphous powder. These characteristics were mainly due to meta linkages in the backbone and to branching. The Yamamoto polymer [53] was obtained as a yellow insoluble powder using the same synthetic procedure described for PATs (see Scheme 1.3), starting from 2,5-dibromobenzene. The polymer was characterized by very low molecular weight (8–10 monomeric units), even though the branching in the main backbone was avoided due to the synthetic procedure followed.

The introduction of side chains in the 2 and 5 positions in 1,4-dibromobenzene has allowed to obtain a soluble polymer. The introduction of the Suzuki coupling for the preparation of PPP opened the way to the production of a great variety of conjugated polymers, not only in the PPP family, but also for polyfluorene (POF) preparation, and represents a strong improvement in the synthesis of conjugated polymers. In Scheme 1.10 the main steps followed by this synthetic procedure are outlined.
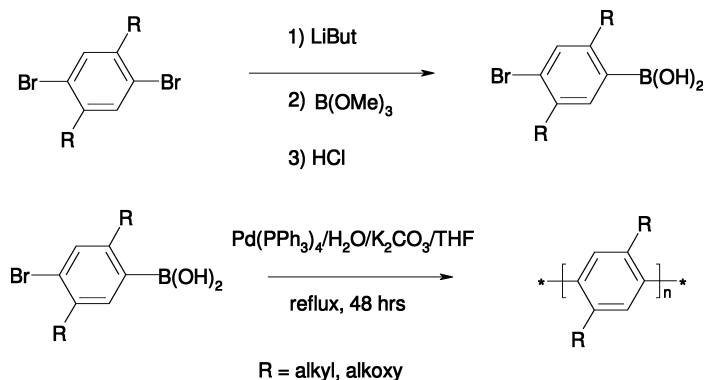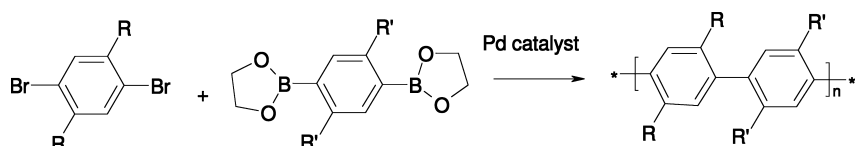
**Scheme 1.10** Suzuki coupling for polyparaphenylene (PPP) preparation.

Polymerization starting from boronic ester is also possible: the advantage of working with boronic ester is in the low amount of water associated with ester with respect to the boronic acid [54]. Reaction of the boronic acid with 1,3-propanediol or ethyleneglycol in excess leads to the formation of the desired ester. Borolane compounds also were synthesized in order to improve the polymerization yields [54].

The main advantage in the use of the Suzuki coupling is related to the possibility of crystallizing the boronic acid or the corresponding esters, because they are stable and can be purified even by flash chromatography. This allows working with highly purified monomers while the Grignard reagents, due to their high reactivity, cannot be purified.

The use of Suzuki coupling has found widespread use for the preparation of alternated copolymers. By following Scheme 1.11, a great number of polymers can be synthesized.

The conjugation length in these compounds is rather low because of the non-planarity between adjacent monomer units due to twisting of adjacent phenyl rings, which are almost perpendicular. A fine tuning of the electrooptical properties of this class of polymers has been obtained by a proper choice of the substituent and by introducing spacers (both with double bond and single bond) in the conjugation path, as shown by Remmers et al. in a series of PPPs [55]: as an example the PPP shown in Fig. 1.4 has an absorption at 331 nm both in so-



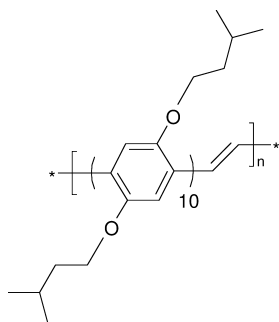**Scheme 1.11** Suzuki coupling for alternated PPP copolymer formation.

**Fig. 1.4** Highly efficient polyparaphenylene (PPP).

lution and solid state and an emission at 395 nm and 441 nm in solution and solid state respectively with a PL QY of 73% for the film.

These compounds are good candidates as the active electroluminescent layer in LEDs.

Polyelectrolytes having the structure of PPP and bearing a cation or anion in the side chain have also been synthesized. These macromolecules are soluble in water in the ionized form, while in the neutral form they are soluble in organic solvents. Some of the most studied structures are reported in Fig. 1.5 [56].
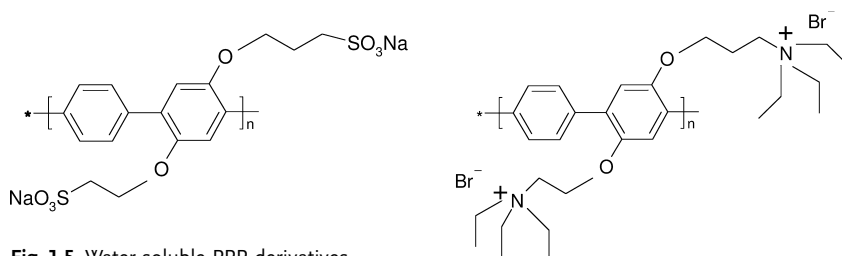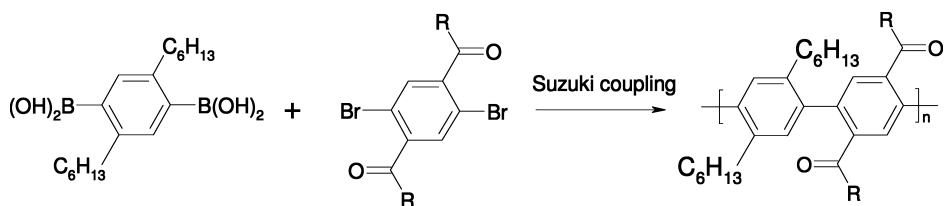


**Fig. 1.5** Water-soluble PPP derivatives.

Suzuki coupling has a wide tolerance towards many functional groups. For example PPP containing keto groups can be prepared as shown in Scheme 1.12 [57].

The introduction of keto groups in a conjugated polymer may be responsible for an increased rate of degradation. The structure reported in Scheme 1.12 has



**Scheme 1.12** Functionalized PPP.
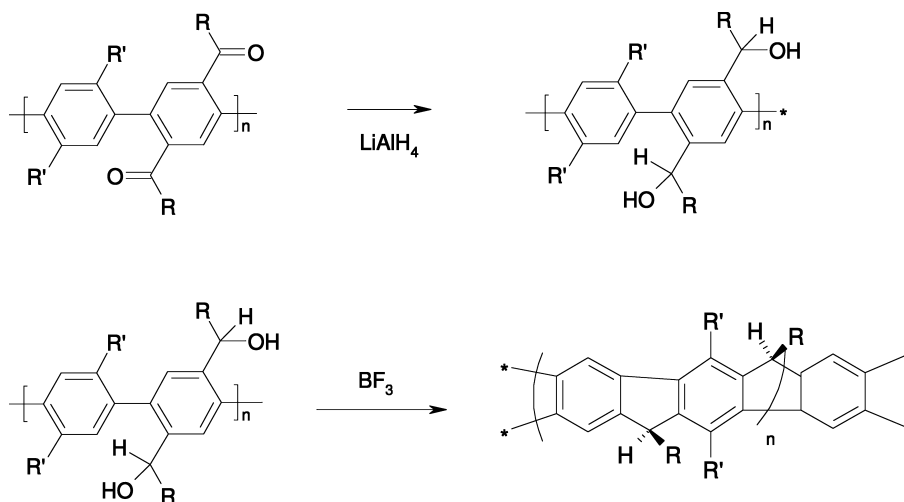
**Scheme 1.13** Synthetic route to phenylene-type ladder polymer.

been used to synthesize a peculiar PPP, a phenylene-type ladder polymer, where all the phenyl rings are forced to be almost coplanar. This structure has been obtained following the synthetic pathway shown in Scheme 1.13 as taken from Ref. [57].

A review on the potential of the Suzuki coupling for many structural modifications of PPP has been recently published [54]. It should be pointed out that by means of this procedure dendronized structures can be realized and easily controlled, even though the number of steps followed and the purification processes necessary to reach a completely controlled structure require a long work-up.

An example of the final step of a polymerization process leading to a dendronized structure having a core of PPP is reported in Scheme 1.14. This gives an idea of the potential of the Suzuki coupling.

Even though the Suzuki coupling is the synthetic procedure most used for preparation of PPP, other methods have appeared in the literature.

Yang et al. reported the synthesis of the PPPs shown in Fig. 1.6 [58] by following a procedure similar to the one proposed by Chen and Rieke for PAT polymerization [41].

More recently, Babudri et al. have shown that palladium-catalyzed cross coupling between aromatic bis-organomagnesium reagents and aromatic dihalides is a good method for synthesizing soluble conjugated phenyl homopolymers and copolymers [59]. In Scheme 1.15 the method followed is reported with some of the structures that have been synthesized. The molecular weight obtained by this method is generally lower than those reached by Suzuki coupling.
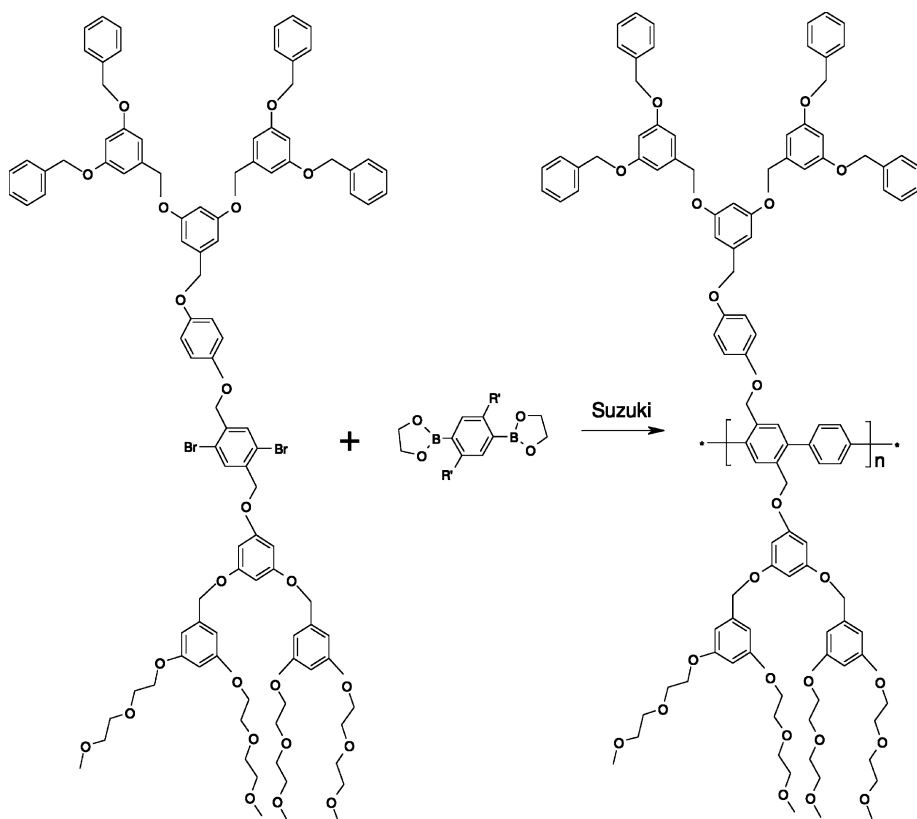
**Scheme 1.14** Preparation of a dendronized copolymer through Suzuki coupling.
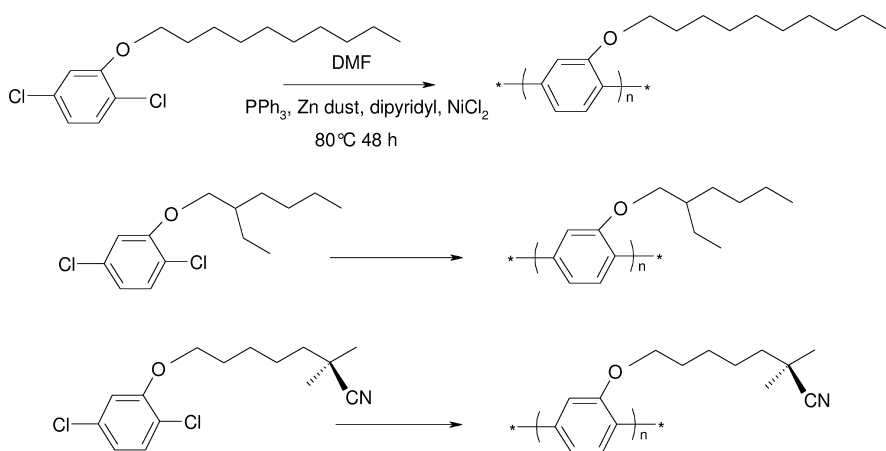


**Fig. 1.6** Soluble monosubstituted PPPs. DMF=dimethylformamide.

**Scheme 1.15** Palladium-catalyzed cross-coupling between aromatic di-Grignard and aromatic dihalides.

### 1.3.3
### Polyfluorenes

Polyfluorenes (POFs) may be considered as polyphenylene derivatives exhibiting an absorption shifted towards higher wavelengths. The $CH_2$ bridge connecting two adjacent phenylene rings induces a planarization of the molecule thus ob-
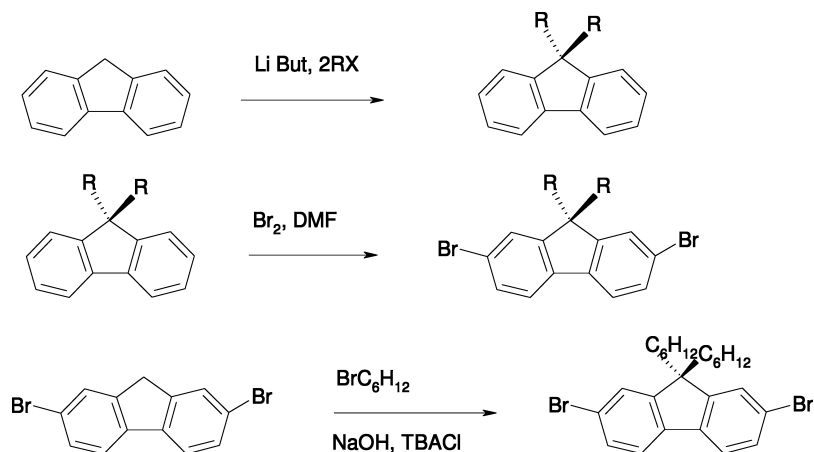
**Scheme 1.16** Synthetic procedures for dialkyl fluorene synthesis.
DMF=dimethylformamide; TBACl=tetrabutylammoniumchloride.

taining a higher conjugation length in the polymer. However the emission of POFs is always in the blue region with typical emission in the range 430–460 nm.

The synthetic strategies used to prepare this kind of polymer are the same as those shown for the PPP family. Usually the 2 and 7 positions are easily substituted by two bromines which are transformed into the corresponding boronic acid derivatives and/or boronic esters by lithiation and subsequent reaction with different borates (Scheme 1.16). As in the case of PPP, the number of combinations to get all possible structures of copolymers depends only on the chemist's creativity.

In order to have a soluble polymer, the 9 position is substituted with two alkyl chains, functionalized chains, alkyl chains containing heteroatoms etc. The properties of the resulting polymers are influenced by the type of substituent used. The reactions leading to the substitution of the two hydrogen atoms in the 9 position are very simple and can be carried out both in aqueous media [60] and in organic solvents by means of alkyl lithium [61].

In Scheme 1.16 two synthetic procedures for this reaction are reported: an accurate control of the purity of the final product is required. If traces of monosubstituted monomer remain in the final products this monomer will be easily incorporated in the polymeric/copolymeric structures.

The hydrogen atom in the 9 position can be removed: oxygen, addition to the C9 of the monosubstituted fluorene unit can occur, leading to a peroxide evolving to a keto derivative as shown in Scheme 1.17 [62]. This oxidation process has been followed by Fourier transform infrared spectroscopy (FTIR), observing the increase of the keto group band at 1721 cm$^{-1}$ (C=O stretching) upon prolonged exposure to air and light. The formation of the keto group in the 9 posi-
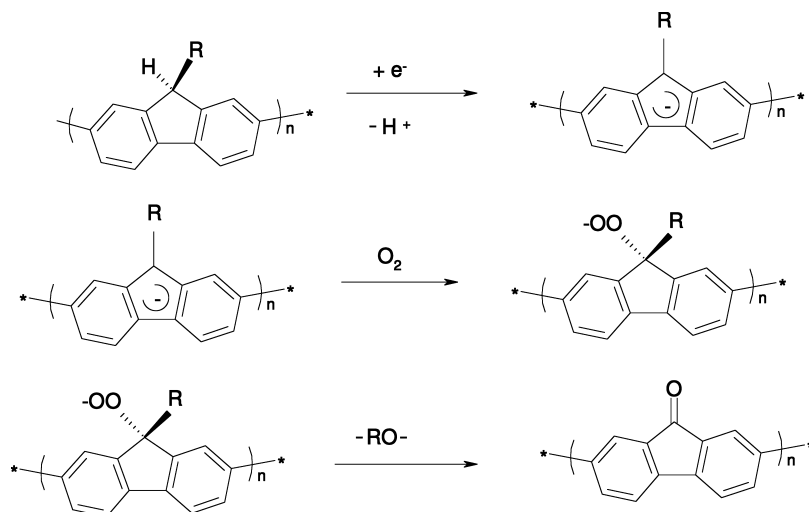
**Scheme 1.17** Oxidation of polyfluorene containing monosubstituted monomers.

tion is responsible for the quenching effect leading to the decrease of PL quantum efficiency and to the appearance of a new band in the PL spectrum at 520 nm. This means that, even in the presence of traces of oxygen, the structure of the polymers having monosubstituted monomers changes, with a marked variation in the emission and decrease of quantum efficiencies.

