

Photochemical Behavior and Optoelectronic Applications of Some Conjugated Polymers

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Abstract The chemical modification of π -conjugated materials offers a wide range of possibilities to design and tailor the structural properties such as conjugation length, molecule-to-molecule interaction, molecular weight, and band gap. This ability to design and integrate materials showing controlled optical and electronic properties is significant for fabricating novel optoelectronic devices such as light emitting diode (LEDs) and solar cells. Conjugated polymer based solar cells (CPSCs), reflect high potential for commercialization as they can be designed to emit desirable electroluminescence, along with ease of fabrication, low production costs as well as low environmental impact. The present chapter focuses on some conjugated polymers used for the preparation of light emitting diodes (CPLEDs) and Organic Solar Cells with special emphasis on poly(phenylenevinylene)s, polyfluorenes, polycarbazoles and poly(thiophene)s.

1 Introduction

Optoelectronic properties of π -conjugated polymers such as polyaniline (PANI), polypyrrole (PPy), poly(thiophene) (PTh) and their numerous derivatives have been extensively explored as the band gap of these polymers can be easily tuned to design a wide range of solar cells/light emitting diodes (LEDs) [1–5]. Moreover, these amazing organic molecules exhibit electroluminescence and photoluminescence when stimulated by light of suitable wavelength. Due to economic advantages over many other device fabrication techniques, conjugated polymers find potential application in designing/fabricating solar cells and LEDs [6–10].

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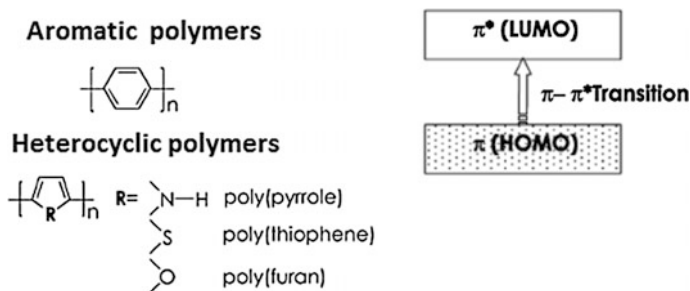


Fig. 1 Formation of HOMO and LUMO in conjugated polymers

Conjugated polymers are generally prepared by chemical/electrochemical polymerization techniques which are initiated by oxidation of the monomer followed by propagation through coupling of two radical cations leading to the formation of polymers in oxidized state [11–15]. The electrical conductivity in these polymers can be increased to several orders of magnitude by altering their band gap and doping is one such technique [16–20]. Conducting polymers exhibit absorption in the visible spectrum which is generally associated with π - π^* transitions [21, 22]. The π -conjugated systems are generally formed by the overlap of p_z orbitals of carbon. In nitrogen containing conjugated polymers, the p_z orbitals of nitrogen also participate in conjugation. The combination of the electron donating/withdrawing substituents are therefore the deciding factors for the semiconducting properties of these polymers and by changing the bond alteration via the introduction of donor/acceptor functional groups, the band gap can be narrowed/widened [23, 24].

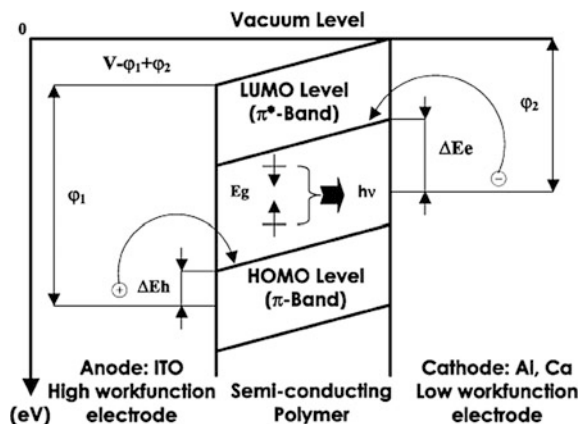
Light in these polymers is generated by the fast decay of excited molecular states, producing color which depends on the energy difference between the excited states and the molecular ground level. As most of the organic conjugated polymers possess low electron affinity, they exhibit hole-transporting properties [25, 26]. The electron affinity of such polymers corresponds to the lowest unoccupied molecular orbital (LUMO) while the ionization potential corresponds to the highest occupied molecular orbital (HOMO), Fig. 1. The ionization potential in these polymers generally lies between 2–3 eV and can be suitably altered by using various functional groups. Most of the conjugated polymer form films that are amorphous and the impurities formed during the synthesis lead to the creation of inner gap states.

2 Fabrication of Polymer Light Emitting Diode (PLEDs) Based on Conjugated Polymers

PLED device can be fabricated by two ways: single layer and multi-layer structures. The former depends on highly emitting material for effective injection and transport of electrons and holes (the majority charge carrier) and also cause the radiative decay of excited molecular states to ground state [27, 28]. The simple technique of fabrication

Fig. 2 Mechanism of charge generation by conjugated polymers in PLED.

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of a polymer based light emitting diode consists of an electroluminescent conjugated polymer and two electrodes. One of the electrodes must be transparent to allow transmission of light during electroluminescence effect and is usually referred to the hole injecting electrode (ITO). Doped conjugated polymers having a high work function (ϕ) are also used as hole injecting electrodes while the electron injecting electrode is made up of a low work function material, Fig. 2. Opposite charge carriers are injected into the conjugated polymer from anode to cathode. Holes are ejected from the valence band (π) (HOMO level) whereas electrons are introduced in the conduction band (π^*) (LUMO level) of the conjugated polymer. There exist barriers on both electrodes for the injection of electrons as well as holes, i.e., ΔE_h and ΔE_e and the barrier for electron injection is higher than the barrier for hole injection. The singlet or triplet states are created by the injected opposite charge carriers and the singlet state radiatively decays to give light. conjugated polymers have either holes or electrons as majority charge carriers [29, 30]. In single layer PLED devices, the electroluminescence takes place in the vicinity of the cathode due to higher mobility of holes in the conjugated polymers which lowers the luminescence efficiency due to non-radiative recombination process. However, it is difficult to balance the injection as well as transport of two charges in a single-material matrix over a specified voltage range and the imbalance between the charges leads to an increase in the voltage causing loss of luminance efficiency. This can be prevented by the addition of an electron transporting layer via the formation of a two-layer device which separates the cathode from the electroluminescent polymer layer [31–35].

3 Synthesis of Conjugated Polymers

Conjugated polymers are synthesized using various organic polymeric reactions to obtain desired chemical structures. Some of these reactions are discussed in the proceeding section.

3.1 Dehydrohalogenation Reactions

These reactions are carried out in presence of strong bases such as potassium *tert*-butoxide, sodium hydride [36]. Dehydrohalogenation has been used to synthesize unsubstituted polyphenylenevinylene (PPV) using dichloroethylene/sodium hydride and DMF solvent, Fig. 3.

Glich polymerization is a dehydrohalogenation reaction which has been widely adopted to synthesize alkyl/alkoxy substituted PPV derivatives [37]. The reaction is a two-step process and is reported to proceed through the formation of quinodimethane intermediate which is generated by radical/living chain anionic polymerization, Fig. 4.

