1

Precision and Purity of Conjugated Polymers – To be Ensured Before Processing

Thorsten Prechtl and Klaus Müllen

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany

1.1 Polymer Design

The performance of electronic or optoelectronic devices fabricated from conjugated polymers depends on three key factors: the structure of the macromolecule, its packing and morphology in a solid thin film, and the interfacing of the film with the outside world. The present book is mainly concerned with devices made by polymer deposition from solution. This formation of thin films is a complex process comprising a subtle interplay of scientific and engineering issues and thus asks for quite different competences. Complications arise when additional criteria come into play such as costs or the speed of the processing upon printing. There is, however, a serious caveat, which must be obeyed right at the beginning of such research and development: *do not commence processing and device fabrication before having optimized and ensured the integrity of the macromolecular structure as well as its reliable and reproducible synthesis.* Understandably, not every reader might be interested in the fine details of synthesis, but every reader, even if leaning toward the physics side of the field, would greatly benefit from knowing

(i) the basic design principles for conjugated polymers as well as
(ii) the concepts behind and potential pitfalls of the synthetic methods used.

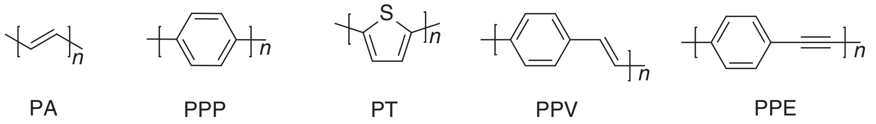
Comprehensive reviews describing conjugated polymer synthesis in all its variations can be found elsewhere [1–9]. Such collections are beyond the scope of this introductory chapter, which is, instead, restricted to preparing the reader's mind before proceeding to polymer processing.

In a conjugated polymer, unsaturated aromatic, olefinic, or acetylenic building blocks are covalently connected by single bonds to create a "box" of delocalized π-electrons. Although some torsion about single bonds is tolerated, too large deviation from coplanarity would hamper π-conjugation. Clearly, π-conjugation would also be interrupted by sp^3-hybridized carbon centers [10]. It is this large domain of mobile, polarizable electrons that qualifies an organic material to interact with light or to undergo electron transfer [11]. The energy levels of the electronic bands (corresponding to HOMO [highest occupied molecular

Solution-Processable Components for Organic Electronic Devices, First Edition.
Edited by Beata Łuszczyńska, Krzysztof Matyjaszewski, and Jacek Ulański.

orbital] and LUMO [lowest unoccupied molecular orbital] energies of small molecules) predict whether a polymer can readily be reduced or oxidized, and thus if it is a p-type or n-type material [10, 12, 13]. The band gap determines whether a material is an insulator, a semiconductor, or a conductor. The extended π-conjugation has originally been considered as being responsible for electrical conductivity, but the pioneering work of Heeger, MacDiarmid, Shirakawa, and coworkers has shown that conductivity requires the formation of charge carriers by doping [14–16], which is nothing other than partial oxidation or reduction [17]. The operation of devices implies an additional process, that is, electron transfer between external electrodes and the active organic component [18], and the efficiency of this interfacial process will again depend on the energy levels of the materials. Finally, the band gap is decisive not only for electron transfer but also for the optical properties in determining the wavelength of light absorption and emission [11].

The classical examples of conjugated polymers are polyacetylene (PA) with an alternating array of single and double bonds, poly-1,4-phenylene (PPP), and its electron-rich, though less stable congener polythiophene (PT). There are also “hybrid” structures such as polyphenylenevinylene (PPV) and polyphenylenethinylene (PPE) comprising both aromatic and olefinic or acetylenic moieties, respectively (see Scheme 1.1). The key difference between PA and PPP is that the former is obtained as an insoluble film upon catalyzed polymerization of acetylene whereby the catalyst can also act as a dopant to yield electrical conductivity, whereas PPP, in an alkyl substituted form, is more commonly synthesized in solution. Solubility in organic solvents is thus a central issue for the success of both synthesis and processing. What should not be ignored is the issue of stability. Thus, PA, for example, is known to readily interact with air with the formation of oxygen-containing functional groups, which hamper the flexibility and conductivity of the material [18, 20].



Scheme 1.1 Structures of classical conjugated polymers. Source: Müllen et al. 2013 [19]. Reproduced with permission of Royal Society of Chemistry.

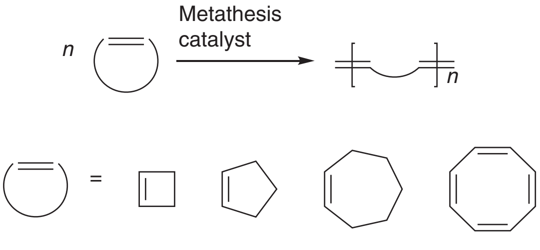
It is impossible not to be impressed by the huge available “toolbox” for conjugated polymer synthesis including

(i) the broad choice of aromatic building blocks,
(ii) the doping of such hydrocarbons with heteroatoms,
(iii) the (regular or irregular) incorporation of different repeat units into one polymer,
(iv) the modes of their connection (e.g. 1,4-, 1,2-, or 1,3-phenylene), and
(v) the attachment of substituents.

All this creates an enormous structural and thus functional manifold. Even if one ignores here their structurally related oligomers and other small conjugated molecules, which would certainly widen the wealth of organic electronic materials, it is this versatility of polymer structures that constitutes one strength of organic electronics and that opens the possibility of tailoring optical and electronic properties. This variety can be further extended into new directions by, for example, co-incorporation of metal centers or by synthesis in confining geometries to furnish discrete nanoparticles [21–27]. The latter are of tremendous use in photonics [28–31].

Materials chemistry has developed powerful rules, either empirical or guided by theory, to predict and explain the chromophoric and electrophoric properties of macromolecules, and it can clearly be understood that these are also determining electrical or optical device function. The art of thus "synthesizing" desired functions and performances is based on reliable structure–property relationships. Clearly, this fundamental concept becomes obsolete without reliable structures. Deviations from an idealized structure of the polymer, whether detectable or not, and impurities will thus not only compromise structure–property relations but also diminish device performance by trapping charges or excited states [32].

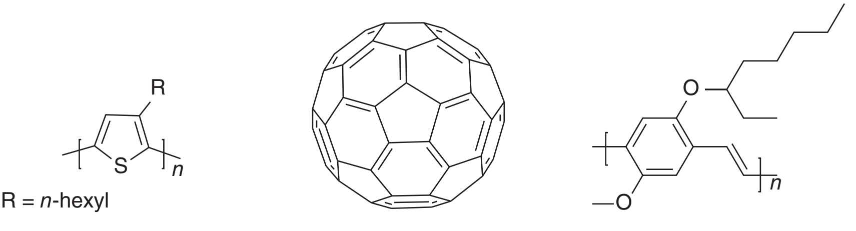
Understandably, the early science and technology of conjugated polymers was more concerned with exploring unknown territory by making new materials, rather than with ensuring whether they possessed sufficiently high structural precision and purity. This was accentuated by the slow rate at which the competences of cutting-edge synthetic organic chemistry were applied to this field. Improvements of synthetic protocols toward conjugated polymers and better analytical methods have, however, tremendously strengthened the validity of the materials science of conjugated polymers. More powerful synthetic protocols included metal-catalyzed bond formation [33–41] and metathesis polymerization [42–46] (see Scheme 1.2), whereas on the analytical side, established methods became more sensitive and new ones were additionally employed. Thus, the power of nuclear magnetic spectroscopy has been significantly enhanced by the availability of higher magnetic fields and multidimensional techniques [47–49]. More importantly, solid-state nuclear magnetic resonance (NMR) measurements [50, 51] have provided insights into the packing of polymers, which could not be ascertained by X-ray scattering [52]. Classical elemental analysis [53] remains of undiminished value but has become complemented by X-ray fluorescence microscopy [54–56].



Scheme 1.2 Representative metathesis polymerization of cycloolefins. Source: Albertsson and Varma 2003 [44]. Reproduced with permission of American Chemical Society.

Consequently, optimizing precise synthesis, scrupulous purification, and sensitive detection of defects must be carefully approached in order to make solution processing of polymers meaningful. Failure to meet these requirements would put the validity of the science and technology of (opto)electronics at risk. Accordingly, no reader should lightly excuse himself by setting aside the chemical fundamentals of the field and by relying only on expertise in physics.

There is, indeed, a tight connection between molecular structure and key physical processes in devices. Historically, conjugated polymers were considered to be candidates for developing electrically conducting “plastics,” which was best illustrated by the notions of obtaining “conducting polymers” or even “synthetic metals” [17]. As has been mentioned, conductivity is bound to the formation of charge carriers and this, in turn, leads to chemical instability. This obstacle together with unintentional doping of low band gap, and thus chemically reactive, polymers has caused loss of interest in this field, and other optical and electronic functions have moved into the limelight. This has then redefined the needs of synthesis, so that, for example, the first use of polymers as emitters in LEDs (light emitting diodes) by the group of Friend required a suitable synthesis of PPV by the Holmes group [57, 58]. In an LED, opposite charges injected from different electrodes must recombine to create excitons, so good device efficiency requires high and balanced concentrations of holes and electrons [59]. High charge carrier mobility is less important, whereas that is the decisive parameter for a polymer-based field effect transistor (FET) [60]. Thus, the availability of a regioregular poly-3-alkylthiophene, first synthesized by McCullough and Lowe [61], was instrumental in enabling Sirringhaus’ work [62] on polymer FETs. A polymer solar cell, in turn, is different from LEDs and FETs because a second component will be required. In order for a solar cell to become efficient, an electron-donating polymer must be combined with an electron acceptor to facilitate charge separation. Here, a breakthrough came when Heeger, Sariciftci, and coworkers [63] added C[60] fullerene (**1**) to a substituted PPV (**2**) to enhance the desired light-induced charge separation (see Scheme 1.3). All these cases nicely document the crucial role in obtaining good device performance of the nature of the material, although, as cannot be stressed enough, supramolecular order in the solid state and morphology of films come into play as well.

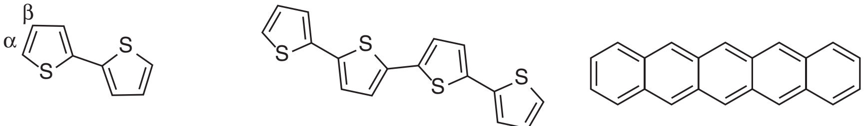


P3HT **1** **2**

Scheme 1.3 Examples of milestones in organic electronics. Source: Müllen et al. 2013 [19]. Reproduced with permission of Royal Society of Chemistry.

Although we will be looking in this chapter at polymer chemistry as the basis of device research, one must admit that efficient organic LEDs and solar cells have also been fabricated from small molecules [64]. Films of small molecules, but not of polymers, can be fabricated by vacuum deposition procedures. Although deposition from solution is cheaper, it requires, of course, sufficiently soluble materials [65]. Additional problems will arise if multilayers are needed. This asks for orthogonal solubility of different materials in different solvents, or loss of solubility by cross-linking before deposition of the subsequent layer [66, 67]. The advantages and disadvantages of employing polymers or small molecules and oligomers as active components of devices must be considered separately for each case. The latter can be purified by vacuum sublimation, and the electronic properties of oligomers, when plotted against the number of repeat units, converge toward those of the corresponding polymers [68–70]. On the other hand, solution-processed polymers give more homogeneous films over large areas, whereas small molecules tend to form crystalline domains, which may not only cause undesired light scattering but also obstruct charge transport because of the presence of grain boundaries [71]. The advantage of polymers does not lie so much in their electronic characteristics, but in their ability to establish controlled morphologies in pure or blended form. It should again be stressed that film formation from solution, in particular during printing, is a complex kinetic process including issues of nucleation [72], phase formation [73], wetting of substrate surfaces, and rheology [74]. All of these can be much better regulated for polymers.