These effects are unwanted and may be avoided only with a careful separation and purification of the starting monomer.

Usually POFs emit at 420 nm; however, emission at higher wavelength (490 nm, 540 nm) has also been observed after aging. This emission has been attributed to interchain excimer formation [61] and is responsible for both a decreased QY and a change in the color emission. This change has been the subject of much experimental work aimed at understanding its real cause. The same emission was observed for POF containing keto groups as the result of chemical oxidation to fluorenone of a monosubstituted fluorene [62].

It should be noted that the advantage of working with boronic acid compounds or their esters is in the purification of the starting monomers. More recently, the direct use of borolanes has been introduced as a tool for improving reaction yields and fastening the overall process. In Scheme 1.18 a procedure used to polymerize fluorene monomers with the use of borolanes is reported [63].

One of the first polymerizations of fluorene was introduced by Fukuda et al. [64]: polymerization of 9,9-dihexylfluorene was achieved by adding this monomer to a stirred solution of $FeCl_3$ in $CHCl_3$ under an Ar atmosphere.

Another synthetic procedure that is widely used mainly for the preparation of soluble POFs is the so-called Yamamoto procedure.
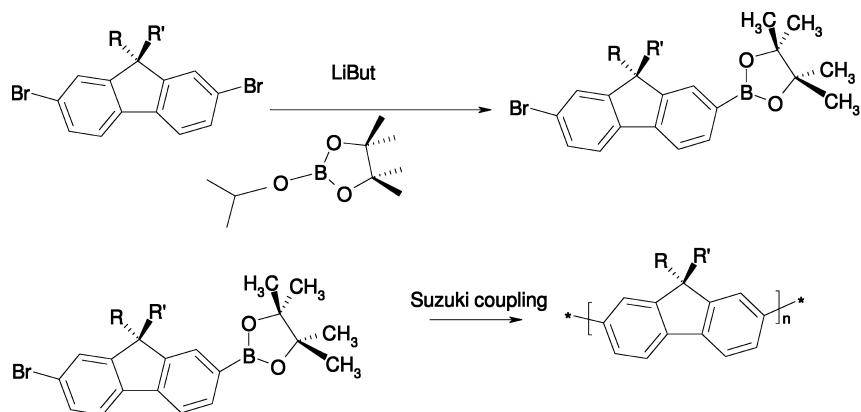
**Scheme 1.18** Use of borolanes in the synthesis of polyfluorenes (POFs).

By this approach, high molecular weight polymers are obtained through the Ni (COD = cyclooctadiene) catalyst and dihalosubstituted fluorene monomers [65]. The control of molecular weight can be obtained by introduction of an end-capper as shown in Scheme 1.19.
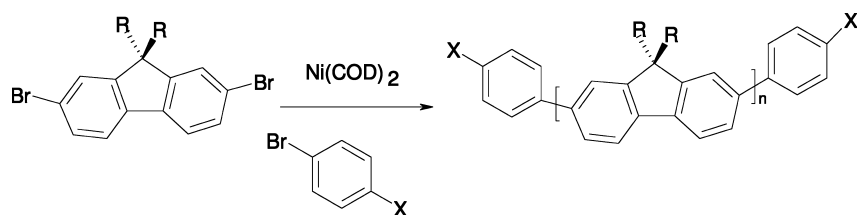


Ni(COD)$_2$ = Nickel (cyclooctadiene)$_2$
X = -NH$_2$, -NPh$_2$, -CH = CH$_2$

**Scheme 1.19** Yamamoto synthesis of POFs.

## 1.3.4
## Copolymers with Phenylenes and Other Aromatics

Copolymerization of fluorene [60] with substituted phenylene gives a polymer with a strongly depressed emission from excimer states. The structure of the polymer is reported in Scheme 1.20. This structure was found to give a QY of about 40% in the solid state with emission centered at 420 nm. LEDs prepared with this polymer gave an external quantum efficiency of about 0.6% and increased color stability compared to the usual poly(dialkylfluorenes). Many co-polymeric structures can be obtained by combining two different monomeric units and following the Suzuki coupling synthetic procedure.
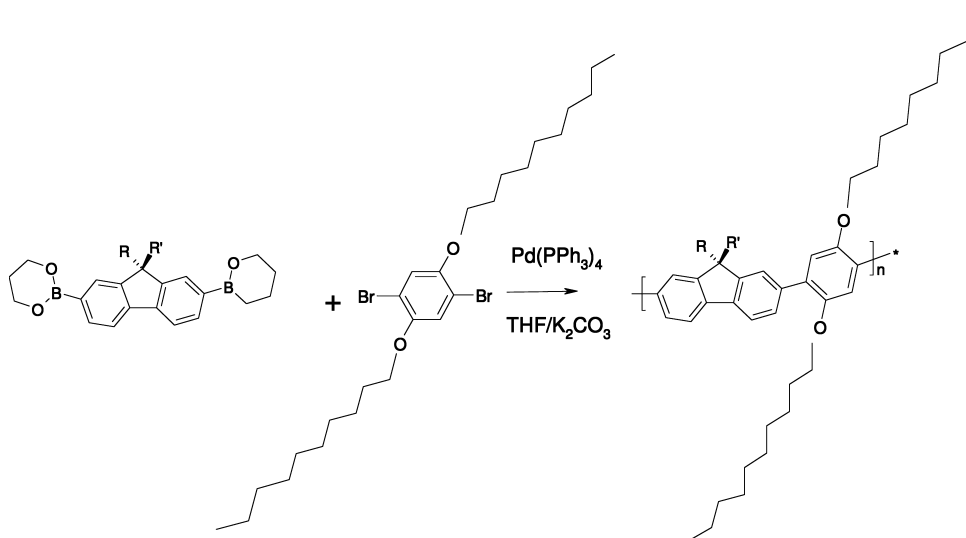
**Scheme 1.20** Synthetic approach to alternated copolymer containing fluorene and benzene units.
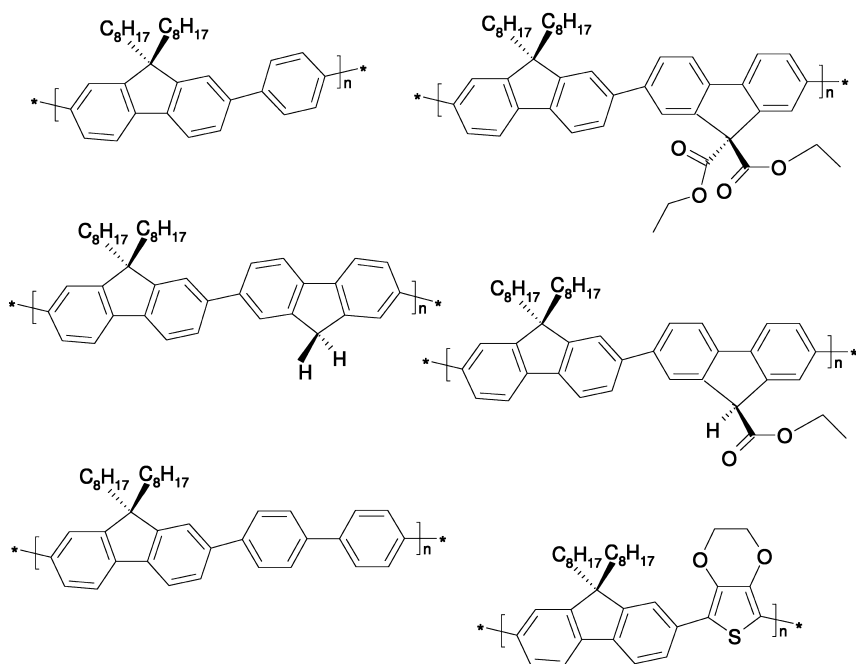


**Fig. 1.7** Fluorene-based copolymers readily accessible from Suzuki coupling.

A list of different copolymers readily accessible is reported in Fig. 1.7. The reader may refer to Refs. [63, 66] for more details.

As POFs are generally better electron transporters than hole transporters, recombination of charges in a LED prepared with these polymers often results in an unbalance of the charges, the negative charges being in excess. To improve the recombination yield, the hole transporter properties can be increased by inserting triphenylamine in the POF backbones [67], or similar compounds that are well known for their good hole-transport properties. This will result in a reduction of the ionization potential of the polymer so that hole injection from ITO is improved.

In Fig. 1.8, examples of these structures are reported: the insertion of the hole transporter unit may be performed in the backbone [68] and at the end of the backbone.

Ego et al. [69] introduced hole transporter molecules onto the monomeric unit; two triphenylamine units were inserted onto each fluorene following the procedure reported in Scheme 1.21.

The ionization potential (IP) of POF has been reported to be 5.8 eV: this value has to be compared with that of ITO (5 eV). For polymer **1** (Fig. 1.8) a value of IP
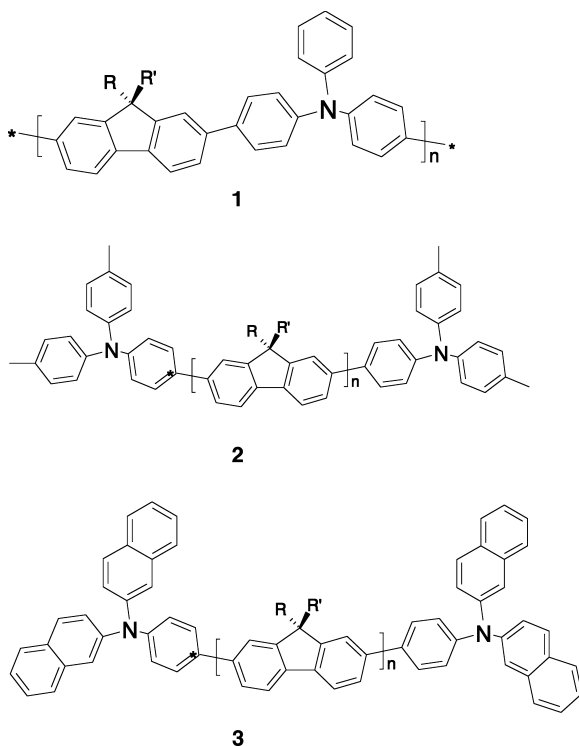


**Fig. 1.8** Polyfluorene containing electron transporter molecules in the main backbone (1) and as end groups (2, 3). R=alkyl chain.
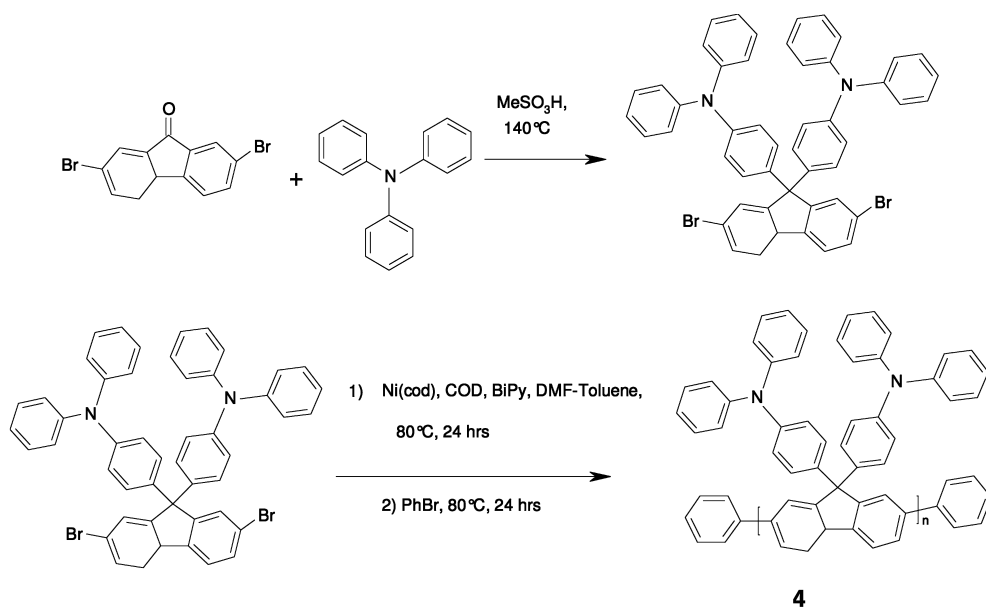
**Scheme 1.21** Insertion of triphenylamine on fluorene.

of ca. 5 eV has been found [68], while for the structure **4** of Scheme 1.21 a value of 5.34 eV has been reported. This is again a clear indication that tuning of the structure is a valid tool for improving the properties of conjugated polymers.

POFs are mainly used for their good emission properties, but they have also been found to be good materials exhibiting high mobility in the solid state. Moreover, they can be aligned into preferential orientation due to their liquid crystalline behavior. These properties have been used for fabrication of polarized LEDs [70] and of FETs exhibiting anisotropy in mobility [71].

It is worthwhile mentioning that, due to their molecular structure, POFs can be oriented by the cooling to room temperature of a thin POF film deposited onto an aligning layer, starting from the temperature where liquid crystalline behavior occurs for this polymer. Preoriented polyimide [72] or PPV [70, 71] films have been used as the aligning layer. Other conjugated systems such as PATs [73] and unsubstituted PPVs can be easily oriented by rubbing the surface of the film with a cloth. A detailed discussion on the orientation properties of conjugated systems is reported in Ref. [74].

In Fig. 1.9 an absorption spectra of a poly(3-decylthiophene) are shown after rubbing and annealing [75]. *R* indicates the dichroic ratios as calculated from the intensity of the absorption at a given wavelength. For this polymer, as in the case of other PATs, the dichroic ratio depends on the wavelength. This is related to the distribution of conjugation segments in the sample. Segments having higher conjugation lengths are better oriented with respect to those having shorter conjugation lengths [76].
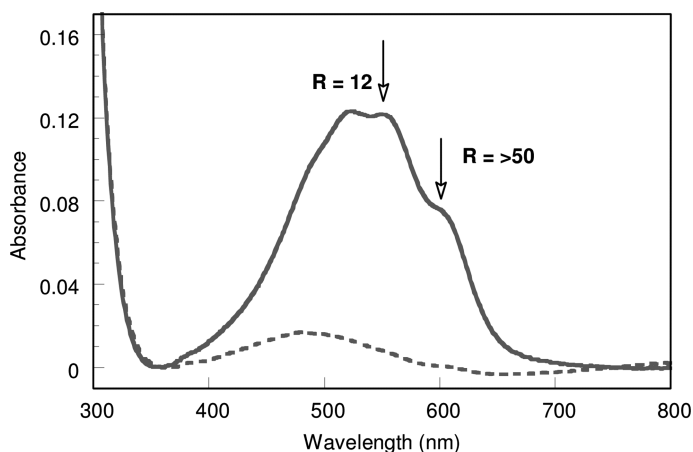
**Fig. 1.9** Absorption spectra in polarized light of a regioregular poly(3-decyl-thiophene). *Dotted line* Absorption with the polarization axis perpendicular to the rubbing direction, *full line* spectrum with the polarization axis parallel to the rubbing, *R* the dichroic ratio as calculated at the wavelengths evidenced by the *arrows*.

1.3.5
**The PPV Family**

Polyparaphenylenevinylene was one of the first polymers studied for its good PL and EL efficiencies. Several synthetic routes have been suggested for the preparation of this polymer. Insolubility is a strong drawback in preparation of high molecular weight materials. For example, step-growth polymerization, like Wittig condensation between terephthaldicarboxyaldehydes and arylene-bisphosphylidenes gives very low molecular weight polymers, because when the growing chain is formed by six–ten repeating units, it is insoluble and the chain growth ends. To overcome these difficulties a soluble form of a precursor was synthesized. A thin film of the precursor is formed by spin-coating or doctor-blade techniques [77]; a subsequent thermal treatment of the film leads to the insoluble conjugated thin film of PPV.

The Wessling method, consisting of the preparation of a sulfonium precursor polymer, was one of the first reported. In Scheme 1.22 the procedure followed to prepare PPV is reported according to Ref. [78].

Several modifications of this general procedure have been introduced, consisting of changing the conditions of the transformation process [79–81] and/or in the nature of the chemical species to be eliminated [82–84].