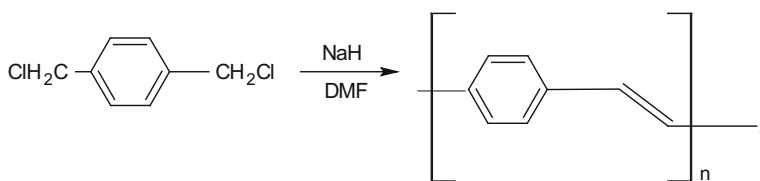


Fig. 3 Dehydrohalogenation polymerization of PPV

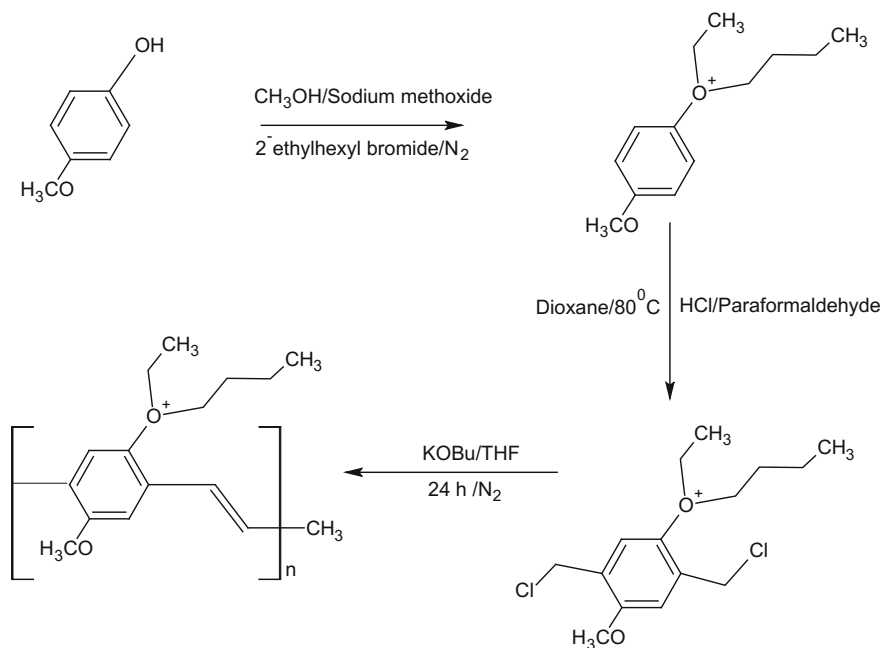


Fig. 4 Glich polymerization of alkoxy substituted PPV derivative

The molecular weight of the polymer can be controlled by optimizing the reaction parameters such as temperature, time, solvent, concentration of the monomer, and amount of base. It has been widely used for the synthesis of homopolymers and copolymers of PPV.

3.2 Precursor Route Polymerization

This polymerization strategy is extensively used for the synthesis of PPV and its substituted derivatives. Wessling and Zimmerman [38] developed a method for the synthesis of PPV via thermo-conversion of sulfonium intermediate (prepolymer) into PPV to yield its film. In the Wessling precursor route 1,4-xylylene-bis-(dialkyl sulfonium)-dichloride is used which upon elimination of tetrahydrothiophene and HCl yields PPV polymer, Fig. 5. The thermo-conversion mechanism yields pin-hole free thin films of conjugated polymers applicable for PLED fabrication. The thermo-conversion temperatures can be lowered to as low as 100 °C using bromide derivatives which can help in the fabrication of flexible PLED devices.

In the halo-precursor route, p-xylylene dichloride is used to obtain a halo precursor which upon elimination of HCl at 250 °C produces either PPV or its derivative. Tetrahydrothiophene salts are generally preferred due to low temperature stability of the prepolymer and also due to ease of conversion to PPV.

3.3 Transition Metal Catalyzed Coupling Reactions

This technique is generally adopted for the synthesis of heterocycles possessing strongly electron-withdrawing groups which generally tend to increase the reaction rate and product yield.

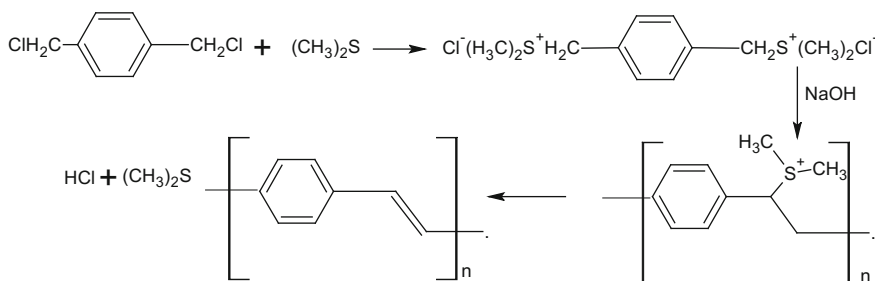


Fig. 5 Wessling Zimmerman Reaction for the synthesis of PPV

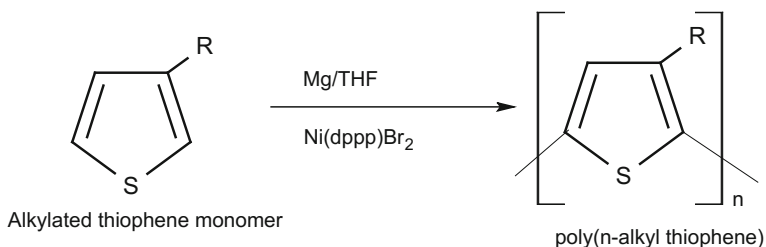


Fig. 6 Synthesis of alkylated thiophenes via Kumada coupling reaction

3.3.1 Kumada Coupling Reaction

This is a cross-coupling reaction, that is utilized for producing C=C bonds via the reaction of Grignard reagents with functional groups such as with alkyl, vinyl or aryl in presence of tetrahydrofuran (THF). Poly(3-alkyl thiophenes) have been synthesized by this reaction, Fig. 6 [39].

3.3.2 McCullough Coupling Reaction

McCullough method has been widely adopted to synthesize poly(3-alkylthiophene). In this method, 2-bromo-3-alkylthiophene is treated with lithium diisopropylamide (LDA) at $-40\text{ }^{\circ}\text{C}$ to form 2-bromo-3-alkyl-5-lithiothiophene which is converted into a Grignard reagent by reacting with $\text{MgBr}_2 \cdot (\text{OEt})_2$ to yield 2-bromo-5-(magnesiobromo)-3-alkylthiophene, Fig. 7. Ni(dppp)Cl_2 catalyzed cross coupling of 2-bromo-5-(magnesiobromo)-3-alkylthiophene is then done to produce poly(3-alkylthiophene) [39, 40]. In the Grignard metathesis polymerization, 2,5-dibromo-3-alkylthiophene monomer is used and is reacted with Grignard reagent to give 2-bromo-5-(magnesiobromo)-3-alkylthiophene followed by cross-coupling reaction in the presence of nickel catalyst to produce poly(3-alkylthiophene).

3.3.3 Suzuki Coupling Reaction

This is a Pd catalyzed coupling reaction in which organic halides are reacted with boronic acids to form aryl derivatives of poly(para-phenylenes), polyfluorenes, Fig. 8 [40].

3.3.4 Heck Coupling

This coupling reaction of Pd mediated olefin arylation is the reaction between an organic halide with a vinylbenzene derivative that produces carbon-carbon double

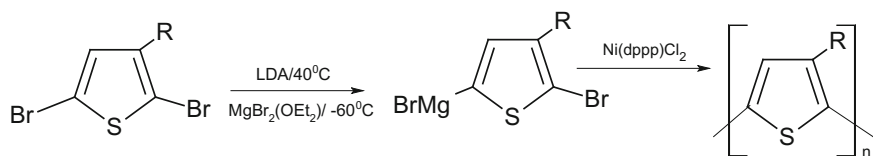


Fig. 7 Synthesis of alkylated thiophenes via *McCullough coupling* reaction

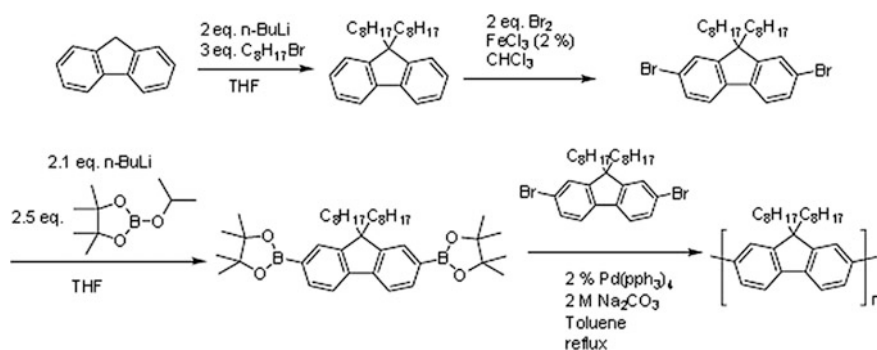


Fig. 8 Synthesis of PF via *Suzuki coupling* reaction

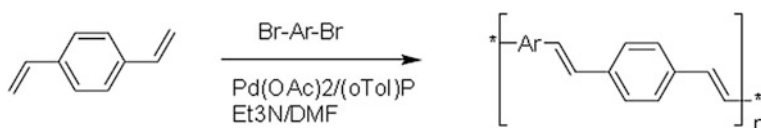


Fig. 9 Synthesis of PPV derivative via *Heck* reaction

bond, with *trans*-selectivity. It is generally preferred for the preparation of PPV related block copolymers, Fig. 9 [41].