Use of small molecules and oligomers, commonly believed to be structurally better defined than conjugated polymers, does not exclude difficulties arising from imperfect synthesis and impurities [75]. The case of organic FETs is instructive. Indeed, the pioneering work of Garnier, Fichou, Horowitz, and coworkers [76–80] on organic FETs might have gained more impact if their oligothiophene semiconductors had been made by controlled coupling of thiophenes rather than by oxidative oligomerization. The dimer (**3**) and tetramer (**4**) (see Scheme 1.4) they used were synthesized from thiophene by lithiation and cupric chloride-mediated oxidative coupling [81]. Further oligomerization was then achieved by oxidative coupling with ferric chloride [82]. It was then already well known that higher oligomers of thiophene tend to couple at both the α- and β-positions [83].



3 **4** **5**

Scheme 1.4 Dimer and tetramer of thiophene and pentacene (**5**). Source: Adapted from Müllen et al. 2013 [19] and Kagan and Arora 1983 [81].

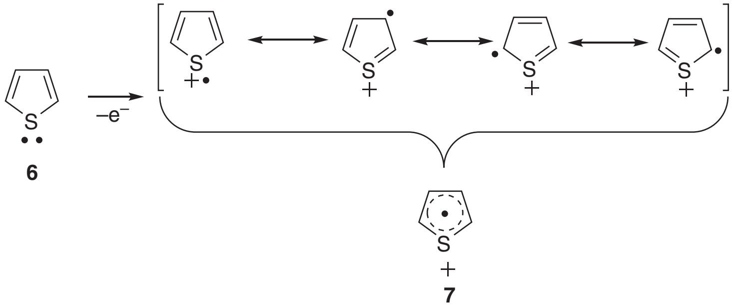
Pentacene (**5**), the prototype of an organic semiconductor, was deposited under vacuum in view of its low solubility. Nevertheless, samples were often contaminated by dihydroderivatives or related quinones arising from the reaction with oxygen and defining an urgent need for purification through repetitive cleaning steps [84–89].

The field of conjugated polymers and their structurally related small molecules has sometimes perceived prospects for technological and/or scientific breakthroughs, which in the end could not be fulfilled. The decline of the synthetic metals was not only due to the above-mentioned stability problem but also due to the fact that the propaganda claim of "replacing copper" had been somewhat exaggerated [90–95]. Likewise, organic electronic devices should not be advanced with the idea of surpassing silicon-based systems, but rather by emphasizing the advantages of organic materials and the new opportunities derived therefrom. Not only the physical functions but also the favorite materials have changed with time, and the attracted attention has often been a matter of fashion. This can best be seen from the hype about carbon materials with 0-, 1-, and 2-dimensional structures [96–105]. What has not changed during all these ups and downs is the need for robust and trustworthy synthesis and fabrication processes.

1.2 Polymer Synthesis

The issues of polymer precision and purity could not be explained better than by a quote from Hermann Mark dating back to the year 1948: "Because high polymers are difficult to purify and identify, the expressions purity and identity should be used with great care." He then went on to list, apart from structural inhomogeneities, the impurities caused by remnants of solvents, catalysts, and, not to forget, smaller oligomers [106]. Although conjugated polymers could mostly not be considered as "high" polymers, the problems there could be even more severe than for commodity polymers without electronic function. This is because even traces of impurities, while being less detrimental to mechanical properties, could seriously influence the physics of charge carriers and excitons [107].

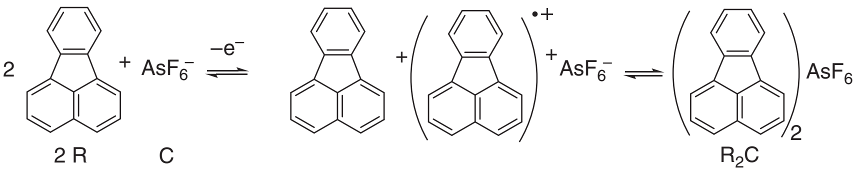
How can a linear, monocyclic, or polycyclic π-system be "activated" for reactions? If thiophene (**6**) donates an electron to an acceptor under formation of its corresponding radical cation **7** (see Scheme 1.5), it needs electrostatic stabilization.



Scheme 1.5 Resonance structures of a thiophene radical cation [108].

This can occur through interaction with a negatively charged counterion that, in a chemical oxidation, comes from the reagent or, in an electrochemical oxidation, from the supporting electrolyte. Other electron-rich (nucleophilic) partners can stabilize the radical cation as well, and one such partner is the neutral molecule.

A π-dimer **8** is initially formed, which under certain conditions will precipitate from solution, deposit at the electrode, and because of its arising electrical conductivity continue to grow to form stacks of discs (see Scheme 1.6). There, the stoichiometry, if R depicts the starting π-molecule and C the counter-anion, corresponds to R_2C. The conductivity of so-called radical cation salts originates from the mixed-valence state with one positive charge per two molecules [109–117] and is illustrated in Scheme 1.6 for the case of fluoranthene. There, the R_2C formula stands for the stoichiometry prevailing in the crystal.

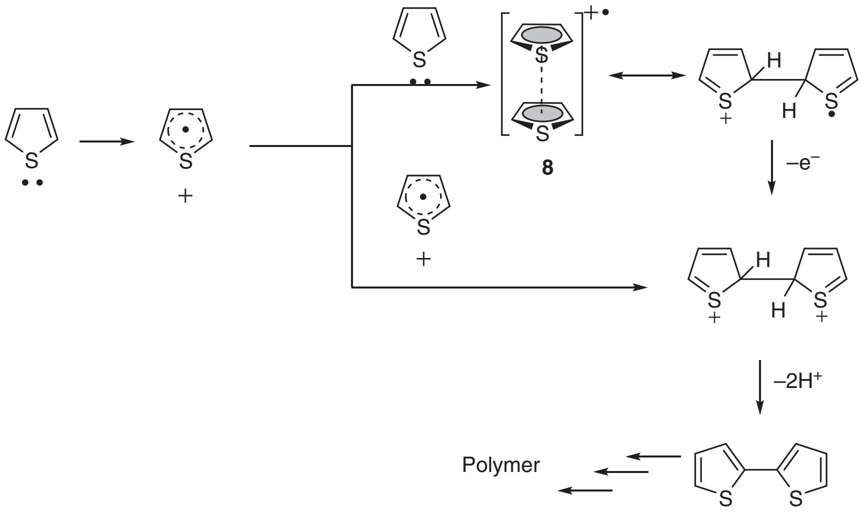


Scheme 1.6 Formation of a radical cation salt illustrated by the interaction between fluoranthene and hexafluoro arsenate. Source: Enkelmann 1982 [109]. Reproduced with permission of John Wiley & Sons.

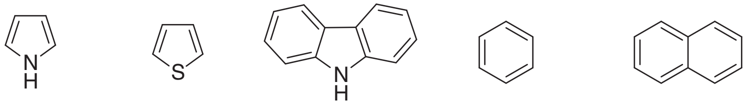
This scheme holds true only for π-systems such as polycyclic aromatic hydrocarbons (PAHs) with extended π-delocalization [109]. If the spin density is, however, highly localized at a single carbon center, the formation of σ-bonded dimers is preferred, which may subsequently lose their positive charge by loss of two protons (see Scheme 1.7). The initial σ-bond formation becomes the starting point of polymerization. The mechanism of growth, however, can be quite complex because oxidation of monomers and oligomers, σ-bond formation, and deprotonation steps can overlap [118]. This oxidative polymerization has been most commonly applied to electron-rich monomers such as pyrroles (**9**), thiophenes (**6**), or carbazoles (**10**) and also to small aromatic compounds such as benzene (**11**) or naphthalene (**12**) (see Scheme 1.8).

The reaction is experimentally simple, starts from an unfunctionalized monomer, and, depending on its redox potential, employs cheap oxidants such as iodine, copper salts, or ferric salts, the latter accompanied by Lewis acids such as aluminum chloride. Not surprisingly, when one considers the underlying reaction mechanisms, the structural precision of the polymers is poor [119]. Thus, monomers can be coupled in a non-regiospecific fashion and coupling products such as **13** in Scheme 1.9 can undergo further oxidative processes under fusion of the monomeric building blocks to larger disc-type π-units [119–122].

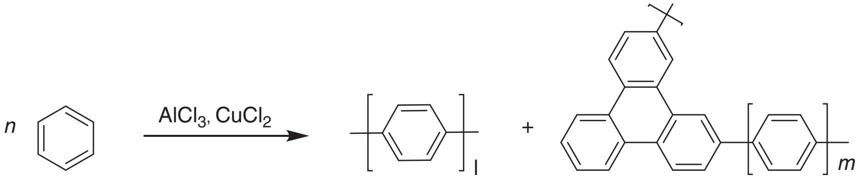
Coming back to the two central issues, that is, electronic design and synthetic realization, a good case could be made for the benzene-based PPP. To begin with, the conjugative interaction between the benzene moieties, i.e. across the inter-ring bonds, is relatively weak, and this leads to a large electronic band gap, which



Scheme 1.7 Radical cation stabilization, dimer formation, and oxidative polymerization starting from thiophene. Source: Enkelmann 1982 [109]. Reproduced with permission of John Wiley & Sons.



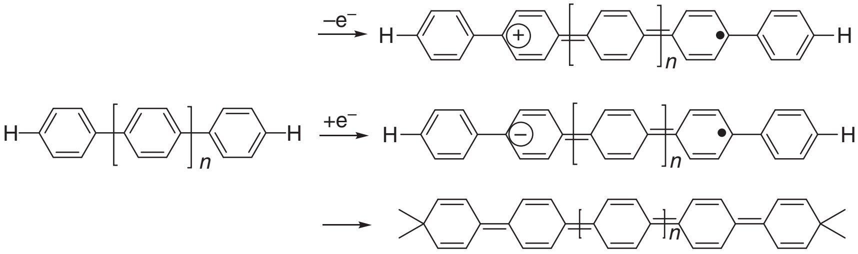
Scheme 1.8 Commonly applied monomers for oxidative polymerization. Source: Müllen et al. 2013 [19]. Reproduced with permission of Royal Society of Chemistry.



Scheme 1.9 Oxidative coupling of benzene and possible side reaction. Source: Kovacic and Jones 1987 [119] and Kovacic and Kyriakis 1962 [120]. Reproduced with permission of American Chemical Society.

results in light absorption and emission occurring at short wavelengths, so that PPPs are blue light emitters. Quite logically, lowering of the band gap can be brought about by increasing the π-bond order of interring bonds. This is possible by transforming the terminal *para*-carbon into a sp^3-center according to Scheme 1.10.

An alternative way is partial oxidation or reduction furnishing singly or multiply charged derivatives as described in Scheme 1.10 [123]. In both cases,



Scheme 1.10 The quinoid structure of PPP enforced by doping or by terminal sp^3-centers. Source: Sengodu and Deshmukh 2015 [123]. Reproduced with permission of Royal Society of Chemistry.

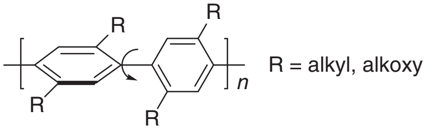
loss of aromaticity of the benzenoid units would also increase kinetic instability. There is, indeed, a typical problem of conjugated polymers and also of small organic π-systems: low electronic band gaps and, correspondingly, small HOMO–LUMO gaps, while leading to useful electronic properties such as long wavelength absorption, often suffer from unavoidable decomposition reactions with, for example, water or oxygen. Understandably, the end products of such reactions could lead to undesirable electronic and optical effects.