It is worthwhile noting that the introduction of alkyl or alkoxy groups on the phenyl ring allows the synthesis of soluble PPVs, which are necessary for the preparation of thin polymeric films by means of simple techniques such as spin-coating or casting. One of the most interesting PPVs synthesized through
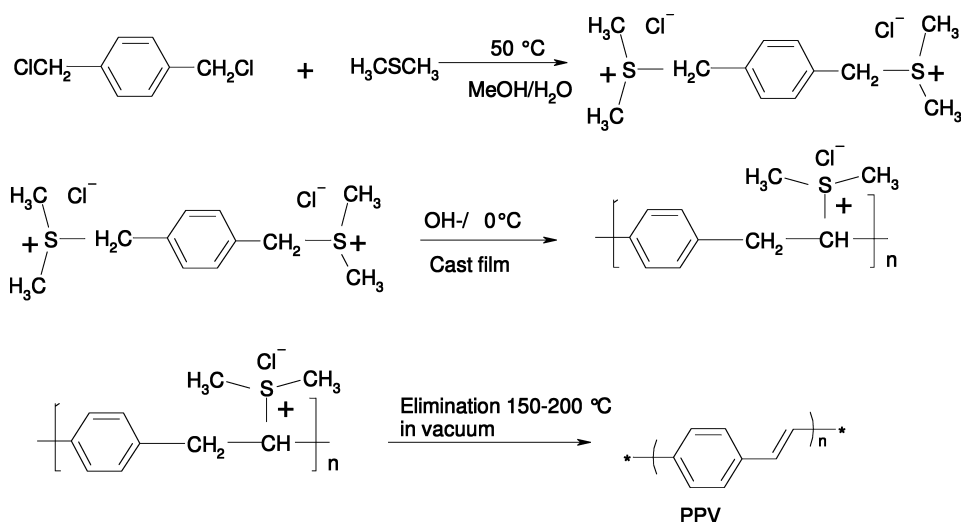
**Scheme 1.22** Preparation of polyphenylenevinylene (PPV) by means of Wessling method.

this method was the so-called MEH–PPV (poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene]) emitting in the red–orange region [85] with good efficiencies both in PL and EL. Its structure is reported in Fig. 1.10.

Another method for PPV preparation is the Gilch route [86]: this consists of the polymerization of dichloro-*p*-xylene with potassium *tert*-butoxide in organic solvents as briefly described in Scheme 1.23.



**Scheme 1.23** Gilch route to PPV.

As in the case of the Wessling route, with this procedure the introduction of side groups on the phenyl ring leads to the formation of soluble polymers.

The Gilch route was also used to synthesize soluble PPVs such as MEH–PPV (Scheme 1.24) [87].
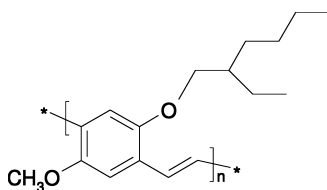


**Fig. 1.10** MEH–polyphenylenevinylene (PPV) structure.

**Scheme 1.24** Gilch route to MEH–PPV: 2-ethylhexyl bromide, KOH, EtOH (*a*), HCHO, conc. HCl, dioxane, 20 °C (*b*), KO*t*Bu, THF, 20 °C (*c*).

The PPVs prepared by means of the Wessling or the Gilch routes contain some defects due to an incomplete deprotection result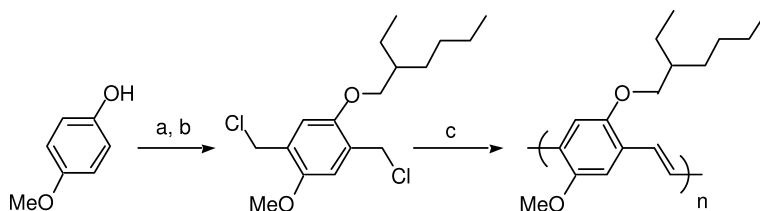ing in a reduction in the conjugation length. This fact, together with the randomness of the regiochemical insertion of the phenyl monomer during polymerization, strongly affects the solid-state properties of the polymers, and hence their electrooptical properties. These polymers are mainly amorphous in the solid state, this fact being responsible for reduced interactions in the solid state, a factor improving the quantum efficiency of PL. Son et al. [88] found that the introduction of cis double bonds in a PPV, which is formed by trans double bonds, interrupting the conjugation and disturbing the polymer chain packing, resulted in the formation of an almost amorphous PPV.

Other synthetic approaches to preparation of PPV, the Heck coupling polymerization, and the Horner-Wittig reaction are reported in Scheme 1.25.

The drawbacks of these reactions are related to the impurities of the catalyst remaining in the polymer. For the Heck reaction [89], stilbene instead of ethene can be used. The polymer obtained by means of the Horner-Wittig [90] reaction reported in Scheme 1.25 has a **n** character, i.e. the polymer better supports negative charges.
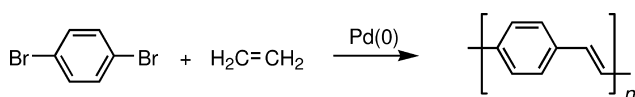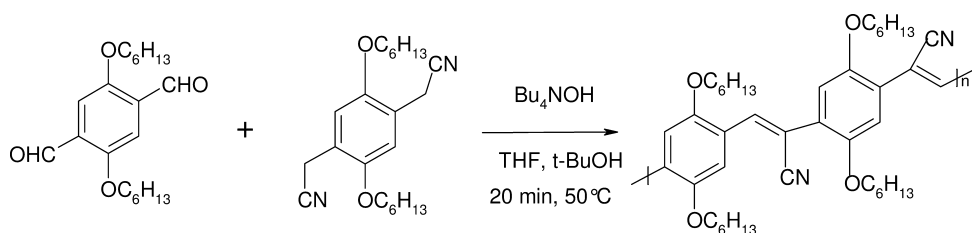


Heck coupling
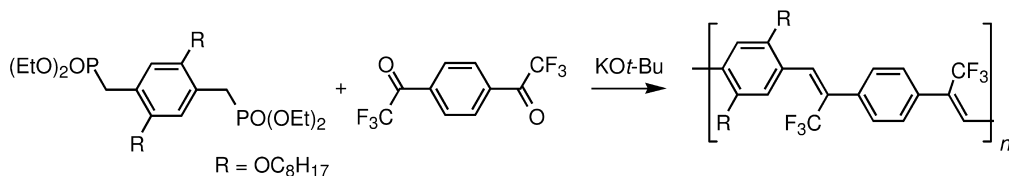


Wittig Horner reaction

**Scheme 1.25** Hecke and Wittig Horner polymerizations for PPV.

**Scheme 1.26** CN–PPV synthesis.

As previously reported for other conjugated polymeric structures, the tailoring of the properties is also achieved by an appropriate choice of substituents: alkoxy groups on the phenyl ring reduce the band gap, with a shift in the emission from green to red.

As an example of a fine-tuning of the electrooptical properties by the proper choice of substituents, we compare the properties of two different PPVs.

Scheme 1.26 reports the synthesis of a soluble PPV bearing cyano groups on the double bonds [91]. The withdrawing effect of –CN groups influences the electronic system so that this polymer, when used as active layer in a LED, gives the same external efficiency both with calcium and aluminum as cathode.

This is the result of the modification of both the band gap and the electronic affinity (EA).

This last parameter is extremely important because the injection of the charges from the cathode is governed by the difference between the work function of the metal and the EA of the polymer. The introduction of the –CN group has an effect in increasing the EA so that the value of work function of the two metals (3 eV and 4.4 eV for Ca and Al respectively) allows the injection of the same number of charges. MEH–PPV LEDs have an external efficiency strongly dependent on the metal cathode; with aluminum the efficiency is 0.02% while the corresponding LED prepared with Ca has an efficiency an order of magnitude higher. CN–PPV exhibits efficiency 0.2% with both metals. Introduction of –CN induces also a red shift of the emission with respect to MEH–PPV.

As PPV is a good hole transporter, the injection of electrons from the cathode in a LED is always more difficult. With the aim of improving negative charge injection, an electron transporter layer can be introduced between the cathode and the electroluminescent polymer. 2-(4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) is a good molecule for this purpose and it can be vacuum-evaporated on top of the electroluminescent layer or blended with it. These approaches have some limitations due to the recrystallization phenomena and aggregate formation of a small molecule such as PBD. To overcome these drawbacks, PPVs having PBD as side chain substituents have been synthesized [92]. An example of these structures is reported in Fig. 1.11.

Other authors [93] have introduced the PBD molecules directly into the backbone of the PPV as shown in Scheme 1.27.
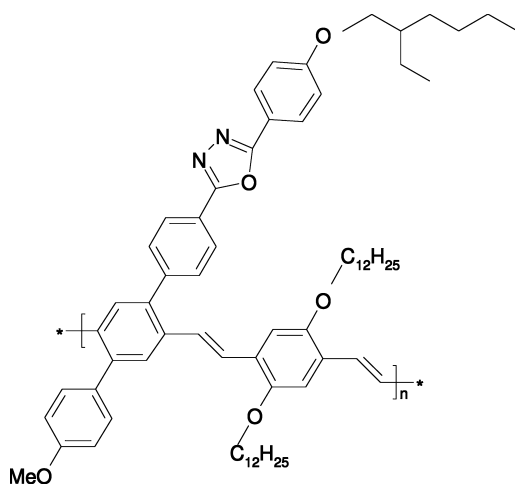
**Fig. 1.11** PPV containing 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) as electron transporter molecule.

A good procedure for improving the electron transport properties in a LED consists of the preparation of polymers containing the PBD unit as side group. The polymer obtained is then mixed with the electroluminescent polymer to form a blend. An example of such a polymer [94] is reported in Fig. 1.12 a.

Following this synthetic approach it has been shown that it is possible to prepare acrylic polymers having both an emitting molecule and the PBD as side chain groups (Fig. 1.12 b).



a)

b)
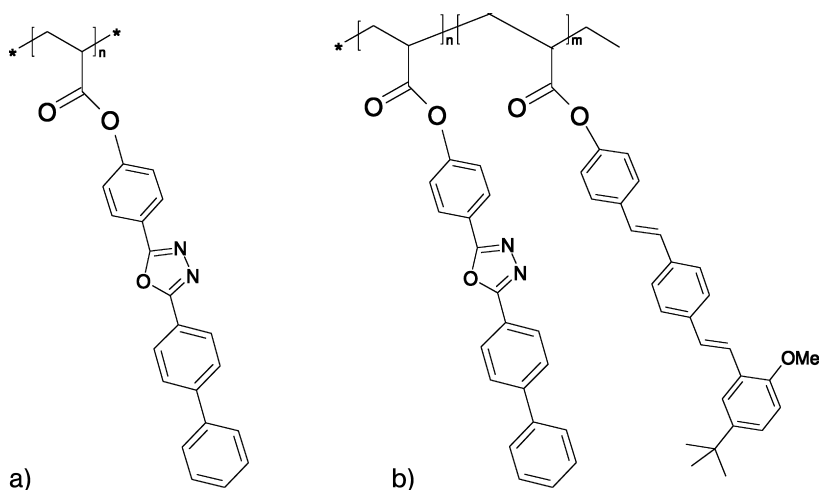
**Fig. 1.12** Polyacrylate containing PBD as side chain (a), and containing PBD and distyrilbenzene as emitting molecule (b).
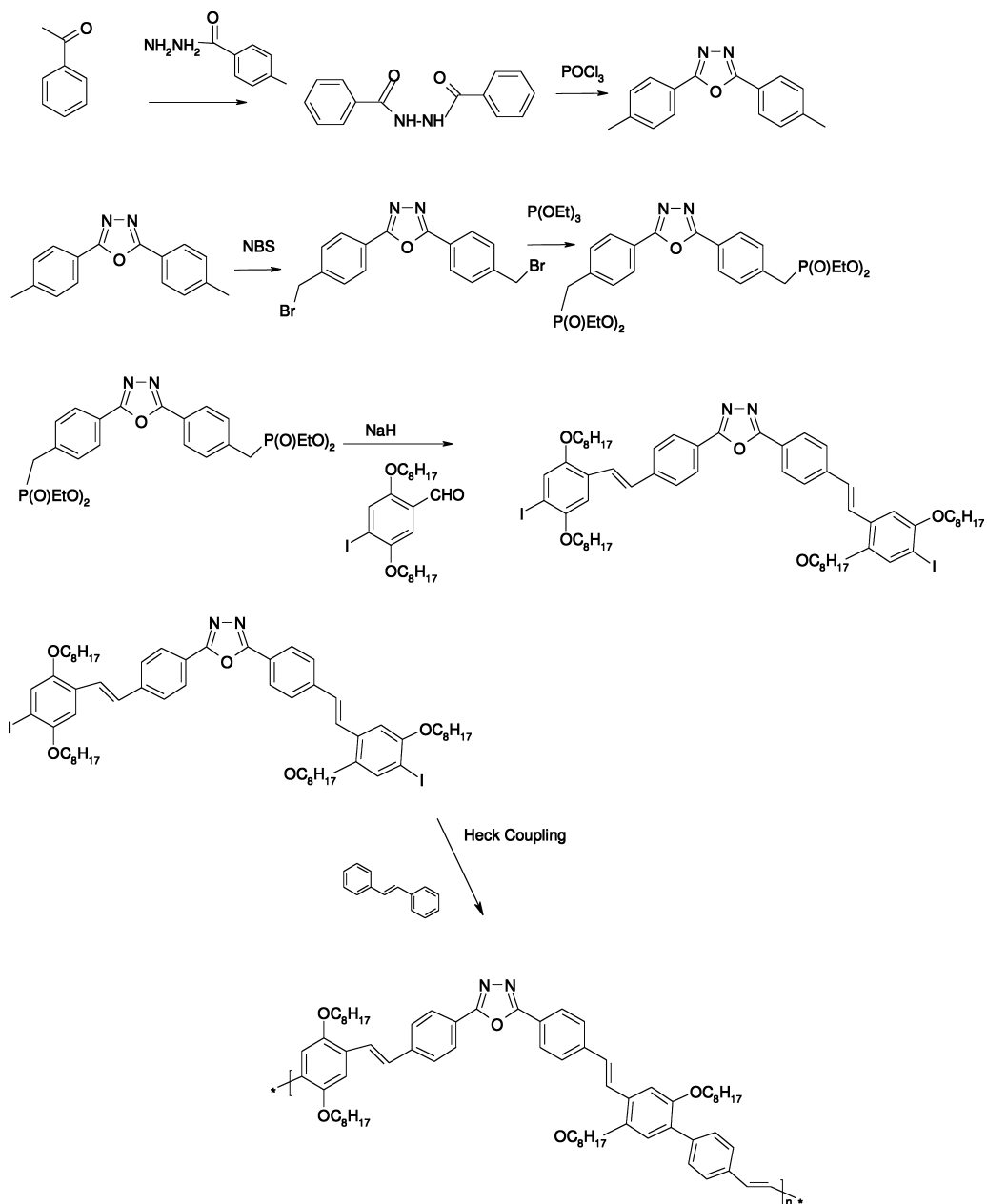
**Scheme 1.27** PPV containing 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-
1,3,4-oxadiazole (PBD) in the main chain.

## 1.3.6
## Poly(phenyleneethynylenes)

Soluble poly(phenyleneethynylenes) alkoxy- or alkyl-substituted were prepared and studied for their interesting electrooptical properties. Introducing triple bonds in the main chain shortens the effective conjugation length. The HOMO–LUMO energy gap is higher with respect to the corresponding PPV structures.

PL emissions in the 550–600 nm region were found [95] in polymeric structures having an average degree of polymerization between 23 and 28. Synthetic approaches mainly consist of the coupling between a 1,4-diethynyl-2,5-dialkyl-(or alkoxy-) substituted benzene and the desired 1,4-dialkyl-(dialkoxy-)substituted 2,5-diiodo-benzene, following Scheme 1.28.

The nature of the substituents can be varied over a large number of groups, including amino and carboxy groups [95].

Copolymers containing alkylthiophene units [96] having PL efficiencies of up to 38% in CHCl₃ solution at 460 nm have also been described (Fig. 1.13).

The synthetic procedure for the preparation of these polymers allows the production of a great number of structures exhibiting different properties, which
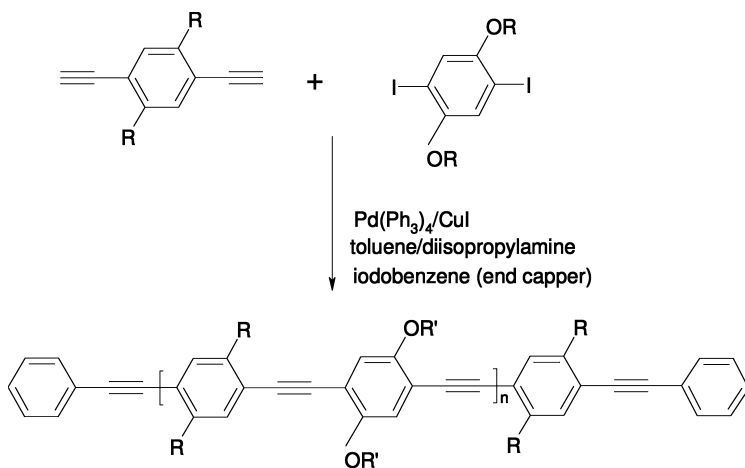


**Scheme 1.28** Pd-catalyzed coupling for preparation of poly(2,5-dialkoxy-*p*-phenylene-ethylene)s. *R* is an alkyl chain. The nature of the substituents can be varied.
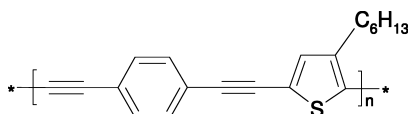


**Fig. 1.13** Alternated copolymers obtained from coupling between *p*-diethynyl-benzene and 2,5-diiodothiophene.
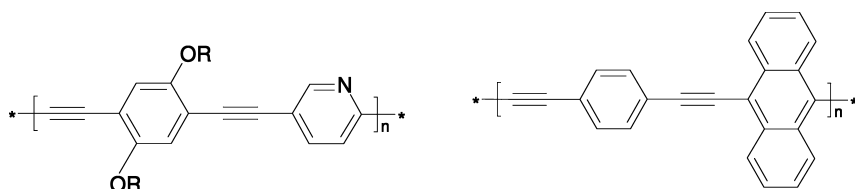
**Fig. 1.14** Conjugated systems containing triple bond in the main backbone.
R=alkyl chains.

can be easily obtained by proper molecular engineering [97]. Some of them are reported in Fig. 1.14.