3.4 Condensation Polymerizations

Condensation polymerization reactions are also utilized to develop light emitting conjugated polymers which are classified as given below.

3.4.1 Wittig Reaction

Wittig polycondensation route has been widely used for the preparation of alternating copolymers in which carbonyl compounds such as aldehyde and ketone are

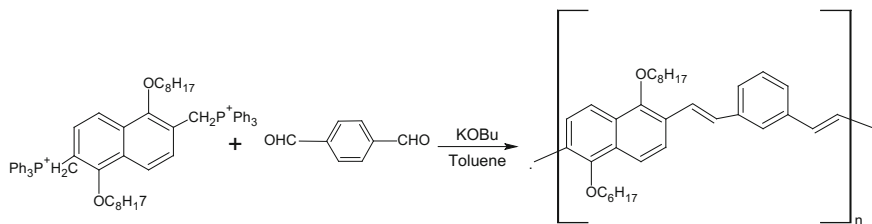


Fig. 10 Synthesis of poly(m-phenylenevinylene) derivative via Wittig reaction

reacted with phosphonium salts of conjugated monomers in presence of base such as KOtBu, Fig. 10 [42, 43].

3.4.2 Knoevenagel Condensation Polymerization

This reaction takes place between aldehyde groups with active methylene species and requires strong electron withdrawing substituent groups such as cyano group [43, 44]. Employing Knoevenagel condensation, numerous PPV related homo and copolymers with CN containing vinylene units have been reported which are prepared using monomers such as 1,5-bis(hexyloxy)-2,6-naphthalenediacetonitrile and 1,5-bis(hexyloxy)-2,6-naphthalenedicarbaldehyde in the presence of a strong base is shown in Fig. 11.

3.4.3 Horner-Emmons Condensation Polymerization

Horner-Emmons condensation consists of substituted phosphonate ester reacted with terephthalaldehyde in presence of potassium *tert*-butoxide to produce alternating copolymer, Fig. 12 [45].

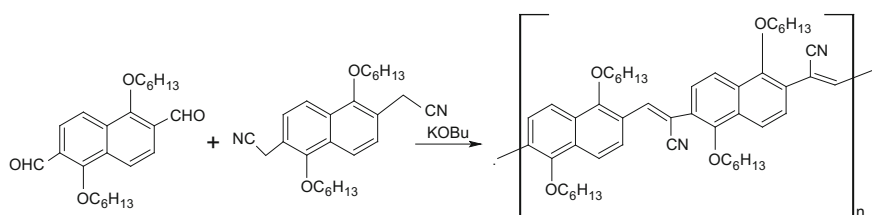


Fig. 11 Synthesis of poly(2,6-naphthylenevinylene) via Knoevenagel method

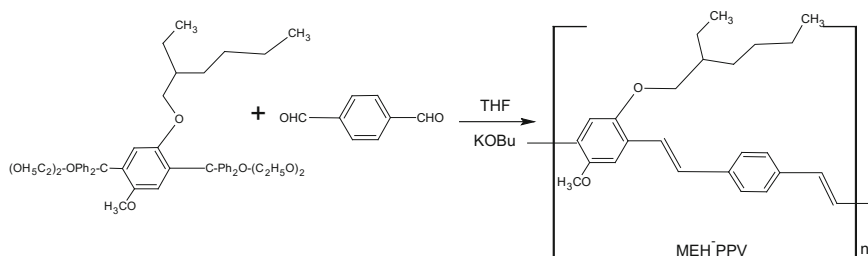


Fig. 12 Synthesis of MEH-PPV via Horner-Emmons condensation polymerization

4 Common Conjugated Polymers Used in PLEDs

Many conjugated polymers are used in PLEDs such as poly(phenylenevinylene) (PPV) [46] and its derivatives [47], poly(carbazole) and its modified derivatives [48], polyfluorenes [49], polyphenylenes [50], poly(phenylene ethynylenes) [51], and polyalkylthiophenes [52]. For most electroluminescent polymers, Calcium provides an effective polymer-metal junction and effectively injects electrons into the conjugated polymer. As internal electric field in a conjugated polymer is lower than that of a semiconductor, it slows down the migration of ions from the ITO to the hole transporting layer. Hence by varying the choice of metal (showing high work function), enhancement of drive voltage and device efficiency are observed. This observation substantiates the tunneling model for cathodic charge injection through the Schottky barrier [53–56].

4.1 Polyfluorene and Its Derivatives

Polyfluorenes are polymers with C₆ or higher substituents at C₉ position which are soluble in conventional organic solvents and are strong blue emitters when excited with UV irradiation [57]. Copolymers consisting of 9,9-dialkylfluorene and various aromatic amines have been investigated [58, 59]. The hole mobility of amine copolymers are quite high and therefore the preparation and properties of alternating copolymers of fluorine with various monomers such as thiophene, bithiophene, triarylamine, etc. have been extensively explored [60–65]. It has been reported that cyano-stilbene based copolymers emit green light, while bithiophene based fluorene copolymers emitted yellow light. Thus, the choice of comonomer can be used as an effective tool to design and optimize polymers with well-balanced hole-electron-transport characteristics, Fig. 13 [66].

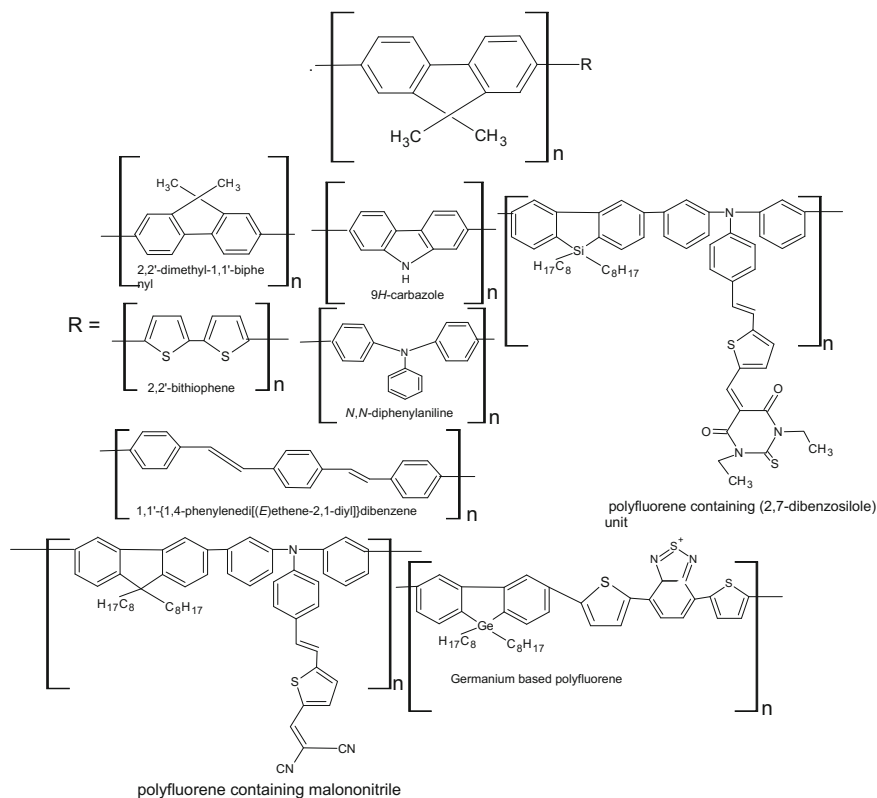
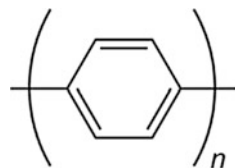