Conjugated polymers have been introduced into the literature, which, due to their small number of repeating units, could, at best, be coined oligomers [1, 124–126], and this points toward the initial synthetic task of polymer synthesis to achieve a high enough molecular weight – although the question of what is high enough must still be discussed. The rigidity of a conjugated backbone fails to produce much free enthalpy upon solvation. As a result, already small oligomers precipitate from solution and thus escape further growth. Alkyl chains, by making conjugated polymers softer and improving solubility, can indeed enhance the achievable molecular weights. Further, although this feature anticipates a key theme of polymer processing, alkyl substitution can assist the formation of supramolecular order, which has even led to the catchy term "side-chain engineering." The downside of making alkyl substituted polymers, next to causing more synthetic steps and diluting the active π-components, is that the steric hindrance of substituents may slow down the coupling of the monomeric units or, in more severe cases, cause increased torsion about interring bonds and thus hinder the desired π-conjugation. The nature and placement of the substituents will thus play a pivotal role [4, 127].

Avoiding the problem of insolubility of PPP by way of alkylation or alkoxylation of the benzene monomer at 2,5-positions did lead to well-soluble polymers such as **14** with high molecular weight. However, because of the increasing nonplanarity of the benzene subunits, the extended conjugation was severely compromised (see Scheme 1.11) [127, 129, 130].

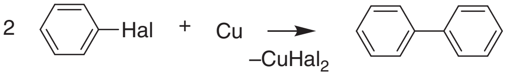
It has for long been known that halobenzenes such as **15**, upon treatment with copper powder, can couple to biphenyl (**16**) under formation of copper halide salts (Ullmann coupling) (see Scheme 1.12) [131].

Already then, concepts such as insertion of metal into the carbon–halogen bond and oxidation of the resulting intermediate have been considered in



14

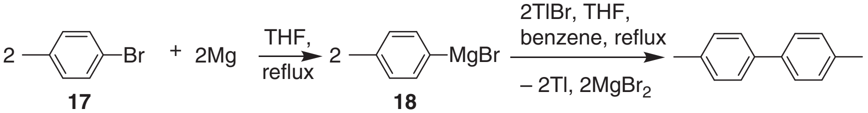
Scheme 1.11 Compromised extended conjugation due to increased nonplanarity. Source: Li et al. 2010 [128]. Reproduced with permission of American Chemical Society.



15 **16**

Scheme 1.12 Biphenyl synthesis by Ullmann coupling. Source: Ullmann and Bielecki 1901 [131]. Reproduced with permission of John Wiley & Sons.

mechanistic discussions. It thus appeared plausible to also use organometallic derivatives of halobenzenes such as magnesium (Grignard) reagents [132, 133] because removal of electrons from the resulting electron-rich benzene species would then allow the coupling of intermediate radicals, again, under extrusion of metal salts. Scheme 1.13 shows how the *in situ* generated Grignard reagent **18** of 4-bromotoluene (**17**) can be used for biphenyl synthesis (see Scheme 1.13) [135].



17 **18**

THF = tetrahydrofuran

Scheme 1.13 4,4′-Dimethyl-1,1′-biphenyl synthesis using a Grignard reagent [134].

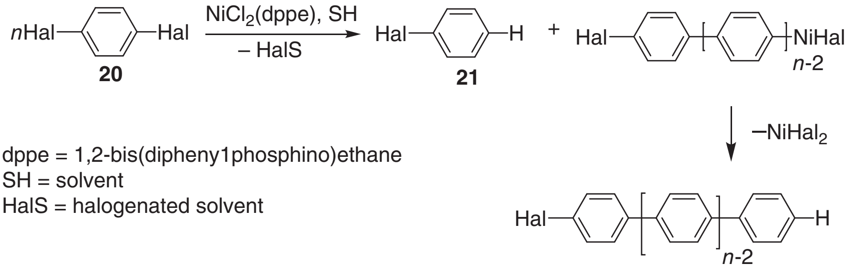
A major achievement was the use of zero-valent nickel metal instead of copper powder as introduced by Yamamoto et al. [136]. This protocol required, however, the chelation of the metal (in Scheme 1.14 through 1,5-cyclooctadiene) to keep it in solution. Independent of the role of the metal, it then appeared straightforward to proceed from monofunctional to a bifunctional 1,4-dihalobenzene monomer **19** and undertake a repetitive coupling toward the desired formation of "polymers" [133, 137].

19

COD = cyclooctadiene

Scheme 1.14 Yamamoto coupling of 1,4-dibromobenzene with chelated zero-valent nickel [136].

Leaving to one side the critical issue of the solubility of PPP, the trouble with this procedure is that such repetitive bond formations are accompanied by side reactions, often involving the solvent, with loss of functional groups to form monohalobenzene (**21**) [133, 138, 139]. This interrupts further polymer growth because a monohalo rather than a dihalo building unit would act as an end-capper as shown in Scheme 1.15.



Scheme 1.15 Polymerization of 1,4-dihalobenzene with end-capping by monohalobenzene [133].

What makes this side reaction even more severe is a characteristic feature of such step-growth polycondensation reactions, which are described by the Carothers equation [140]. When plotting the degree of polymerization $\overline{X}_N$ as a function of conversion *p*, it appears that polymers can only form toward the end of the reaction, i.e. by the coupling of initial oligomers, and this requires perfect stoichiometries. This is shown in Figure 1.1 where the Carothers equation for a bimolecular AA-BB-polymerization is used to display the influence of different

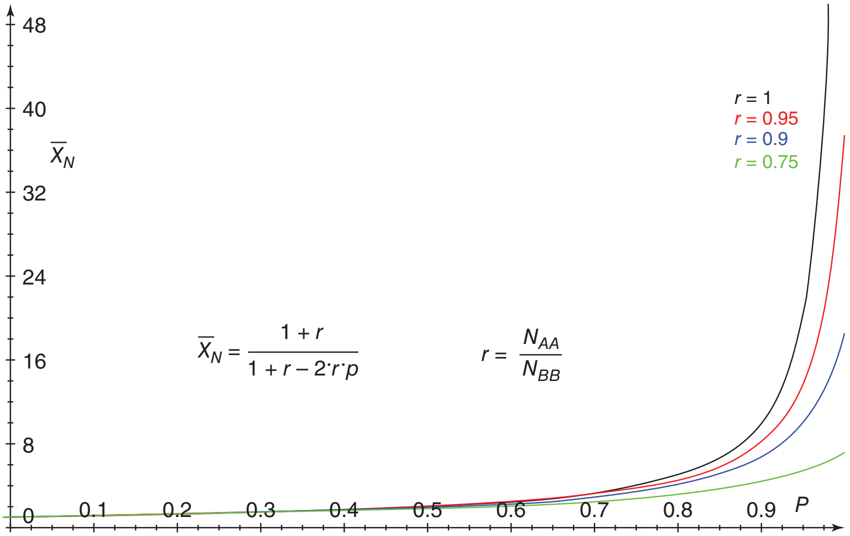
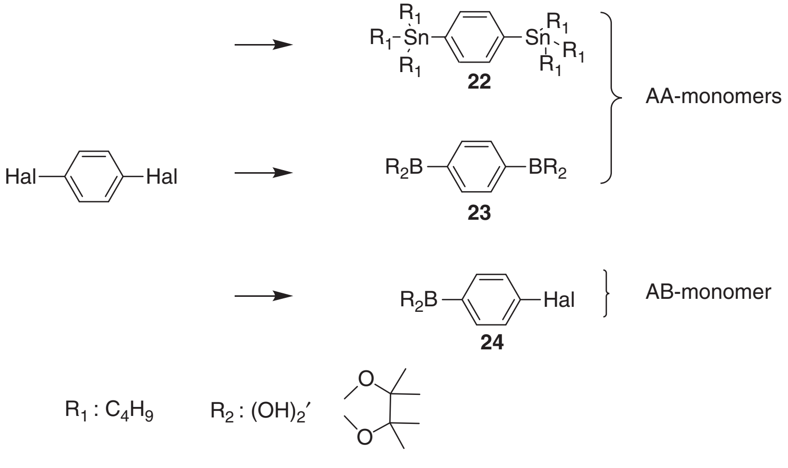


Figure 1.1 Plot of the degree of polymerization $\overline{X}_N$ as a function of the conversion *p* with different molar ratios of the monomers *r*.

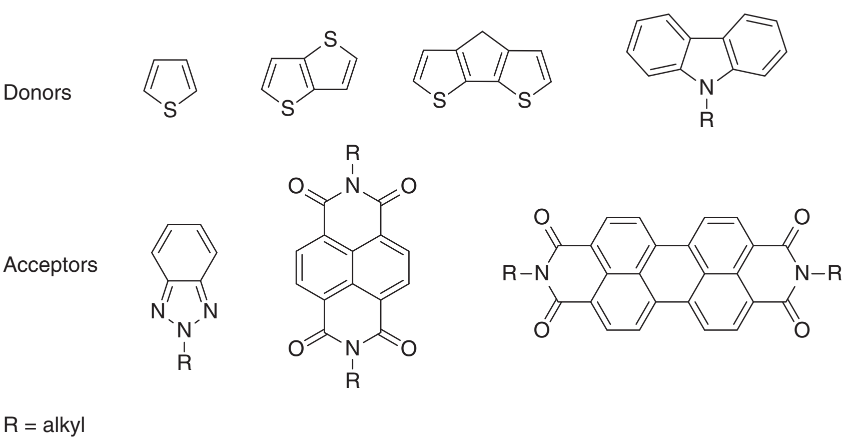
stoichiometries on the degree of polymerization. The molar ratio of the two monomer units is expressed by *r*, that is, the relative concentrations of the AA- and BB-monomers.

In gaining better control over such chemistry, two steps have reached tremendous importance: (i) transformation of halobenzenes into stable and purifiable boronate (**23**) or tin derivatives (**22**), which could then be subjected to coupling with halobenzene components in (ii) a transition-metal-catalyzed process (see Scheme 1.16) [33, 40, 141, 142]. The concept of catalysis must be emphasized as it stands in contrast to the above nickel-mediated coupling of halobenzenes, which requires stoichiometric amounts of metal. These synthetic protocols have been developed within the field of synthetic organic chemistry and have justly been awarded with the Noble Prize for Suzuki, Negishi, and Heck in 2010 [142–151]. Although these reactions, mostly referred to as name reactions, would certainly deserve more attention here in view of their broad synthetic scope and mechanistic implications, it is important that they have then been adjusted to the needs of polymer chemistry [129, 130, 152]. This achievement has revolutionized the synthesis of conjugated polymers and helped to put materials chemistry on a sounder basis. An additional advantage is that one can now, rather than reacting bifunctional AA- and BB-type components (such as diboronate and diahalo monomers), allow polymerization starting from (only) the corresponding bifunctionalized AB-building block **24** [153–155].



Scheme 1.16 Bifunctional tin and boronate reagents and a corresponding AB-monomer for cross-coupling reactions [108].

Further, although statistical incorporation of different dihalo monomers in a Yamamoto coupling can be achieved, it now becomes possible to create a strictly alternating sequence of building blocks in, for example, donor–acceptor (D–A) polymers (see Scheme 1.17) [156–160]. The access to defined D–A-polymers allowed fabrication of semiconductor materials with hole-transporting and electron-transporting properties [160]. A critical issue, that is the availability of the pure, functionalized building blocks, will be discussed later.



Scheme 1.17 Selected donor and acceptor building blocks for donor–acceptor polymers. Source: Müllen et al. 2013 [19]. Reproduced with permission of Royal Society of Chemistry.