These polymers were recently studied for their liquid crystalline behavior [98] and for their possible orientation to give polarized EL [99, 100].

### 1.3.7
### Copolymers for Triplet Emitters

One of the most widespread applications for conjugated polymers is the fabrication of LEDs. The greatest effort in this area, from the synthetic point of view, has been focused on the increase of the PL efficiency in the solid state, which is the bottleneck for obtaining LEDs with high efficiencies. External efficiencies up to 3–4% have been reached with polymeric materials used as active layers. In these devices the process of charge injection from the electrodes and recombination generates radiative singlet excitons with a theoretical [101] maximum in quantum efficiency of 25%. It is expected that the radiative decay from both singlet and triplet states should lead to a strong increase of efficiencies in LED. Recently it has been shown that very high efficiencies in LEDs can be obtained by using transition metal complexes as emissive phosphorescent species [102]. In these complexes, usually called triplet emitters, the intersystem crossing (decay from a singlet to a triplet state) is very efficient and a highly emissive state is generated with high triplet content. If these triplet emitters are incorporated in a device, the internal efficiency can be as high as 100% because they can collect both singlet and triplet excitons [103].

In order to assemble a phosphorescent polymer LED, a phosphorescent dye is added to a charge-transporting polymer matrix. The energy of the lowest lying triplet state of the polymer matrix must be higher than that of the phosphorescent emitter. Polyvinylcarbazole (PVK) is one of the suitable semiconducting polymers to be mixed with green emitter (iridium complexes) acting as triplet emitters, while PPV and POF are more suitable for red or yellow emitters. Matching between its triplet energy and that of the emitter can be reached by a proper tailoring of the PVK electronic structure by means of carbazole-based copolymers. This is a good example of how the precise chemical modification of a material can be used for fine-tuning its electronic properties.
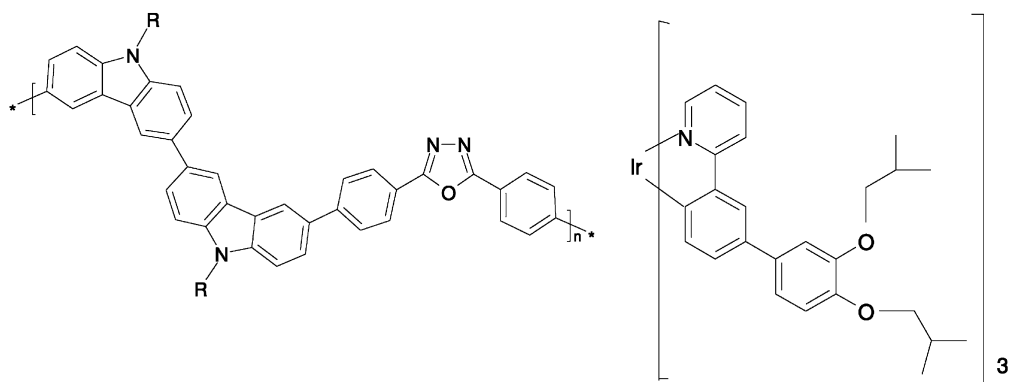
**Fig. 1.15** Polyvinylcarbazole (PVK) structure modified to be used with green emitters, whose structure is also reported.

The electronic modification of this polymer has to fulfill some requirements: besides the need to exhibit a triplet state higher than the incorporated phosphorescent dye, it must exhibit good charge injection from the electrodes. For this reason, in Ref. [103] some copolymers of carbazole and oxadiazole were prepared and tested in order to optimize both triplet–triplet energy exchange and charge injection from the electrodes. An example of one of these structures is reported in Fig. 1.15 together with the structure of the green emitter studied in Ref. [103].

### 1.3.8
### Polyazines and Polyazomethines

Two important families of conjugated polymers exhibiting interesting optical and electronic properties are those of polyazines (PAZs) and polyazomethines (PAMs), both belonging to the general class of Schiff base polymers [104–106]. They are characterized by the presence of HC=N linkages, which are isoelectronic with the HC=CH groups present in many prototypical conjugated polymers such as PA and PPV [107, 108].

Polyazine is formally isoelectronic with PA, but, unlike PA, is very stable in air [109]. Conjugated PAZs contain direct N–N bonds because they derive from acid-catalyzed condensations of hydrazine with aromatic dialdehydes or diketones (see Scheme 1.29). They can be doped with iodine to give air-stable, electrically conducting materials with room temperature conductivity as high as 1.3 S cm$^{-1}$.

On the other hand, PAMs are the product of condensation of aromatic dialdehydes with aromatic diamines (Scheme 1.29). The first PAMs were prepared by Adams and coworkers from terephthalaldehyde and benzidine and dianisidine in 1923 [110]. The basic aromatic conjugated PAM is the structure of poly(1,4-phenylene-methylidenenitrilo-1,4-phenylenenitrilomethylidene) (PPI), reported in Fig. 1.16 which is isoelectronic with PPV. Unlike PPV, the imine nitrogen of the PPI backbone introduces additional useful features and chemical flexibility,
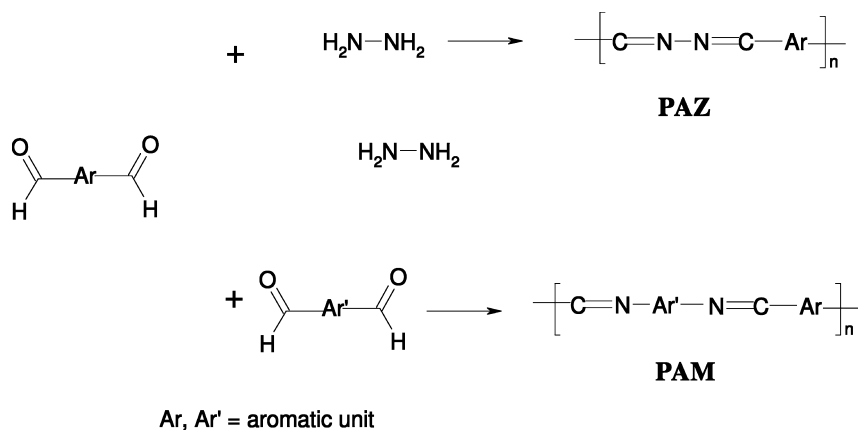
**Scheme 1.29** Synthetic pathways to obtain conjugated polyazines (PAZs) and polyazomethines (PAMs).
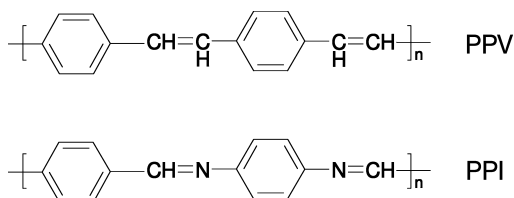


**Fig. 1.16** Poly(1,4-phenylene-methylidynenitrilo-1,4-phenylenenitrilomethylidene) PPI isoelectronic with PPV.

including high solubility in concentrated sulfuric acid and complexation with Lewis acids [111, 112]. Conjugated PAMs, containing only phenylenic moieties, have been synthesized even in vacuum by using chemical vapor deposition and tested as active layer or hole-transport layer in electroluminescent devices [113, 114].

Lateral alkyl chains should be present in order to overcome the drawback of insolubility in organic solvents, which limited the early investigations on these systems.

Soluble PAMs and PAZs containing different aromatic hydrocarbon moieties in the backbone and various side group substituents have been prepared and used to investigate the effects of the molecular structure on the electronic and optical properties of conjugated polymers [115–117]. In particular Destri et al. synthesized soluble PAMs and PAZs containing thiophene rings used for the preparation of optical waveguides; the peak values of the third-order susceptibility are about $10^{-10}$ to $10^{-11}$ e.s.u. [118, 119].

Novel poly-Schiff bases containing 4,4′-diamino-triphenylamine as hole-transport material for organic electronic devices were synthesized by Niu and the

mobility of polymer film was also measured to be $1.68 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ by means of the time-of-flight (TOF) technique [120].

## 1.4
## Block Copolymers

Many methods have been proposed for the preparation of smart materials able to perform many functions. This requirement, together with the need to operate at reduced size, has induced many researchers to look for systems that can be organized and controlled at the nanoscale level. Photolithography is a good tool for manipulating matter at the submicrometric scale, but the need for smaller feature size and simpler methods based on self-organization of matter are forcing material scientists to explore new fields of planning and building materials.

In this race, research on block copolymers (BCs) offers a new chance to contribute to an expanding area that is extremely interesting both for fundamental research and technological activity.
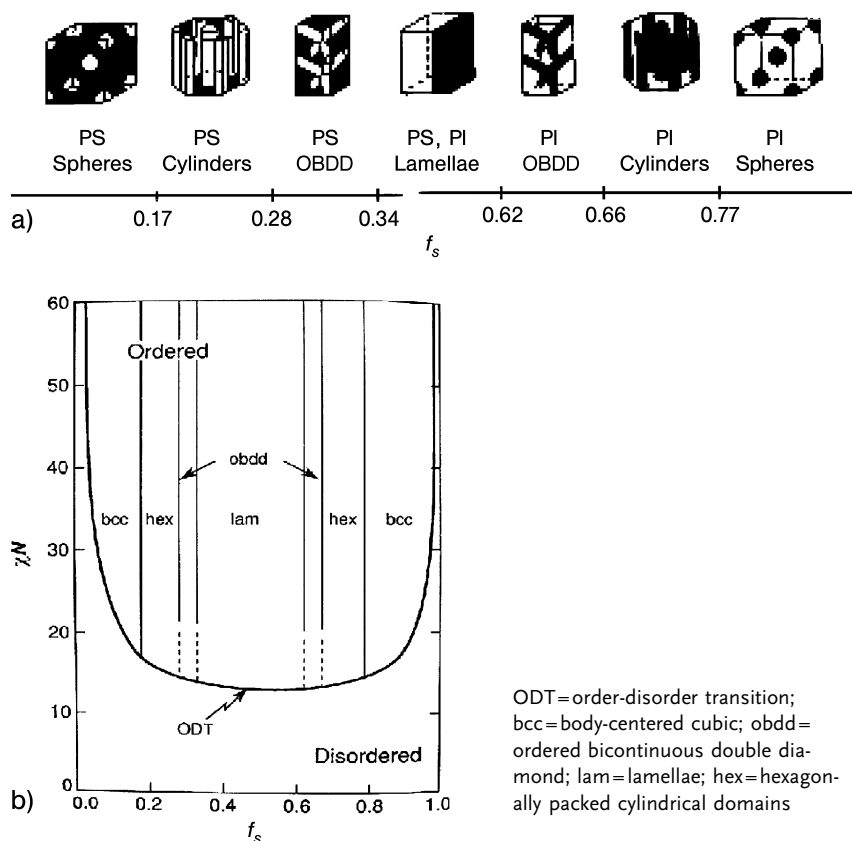
From the chemical point of view a BC may be considered as two or more different chemically linked species. In most cases, as they are incompatible, the thermodynamics associated with the behavior of the constituting block is the driving force for the nanophase separation occurring in the solid state: the unfavorable mixing enthalpy and the small mixing entropy drive the assembling process. Macrophase separation is not present because the covalent bond connecting the two blocks prevents it. The incompatibility arises from the difference between the constituting blocks, which can be hydrophobic/hydrophilic, soft/hard, semiconducting/insulator.

The behavior of coil–coil diblock copolymers is relatively well understood [121] and depends on the following factors:

- the sum of the degree of polymerization $N$ of the blocks (in the case of a diblock of monomer A and monomer B it is $N=N_A+N_B$);
- the Flory-Huggins $\chi$ parameter, which represents a measure of the incompatibility of the two blocks;
- the volume fraction of the constituting blocks ($f_A$ and $f_B$ with $f_A=1-f_B$).

The segregation product $N\chi$ determines the microphase separation degree. In most of the cases $N>50$ and in this condition the morphology of the separated nanophases changes with a variation of the volume fraction of the blocks. The possible morphologies in polystyrene–polyisoprene BCs at different volume fractions of polystyrene (PS) are reported in Fig. 1.17a. In Fig. 1.17b the phase diagram shows phase behavior of the same diblock copolymer.

If a block of a coil–coil diblock copolymer is replaced by a stiff macromolecule, like a conjugated polymer, the $\chi$ parameter increases [19]. A general theoretical approach to the phase behavior of rod–coil diblock copolymer is not yet available because the system is more complicated. One of the competing factors influencing the phase separation is the aggregation of rigid segments to give

a)



b)

ODT=order-disorder transition; bcc=body-centered cubic; obdd= ordered bicontinuous double diamond; lam=lamellae; hex=hexagonally packed cylindrical domains

**Fig. 1.17** (a) Ordered nanophase separation in polystyrene (PS–PI) diblock copolymers. (b) Phase diagram of PS–PI block copolymer. (Reprinted with permission from AAAS [121]).

crystalline or liquid–crystalline domains. The regular pattern which can be reached by playing with the compositional ratio of the blocks and their chemical characteristic can be used as a template to form a patterned surface, opening new perspectives in the area of electronics with length scales that are difficult to obtain with conventional lithographic processes.

1.4.1
**Anionic Polymerization Processes**

One of the first parameters that a polymer chemist should control during a polymerization process is the molecular weight and its distribution: these parameters are very important because morphology control may be achieved through control of them.
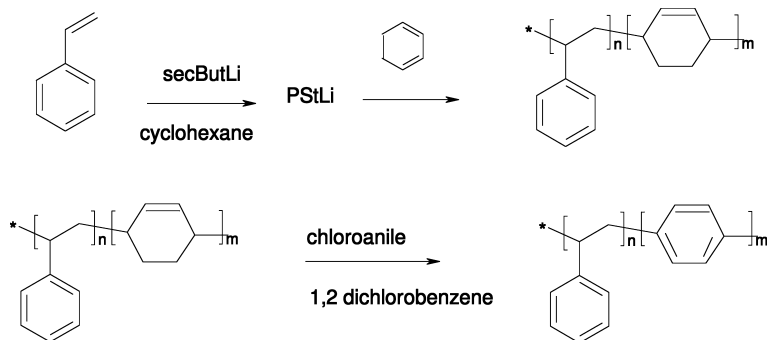
**Scheme 1.30** PS–PPP block copolymer.

"Living" polymerization processes guarantee a direct relationship between molecular masses and conversion, together with a very narrow distribution.

François et al. [122] prepared diblock copolymers, one block being a semiconducting polymer, polyparaphenylene (PPP), the second block being PS, by using anionic polymerization. He started the living anionic polymerization of styrene by *sec*-BuLi. When the styrene monomer was consumed, the second monomer, cyclohexadiene, was introduced and anionically polymerized according to Scheme 1.30.

The last step in Scheme 1.30 refers to the introduction of double bonds in cyclohexene. A similar procedure was followed by the same authors to prepare polymethylmethacrylate–polyparaphenylene (PMMA–PPP) copolymers [122].

### 1.4.2
### BCs from Tetramethylpiperidinoxyl-mediated Polymerization

Tetramethylpiperidinoxyl (TEMPO) is one of the most widespread initiators for living radical polymerization and can be conveniently used to form BCs.

For a TEMPO-mediated polymerization, the mechanism commonly accepted is reported in Scheme 1.31 as taken from Ref. [123].

In the example reported, initiator **1** is synthesized starting from benzoyl peroxide, styrene and TEMPO. Other authors reported the formation of initiators starting from *tert*-butyl peroxides [124] or other radical initiators [125]; however these TEMPO initiators are used to start the polymerization (in Scheme 1.31 with styrene) by heating at a temperature where dissociation of the initiator takes place. In fact, at high temperature dissociation takes place in an equilibrium process giving TEMPO and a radical **2**. In the presence of an excess of monomer, the radical **2** initiates a single growing polymer chain while the presence of TEMPO as counter radical suppresses the chain-ending reactions.