Fig. 13 Various derivatives of polyfluorene

4.2 Polyphenylene (PPP) and Its Derivatives

Poly(p-phenylene) (PPP) is a widely explored conjugated polymer in the field of PLED materials, Fig. 14 [67]. The presence of large band gap in the polymer reveals its blue emission characteristics. PPPs are insoluble and intractable in nature and therefore researchers have explored routes to synthesize soluble PPP films and a variety of PPP precursor routes have been discussed in literature [68]. PPP precursor routes involve the thermal elimination such as the elimination of two equivalents of acetic acid (per monomer unit) from poly-1,4-(5,6-diaceto-2,3-cyclohexene). This

Fig. 14 Structure of poly(phenylene)



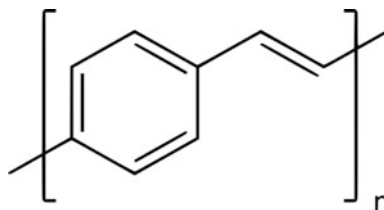
enables aromatization of the polymer chain rings and formation of PPP structure [68, 69]. As the reactions require relatively high temperatures, reduction of molecular weight takes place. Therefore, limited success has been achieved in the precursor approach to synthesize PPP and more interest has been focused on the preparation and characterization of PPPs bearing alkyl, alkoxy, and aryl units [70–75]. Polymerization reaction in these derivatives has been carried out via aryl/Suzuki coupling approaches. High molecular weights have been achieved which are good enough to cast films, and blue-emitting diodes having reasonable efficiencies have been formulated [74, 75].

Schlüter and Wegner [76] have formulated PPP derivatives with alkyl side chains through transition-metal-catalyzed polycondensations, Suzuki coupling of arylboronic acids and bromoarenes while Yamamoto [77] reported nickel-catalyzed coupling of substituted dihalobenzenes, hydroquinone bistriflates, and bis(mesylates) [78–80]. The inclusion of solubilizing side groups on the PPP backbone suffers from a major drawback that the additional substituents considerably twist the substituted phenylene rings out of plane causing a decrease in the interaction of the aromatic π -electron system accompanied by a drop in fluorescence quantum yield. The twist cannot occur if the PPP backbone is planarized by transforming it into a ladder polymer. Scherf and Müllen [81] synthesized regular ladder-type polymers derived through a two-step route in which a soluble poly(p-phenylene) was prepared by Suzuki aryl-aryl coupling of monomers. The ladder formation occurred with high regularity, with no defects such as cross-linking or incomplete cyclization. The molar masses of soluble, ladder-type poly(p-phenylene)s (LPPPs) were reported to be high. The phenylene rings in the ladder polymers are highly planar and the homopolymer shows a broad emission between 650 and 450 nm in the solid state, in contrast to the polymers sharp fluorescence emission around 450 nm in solution. The large Stokes shift (yellow emission) is especially enhanced after annealing, and has been attributed to the formation of excimers owing to interchain interactions and π -stacking between the planarized conjugated segments. The mechanism of generation of an intra-chain polaron-exciton involves coupling between electron and vibrational excitations as each inserted charge causes strong geometric distortion of the lattice, which displays a quinonoid-based structure. When radiant combination takes place, photons with an energy higher than that which separates the energy levels of two polarons (or bipolarons) are formed, which generates lattice coupling. The excited electron-hole pair can be localized on the same molecule (Frenkel exciton) or over different molecules (Wannier exciton) [82, 83].

4.3 Poly(Phenylene Vinylene) (PPV) and Its Derivatives

Poly(phenylene vinylene) (PPV) exhibits linear rigid-rod-like structure, with a good tendency to form crystalline morphology, Fig. 15 [84–88]. However, due to lack of functional groups to enhance solubility, this system is intractable and not

Fig. 15 Chemical structure of poly(phenylene vinylene)



processable directly from solution but shows the tendency to emit yellow light under electrical stimulation. A variety of solvent-processable versions of PPV, and PPV copolymers have been synthesized [89, 90]. Since solvent processability is a desirable property for polymeric emitting systems, PPVs that can be cast as films have been developed [90]. Solution processable PPV precursors have been synthesized via thermal elimination of tetrahydrothiophene and hydrogen chloride at temperatures between 150–300 °C via Wessling condensation route [38].

2-methoxy-5-(2-ethylhexyloxy) derivative (MEH-PPV) is the most investigated derivative of PPV. The presence of alkoxy substituent have shown to impart red emission and hence, MEH-PPV exhibits an orange electroluminescence as compared to yellow-green emitted by PPV. The Wessling sulfonium reaction is generally adopted for the synthesis of the dialkoxy PPVs which involves base-initiated dehydrohalogenation polymerization of 1,4-bis(halomethyl)-2,5-dialkoxybenzene monomers [83, 84]. This reaction produces highly soluble and highly pure PPVs. LED devices based on soluble PPVs have shown very good performance and have led to considerable commercial interest in developing materials of this type. The choice of the monomer is significant because those monomer units which cause weak π interactions between phenyl rings, result in the production of a large band gap. The introduction of non-conjugated sequences, which diminish the degree of conjugation, have been used to induce a blue shift in the emission of PPV.

PLEDs based on poly(phenylene ethynylene) (PPE) have been developed via Sonogashira coupling of diethynylbenzenes and dihalobenzenes [91–93]. Poly(phenylene ethynylene) exhibits yellow emission ($\lambda_{\text{max}} = 600$ nm) [94] whereas its alkoxy derivative reveals red-orange emission [94]. A blue green emission can be attained via the introduction of 2,5-pyridinediyl unit ($\lambda_{\text{max}} = 480$ nm). Poly(3,4-dialkyl-1,6-phenylene ethynylene)s reveal blue emission ($\lambda_{\text{max}} = 410$ nm) which can be prepared by palladium cross-coupling reaction of a 3,4-dialkyl-1,6-diiodobenzene with 3,4-dialkyl-1,6-diethynylbenzene [94]. Apart from several other factors, steric interactions in PPEs cause twisting of the polymer chains thereby reducing the effective conjugation length, which limits their effective application as stable PLEDs.

4.4 Polythiophene and Its Derivatives

Thiophene derivatives represent a good example of how color of emission can be varied in PLEDs by modifying the polymer structure, Fig. 15 [95–99]. Soluble poly(3-alkylthiophene)s have been prepared by polymerization of 3-alkylthiophene monomers in the presence of excess ferric chloride, or by nickel-catalyzed coupling of dihalothiophenes with thiophene-bis(magnesium halide)s [100, 101]. 3-alkylthiophenes homopolymers and copolymers exhibit red electroluminescence ($\lambda_{\text{max}} = 640 \text{ nm}$) having alkyl chain lengths in the range of 6–22 carbon atoms [102–105].

Doping these alkyl thiophenes with fluorescent dyes is reported to enhance the device efficiency and the frequency of emission is found to be dependent on regularity of the side chains on the polymers, Fig. 16. Alkylated polythiophenes were reported by Hadziioannou et al. [105] who found a correlation between emission maxima and the inverse number of alkylated thiophenes between two consecutive head-to-head coupled dyads.