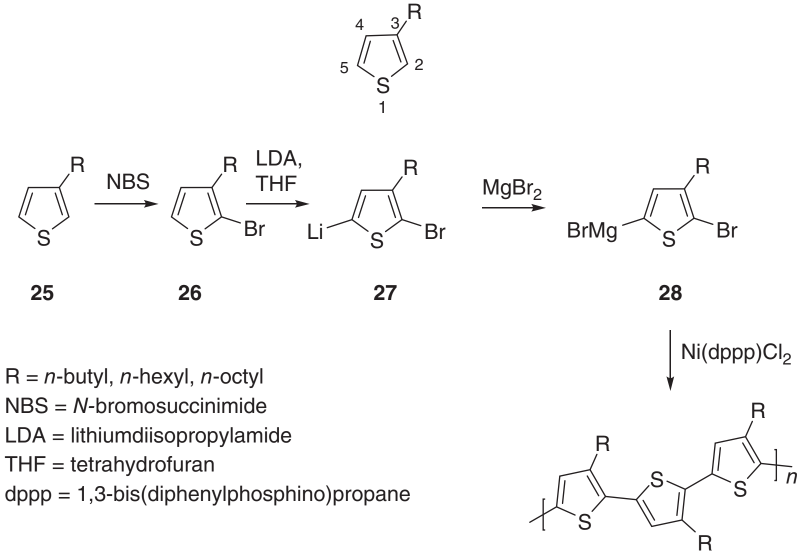
It then makes a difference, of course, whether the donor or acceptor unit is used as the halo component. These improved coupling protocols do not guarantee high molecular weights because side reactions can still occur such as loss of the tin or boronate functions or electron transfer processes between reagents leading to homocoupling [161]. The latter furnish deviations from a strictly alternating sequence of building blocks in D–A-polymers [162–164].

The synthesis of polythiophenes has played an important role in the development of conjugated polymer synthesis wherein the regioregular formation of head-to-tail polymers from 3-alkylthiophenes (see Scheme 1.18) presented a particular challenge that was solved by McCullough and Lowe [61]. According to Scheme 1.18, 3-alkylthiophene **25** was first subjected to bromination to yield **26**, followed by lithiation of the other α-position. Transmetallation of **27** provided the bifunctional AB-type monomer **28**, which was then polymerized to yield poly-3-alkylthiophene with a regioregularity of 91% [61].

The synthesis of polythiophenes has found an interesting variant discovered independently by McCullough and coworkers [165, 166] and Yokozawa and coworkers [167, 168], namely a polymerization rather than polycondensation according to Scheme 1.19. One implication of such a mechanism, which cannot be described in detail herein, is that it furnishes a living end as is obvious from structure **30**.

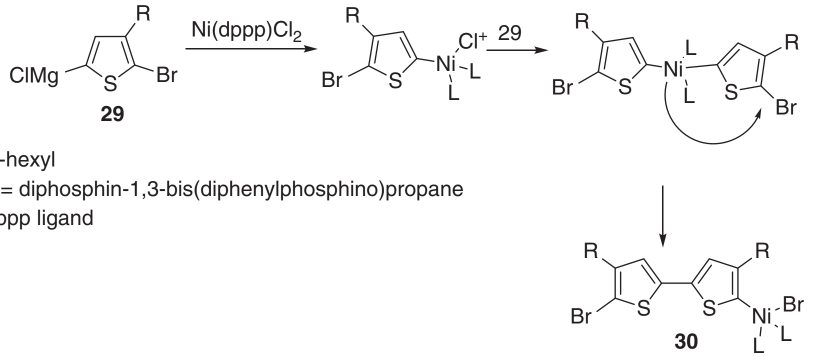
Thus, it now becomes possible to synthesize a copolymer which, for example, combines a rigid rodlike conjugated segment with a flexible, coil-type one [170–172]. An important consequence of this molecular design is that the coil can assist in the assembly of the conjugated unit [173]. It should also be mentioned that Yokozawa disclosed the possibility of a polymerization mechanism in the Suzuki synthesis of PPPs [174, 175].

Polyphenylenes as shown in Scheme 1.20 have then been widely synthesized employing either Yamamoto or Suzuki and Stille coupling reactions [128, 176, 177].



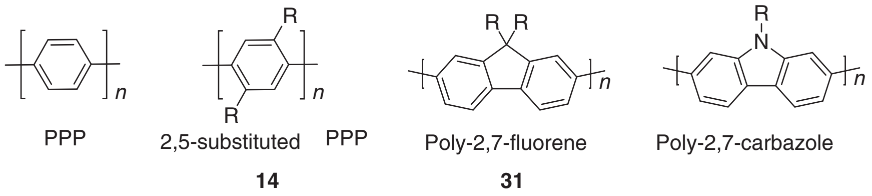
R = *n*-butyl, *n*-hexyl, *n*-octyl
NBS = *N*-bromosuccinimide
LDA = lithiumdiisopropylamide
THF = tetrahydrofuran
dppp = 1,3-bis(diphenylphosphino)propane

Scheme 1.18 Synthesis of AB-thiophene monomer **28** to yield regioregular poly-3-alkylthiophenes. Source: McCullough and Lowe 1992 [61]. Reproduced with permission of Royal Society of Chemistry.



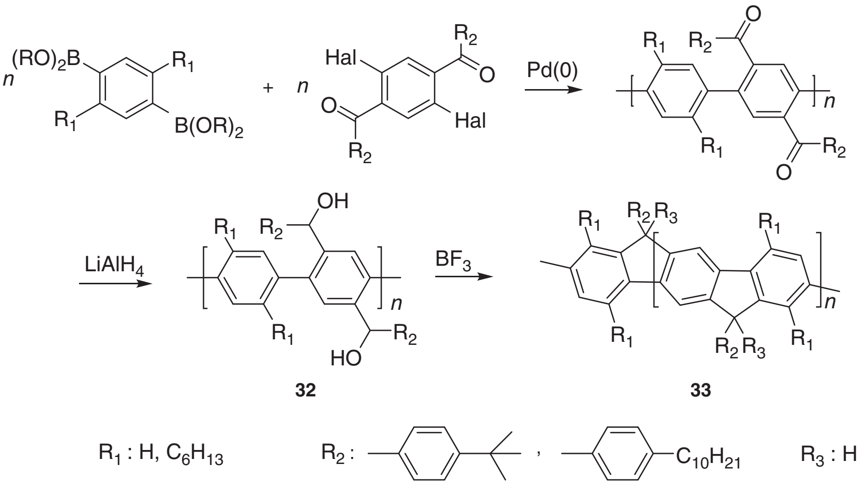
R = *n*-hexyl
dppp = diphosphin-1,3-bis(diphenylphosphino)propane
L = dppp ligand

Scheme 1.19 Mechanism of chain growth polymerization proposed by Yokozawa. Source: Cheng et al. 2009 [169]. Reproduced with permission of American Chemical Society.



R = alkyl

Scheme 1.20 Different poly-*para*-phenylene structures. Source: Müllen et al. 2013 [19]. Reproduced with permission of Royal Society of Chemistry.

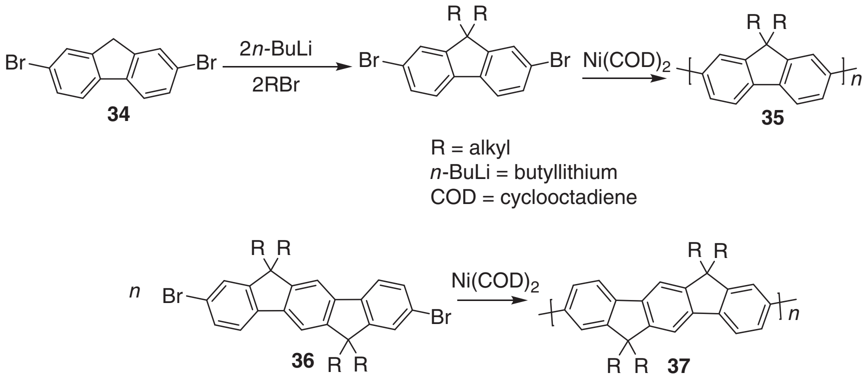


Scheme 1.21 Synthetic route toward LPPP. Source: Scherf and Müllen 1991 [178]. Reproduced with permission of John Wiley & Sons.

A special case of PPPs is presented by the ladder poly-1,4-phenylenes LPPPs **31** shown in Scheme 1.21. There, neighboring benzene rings are connected by methylene bridges so that the whole π-system is forced into a plane, thus favoring conjugation. Solubilizing alkyl substituents can be attached to the bridging carbons and no longer cause torsion between benzenes as occurring in alkyl substituted PPPs **14**. LPPPs have played a useful role as blue emitters in LEDs [179].

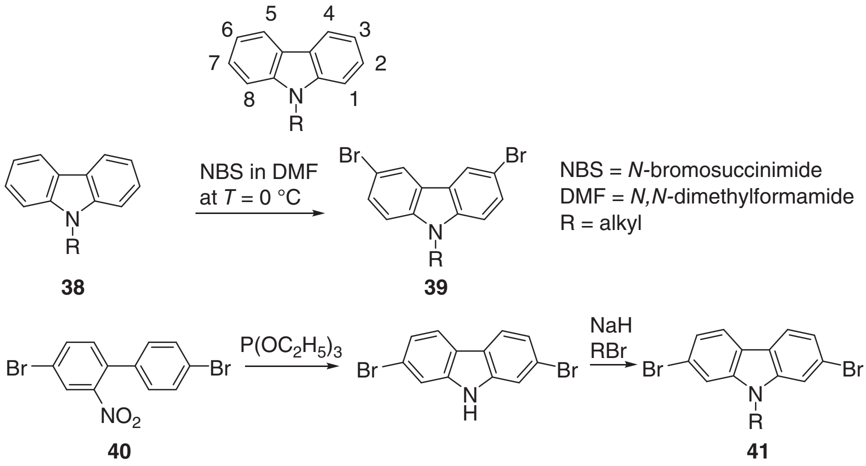
LPPPs highlight the opportunities of more sophisticated synthesis of conjugated polymers, but also the potential drawbacks. This is readily understandable from the synthetic protocol in which a functionalized PPP **32** must be transformed into the ladder structure **33** by polymer-analogous ring closures [178]. Failure to do this quantitatively will leave defects with twisted benzene rings, and we shall come back to the synthesis of ladder structures by improved methods later. There is yet another feature that again documents the close connection of physical properties and perfection of synthesis. The emission of the blue emitting LPPP is a little bit too greenish for a blue LED and can be somewhat hypsochromically shifted by going to step-ladder PPPs. There, planarized moieties such as fluorene (**34**) or indenofluorene (**36**) are coupled via single bonds to establish step-ladder polymers **35** and **37** [180–185]. Understandably, the bridging units can be more smoothly closed for a monomer rather than for a polymer allowing purification before polymerization (see Scheme 1.22).

This is also a good opportunity to consider the availability of the monomeric buildings blocks as starting materials of polymer synthesis. First, it should be mentioned that coupling of unsaturated monomers can also be achieved in a catalytic process by way of CH-activation, thus avoiding the initial formation of halogen-functionalized building blocks [187–191]. Dihalobenzenes are commercially available, whereas the benzene precursors of LPPPs require special synthesis. Often, regioselectivity is a critical issue in the syntheses of dihalo building blocks. Although 3,6-dibromocarbazole (**39**) is readily accessible by bromination



R = alkyl
n-BuLi = butyllithium
COD = cyclooctadiene

Scheme 1.22 Fluorene (**34**) and indenofluorene (**36**) polycondensation after regioselective bromination. Source: Setayesh et al. 2000 [184] and Bernius et al. 2000 [186]. Reproduced with permission of American Chemical Society.