It has to be pointed out that after the polymerization process, the TEMPO molecule remains linked to the grown polymer. By heating at a temperature of
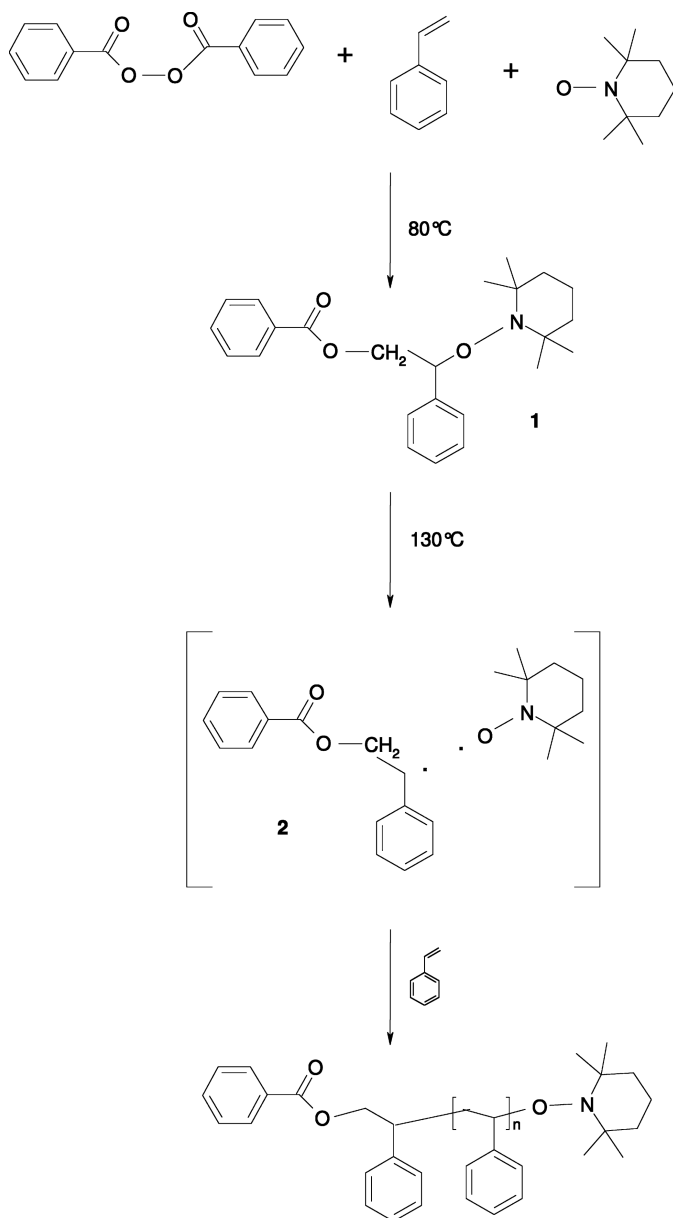
**Scheme 1.31** Polymerization of styrene by means of tetramethylpiperidinoxyl (TEMPO).
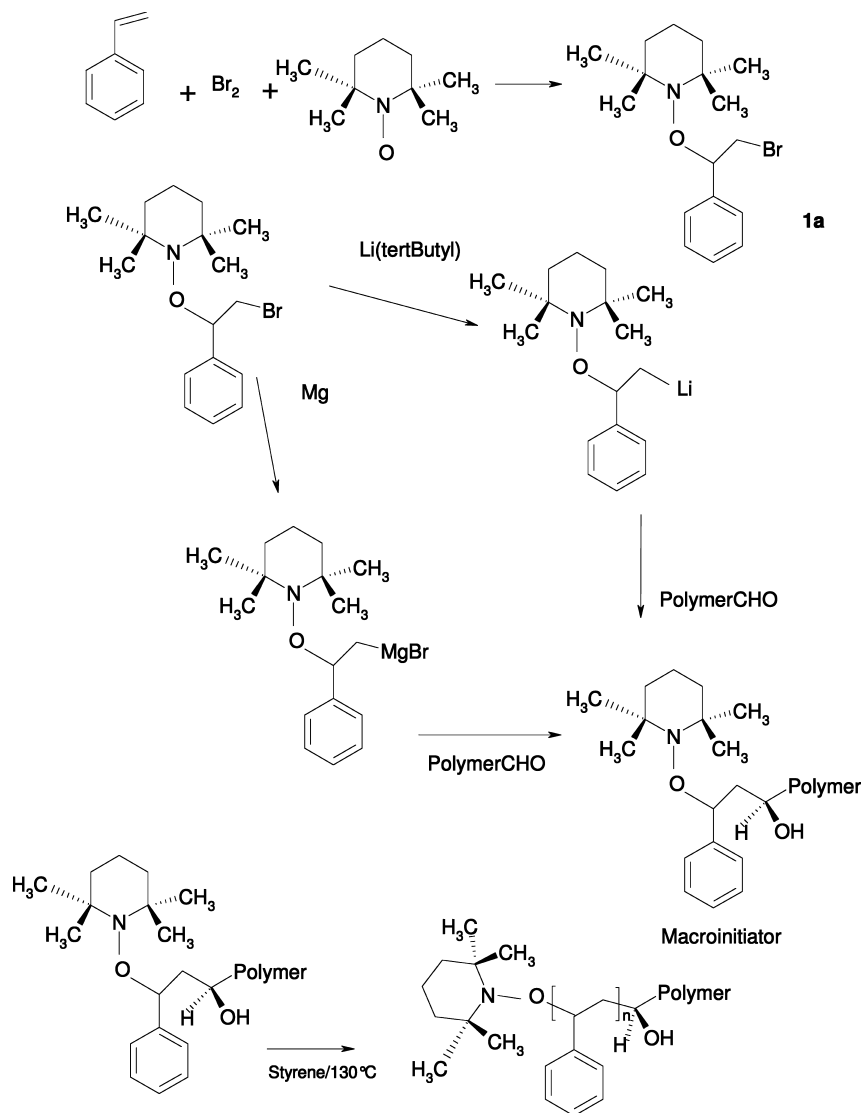
**Scheme 1.32** PS–PPV block copolymer.

125–130 °C in the presence of another monomeric unit (suitable to be polymer-ized by TEMPO) polymerization occurs and the molecular weight increases. This is the way to produce a BC.

The following example will show how TEMPO can be conveniently used to form copolymers between conjugated polymers and insulating polymers (Scheme 1.32).

The first step is the formation of a macroinitiator, i.e., linking between TEM-PO and a semiconducting polymer (PPV). Hadziioannou formed a macroinitiator starting from TEMPO-Br-styrene (1a) according to Ref. [126], as shown in Scheme 1.32.

The presence of bromine makes this compound suitable to react with Mg or Li (tert-But) giving the corresponding organometallic compound. This reactive species can react with carboxy-functionalized conjugated polymer PPV [126] (in Scheme 1.32 it is indicated PolymerCHO). This is a very clear example of a synthetic approach to a multifunctional material which arises from accurate planning of the macromolecule:

- A synthetic approach has been chosen in order to have a control of the PPV block.
- The PPV block has been functionalized.
- The PPV block has been transformed into a macroinitiator.
- The polymerization of styrene occurs from the PPV block by means of a living radical polymerization which allows the control of the molecular weights.

The scheme reported is suitable for the preparation of many different copolymeric systems by means of TEMPO-mediated polymerization.

As we have mentioned above, the key step of this procedure is the preparation of a macroinitiator, containing TEMPO, which allows the starting of the polymerization of a block directly from an already prepared block. This requires a modification of the starting TEMPO molecule, which has to react with an end group of a macromolecule already formed.

There are different synthetic procedures in the literature following the same strategy; they mainly differ in the kind of nitrosyl used to start the polymerization. In fact, TEMPO mainly polymerizes styrene-based systems, but not other monomers such as acrylates [127]. A number of alkoxyamines suitable for living free radical polymerization have been investigated. With a procedure similar to the one reported in Scheme 1.32, Stalmach et al. have shown that 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) (Fig. 1.18) can be conveniently used to synthesize BCs between a soluble PPV derivative and *n*-butylacrylate [128].
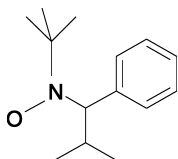


**Fig. 1.18** TIPNO living radical initiator.

The key step in these synthetic procedures is the linking between the nitrosyl compound and an already preformed conjugated polymer. This is a necessary step because conjugated polymers cannot be obtained by means of nitroxide-mediated polymerization.

### 1.4.3
### BCs from Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a radical polymerization which allows, as in the case of the nitroxide-mediated polymerization, control of the molecular masses and of their distribution. The mechanism is different with respect to the process described in the previous paragraph, because a metal is necessary. With this procedure a great variety of vinyl monomers can be easily polymerized and the control of the polymerization reaction is mediated by the atom transfer equilibrium shown in Scheme 1.33.

$$RnX + Mt^z L_m Y \quad \xrightarrow{k_{act}} \quad Rn \bullet + XMt^{z+1} L_m Y$$

$$k_{deact}$$

$$+ \; M \qquad k_t$$

$$k_p$$
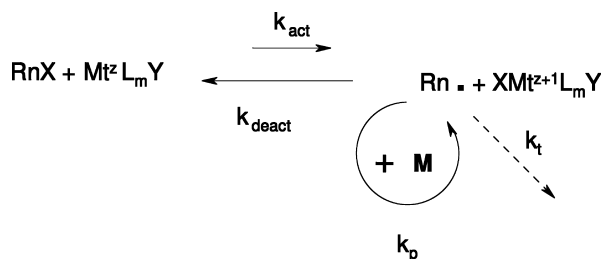
**Scheme 1.33** Mechanism for an atom transfer radical polymerization (ATRP).

The metal complex $Mt^z L_m Y$ cleaves the Rn–X bond (X is a halogen) homolytically and reversibly with the rate constant $k_p$. In the subsequent step, the generated Rn radical adds to a monomer M with a rate depending on $k_p$ before its deactivation with a rate constant $k_{deact}$ to give the dormant species RnX by reaction with the oxidized metal complex ($Mt^{z+1} L_m Y$). The repetition of these cycles leads to well-defined polymers with high molecular weights and narrow distribution; as the concentration of radicals is low, the termination process can be neglected [129].

Lui et al. used ATRP to prepare BCs between poly(3-alkylthiophenes) (PATs) and PMMA or PS [130]. ATRP allows the polymerization of both styrene and methylmethacrylate.

The procedure used is similar to the one described for TEMPO-mediated polymerization. In this case the conjugated polymer also has to be functionalized with the ATRP initiator. The addition of a new monomeric unit allows the polymerization to start directly from the already prepared block.

In Scheme 1.34, the procedure followed by McCullough is reported. Diblock and triblock copolymers were synthesized and characterized and diblock copolymers formed by poly(3-hexylthiophene) and polyurethane were also prepared. The distribution of molecular weight is narrow ($M_w/M_n = 1.2–1.6$) and the morphology of the films obtained from these copolymers is fibrillar. Depending on the ratio between the semiconducting block and the insulating one, conductivity of the film upon doping was observed.
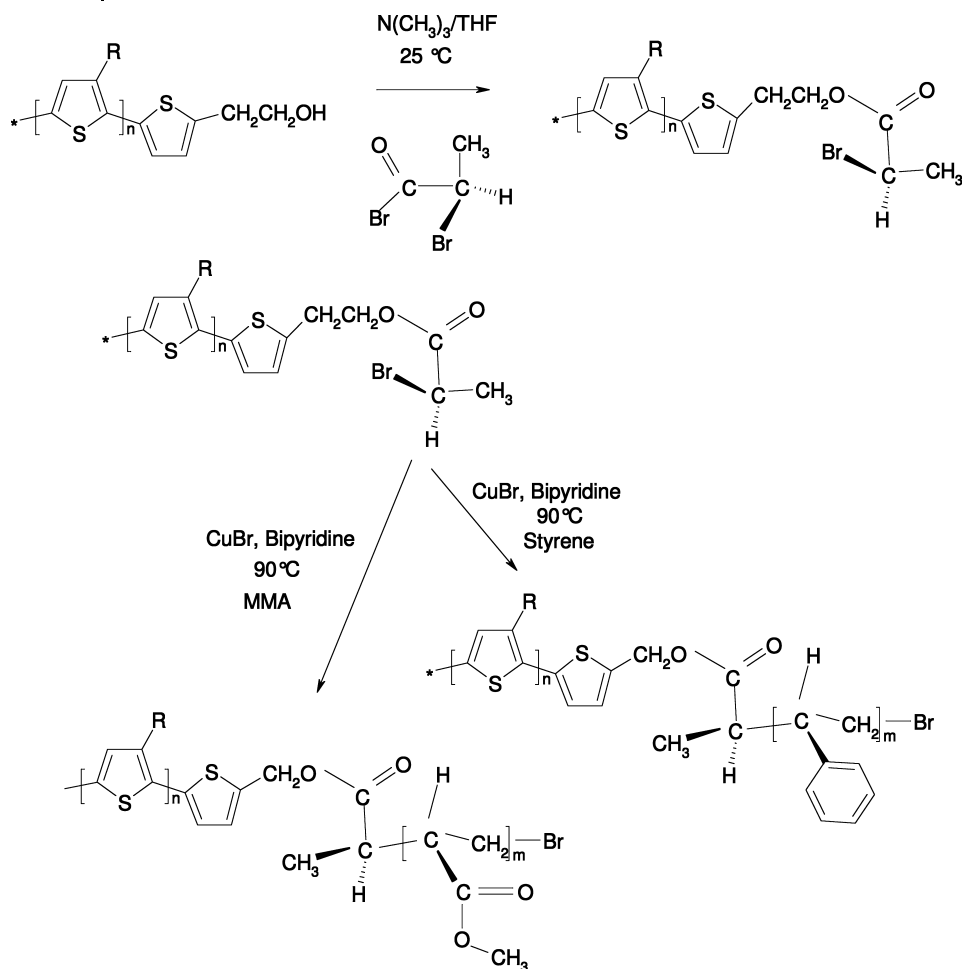
**Scheme 1.34** McCullough approach for PAT–polymethylmethacrylate (PMMA) and PAT–PS diblock copolymer synthesis.

### 1.4.4
### BCs from Polyfluorenes

BCs of POF and poly(ethyleneoxide) (PEO) have been reported by Marsitsky et al. [131]; the procedure is reported in Scheme 1.35. The copolymer structure was evidenced by comparing the molecular weight as detected by gel permeation chromatography (GPC) before and after the reaction with ethylene oxide, and by $^1$H-NMR.

An approach consisting of the use of ATRP [132] has allowed preparation of a triblock copolymer according to Scheme 1.36, one block being POF and the other polyacrylate.
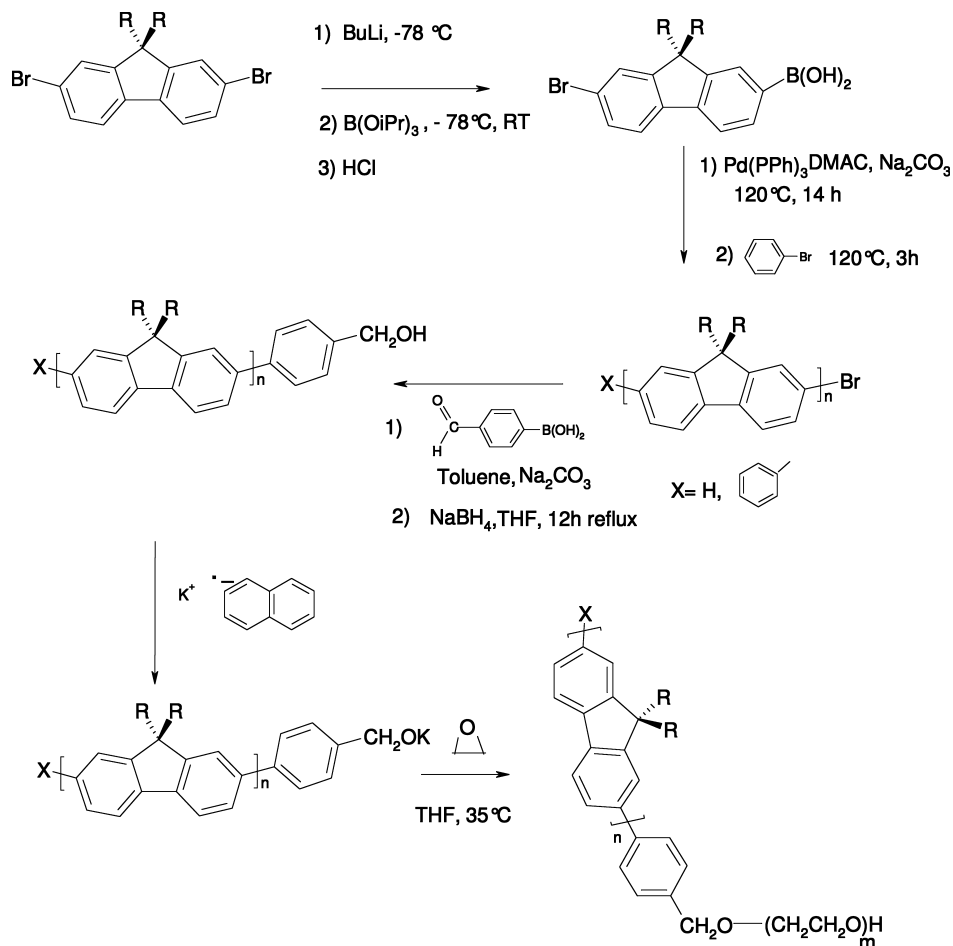
**Scheme 1.35** POF–(polyethyleneoxide) (PEO) diblock copolymers.
DMAC = N,N-dimethylacetamide.

The first-order kinetic plot was linear, and the molecular weights and their distribution (1.21 to 1.33) were controlled; it was concluded that the polymerization process for the growing of the two blocks has a living character.