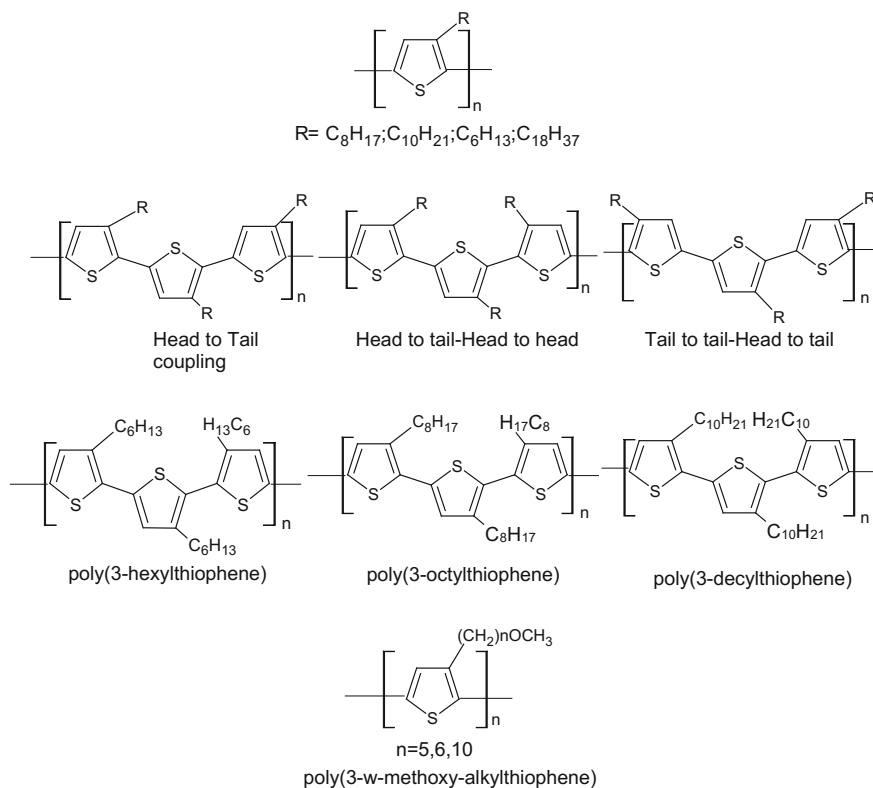


Fig. 16 Derivatives of thiophenes

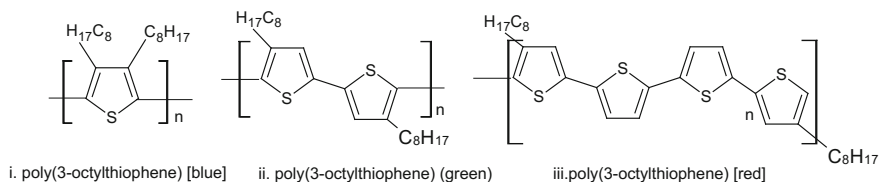


Fig. 17 Chemical structures of poly(3-octyl thiophene)

Thus, (i) showed an emission maximum at 460 nm (2.7 eV), while (ii) and (iii) had emission maxima at 530 (2.35 eV) and 550 nm (2.25 eV), respectively. Similarly, poly(3-hexylthiophene) revealed a blue-shift with increasing amounts of head-to-head dyads as reported by Holdcroft and Xus, Fig. 17 [98, 99]. The blue shifts were obtained by introducing bulky substituents and also by substitution at both the 3rd and 4th positions of poly(3-hexylthiophene) [104–106]. The blue shifts can be attributed to twisting of the conjugated backbone due to the presence of bulky substituents. Greater control of emission colors requires the ability to control polymer regioregularity. When thiophenes were polymerized using ferric chloride as initiator, the resulting polymers showed region-randomness with head-to-tail (2,5'-) coupling, varying from 52 to 80 % [105, 106], while coupling of oligomeric alkylthiophenes resulted in the formation of regioregular copolymers [107, 108]. More general routes for the synthesis of regioregular (head-to-tail) poly(3-alkylthiophene)s have been developed by McCullough et al. [108, 109] and Rieke et al. [100–111]. They carried out nickel-catalyzed coupling of 2-halo-5-metalthiophenes. Poly(3-alkylthiophene) copolymers with side chains containing terminal azide groups have also been synthesized revealing polarized emission from stretch-oriented polythiophenes [111]. Oriented films of poly[3-(10-methoxydecyl) thiophene] deposited by Langmuir ± Blodgett techniques were reported to emit polarized electroluminescence [105–111].

5 Fabrication of Solar Cells Using Conjugated Polymers

Organic semiconductor films are generally photo-sensitive and photo-induced electron transfer from a donor-acceptor-type moiety/functional group introduces free charge carriers. The positive charge carriers are created on the donor layer, i.e., p-type, whereas negative charge carriers are created on the acceptor layer, i.e., n-type. These donor-acceptor-type bilayer devices thus work like p-n junctions, Fig. 18. The most common representatives of hole conducting donor-type semiconducting polymers are: derivatives of phenylene vinylene such as poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMOPPV), poly(3-hexylthiophene) (P3HT), fluorine derivatives such as (poly(9,9'-dioctylfluorene-co-bis-*N,N'*-(4-butylphenyl)-1,4-phenylenediamine) (PFB), Fig. 19. These polymer-based photovoltaic materials are commonly solution processed at low temperatures [112–117].

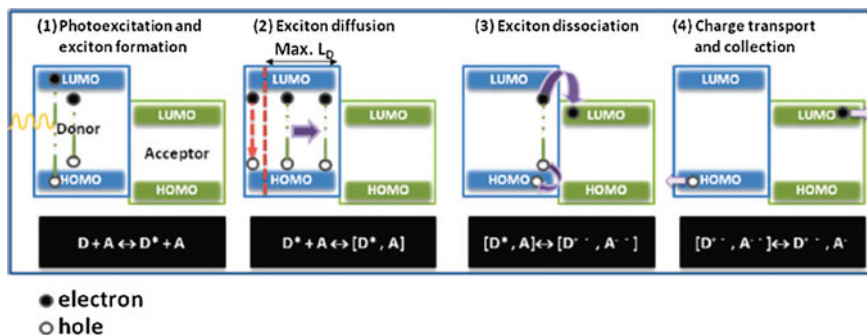


Fig. 18 Mechanism for donor-acceptor heterojunction solar cells. (1) Photoexcitation of the donor to generate a Coulomb correlated electron-hole pair, an exciton. (2) Exciton diffusion to the D-A interface. A distance longer than the maximum diffusion length ($max LD$) will lead to relaxation of the exciton. (3) Bound exciton dissociation at the D-A interface to form a geminate pair. (4) Free charge transportation and collection at electrodes. Reprinted with permission from ACS, Y.-J. Cheng, S.-H. Yang, and C.-S. Hsu, Synthesis of Conjugated Polymers for Organic Solar Cell Applications Chem. Rev. 2009, 109, 5868–5923

Soluble precursor polymers can also be converted into the final semiconducting form with a post-deposition conversion reaction [118]. For the formulation of organic solar cells spin-coating, doctor blading, as well as screen-printing methods are generally applied as they lead to upscaling of the production with low-energy consumption. For the fabrication of a bilayer heterojunction device, p-type and n-type organic semiconductors are sequentially stacked on top of each other in various combinations [119]. The excitons created within a distance of 10–20 nm are only able to reach the interface which results in loss of absorbed photons away from the interface leading to low quantum efficiencies [120]. Hence, the efficiency of bilayer solar cells is limited by the generation of charges within the range of 10–20 nm from donor-acceptor interface. The thickness of the film also plays a crucial role and thick film affects the absorbing material, resulting in a minimum photocurrent at the maximum of optical absorption spectrum. In bulk heterojunction devices, the donor-acceptor moieties are taken in bulk volume which creates donor-acceptor phase separation within 10–20 nm length scale and each interface is within a distance less than the exciton diffusion length from the absorbing site. This increases the interfacial area between the donor and acceptor phases and results in improved solar cell efficiency [121, 122].