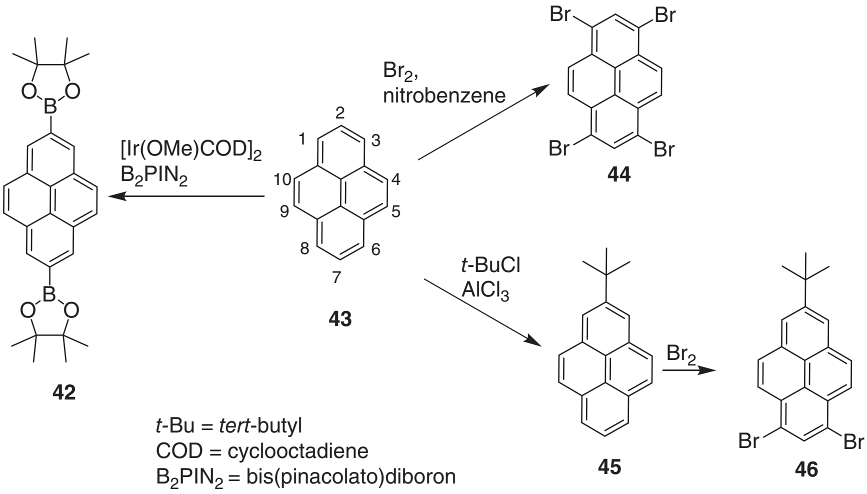


NBS = *N*-bromosuccinimide
DMF = *N*,*N*-dimethylformamide
R = alkyl

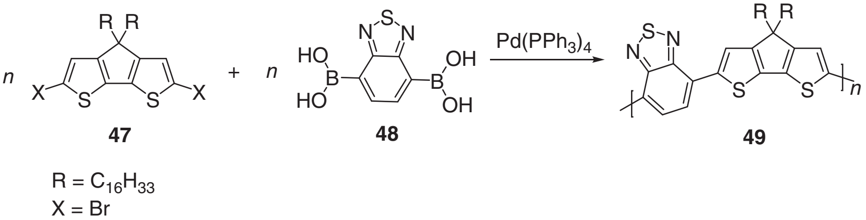
Scheme 1.23 Regioselective monomer synthesis as demonstrated for 3,6-dibromocarbazoles and 2,7-dibromocarbazoles. Source: Majchrzak et al. 2016 [192] and Dierschke et al. 2003 [193]. Reproduced with permission of Royal Society of Chemistry.

of carbazole (**38**) [192], the 2,7 regioisomer **41** requires a more expeditious route starting from a biphenyl precursor **40** (see Scheme 1.23) [193].

Using pyrene (**43**) as a monomeric building block of conjugated polymers is very attractive in view of its unique optical properties, but synthetically more complicated. Pyrene undergoes halogenation in the 1,3,6,8-positions [194] rendering access to a pure dihalo isomer difficult. A synthetic trick employs a Friedel–Crafts alkylation yielding the 2-*tert*-butylpyrene (**45**). The latter serves as a useful intermediate by blocking the 1 and 3 positions [195, 196]. Monomer **46** then furnishes a high-molecular-weight poly-1,3-pyrene as a blue emitter (see Scheme 1.24) [195].



Scheme 1.24 Pyrene (**43**) in different reaction protocols. Source: Figueira-Duarte et al. 2010 [195], Miura et al. 1994 [196], and Coventry et al. 2005 [197]. Reproduced with permission of John Wiley & Sons.

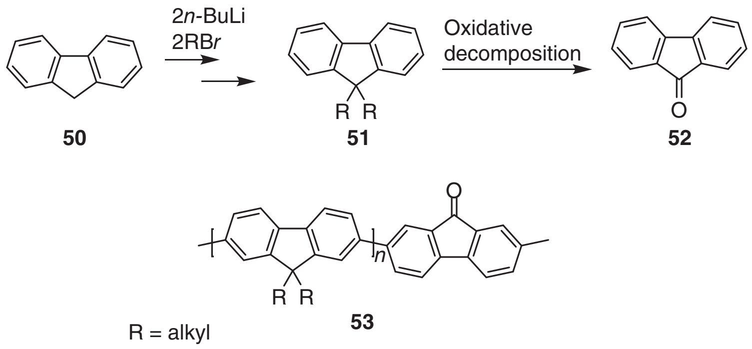


Scheme 1.25 Use of bifunctionalized cyclopentadithiophene (**47**) and the diboronate of benzothiadiazole (**48**) to achieve an alternating D–A-polymer. Source: Zhang et al. 2007 [202] and Hinkel et al. 2015 [203]. Reproduced with permission of American Chemical Society.

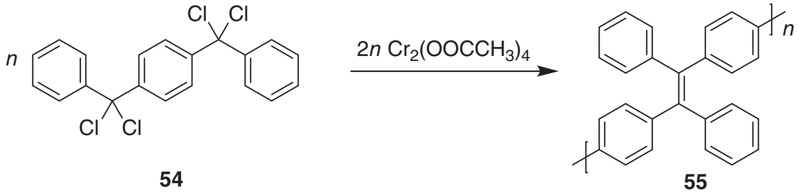
Stannyl and boronate derivatives can be obtained from the corresponding halo compounds, but sometimes from the hydrocarbons directly. Thus, the diboronate **42** can be made from pyrene in an iridium-catalyzed reaction [197].

Purification of all monomers is a mandatory step. It is, for example, recommended to crystallize boronate reagents [198], and in the case of the D–A-polymer **49** has furnished an "inverse" Suzuki coupling by the use of cyclopentadithiophene **47** [199–202] and of a crystalline derivative of diboronate **48** (see Scheme 1.25) [202–207].

There are other sources of trouble in providing monomers for conjugated polymer synthesis. One readily understands that 9,9-dialkyfluorenes are obtained from fluorenes with CH$_2$-bridges by deprotonation and subsequent alkylation (see Scheme 1.26) [208]. The intermediate monoalkyl species, which is difficult to remove before polymerization [176], but even the complete dialkyl analog **51** can undergo oxidative decomposition, thus producing a carbonyl group. The resulting fluorenone **52**, which can then not be removed from the polymer chain



Scheme 1.26 Alkylation of fluorene (**50**) and poly-2,7-fluorene containing a fluorenone defect. Source: Adapted from Perumattam et al. 1994 [208] and Romaner et al. 2003 [209].



Scheme 1.27 1,4-Bis(phenyldichloromethyl)benzene (**54**) yielding poly-1,4-phenylene-1,2-diphenylvinylene (**55**). Source: Hörhold et al. 1977 [213]. Reproduced with permission of John Wiley & Sons.

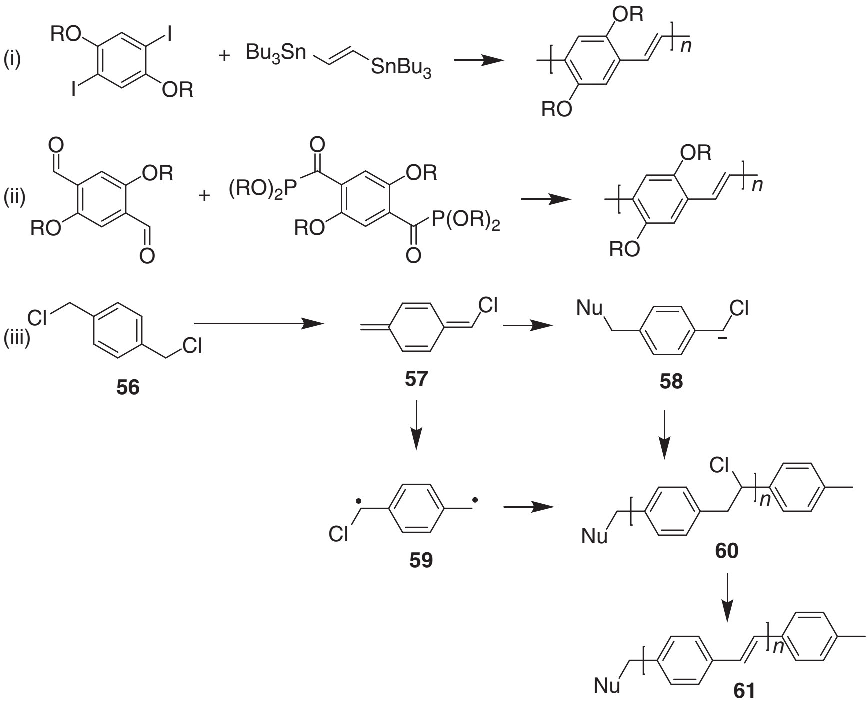
53, is a chromophor in its own right and severely changes the emission behavior by giving rise to additional bands at longer wavelengths [209].

PPPs and PPEs exist as rigid rods that qualify them to assemble to lamella-type aggregates via side-by-side packing of the chains [5, 8, 50, 177, 210–212]. In contrast, the flexible vinylene groups of PPV, which exist in both cis- and trans-configurations, impart a lower tendency toward packing and even give rise to coiled conformations. A characteristic case is the diphenyl derivative of a PPV (**55**) introduced by Hörhold et al. (see Scheme 1.27) [213].

This polymer is soluble even without attached alkyl chains, which can be assigned to the twisted conformation of the chain. The latter is less favorable for tight packing.

There are three conceptually different ways of PPV synthesis (see Scheme 1.28): (i) suitably functionalized benzene and olefin derivatives are coupled under σ-bond formation in a manner analogous to PPP synthesis [214], (ii) 1,4-xylenes are subjected to chemical transformations furnishing both electrophilic and nucleophilic reagents prone to a connective double bond formation [215], and (iii) xylene derivatives such as **56** are treated with base. After 1,6-elimination, a quinoid intermediate such as **57** is formed, which polymerizes to **60** containing saturated vinylidene units. These are then subjected to polymer-analogous 1,2-eliminations to establish the desired vinylene groups and thus the PPV [216].

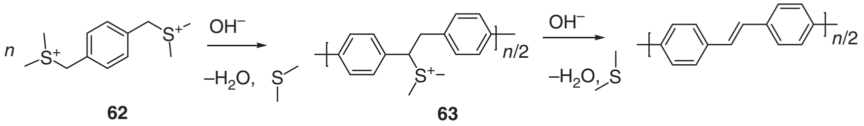
Depending on temperature, solvent, concentration, and additives, the polymerization can proceed by a radical or anionic mechanism: the anionic pathway,



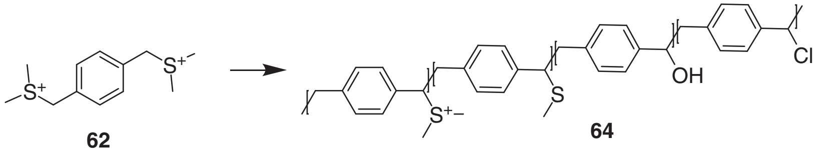
Scheme 1.28 Concepts of PPV synthesis through σ-bond formation (i), connective double bond formation shown here for the polycondensation according to Horner (ii) and the Gilch precursor route (iii) [214–216].

which prevails in the presence of large amounts of base, is described by the reaction from **57** to **58**. The molecular weight of the resulting precursor polymer **60** is often low. The radical pathway comprises the formation of the diradical intermediate **59** from **57**. This diradical undergoes polymerization and yields polymers with relatively high molecular weight. Polymerization of **56** often affords products with a bimodal polymer weight distribution, which can be explained by the presence of both mechanisms [217–219].

The latter protocol implies a so-called precursor route. This method deserves special attention here because it has played an important role in the evolution of polymer synthesis and is, again, perfectly suited to highlight the issue of structural perfection. Casting a thin solid polymer film from solution is often hampered by insufficient insolubility of the material. It has already been pointed out, on the other hand, that after deposition, one may prefer insolubility, for example, for depositing a further layer without redissolving the first one. The precursor **60** comprises saturated bridges, is flexible and soluble, but can re-establish the desired (insoluble) conjugated polymer PPV. This looks good on paper, but is not trivial. The elimination in film form by either a base-induced or thermally stimulated process must proceed quantitatively and should not obstruct the film or the substrate underneath. Thus, PPV has originally been synthesized via the so-called Wessling–Zimmermann route (see Scheme 1.29) [220].