If R is a $-(CH_2)_2N(CH_3)_2$ group, the further reaction of the triblock copolymer, as shown in Scheme 1.36, with $CH_3I$ allows the preparation of an ionic polymer with amphiphilic properties. The copolymer forms aggregates in water as the POF block is not soluble in water; a broad tail in the emission band of POF is observed in the PL spectrum in tetrahydrofuran (THF)/water suspension, together with a decrease in the PL quantum efficiency with respect to THF solutions (49% versus 83%).
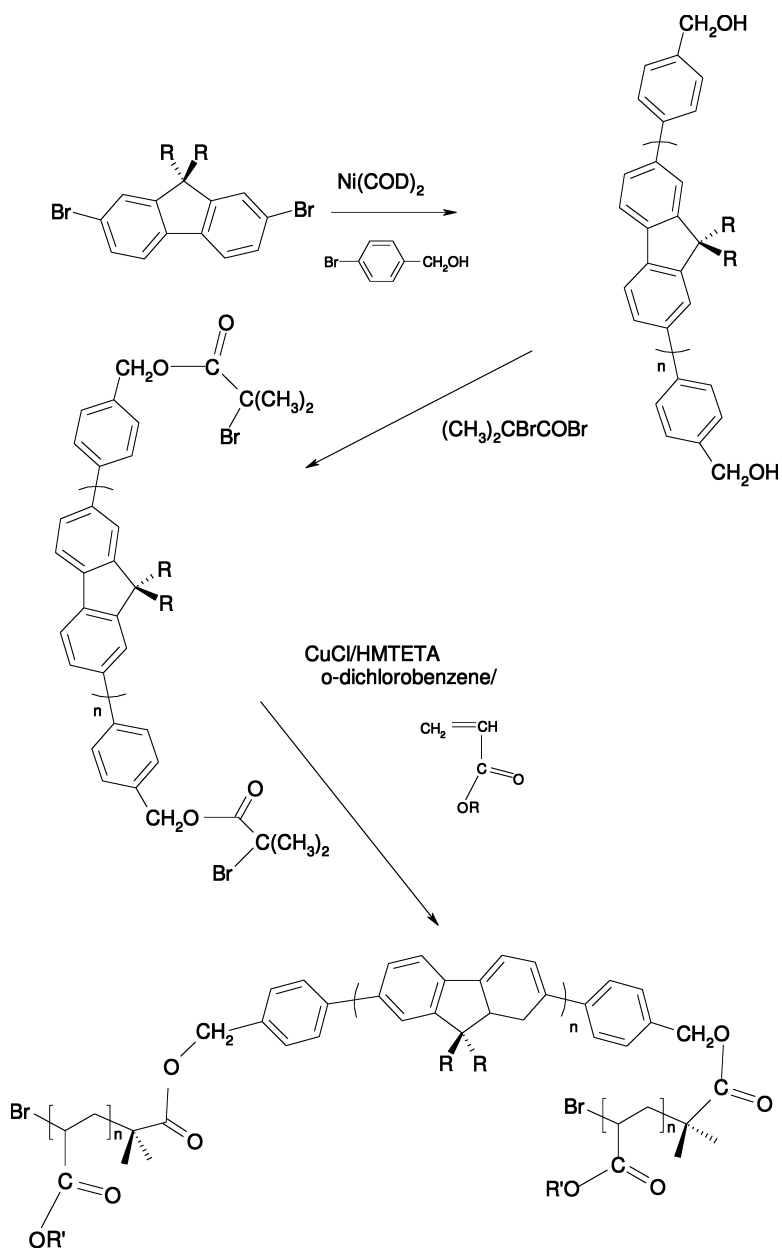
**Scheme 1.36** Triblock polymer polyacrylate (PAC)–POF–PAC.
HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine.
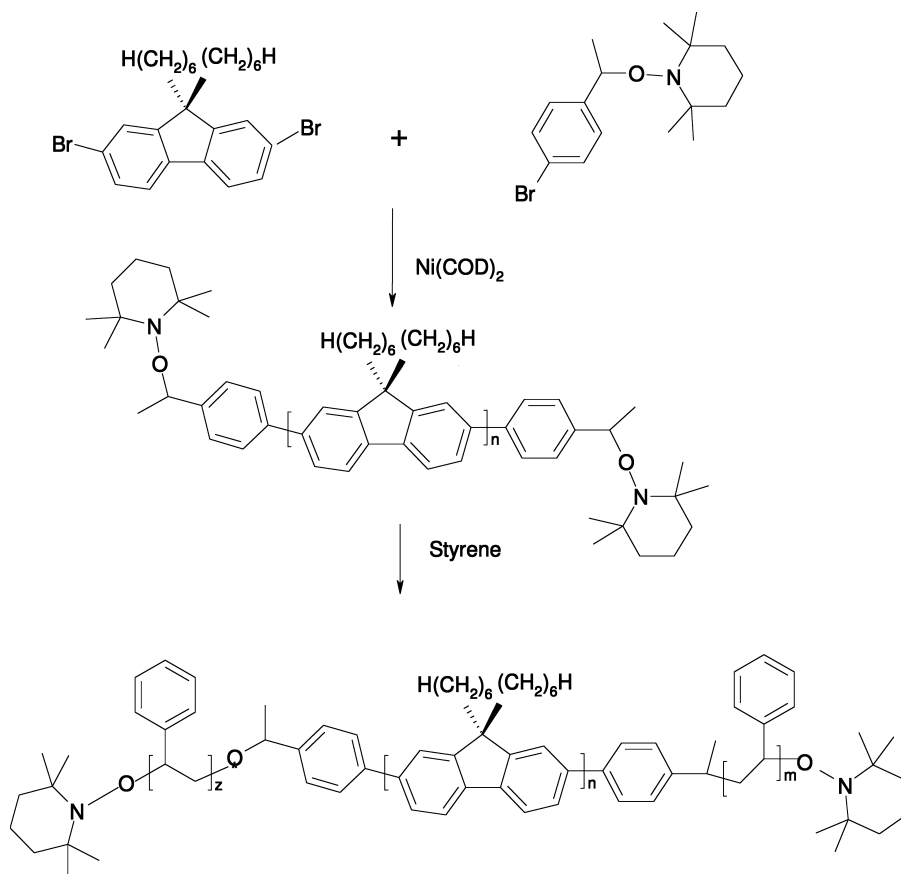
**Scheme 1.37** Triblock copolymer: PS–POF–PS.

By using the Yamamoto synthesis of POFs, Klaerner et al. [133] were able to prepare triblock copolymers with one block of POF linked to two blocks of PS (Scheme 1.37).

They used the TEMPO derivative shown in Fig. 1.19 as endcapper/initiator in the polymerization of fluorene monomers.
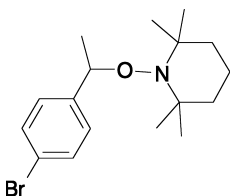


**Fig. 1.19** Tetramethylpiperidinoxyl (TEMPO)-modified initiator.

This molecule was added to the polymerization of 2,7-dibromo-9,9-dihexyl-fluorene in order to control the molecular weight and to introduce a living radical polymerization initiator. The overall procedure is described in Scheme 1.37.

The authors reported that the reaction can be performed in one step; they have also described the preparation of triblock copolymers by copolymerizing 2,7-dibromo-9,9-dihexylfluorene in the presence of an endcapper/initiator and $\varepsilon$-caprolactone and $Sn(Oct)_2$ as catalyst for $\varepsilon$-caprolactone polymerization.

### 1.4.5
### *p–n* Diblock Polymers

These structures are very interesting because a BC linking two different polymeric semiconductors, with a *p* and *n* character, is a good tool to control the morphology and also the interface between the *p* and *n* blocks. In most of the electrooptical applications an increase in the interface area between a *p* and *n* material is a valuable goal since the interface is the active area for charge recombination or separation.

An interesting approach for producing this kind of copolymer was recently introduced by Thelakkat et al. [134], who used the TEMPO-mediated polymerization procedure to prepare a *n–p* diblock copolymer.

The copolymer prepared is not formed by two conjugated blocks; two different vinyl monomers bearing a triphenylamine (hole conductor) and perylene-3,4:9,10-tetracarboxylic bisimide (electron transporter) respectively are polymerized by TEMPO macroinitiator according to Scheme 1.38. Polydispersities range from 1.22 to 1.97 and the increase in molecular weight with the conversion is linear thus indicating the living nature of the polymerization process.

The films obtained from these copolymers exhibited phase separation at the nanometer scale showing nanophase of bisimide in a matrix of poly(vinyltriphenylamine).

Boiteau et al. [135] prepared *p–n* diblock copolymers between 4-*tert*-butyl-4-(4′-vinylstyril)-*trans*-stilbene and 2-[4-(4′-vinylbiphenyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole by means of a TEMPO-mediated copolymerization. The main idea was to introduce into the same backbone a good electron transporter and a good emitter in order to improve the electron injection in a LED device. The structure of the polymer is reported in Fig. 1.20.

### 1.4.6
### Conjugated–Conjugated BCs

The possibility of having on the same macromolecules two conjugated blocks with different reduction and oxidation potentials is very attractive. For example, if a good nanophase separation occurs, a good charge separation may be obtained with an efficient transport of the charges to the electrodes.
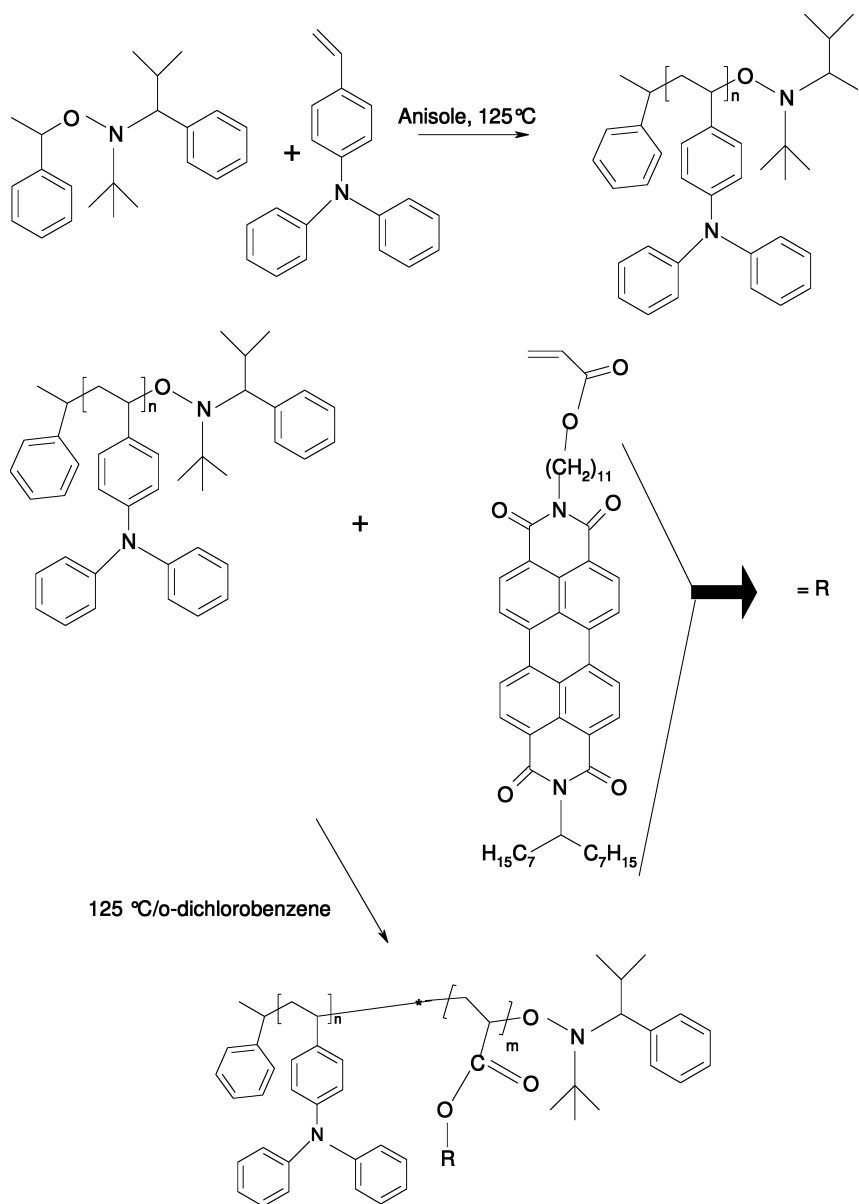
**Scheme 1.38** A *p–n* type block copolymer.
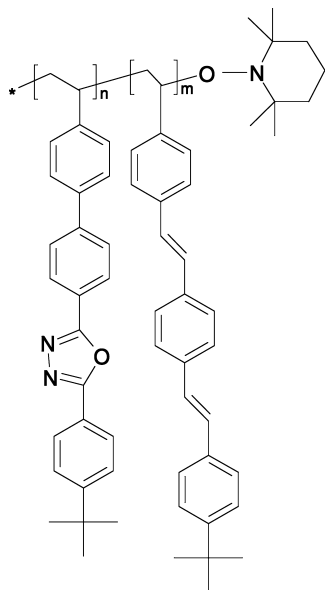
**Fig. 1.20** *p–n* Diblock copolymers between 4-*tert*-butyl-4-(4′-vinylstyril)-*trans*-stilbene and 2-[4-(4′-vinylbiphenyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole.

Up to now there are not many examples in this area that is very attractive. Schmitt et al. reported the synthesis and characterization of POF/polyaniline BCs [136]. The synthetic procedure followed is an example of how the formation of a copolymer may be reached by using completely different synthetic approaches for the preparation of the two blocks.

In fact, while POF is obtained through a Suzuki coupling, the polymerization of aniline follows an oxidative coupling by means of a $(NH_4)_2\ S_2O_8/H^+$ system. The synthetic procedure requires the preparation of the first POF block, its functionalization and the subsequent polymerization of aniline. In order to make the copolymer more soluble in common organic solvents, 2-undecylaniline was used because the resulting block is more soluble due to the side-chain solvating effect. Poly(2-undecylaniline) (PUNI), which is formed as undesired product, is soluble in polar solvents such as THF, but insoluble in toluene. So the unwanted PUNI produced during the second block formation can be removed by extracting the crude copolymer mixture with toluene: PUNI is not extracted and toluene dissolves only the copolymer.

In Scheme 1.39 the main steps of this synthetic procedure are outlined. The proof that the two blocks are covalently linked comes from a detailed GPC analysis by comparing the molecular weight of the POF block before and after the polymerization of 2-undecylaniline with both refractive index and UV-visible detectors. After thermal treatment, thin films of the copolymer showed a nanoscopically structured morphology with phase separation in the meso scale (100 nm).

**Scheme 1.39** POF–poly(2-undecylaniline) (PUNI) diblock copolymer.
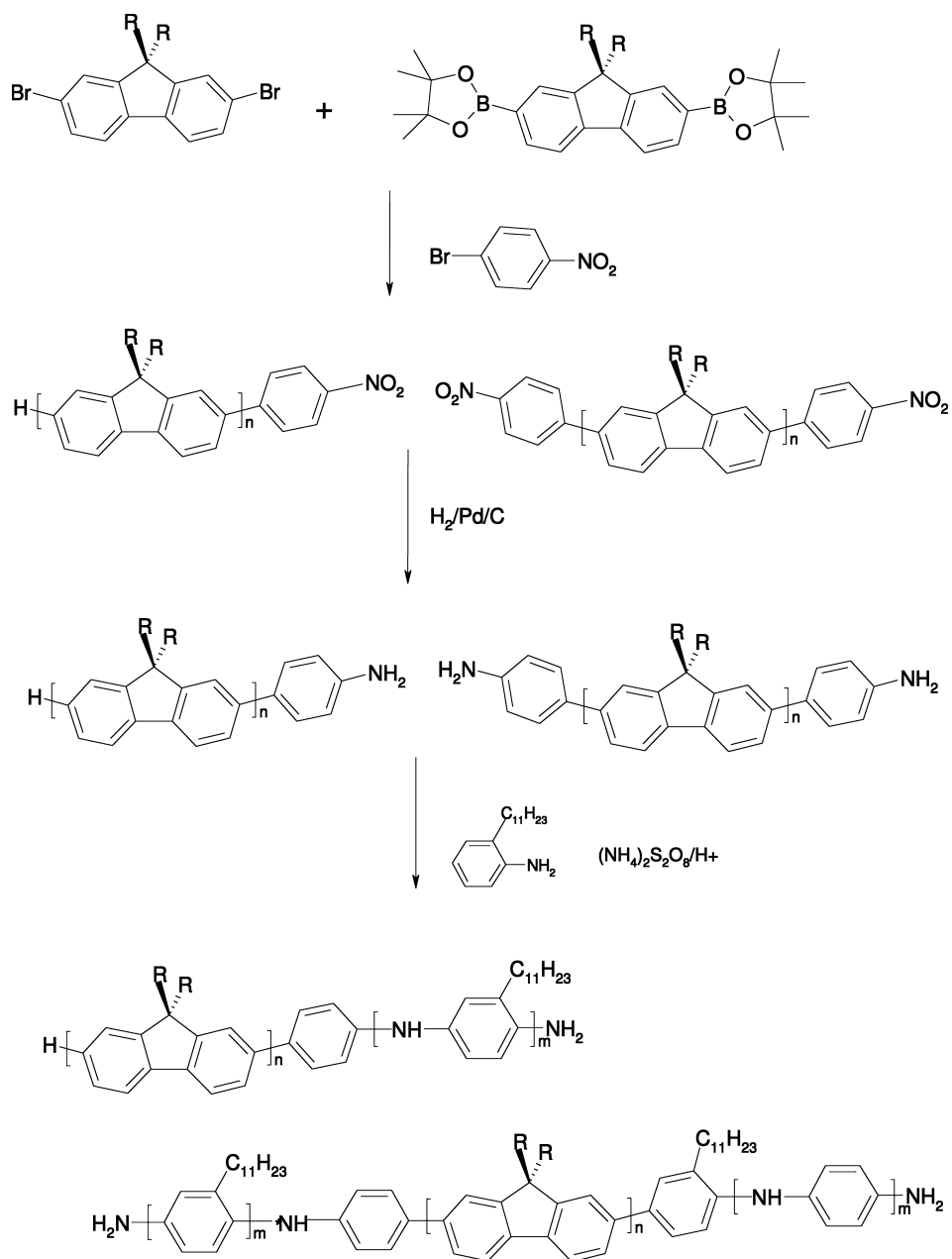
1.4.7
**The Oligomeric Approach**

The requirement of well-defined structures has induced many research groups to enter the field of high-purity materials, starting from oligomers that can be chemically decorated to reach a good solubility and processability. Sexithiophene has been found to be a promising material for FETs, but it is almost insoluble and high-vacuum procedures are necessary to deposit thin films suitable for application.