In the bilayer heterojunction devices, the donor-acceptor phases are separated from each other and can selectively contact the anode and cathode, whereas in the bulk heterojunction both phases are intimately mixed and there is no preferred direction for the internal fields of separated charges, Fig. 20. The electrons and holes are thus created within the volume having concentration gradient (diffusion) as driving force. The separated charges require percolated pathways and the donor-acceptor phases form bicontinuous interpenetrating network [123]. Bulk heterojunction devices are sensitive to the morphology in the blend [124]. Majority of

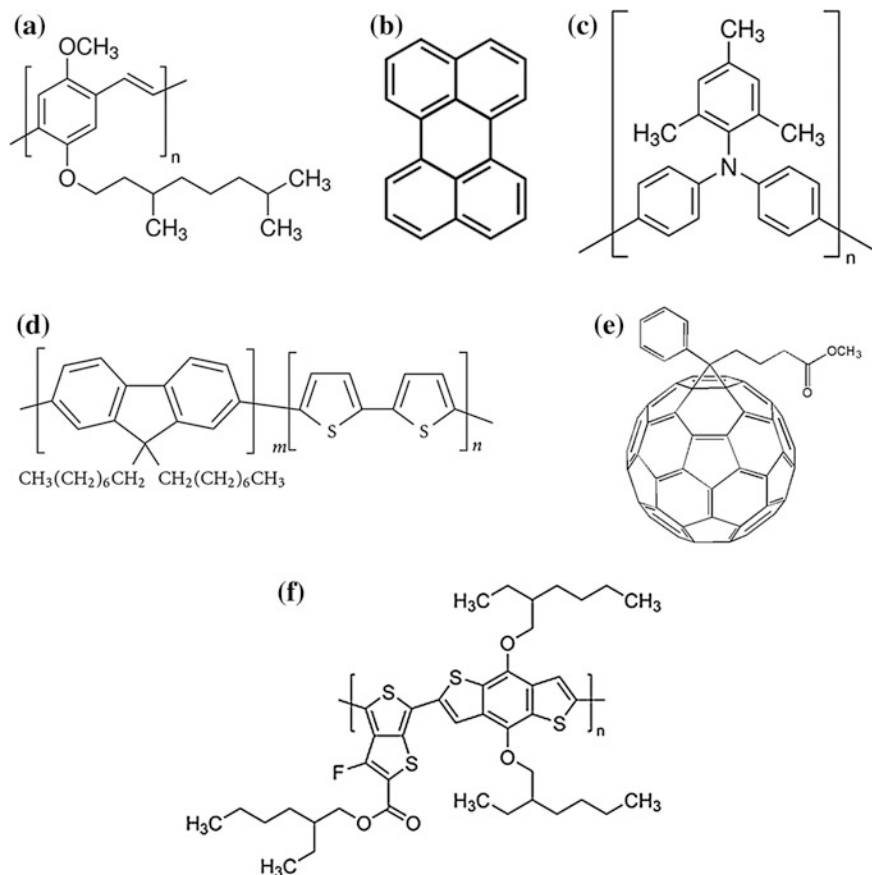


Fig. 19 Common organic semiconductors used in organic solar cells **a** poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV), **b** perylene, **c** poly(triaryl amine), **d** poly[(9,9-di-n-octylfluorenyl-2,7-diyl)] ((F8T2)), **e** Phenyl-C₆₁-butyric acid methyl ester-alt-2,2'-bithiophene-5,5'-diyl] (PCBM), **f** poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl}) (PTB7)

conjugated polymers have band gaps higher than 2 eV, which limits the possibility of harvesting solar photons to about 30 %. This is because organic materials have a large band gap (2–3 eV), which can absorb only a small portion of the incident solar light. A band gap of 1.1 eV can absorb 77 % of the solar irradiation and because the absorption coefficients of organic materials are as high as 10⁵ cm⁻¹, a layer of 100 nm thickness is enough to absorb most of the photons [124, 125]. The primary photo-excitations in organic materials do not directly produce free charge carriers but to coulombically bound electron-hole pairs, called excitons. Hence for optimum dissociation of excitons, strong electric fields are necessary which can be supplied via externally applied electrical fields or via interfaces. The exciton diffusion length should be of the same order of magnitude as the donor acceptor phase

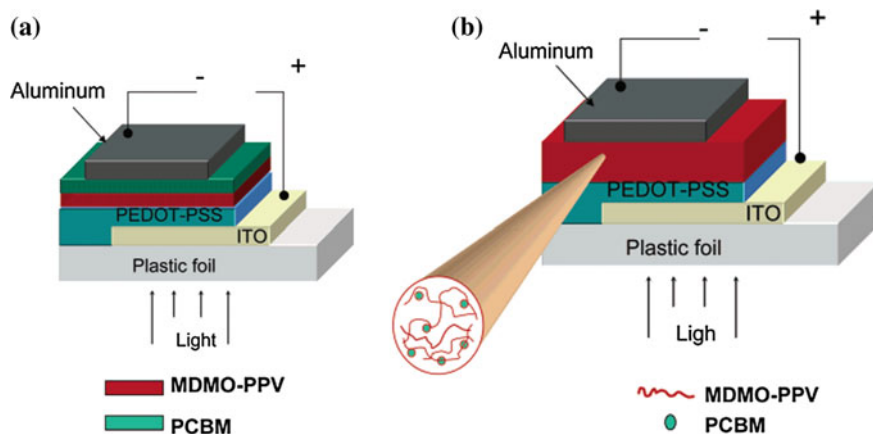


Fig. 20 **a** Bilayer Device fabrication and **b** Bulk heterojunction device fabrication. Reprinted with permission from ACS, S. Gunes, H. Neugebauer, and N. S. Sariciftci, *Chem. Rev.* 2007, 107, 1324–1338

separation length otherwise, their energy is lost for the power conversion before reaching the interface due to exciton decay via radiative/nonradiative pathways. The exciton diffusion lengths in conjugated polymers are usually reported to be in the range of 10–20 nm.

Blending of conjugated polymers with electron acceptors is a very efficient way to break photo-excited excitons into free charge carriers. Ultrafast photophysical studies reveal that photo-induced charge transfer in such blends is much faster than other competing relaxation processes. For producing highly efficient photovoltaic devices, the charges generated need to be transported to the appropriate electrodes within their lifetime and the charge carriers need a driving force to reach the electrodes. A gradient in the chemical potentials of electrons and holes (quasi Fermi levels of the doped phases) is built up in a donor-acceptor junction which is determined by the difference between the highest occupied molecular (HOMO) level of the donor and the lowest unoccupied molecular orbital (LUMO) level of the acceptor. This internal electrical field determines the maximum open circuit voltage (V_{oc}) and contributes to a field-induced drift of charge carriers.

6 Conjugated Polymers Used in Organic Solar Cells

6.1 Phenylene-Vinylenes and Its Derivatives

Poly(p-phenylenevinylene) is reported to be insoluble as discussed earlier and therefore difficult to process in solid state. Wittig reaction has been used to develop

PPV but the major drawbacks of precursor approach include the generation of toxic side products during the solid-state, incomplete thermal conversion or oxidation causing structural defects as well as undefined molecular weight. The incorporation of long alkyl or alkoxy chains into the phenylene monomer is seen to produce solubility, Soluble derivatives of phenylene-vinylenes, such as poly(2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylenevinylene) (MEH-PPV), poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) mixed with soluble derivatives of fullerenes, such 1-(3-methoxycarbonyl)propyl-1-phenyl-[6, 6]-methanofullerene (PCBM) are known to produce 2.5 % efficient solar cells [126]. Shaheen et al. [123] prepared MDMO-PPV: PCBM in the weight ratio of 1:4 for obtaining a power conversion efficiency of 2.5 % using chlorobenzene as a solvent. The electron mobility of pure PCBM has been reported to be higher than the hole mobility of pure MDMO-PPV [124]. Hoppe et al. [75] demonstrated that increasing PCBM content increases the size of these PCBM nanoclusters. To study the relationship between morphology and performance in bulk heterojunction solar cells, MDMO-PPV/ PCBM blends have been investigated in detail [126–128]. Mihailetschi et al. [128] developed a model for quantitative description of the behavior of PPV:PCBM bulk heterojunction solar cells.