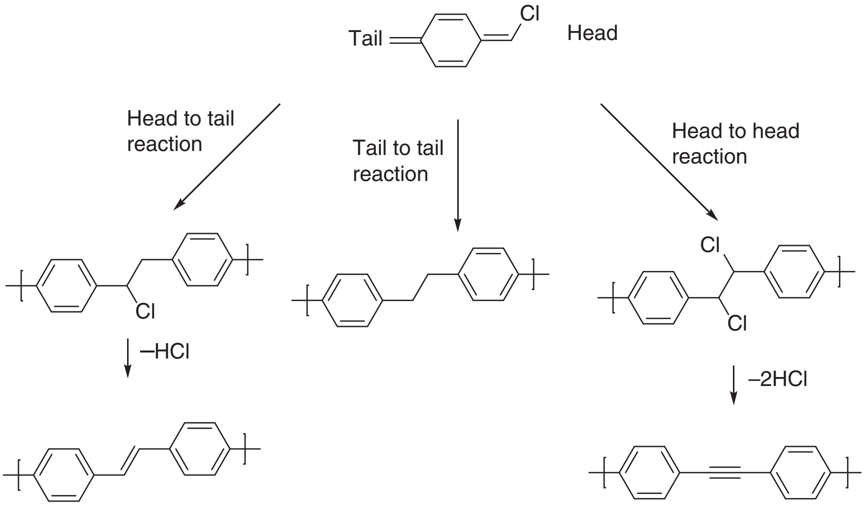
Scheme 1.29 Wessling–Zimmermann route toward PPV. Source: Wessling 1985 [220]. Reproduced with permission of John Wiley & Sons.



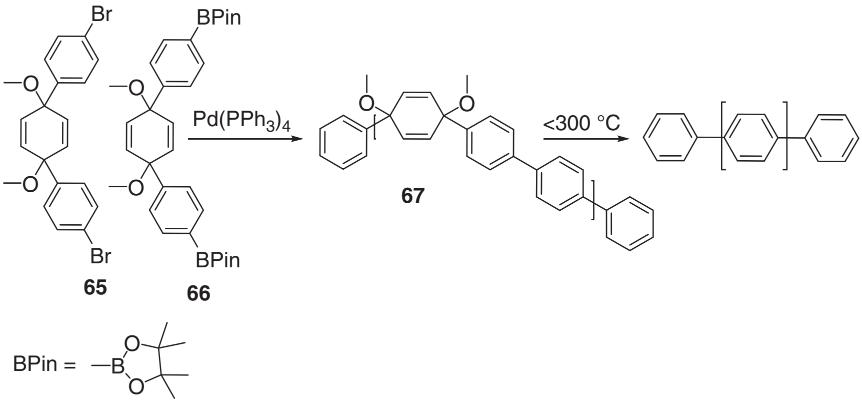
Scheme 1.30 Side reactions within the Wessling–Zimmermann route [221].

This procedure starts from **62**, which gives rise to the precursor polymer **63**. If the elimination of **63** is not quantitative, saturated units are left, which interrupt π-conjugation. What is more problematic is that elimination in the presence of water can lead to substitution rather than elimination of the sulfonium substituent (see Scheme 1.30). This forms alcohols that can give rise to ketone impurities [221–223]. The latter act as traps for excitons, which will, of course, obstruct efficient light emission.

Interestingly, this route has been optimized, but even the so-called Gilch route (shown in Scheme 1.28) has been shown by impressive studies performed in industry to produce a whole zoo of side products [224, 225] (see Scheme 1.31).



Scheme 1.31 Side products in the Gilch polymerization depending on the mode of connection of the monomers. Source: Becker et al. 1999 [224]. Reproduced with permission of American Chemical Society.

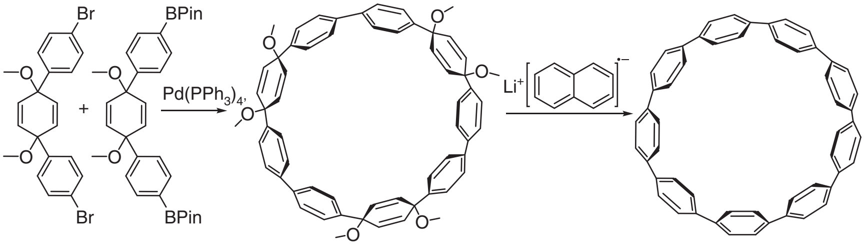


Scheme 1.32 *syn*-1,4-Bis(4-halophenyl)-1,4-dimethoxycyclohexadienes (**65**) to achieve a well-soluble and processable precursor polymer **67**. Source: Abdulkarim et al. 2016 [226]. Reproduced with permission of American Chemical Society.

It is clear that the precursor protocols define a rich playground for exercises in precision synthesis. It might therefore be instructive to revisit PPP and PA synthesis (see Scheme 1.32). Various benzene derivatives have been synthesized and subjected to the synthesis of a PPP precursor polymer. A recent and particularly successful case uses the kinked disubstituted 1,4-*syn*-dimethoxycyclohexadienylene monomer **65**, which is obtained by nucleophilic attack of an organometal reagent upon benzoquinone [226]. This reaction is not stereoselective and anti-1,4-bis(4-halophenyl)-1,4-dimethoxycyclohexadiene (as one configurational isomer) can also be formed. To achieve pure syn- or anti-product, separation by column chromatography or recrystallization is quite demanding [227, 228].

This kinked structure **65** has originally been used to make cycles such as **68**, which could then be transformed into aromatic macrocycles (see Scheme 1.33) after reductive removal of the methoxy groups and re-formation of the benzene rings [227, 229, 230].

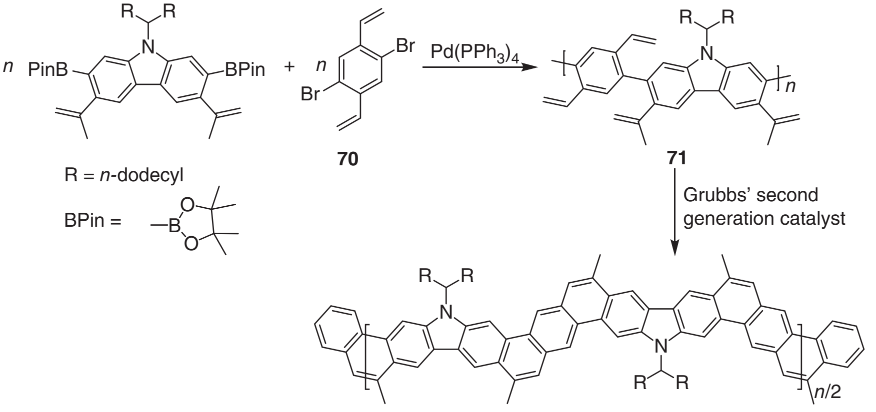
What allows ring formation is also instrumental in avoiding the tight packing of the linear polymer **67** in the solid and in affording solubility. Forming the target



Scheme 1.33 *syn*-1,4-Bis(4-halophenyl)-1,4-dimethoxycyclohexadienes leading to cyclo[*n*]phenylene (**69**). Source: Jasti et al. 2008 [227]. Reproduced with permission of American Chemical Society.

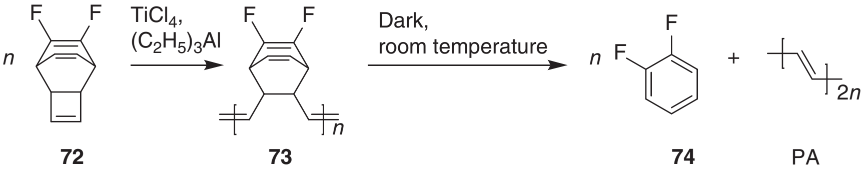
PPP polymer by reductive elimination does not make sense because it would afford insoluble materials. Also, treating a film of **67** with a reducing agent causes problem because of limited diffusion of the reagent. It was therefore critical that the elimination starting from **67** could be achieved in a thermal rearomatization process providing a perfect PPP.

Coming back to the synthesis of ladder polymers as a critical case of polymer-analogous reactions, 1,4-dibromo-2,5-divinyl benzene (**70**) was used to achieve **72** by Suzuki cross-coupling (see Scheme 1.34). The ring-closing metathesis reaction of **71** was optimized, and analysis of the resulting ladder polymer showed that less than 1% of the vinyl groups had not reacted and, instead, produced defects by interrupting the ladder-type backbone. This small amount of defects has also been confirmed by analysis through scanning tunneling microscopy (STM) [231], but still influences the observed length of exciton delocalization.



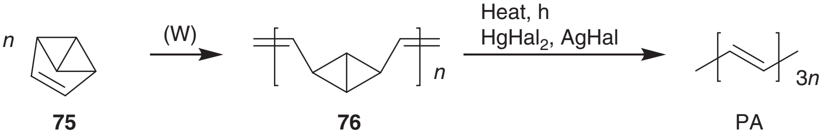
Scheme 1.34 Ring-closing metathesis reaction to achieve a ladder-type polymer with a small degree of defects. Source: Lee et al. 2016 [231]. Reproduced with permission of Royal Society of Chemistry.

Thermally stimulated transformations without the involvement of additional reagents and the metathesis reaction have also proven their value in precursor routes toward PA. The "Durham" route introduced by Feast and coworker [232] utilized a ring-opening metathesis from **72** to polymer **73**, followed by thermally induced extrusion of benzenes **74** from **73** (see Scheme 1.35). The perfection of this process follows from the stability of the extruded benzene building block.



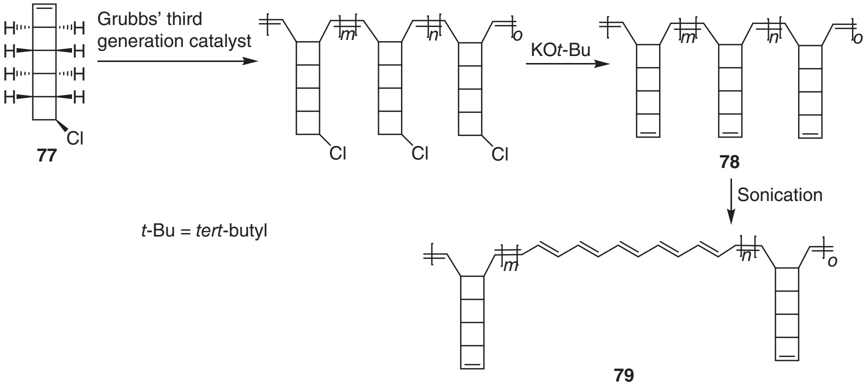
Scheme 1.35 PA through the Durham route [232].

Somewhat related, PA formation from **75** relied on a skeletal rearrangement of **76**, although the explosive nature of its benzvalene subunits made its application less favorable (see Scheme 1.36) [233–235].



Scheme 1.36 Ring-opening metathesis polymerization of benzvalene and rearrangement of the intermediate polymer **76** to polyacetylene [233].

To complete the possibilities of PA formation, a recent and particularly original way to obtain PA should be mentioned. It is based on unzipping of a ladderene precursor polymer **78** through sonication (see Scheme 1.37). This is obtained by ring-opening metathesis polymerization of the ladderene **77** and then unzipped to yield the PA copolymer **79** [236].



Scheme 1.37 Ring-opening metathesis polymerization of ladderene **77** and its unzipping through sonication to polyacetylene copolymer **79**. Source: Chen et al. 2017 [236]. Reproduced with permission of American Association for the Advancement of Science.

1.3 Molecular Structure, Supramolecular Structure, and Interfaces

Although in the previous sections we have mostly been dealing with overarching principles and general guidelines of polymer synthesis, the following one will focus more on reviewing detailed literature examples. Before that, an introductory comment on how we depict polymer structures seems appropriate. This is normally done by a molecular formula comprising the repeat unit and its average number, which then also reflects the molecular weight. Inspection of this formula tells us a lot about the nature of the polymer in terms of the above design criteria. Experience would readily tell us, for example, whether we are dealing with a p- or n-type material or in which wavelength domain the polymers absorb light. In principle, this description also holds for "infinite" structures, but becomes less compelling for increasingly complex π-systems such as carbon nanotubes (CNTs) or holey graphenes, where a "repeat unit" cannot be defined easily if at all.