Kilbinger and Feast [137] developed a soluble kind of sexithiophene by connecting oligomers of thiophenes (from terthiophenes to sesquithiophenes) with flexible and soluble PEO chains of defined length. The structures prepared are reported in Scheme 1.40 together with the synthetic procedure followed. The co-polymer was used as active layer in a FET reaching a mobility of $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and an on/off ratio of about 1000.
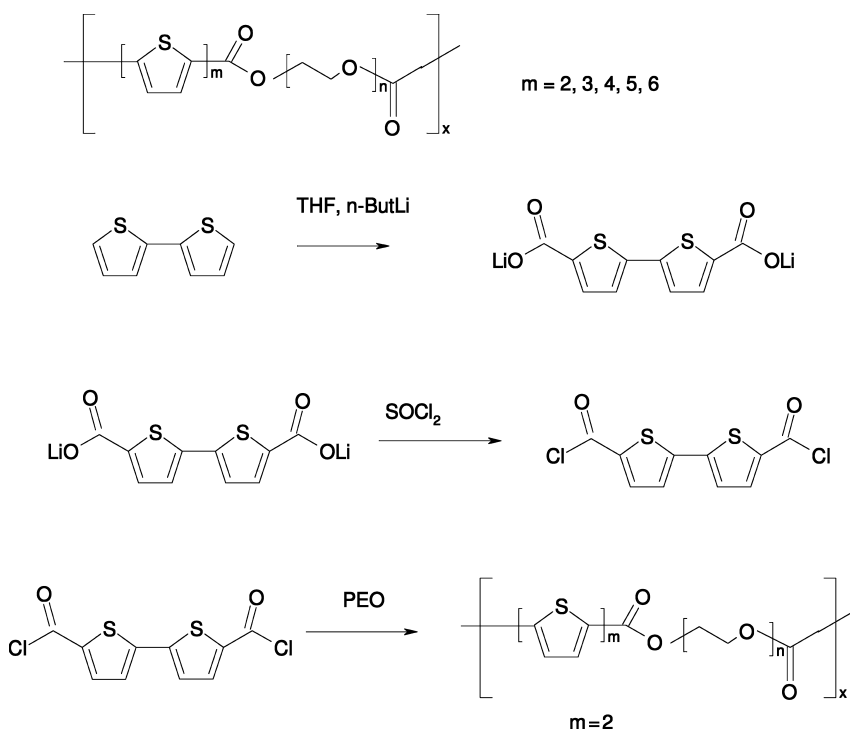


**Scheme 1.40** Sexithiophene–PEO diblock copolymer.

**1.5**
**Towards Autoorganized Devices**

The autoorganization of matter in view of the specific application is the object of many investigations. The great interest here is mainly due to the chance of obtaining an autoorganized material which does not have to be further organized by external techniques and is already suitable for use as active component of a device. As we have already mentioned in the previous paragraphs, the required organization of materials can only be reached through a proper planning of the molecules.

Polymers and copolymers are well known to give autoorganization under certain conditions that can be useful for technological applications.

Dewetting phenomena have been studied recently and have been shown to be very promising for obtaining patterned films of polystyrene with the help of an electric field. Schaffer et al. [138] produced, starting from a brominated PS (PSBr) film (45 nm thick) by means of electrostatic lithography, polymer stripes of 125 nm height and 140 nm wide (Fig. 1.21).
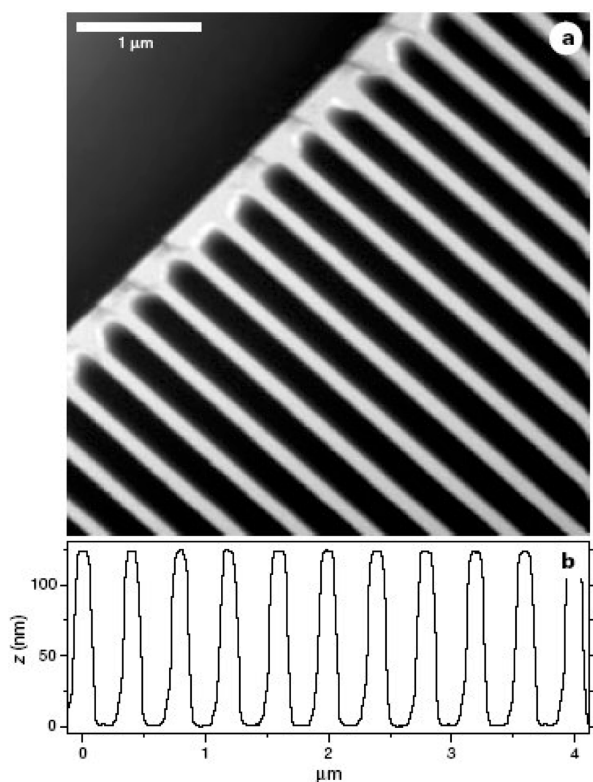


**Fig. 1.21** Stripes of PS on doped silicon substrate (see text) [138].
(Reproduced with permission by Nature Publishing Groups).

These stripes were obtained by heating the preformed polymeric film between two electrodes, one being a doped silicon substrate for the polymer film and the other a regularly patterned silicon substrate acting as a master which was maintained at 125 nm distance from the other electrode while 42 V was applied between the master and the substrate. This structure can be easily obtained and no particular or expensive apparatus is necessary to reach the goal; the patterned PSBr film can be used as a cheap mask for many purposes where submicrometric features are necessary. For this kind of structure, however, a master, which is previously prepared through lithographic processes, is necessary.

Obtaining completely self-organized systems without the use of a master would be a valuable improvement, contributing to further decrease the gap between organic materials and inorganic systems.

A great number of works has recently appeared in the literature on this subject; polymeric and copolymeric materials are very promising [139, 140].

As reported in the introduction, BCs are well known to give ordered morphologies due to a nanophase separation occurring between the two blocks. This characteristic, which was studied years ago in coil–coil BCs [19], has been found very promising in the case of BCs where a semiconducting block is linked to an insulating block [141].

Surin et al. [142] have studied in detail the structural behavior of diblock copolymers where a semiconducting block is linked to a flexible chain. It was possible to correlate the morphological structure, observed by AFM, with the structure of the macromolecules.

In a POF–PEO (i.e., $(F)_8$–$(EO)_8$) BC film (Fig. 1.22), the formation of fibrillar nanostructures with a typical width of a few nanometers and a length varying from 100 nm to several micrometers was observed by AFM.

By analyzing many fibrils they found that the width and height of the fibrils were almost constant, i.e., 11 nm and 1 nm respectively, suggesting a ribbon-like structure rather than a real fibril. They also evidenced that the fibrils are almost straight and parallel to each other (Fig. 1.23).

Molecular modeling calculations evidenced the tendency of dioctylfluorene oligomers to form $\pi$ stacks with an interplane distance of 5 Å. This observation, together with the value of 9.7 nm estimated for the polymer chain in its fully extended conformation, induced the authors to propose a model where the chain axis is parallel to the plane of the substrate and perpendicular to the axis of the fibrils.

It is assumed that the particular fibrillar morphology is due to the interactions between the facing conjugated backbones, whose planes tend to be per-
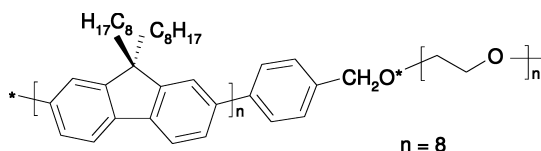


**Fig. 1.22** Polyfluorene (POF)–poly(ethyleneoxide) (PEO) diblock copolymers with short segments.

a)

b)

c)
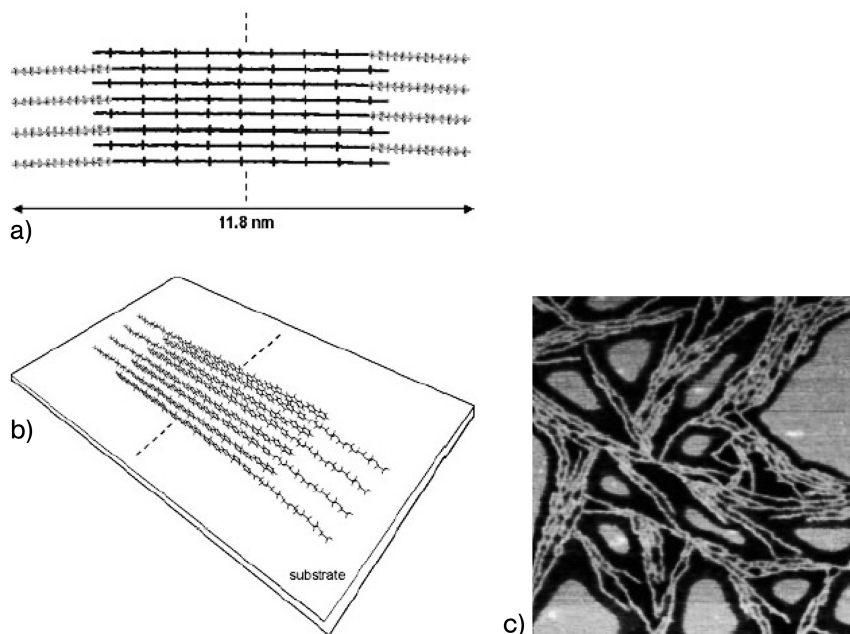
**Fig. 1.23** View of the stacking of copolymer polyfluorene–poly(ethyleneoxide) [(F)$_8$–(EO)$_8$] macromolecules to give nanoribbons. The conjugated chains form a $\pi$-stacking with the plane of the fluorene units almost perpendicular to the substrate. The PEO chains alternate on each side of the ribbons. (a) Top view; plane of the conjugated segments perpen- dicular to the view. POF block in *black*, PEO block in *grey*. (b) Perspective view; the alkyl chains on fluorene units are not represented. (c) Atomic force microscopy (AFM) image in tapping mode of fibrils of (F)$_8$–(EO)$_8$ on mica as obtained from tetrahydrofuran (THF) solution [142].

pendicular with respect to the substrate plane. Other BCs formed by a conjugated stiff macromolecule connected with flexible chain were found to give the same kind of morphological structure: poly(paraphenylenevinylene)–PS [143], poly(paraphenylenevinylene)–PEO [144].

Fibrillar morphology was also found in triblock copolymers with the following structure (EO)$_{45}$–(F)$_{20}$–(EO)$_{45}$ suggesting in this case also that the $\pi$ stacking is a driving force for the specific morphological situation.

By increasing the molecular weight of one of the blocks, as for copolymer (EO)$_{116}$–(F)$_{29}$–(EO)$_{116}$, atomic force microscopy (AFM) investigations showed no fibril formation for films prepared from both THF and toluene. Nonorganized aggregations are observed and the authors proposed that the driving force of the morphology formation was due to the assembly of the PEO overcoming the effect of the $\pi$ stacking.

These observations are evidence of morphological control by means of the structural parameters: when the amount of PEO block is relevant with respect to the conjugated system, it will be the driving force for nonordered aggrega-

tions, while if both PEO and POF have the same length, an ordered fibrillar morphology will be present.

The morphology was also found to change with the type of substrate used to deposit the film and with the solvent; rapidly evaporating solvents lead to less textured structures, while with a slow evaporation molecules are arranged in highly ordered structures.

The study performed on these materials shows very well that, with BCs, tuning of the nanostructures can be easily achieved. The control of the above-mentioned parameters might lead to the choice of application for this material. For example, nanoribbons formed by overlapped $\pi$ backbones can be directly obtained as a bridge connecting the source and drain of a FET thus providing an ordered arrangement suitable for charge motion through the molecular structures.

Oligoethyleneoxide-functionalized sexithiophene shows strong $\pi$–$\pi$ interactions in the solid state, also leading to a $\pi$-stacked system.

The interaction with the substrate is a key parameter in determining the orientation of the molecules, which can be a relevant parameter in controlling the properties of the material. In fact, highly regioregular poly(3-hexylthiophene) – P3HT – can be arranged to give high mobility only when the substrate is hydrophobic [145]. This has been carefully studied by grazing-incidence X-ray diffraction on P3HT film obtained by spin-coating directly onto the Si/SiO$_2$ substrate where the device was fabricated. The film was 70–100 nm thick and the structural investigation revealed that with a SiO$_2$ surface treated with a silylating agent (hexamethyldisilazane), highly regioregular P3HT can arrange on the surface of the dielectric with the plane of the thiophene ring almost perpendicular to the plane of the devices and with the main backbone parallel to the surface. This is a condition which optimizes the overlap of the conjugated system and allows a good charge mobility of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$. If the polymer is not regioregular, i.e., its regularity is lower than 81%, this kind of orientation is not reached and mobilities of 2–3 orders of magnitude lower are found.

A number of different structural factors influencing the mobility have been recently found for P3HT. High molecular weight gives higher mobility, this factor probably influencing the dimensions of the crystallites of polymers [146]. However it is well-established that the orientation of the polymer chain in the ordered domain with respect to the substrate is the key factor for high mobility. In Fig. 1.24 a structure of a soluble polythiophene suitable for FET assembling is reported. The macromolecule was synthesized after proper structural planning with the aim of preparing a suitable material for FET focusing on the following parameters [147]:

- appropriate length for the alkyl side chains;
- regularity in the structure in order to induce molecular assembly;
- control over the extended $\pi$ conjugation in order to reach a good balance between the functionality of the transistor and stability against oxygen.

The polymer in Fig. 1.24, with R = $n$-C$_{12}$H$_{25}$, after annealing at 120–140 °C showed highly crystalline patterns and a $\pi$–$\pi$-stacking with interlayer spacing of

3.8 Å
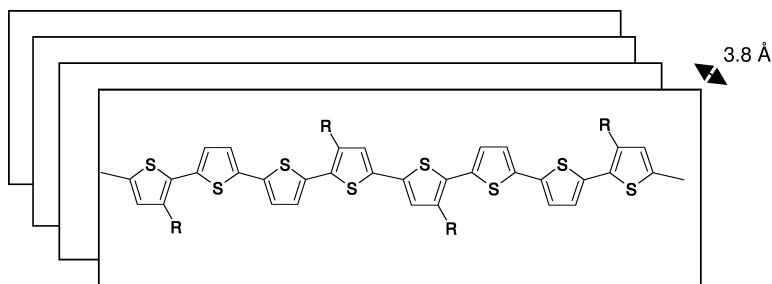
**Fig. 1.24** $\pi$-stacked system in regiodefined soluble polythiophene (see text).
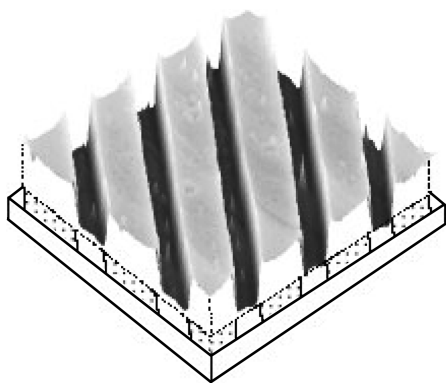


**Fig. 1.25** Patterned surface in a polymeric blend deposited on a treated substrate [148]. (Reproduced with permission by Nature Publishing Group).

3.8 Å. It was also found that deposition of thin film on silicon wafer modified with octyltrichlorosilane results in the formation of highly ordered lamellar $\pi$ stacks with an orientation perpendicular to the substrate in a way similar to the behavior of P3HT. The authors found that with this kind of arrangement and after a proper thermal treatment the mobility was 0.14 cm$^2$ V$^{-1}$ s$^{-1}$ with an on/off ratio of 10$^7$. This material showed good stability against oxygen and only a slight decrease in the mobility and on/off ratio after 1 month in the dark.