The introduction of cyano linkages in place of vinylene linkages is seen to lower both LUMO and HOMO levels by ~ 0.5 eV, with little effect on the magnitude of the band gap. With the introduction of cyano groups, the conjugated backbone undergoes twisting due to steric hindrance. Cyano functionalized PPVs exhibit high electron affinities and electron-transport properties as a result of the electron-withdrawing effect of the cyano side group. It therefore acts as a suitable electron acceptor in photovoltaic devices in either bilayer or bulk heterojunction device configuration [129–133].

To further lower the band gap of cyan based PPVs below 2 eV, thiophene units with lower aromaticities have been incorporated into the main chain to form a D-A arrangement. Vanderzande et al. [132] developed copolymers based on the bis (1-cyano-2-thienylvinylene) phenylene prepared by Knoevenagel condensation to construct cyanovinylene linkages, Fig. 21.

Reynold et al. [133] developed CN-PPV derivatives containing dioxythiophene moieties in the main chain which revealed narrow band gaps ranging between 1.5–1.8 eV and good solubilities in common organic solvents, Fig. 22.

6.2 Poly(3-Alkylthiophenes) and Its Derivatives

Poly(3-alkylthiophenes) (P3ATs) and regioregular poly(3-alkylthiophenes) (RRP3AT) (P3HT:poly(3-hexylthiophene), P3OT:poly(3-octylthiophene), and P3DDT:poly(3 dodecylthiophene) are used as electron donors in heterojunction solar cells showing conversion efficiencies up to 5 % [134–137]. The influence of the alkyl side chain length of regioregular P3HT, P3OT, and P3DDT on the electrochemical and optical properties was studied by Al Ibrahim et al. [134]. It was

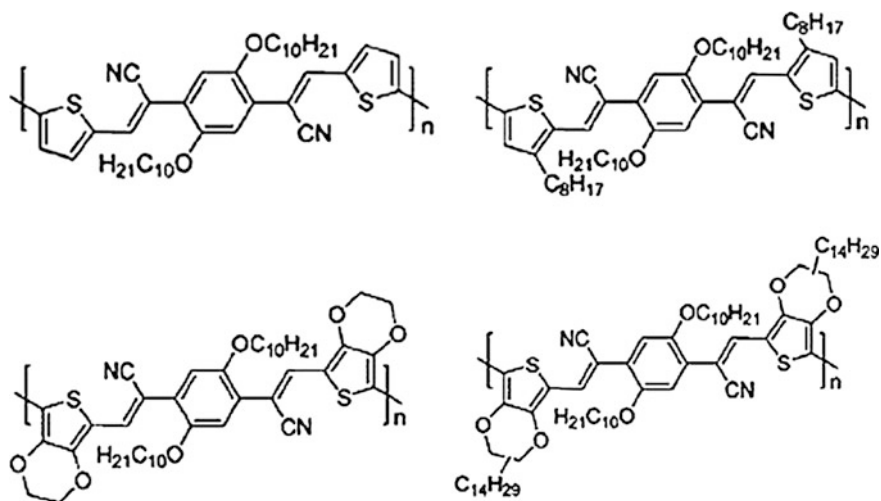


Fig. 21 Structures of CN-PPV derivatives

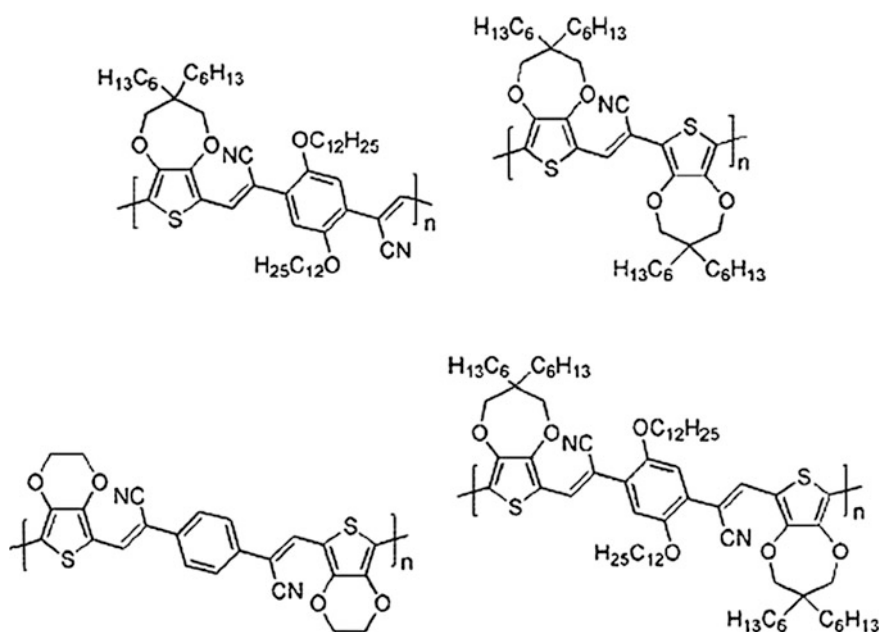
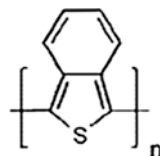


Fig. 22 Structures of CN-PPV derivatives containing dioxithiophene

found that with longer side chain length, the band gaps were slightly increased while absorption coefficient revealed a decrease upon increasing the side chain length containing polythiophenes due to chromophore dilution. Using regioregular

Fig. 23 Structure of Polyisothianaphthene (PITN)



poly(3-hexylthiophene) (RR-P3HT) as donor and PCBM as acceptor, bulk heterojunction solar cells have been developed revealing 75 % quantum efficiencies and power conversion efficiencies up to 5 % [135, 136]. The high efficiency of these devices has been reported to be due to the presence of microcrystalline lamellar stacking in the solid state packing which reduces recombination of electrons and holes. Regioregular P3HT shows interchain interactions that cause a red shift of the optical absorption due to stacking. Padinger et al. [138] investigated the effect of annealing on P3HT based solar cells by applying an external voltage which was shown to cause recrystallization along with reduction in the free volume as well as density defects at the interface. Chiravaze et al. [139] investigated that P3HT showed pronounced red shift upon thermal annealing at a temperature above 110 ° C for 4 min. The hole mobility in the P3HT component was found to increase by more than 3 orders of magnitude.

Polyisothianaphthene (PITN), Fig. 23, is also a polythiophene derivative where all the thiophene rings are fused to a benzene ring at the 3,4-positions of thiophene. It possesses a band gap of 1 eV, which is smaller than that of polythiophene. The PITN main chain favors the quinoid form to preserve aromaticity causing a change in the thiophene aromaticity [140].

Hillmyer and co-workers [141] developed Isothianaphthalene (ITN)—thiophene copolymer using distannyl-isothianaphthene (obtained via lithiation of isothianaphthalene in presence of *n*-butyl lithium in tetramethylethylenediamine (TMEDA) and THF followed by reaction with trimethyltin chloride). It was found that this molecule could be used as a precursor to prepare the ITN-fluorene copolymer/ITN—thiophene through Stille coupling with 9,9-dihexyl-2,7-dibromofluorene/ bis(bromothiényl)-isothianaphthene, Fig. 24.