Regarding the molecular weight of polymers and thus high values of n, first of all, these hold promise for more robust and more homogeneous films upon deposition. Beyond the mechanical aspect, higher molecular weights are expected to favor charge carrier transport for, both, molecular and supramolecular reasons, i.e. transport along a molecular chain and between chains in a given morphology [176, 237].

The length of a polymer chain can differ significantly from batch to batch, even if seemingly identical experimental conditions have been established [238]. This stresses the need for efficient methods of purification and a short overview over the appropriate approaches is necessary. Further, as the quality of polymer synthesis cannot be decoupled from the power of the analytical methods, these must be covered as well.

In general, the length of a polymer is described by M_n (the number-average molecular weight), M_w (the weight-average molecular weight), and the ratio between weight- and number-average molecular weight, which is called dispersity D_M [239]. To achieve small values of D_M, several protocols can be followed such as precipitation from solution [240], Soxhlet extraction [241], and preparative [242] and recycling gel permeation chromatography (GPC) [243–247]. Purification by precipitation from solution does not only influence the average molecular weight, but also the dispersity, because small oligomers often do not precipitate as opposed to polymers. This method has severe limitations as higher polymers cannot be further separated [226, 240]. Additional separation of higher molecular weights can be achieved by Soxhlet extraction where the solid polymer is washed with different ("matching" or "mismatching") solvents, thus furnishing molecular weight fractions with smaller dispersity [240].

Within preparative GPC, the polymer solution is eluted through a column filled with a porous gel. Separation of the polymers is based on different hydrodynamic volumes. Polymers with smaller hydrodynamic volumes enter the pores so that fractions with higher hydrodynamic volumes elute more readily and fractionation becomes possible [240]. Further, if the eluted fractions are reinjected onto the column in a so-called recycling GPC, the desired fractions can be separated, whereas the undesired fractions are subjected to another passage [243–247].

Analytical techniques are needed to assess the success of the fractionation method. The importance of solution and solid-state NMR spectroscopy has already been emphasized for a detailed structural analysis. Given that a polymer possesses defined end group(s), one can relate the intensity of the corresponding NMR signals to that of the repeat units, thus obtaining information on n [248]. Clearly, such a method becomes less reliable with higher molecular weights. The same holds true for matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry. One may be able to identify the nature and number of repeat units, but higher molecular weights will escape detection as they will no longer desorb. This method is thus mostly restricted to oligomers [249–251].

If a polymer solution is irradiated by a laser beam, the intensity of the scattered light at different scattering angles yields direct information on the molecular weight and the size of the scattered moiety. As the intensity of the forward scattered light correlates with the particle size, one limitation of the static light scattering is that the scattering intensity increases with the third power of the particle size, so that small particles cannot be detected in the presence of large ones. Static light scattering therefore requires a small D_M. In cases where small particles in the presence of large ones should be investigated, it is recommended to utilize dynamic light scattering to resolve the contribution of the small sizes. Also, the detection of large particle sizes and the corresponding molecular weights has upper limits, as for large particles, the necessary access to scattering angles close to zero is not straightforward. Nevertheless, this method has the advantage that it does not require calibration [252, 253]. This does not hold true for GPC. The problem there is that the rigid-rod-conjugated polymers have a different hydrodynamic volume than the random-coil polymers normally used for calibration. Toward a semiquantitative analysis, standard polymers with a rigid-rod character would be required. The latter are, however, often available only for lower molecular weights, making an extrapolation toward higher chain lengths less reliable [254].

Returning to the electronic properties of different molecular weights of conjugated polymers, studies by Kline et al. [255, 256] become relevant who investigated the charge carrier mobilities for different chain lengths of regioregular poly-3-hexylthiophene (P3HT). The polymer was synthesized following the McCullough route (as shown in Scheme 1.18) and compared with commercially available regioregular P3HT. The commercially available one showed a large dispersity and was subjected to Soxhlet extraction yielding three fractions (<10 kDa, ≈10 kDa, and >30 kDa) with a dispersity ranging from 1.3 to 1.9 and a regioregularity >95%. The molecular weight of the polymer made by the McCullough route was monitored over time and showed a dispersity ranging from 1.1 to 1.5 and a regioregularity >98%. In FET devices fabricated under identical conditions, the differently made polymer samples gave the same trend of increasing charge carrier mobility with increasing molecular weight, but no saturation effect could be achieved [255].

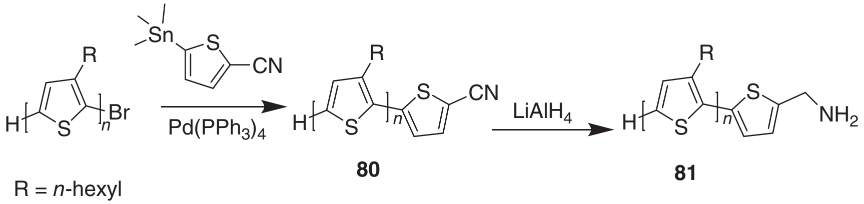
In a related work, different fractions (<4 kDa, ≈10 kDa, >30 kDa) of P3HT were cast to films using different solvents and different annealing protocols. Low-molecular-weight polymers appeared to be more sensitive to processing conditions, most probably because of more profound morphology changes. Indeed, the charge carrier mobilities differed by a factor of 100. Even under optimized processing conditions, however, low-molecular-weight polymers could not reach the charge carrier mobilities of their high-molecular-weight congeners [256].

Related works on poly-3-alkylthiophene lead to the conclusion that M_n values of about 20–30 kDa and a D_M of 1.2–1.8 were preferable to achieve robust devices with a high charge carrier mobility [257–259], but it was speculated that even much higher charge carrier mobilities could be achieved by longer, defect-free chains [255].

Similar conclusions could be drawn from FETs using the widely known PPV 2 (shown in Scheme 1.3) as a semiconductor whereby polymer fractions with 100 kDa, 1, and 2.8 MDa were cast from toluene followed by annealing of the films [260].

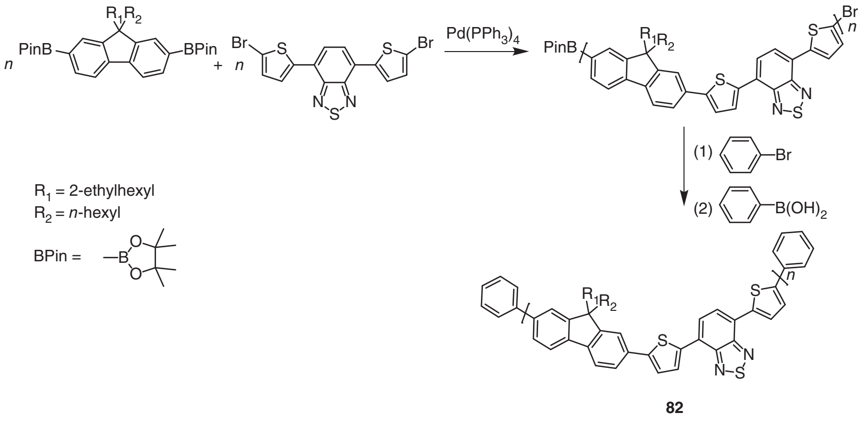
Astonishingly enough, the syntheses of many polymers have been reported in the literature without the terminal functions ever being specified. This is careless because functional groups at the chain ends may interact with charges or excitons or undergo decomposition reactions. End-capping is therefore indispensible as a final synthetic step. Of course, this can become complicated if different functional groups are involved. Thus, a repetitive Suzuki coupling, if no dehalogenation and deboronation has occurred, will result in both kinds of end groups, which will then have to be "deactivated" by reaction with an excess of the corresponding reagent. In any event, a strong plea is made herein to specify the end groups within the molecular formula.

Next to problems of undesirable decomposition, defined end groups are relevant for controlling (i) the interaction between polymers and functional nanoparticles in a device [261] and (ii) surface properties of polymer films [262]. Liu investigated the interaction between CdSe nanorods and regioregular P3HT equipped with terminal amino functions. The polymer was synthesized through a modified McCullough polymerization [165, 263, 264] followed by *in situ* end functionalization with an organotin reagent bearing a cyano group (**80**). Reduction with $LiAlH_4$ resulted in the desired end-functionalized polymer **81**. The precursor polymer shown in Scheme 1.38 with undefined bromo and hydrogen end groups and the polymer with defined amino termini were both applied in film formation with CdSe nanocrystals. Different composites were introduced into photovoltaic devices furnishing power conversion efficiencies sensitively depending on the end functionalization [261].

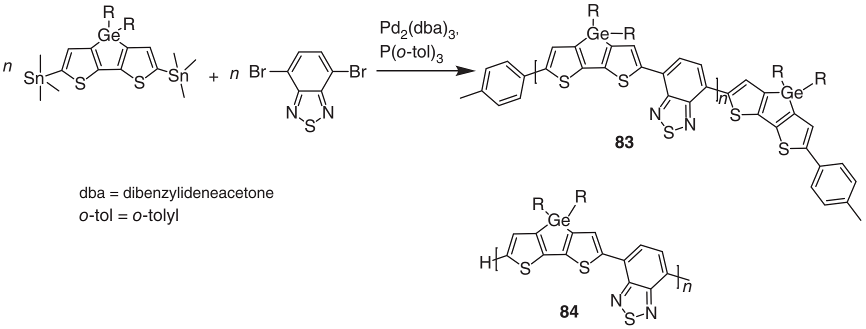


Scheme 1.38 Random hydrogen and bromo end groups and defined amino termini of poly-3-hexylthiophene. Source: Liu et al. 2004 [261]. Reproduced with permission of American Chemical Society.

Svensson described a protocol for precise end-capping via Suzuki cross-coupling. The termination of the polymerization was realized by adding first bromobenzene and second an excess of phenylboronic acid to the reaction as shown in Scheme 1.39 [265]. The photovoltaic devices fabricated from **82** showed impressive power conversion efficiencies and this can also be attributed to the defined end groups. This concept of end-capping was followed in many successive polymerizations by the groups of Inganäs, Andersson, and coworkers [265–267].



Scheme 1.39 End-capping protocol used to terminate a Suzuki polymerization. Source: Svensson et al. 2003 [265]. Reproduced with permission of John Wiley & Sons.



Scheme 1.40 D–A-polymer with and without precise tolyl end-capping. Source: Koldemir et al. 2015 [262]. Reproduced with permission of American Chemical Society.

Koldemir applied a Stille coupling for the D–A-polymer shown in Scheme 1.40 with defined tolyl end groups **83** for comparison with a polymer not possessing defined end-capping **84** and both D–A-polymers were used to fabricate FETs. Films were deposited under a variety of conditions to make sure that the results were independent of processing parameters. The charge carrier mobilities appeared to be an order of magnitude higher if FET devices were built from the tolyl end-capped polymer [262].

Although end groups and their decomposition can produce impurities, there are other sources of impurities not directly related to the polymer itself. Established methods such as NMR spectroscopy or GPC can be employed to detect contaminations from (catalyst) ligands or oligomers [268]. A troublesome issue is inorganic residues, for example, from metal catalysts, which asks for efficient methods to remove and detect them.