The above-reported examples are clear indications of the role played by supramolecular organization at the nanoscale in the performance of a device. Micro- and nanostructuring of materials is a very promising area and some recent studies have opened new perspectives in this field.

Böltau et al. showed [148] that the domains of a mixture of two polymers can be organized in given structures if the substrate surface, where deposition of the film takes place, is prepatterned through a variation of the surface energies. The patterning of the surface can be easily obtained through the methods currently used for deposition of microstructured molecular films [148, 149]: follow-

ing the described simple approach such patterns can be reached on the two-component polymer film.

The procedure is based on the phase separation occurring in a binary fluid and on the selective absorption from a two-component mixture. In fact, one component of a polymeric blend will migrate away from the region exhibiting high surface energy.

A gold substrate (which is polar) was partially covered with a self-assembled monolayer which formed a regular pattern of nonpolar stripes. After spin-coating a PS/polyvinylpyridine (PVP) mixture onto the prepatterned surface and removing PVP with ethanol (a good solvent only for PVP), the structure represented in Fig. 1.25 was found. Only PS remained on the nonpolar stripes of the surface.

Friend et al. followed a similar approach to build up a self-organized structure for the preparation of LEDs [150]. In fact, they prepared a blend of two different semiconducting polymers exhibiting good EL in the blue [poly(9,9-dioctylfluorene) (PFO)], and green [poly(9,9-dioctylfluorene-alt-benzothiazole) (F8BT)] regions. The PFO emission peak overlaps with the absorption peak of the F8BT and the EL spectrum is due to F8BT emission in the green region. These two polymers give phase separation in a film obtained from xylene solution: 2–4 µm-wide domains of PFO are homogenously distributed in a F8BT matrix. A xylene solution of a PFO/F8BT mixture (1/4) was spin-coated on an indium tin oxide glass which was covered by a PEDOT/PSS film which was briefly treated with oxygen–plasma in order to oxidize the surface. A pattern consisting of alternating hydrophobic and hydrophilic surfaces was introduced by transferring 7-octenyltrichlorosylane spots onto the PEDOT/PSS-treated surface by means of microcontact printing [151]. The desired morphology, obtained with the same structure of the patterned stamp, was formed when the film was allowed to dry for 30 min in an atmosphere saturated with xylene. Inspection of the formed photoluminescent patterned film by fluorescent micrographs confirmed the formation of a 2D patterned structure with the same features as the patterned PEDOT/PSS underlying layer. The blend layer was found to be formed by well-defined spots with a diameter of 2–2.5 µm made up of POF blue-emitting polymers which were embedded in a green emitting matrix of F8B7 (Fig. 1.26).

Owing to the similar chemical structure of the two polymers, the phase separation is not complete. Micro-Raman spectroscopy showed that the blue-emitting spots were 56% POF, while the green matrix was 90% F8BT. The blue spots were formed on the hydrophobic dots of the underlying surface, while the green matrix was found to cover the more hydrophilic, not silanized PEDOT/PSS surface.

The patterned layer was incorporated into a LED by evaporating on its top, calcium and subsequently aluminum. No variation in the electrical behavior was found with respect to the device where the PEDOT/PSS film was not treated with silanizing agent, indicating that the treatment of the PEDOT/PSS surface was not influencing the charge injection in the device. The authors found an external QY that was increased by a factor of 2 with respect to an un-
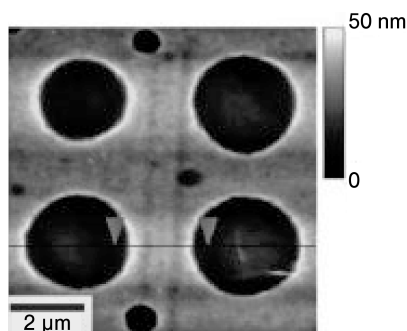
**Fig. 1.26** Phase separation obtained in a blend of two electroluminescent polymers [150].

patterned device. They ascribed this improvement to the extraction of the wave-guide mode from the device.

This example shows that controlling the interaction among different structures in the solid state may be a useful tool for preparing patterned morphologies almost automatically. In this case, the kind of pattern has been decided previously and realized by lithographic techniques. However, the reproduction of the given pattern on the PEDOT/PSS substrate was realized by microcontact printing making use of polydimethylsiloxane elastomer. The technique is very cheap and the stamp can be used many times to reproduce the same pattern on many devices.

A further effort towards a high level of autoorganization of semiconducting polymeric materials has been shown recently by Song et al. [152], who showed that the mesostructuring of semiconducting polymers can be obtained with simple methods. The so-called "breath figure method" was used as a tool to prepare hexagonally ordered bubble arrays in rigid-rod polymers.

The breath figure approach has been extensively studied in recent years. François et al. [153] was the first to show how BCs formed by PS and PPP dissolved in $CS_2$ exhibits, after evaporation of the solvents, thin films presenting hexagonally ordered arrays of holes (with a diameter of 0,5–2 µm) on the surface. The pattern formation occurs only if some degree of humidity is present in the atmosphere. In fact the holes on the surface are created by condensation of microdroplets of water on the evaporative cooling surface of the solution giving rise to the film. A definitive description of the pattern formation has not yet been reported even though some interesting models have been proposed. In Fig. 1.27 a scheme of the mechanism of patterned surface formation is reported according to Srinivasarao et al. [154].

More recently Kumacheva et al. have established that self-organization of holes can be due to Bènard-Marangoni convection [155]. They showed that in some fluids, under particular conditions, vertical temperature gradients induce various types of convection phenomena, forming, on the fluid surface, ordered patterns [156].

(a)

Moist air    Solvent

(b)

(c)

(d)
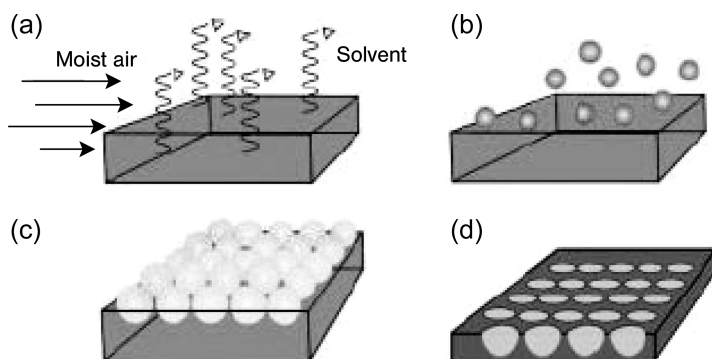
**Fig. 1.27** Patterned film formation. (a) Cooling of the solution surface due to solvent evaporation. (b) Water droplets condensation on the cooled surface of the liquid. (c) Organization of water droplets into 2D

hexagonal array. (d) The water droplets sink into the solution and after film formation droplets evaporate leaving their imprint in the polymeric film [152].

In Ref. [152] a 2D pattern has been prepared by evaporation of $CS_2$ solutions of semiconducting polymers. Highly ordered arrays of holes with hexagonal symmetry with the order extending over a large area and without grain boundaries were found for poly(paraphenyleneethynylene) films prepared in the presence of moisture in the atmosphere (Fig. 1.28). The bubbles below the surface were 3–5 μm in diameter depending on the preparation conditions. Other conjugated polymers were found to give a 2D ordered pattern similar to the one reported in Fig. 1.28; according to Srinivasarao this procedure opens new possibilities in the preparation of systems for energy transfer and charge transfer.

All the methods above described are direct ways to assemble polymeric materials at an organization level that is beyond the molecular architectures. As mentioned at the beginning of this section, these are highly innovative methods which are at the frontier of material science and represent the trend towards the self-organization of matter. Other methods, involving, for example, litho-

R

$*\left[\phantom{x}\right]_n *$    R = -O(CH$_2$)$_6$H

R
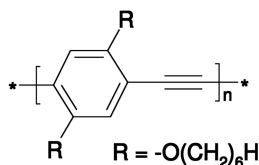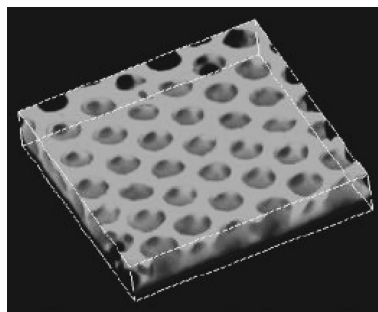
**Fig. 1.28** Confocal laser micrograph of an ordered pattern of micrometric holes on the surface of a poly(paraphenyleneethynylene) film.

graphic and soft lithographic processes are still of great interest for their potential in technological applications.

The micro/nano-fabrication of electroluminescent polymeric LED pixel arrays is an important field because this system can be directly used in the preparation of displays with high resolution.

Faraggi et al. [157] used a laser beam to ablate both the polymer and the electrodes through a mask to get a pixel array of electroluminescent polymer. The ITO-coated glass was irradiated by a 193 nm excimer laser through a simple mask of an electron microscope bar grid with a line width of 20–25 μm and a spacing between the bars of the same size.

By adjusting the number of pulses, an exact replica of the grid was reproduced on ITO, which presented an ordered pattern of strips of ITO alternating with glass stripes of the same width. A copolymer, copoly-(1,4-phenylenevinylene-2,6-pyridylenevinylene) emitting in the yellow-green region, was spin-coated on the ITO-patterned glass producing a uniform thin film with a thickness of about 1000 Å. The following step was deposition of a 2000-Å-thick layer of aluminum acting as electrode, which was subsequently ablated with the excimer laser beam through the same mask. The mask was rotated by 90° with respect to the direction of the ITO lines. The pixel dimensions were 20×20 μm.

Soft lithography is a powerful technique which has been shown to be extremely useful for the preparation of patterned surface of electroluminescent polymers. Bolognesi et al. recently reported that, by means of soft lithography, the reproduction of the pattern of holes generated by water droplet condensation on the cooling surface of an evaporating solution of PS, can be easily achieved, obtaining a negative replica of the starting PS film [158]. This replica, made of polydimethylsiloxane (PDMS), can be used to reproduce, by micromolding in capillaries (MIMIC) [151], the regular pattern of the pristine PS film.

In Fig. 1.29a the AFM image of the negative mold of the PS film is reported together with the positive replica (Fig. 1.29b) obtained by MIMIC by using a poly(dioctylfluorene) solution.

A simple procedure for the preparation of ordered arrays of semiconducting polymers, making use of solvent-assisted micromolding of a film precursor to poly(*p*-phenylenevinylene) (PPV) was presented by Rogers et al. in [159].

A thin film of precursor PPV was spin-coated on ITO-covered glass. The film, which is still soluble in methanol, was molded to produce a patterned LED. Molding was performed through a PDMS mold, which was produced by soft lithography [151] from an original pattern prepared by conventional lithographic procedures. The PDMS stamp was wetted with methanol and during the contact between the stamp and the polymeric precursor film, the methanol partially dissolves the precursor causing it to wick into the channels formed by contact of the elastomer with the film. After methanol evaporation followed by removal of the mold the heating of the film in vacuum produces a patterned structure onto ITO glass of PPV.

The subsequent evaporation of calcium and aluminum leads to the formation of the second electrode: by applying a voltage the emission of light is observed
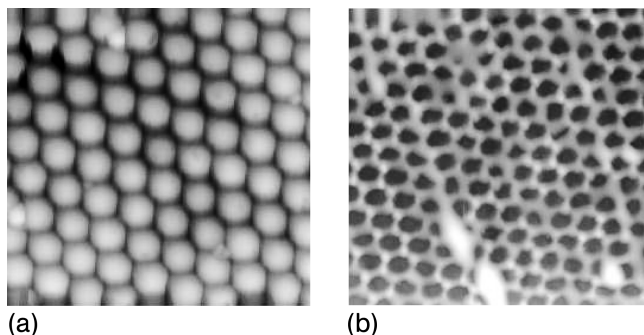
**Fig. 1.29** (a) AFM images (tapping mode) of the negative polydimethyl-siloxane (PDMS) mold as obtained from a PS patterned film (see text). (b) Replica of the pristine PS-patterned film obtained by micromolding in capillaries (MIMIC) with poly(dioctylfluorene). (Reproduced in part with permission from [158]).

through ITO. Emission of light was preferentially obtained from the thin region of the PPV film which was created during embossing with the wet mold.

The hole mobility of semiconducting polymers is relatively low (ranging from $10^{-7}$ to $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) and this can be a benefit because such values restrict current-spreading, thus making possible the localization of the emitted light in a LED of reduced dimensions.

Boroumand and coworkers [160] were able to achieve emission from nanometric spots arranged in a regular pattern by using high-resolution lithography (an electron-beam writer). By this method, the hole-injecting electrode was patterned creating a 50×50 array of disks having a diameter of 100 nm or 200 nm with a pitch of 10 μm. On the top of this array a usual LED was prepared by subsequent deposition of PEDOT/PSS, of a green-emitting POF-based polymer as the active emitting layer and of the cathode (calcium and aluminum). The authors reported that the emissive diameter of the nanometric LEDs is larger than their hole-injecting contact (170 nm compared to 100 nm). This phenomenon has been ascribed to the current-spreading effect, which occurs even in systems that are characterized by low mobility of the carriers.

The potential of polymeric materials in electronic applications is still increasing, because feature sizes less than 30 nm are not easily obtained by standard semiconductor lithography techniques.

BCs are attracting much attention because they self-assemble into a microphase formed by nanophases exhibiting ordered morphologies at the equilibrium. These morphologies can be used as template for developing highly dense periodic arrays of dots or holes on silicon substrate.

Park et al. [161] used diblock poly(styrene)–poly(butadiene), PS–PB, to obtain thin films, 50 nm thick, with well-defined morphologies, over silicon nitride. These films were formed by a matrix of PS with spherical domains of PB ordered in a 2D hexagonal lattice between a thin layer of PB wetting the silicon
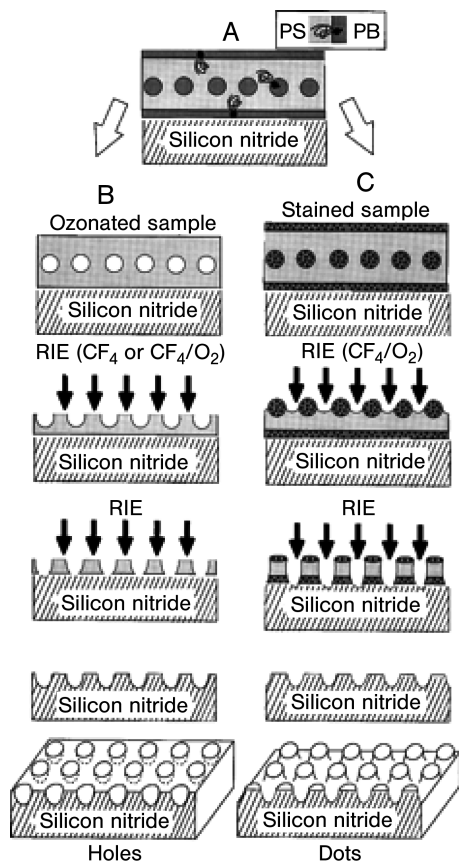
**Fig. 1.30** Patterning a silicon nitride substrate using a block copolymer as a template, *RIE* = reactive ion etching (Reprinted with permission from AAS [161]).

nitride and another thin layer of PB in contact with air (see Fig. 1.30). Two different processes can be followed to obtain holes or dots on silicon nitride respectively.

Following process B (Fig. 1.30), the PB domains are easily oxidized by ozone leading to a structure containing some holes regularly arranged: a periodic variation of the film thickness is reached. The subsequent treatment with reactive ion etching (RIE) easily removes the polymer underneath the empty spheres, while in the remaining areas, where a thicker film is present, removal is slower. In this way a thin film of silicon nitride is also removed. After dissolving the PS film remaining on the substrate with a solvent, a patterned structure made of holes appears on the substrate. On the other hand, by following the C method (Fig. 1.30) a regular pattern of dots can be formed on the silicon nitride substrate.

The starting copolymer film was exposed with $OsO_4$ vapors. This results in a selective staining of PB domains because $OsO_4$ reacts with the double bonds of PB. The RIE action on the osmium-treated film produces a selective etching of the PS, because the PB domains are protected by osmium. In this way, regularly arranged dots are formed on the substrate after dissolving the rest of the polymer with a solvent. A density of $7 \times 10^{10}$ holes $cm^{-2}$ was reached.

A further example showing the potential of semiconducting polymers towards self-organized devices was developed by Elsenbaumer and his group [162]. They prepared a precursor of a PPV derivative, containing $-CH_2OH$ functions [163], which was spin-coated onto an ITO-coated glass. After conversion to the conjugated PPV, the silver cathode was deposited on top of the film by using Brashear's method for deposition of silver mirrors [164]. The chemistry of this method is mainly based on the Tollen's test used to identify aldehydes. The $-OH$ groups on the semiconducting polymers are oxidized to aldehydes in mild conditions and subsequently treated with silver nitrate solution. Silver ions are reduced to metallic silver, which is deposited on the semiconducting polymer forming a thin shiny film of silver acting as cathode.

The authors reported that a LED prepared with this approach has an efficiency an order of magnitude lower than one prepared with the cathode formed by vacuum evaporation. The advantage of this approach is in its low cost and in the possibility to selectively cover part of a polymer film.

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