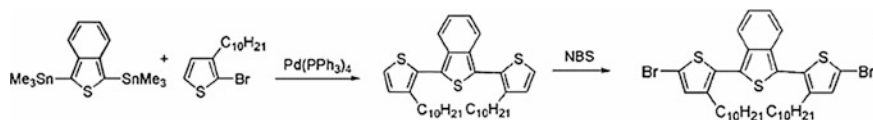


Fig. 24 Synthesis of ITN—thiophene copolymer using distannyl-isothianaphthene and bis(bromothiényl)-isothianaphthene

6.3 Polypyrrole and its Derivatives

Pyrrole ring containing polymers have been synthesized via Stille coupling of 2,5-bis(5-(trimethylstannyl)-2-thienyl)-*N*-dodecylpyrrole and 4,7-dibromo-2,1,3-benzothiadiazole using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ as the catalyst and higher molecular weights are attained using distannyl monomer, Fig. 25 [142–144]. This polymer reveals a low band gap of 1.6 eV and efficient photoinduced electron transfer, was reported by photoinduced absorption and photoluminescence quenching of the former. The solar cell device based on the pyrrole ring derivative with /PCBM exhibited 1 % efficiency when used in the weight ratios P131:PCBM ratio of 1:3. The addition of diketopyrrolopyrrole unit has shown to impart high electron and hole mobility both close to $0.1 \text{ cm}^2/(\text{V s})$ in an FET device. Janssen and co-workers [144] reported a conjugated polymer synthesized using quaterthiophene and diketopyrrolopyrrole units, Fig. 26.

6.4 Porphyrin Based Polymers

Porphyrin derivatives reveal good photochemical and thermal stabilities due to their large π -conjugation systems which have been found suitable for organic photonic and electronic applications [145–147]. Porphyrin molecules have been well established to serve as potential photosensitizers in dye-sensitized solar cells. Soluble porphyrin-dithienothiophene copolymers have been synthesized using Sonogashira

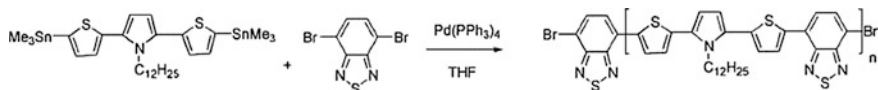


Fig. 25 Synthesis of pyrrole containing copolymer via Stille coupling of 2,5-bis(5-(trimethylstannyl)-2-thienyl)-*N*-dodecylpyrrole and 4,7-dibromo-2,1,3-benzothiadiazole

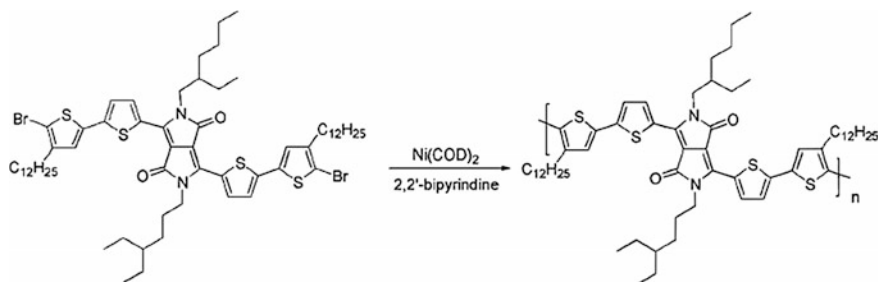


Fig. 26 Synthesis of diketopyrrolopyrrole containing polymer via Yamamoto coupling

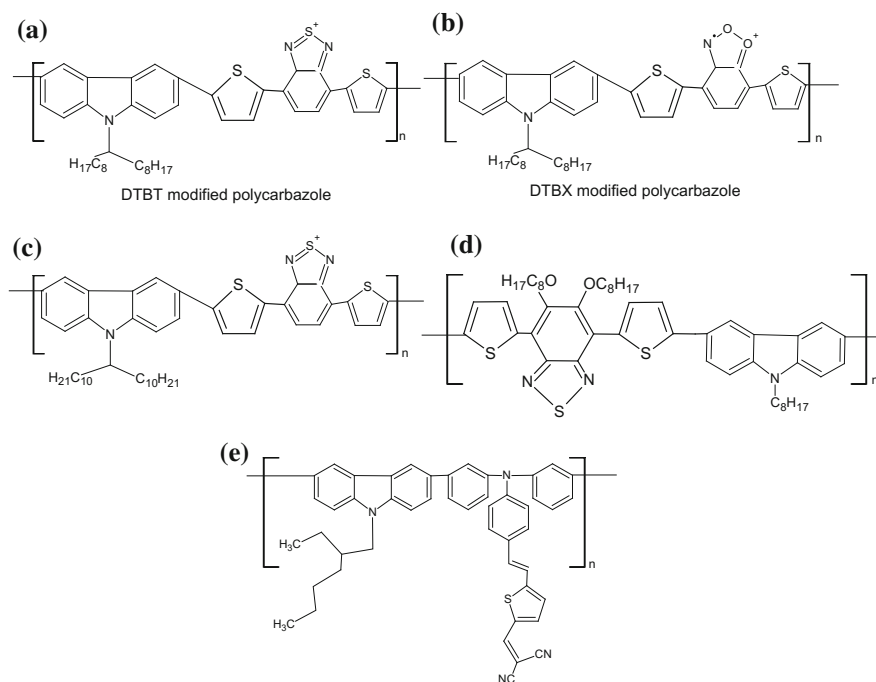


Fig. 27 Various derivatives of carbazole containing conjugated polymers

coupling reaction [147]. The introduction of diethynyldithienothiophene into the porphyrin main chain is found to reduce steric hindrance, and enhances conjugation, which helps in improving the charge-transport property. However, to ensure sufficient solubility of the porphyrin-containing polymer for solution processing, a large aliphatic chain insulating portion must be incorporated into the porphyrin unit, and this is known to have a negative effect on the charge transport.

6.5 Poly(Carbazole) and Its Derivatives

The carbazole monomer has a fused pyrrole ring which makes tricyclic carbazole fully aromatic and electron-rich due to the presence of nitrogen group. The introduction of alkyl chains showing good solubility when alkylation is carried out at 9-position, Fig. 27. Leclerc et al. [148, 149] developed 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) based poly(N-alkyl-2,7-carbazole) (PC) exhibiting enhanced thermal stability, relatively high molecular weight and good solubility. He also developed 4,7-dithien-2-yl-2,1,3-benzothiadiazoxaline (DTBX) based polycarbazole as accepting unit which showed good hole mobility due to its symmetrical backbone and well organized structure.

In order to improve the solubility and close packing of polymer, Hashimoto developed a 10-carbon chain alkyl derivative of polycarbazole which also exhibited similar photovoltaic parameters as those of DTBT based polycarbazole. Qin et. al. [150] designed a carbazole derivative showing planar polymer conformation by introducing two octyloxy chains onto benzothiazole (BT) ring and an octyl chain onto carbazole ring. Cao [151] developed a series of carbazole-based two-dimensional polymers having HOMO energy levels as the conjugated backbone but their LUMO levels were governed by narrow band gap side chains. The 2-ethyl-hexyl chains had little influence on the photovoltaic performance but heptadecanyl chains on carbazole led to a significant decrease in the photovoltaic performance. Hence, alkyl chains on carbazole unit had important influence on the hole transporting ability of the resultant polymers. The presence of short alkyl chains resulted in high mobility than bulkier alkyl side-chains. The bulky alkyl chains possibly cause imbalanced electron transport and consequently decreased fill factor of polymer [152].

7 Conclusion and Future Prospects

Several strategies have been adopted to tailor the band gap of conjugated polymers and significant progress has been made in synthesis, as well as structural modification of conjugated polymers. These materials show impressive applicational potential in energy harvesting, as well as designing of opto-electronic devices. However, large-scale synthesis of these materials with optical tunability is highly desirable. Fabrication of highly crystalline conjugated polymers is still a challenge. The reproducibility and stability of doping level is also required. Conjugated polymer based organic-inorganic hybrid structures is a highly promising field of research, to enhance the above-mentioned properties and to address the corresponding challenges multifunctional conjugated polymers need to be designed and developed to open up new avenues of research in the field of energy harvesting and opto-electronic device fabrication.

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