It has, indeed, been reported that palladium concentrations of 0.07 wt% can influence the performance of organic photovoltaic (OPV) cells [269]. First attempts at, indirectly, checking for metal impurities by time-resolved microwave conductivity measurements showed unsatisfactory results [270]. Nikiforov et al. presented a direct and quantitative method utilizing synchroton-based X-ray fluorescence and thus arrived at a limit of the metal concentration not compromising device performance [271]. Abdou et al. [272] used P3HT made by oxidative coupling with ferric chloride and studied the role of iron(III) salts in the performance of thin film FETs after several fractionation steps via Soxhlet extraction. The purification techniques were quite tedious including 2 days of Soxhlet extraction with methanol, 5 days of acetone Soxhlet extraction, and treatment with aqueous ammonia. The whole process was monitored by measurements of the electrical conductivity [272].

Metal residues other than iron, for example, Na, Mg, or Ca, can also influence the performance of FETs or OPVs and thus need to be removed. The efficiency of several purification protocols for P3HT synthesized via a chain growth polymerization with a nickel complex as catalyst (according to Scheme 1.14) were investigated [61, 169]. ICP-MS (inductively coupled plasma mass spectrometry) was used to determine the amount of Ni, Fe, K, Mg, Ca, Cu, Na, and Zn after (i) no purification, (ii) classical Soxhlet extraction, and treatment with (iii) dimethylglyoxime/15-crown-5 or (iv) ethylenediamine/15-crown-5. Chelating agents such as ethylenediamine and crown ethers turned out to be indispensable to obtain polymer samples with high power conversion efficiency in OPVs and low hysteresis together with a high on/off current ratio in FETs [107].

It has been emphasized that the solvent is the key factor in controlling the film-forming process and the deposition kinetics. Figure 1.2 illustrates that no structural orientation is to be expected in the case of fast evaporation of the

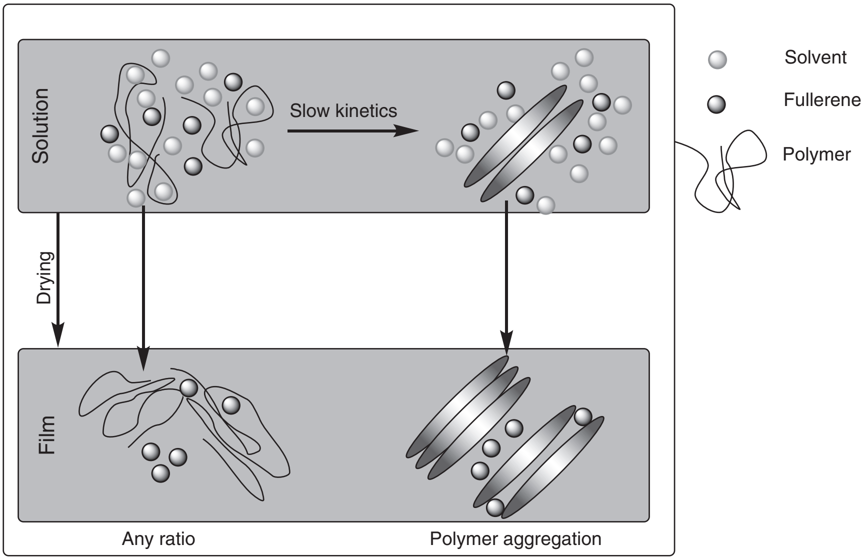


Figure 1.2 Schematic description of solvent-assisted film formation of polymer chains and fullerene. Source: Grand and Reynolds 2015 [273] and Kouijzer et al. 2013 [274]. Reproduced with permission of American Chemical Society.

solvent, whereas slower evaporation can allow for a preaggregation and even incorporation of fullerene acceptors in the formed aggregates. More detailed descriptions of such deposition kinetics will be given later in this book. It should not be overlooked, however, that the solvent can also contain contaminants such as hydrogen chloride in chlorobenzene [275], stabilizing agents such as ethanol in chloroform [276], or butylated hydroxytoluene in tetrahydrofuran [277]. One problematic impurity is water, which is often not easy to remove [278–280]. Moreover, there is evidence [279, 281–284] of a water–oxygen complex, which acts as a dangerous trap for electrons. Needless to say that at the end of the deposition, there should be no residual solvent left, although small molecules such as 1,8-disubstituted octanes are often added to favor nanophase separation of different components in the fabrication of solar cells [285–287].

The emphasis of this book is on solution processing of conjugated polymers and the impact of the resulting film structures upon device function (see Figure 1.2). This process, as has been outlined above, is governed by a complex interplay of intermolecular and interfacial forces and requires extensive experimental optimization. At this point, one must admit a key problem in the use of conjugated polymers: although we have accumulated empirical rules for intramolecular control of structure and function, the “design” of desired supramolecular structures and the avoidance of unwanted packing modes are still in their infancy. Although we are not going to anticipate these discussions here, one important question remains: can we build functions into the macromolecular structures, which allow a rational construction of packing modes? This concept, also supported by simulation of polymer assemblies, is attracting increasing attention [288]. Indeed, we have indirectly touched upon relevant factors when targeting high solubility of polymers: any irregularity of structure such as cis–trans isomerization of double bonds, bending of aromatic building blocks, branched alkyl chains, irregular placement of alkyl substituents, or co-incorporation of 1,4- and 1,3-phenylene units help to avoid ordered packing and improve solubility [289, 290]. Conversely, any structural regularity, size and shape of the repeating units, regular placement of substituents, as well as alkyl group interdigitation between macromolecules will favor the built-up of supramolecular order [291–293]. The molecular design could also include substituents enabling noncovalent interactions such as Coulomb forces or hydrogen bonds, but there again, their precise location is essential [292–296].

Supramolecular motifs such as lamellae of chains or columns of discs (see Figure 1.3) have already been mentioned above where order favors high charge carrier mobility and local defects can act as scattering sites. Insofar, the whole device function is defect-controlled even if no structural analysis such as X-ray diffractometry would be able to detect it [301]. The device function must also include consideration of packing motifs with the outside world. Thus, the molecular π-system inside a supramolecular array can produce either a face-on or edge-on arrangement with different implications for the hopping of charges and the reorganization energy of molecules involved. This arrangement can depend on the molecule and its alkyl substitution pattern [1], but also on the nature of either electrode or substrate surface [302].

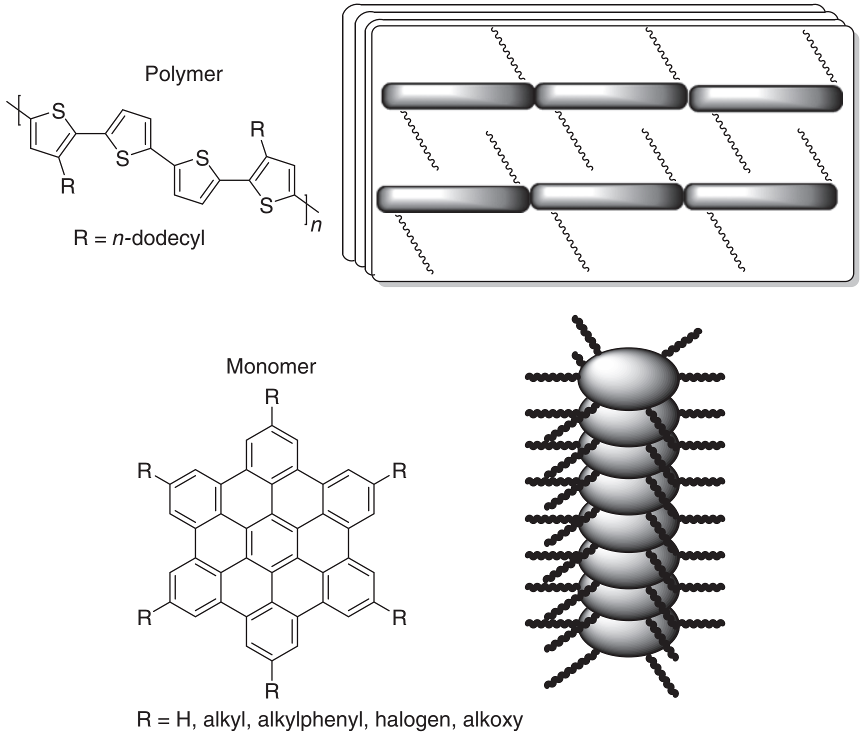


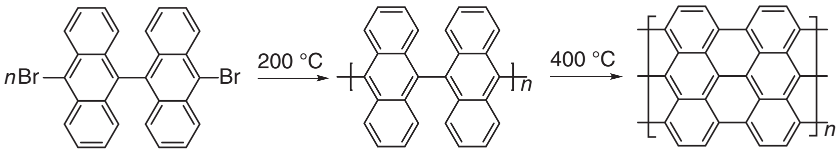
Figure 1.3 Schematic illustration of lamellar packing of chains and columns of discs [297–300].

Further, avoiding contact resistance between electrodes and organic semiconductors or removing polar impurities on the insulator surface is critical for device performance, but can only be addressed with chemical techniques [303, 304]. Treatment of electrodes with aromatic thiols, for example, appeared to reduce the contact resistance of a thin film transistor produced from pentacene [305]. Hydrophobization of the SiO_2 layer becomes possible by hydrophobic self-assembled monolayers (SAMs) [306–308]. Their role is to remove residual surface water from the gate dielectric [306].

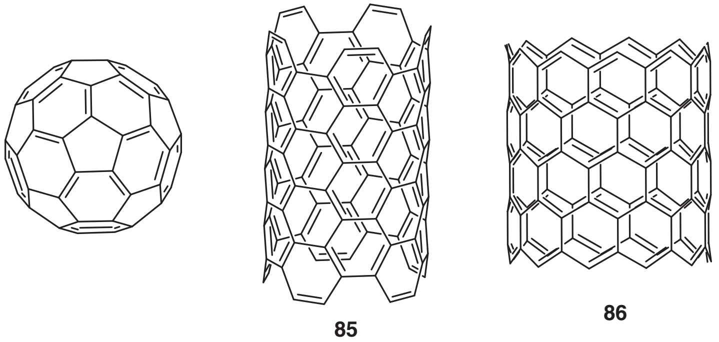
1.4 Beyond Solution Synthesis

The synthesis of PA by blowing a stream of acetylene over a thin film of silicon oil containing the catalyst nicely documents the fact that conjugated polymers must not necessarily be executed in (homogeneous) solution. This was possible due to the discovery of catalysts that work at moderate temperatures and pressure [309, 310].

More recently, dihaloarenes have been immobilized on metal surfaces and their polymerization been thermally mediated under STM control. This can even lead to polymer structures not available by conventional solution synthesis (see Scheme 1.41) [301–306].



Scheme 1.41 10,10′-Dibromo-9,9′-bianthryl precursor monomer to achieve a defined graphene nanoribbon (GNR). Source: Cai et al. 2010 [306]. Reproduced with permission of Springer Nature.

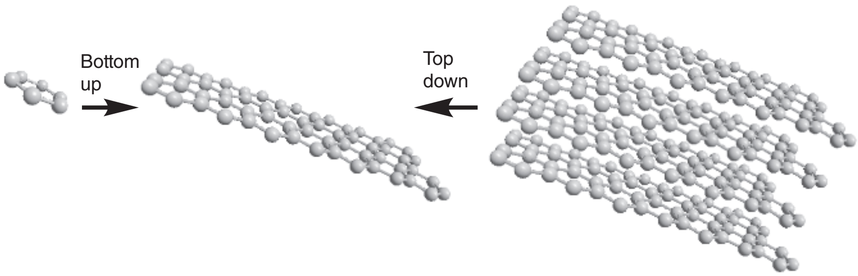


Scheme 1.42 Fullerene, armchair carbon nanotube (**85**), and zigzag carbon nanotube (**86**).

The world of carbon-based electronic materials nicely documents that the toolbox of synthetic chemistry is extremely diverse and even includes reactions under extreme conditions such as high temperature or pressure (see Scheme 1.42) [307].

Fullerenes are mostly obtained by arc and combustion methods [308, 311]. Solution chemistry comes again into play again when chromatographic purification or modification by cycloaddition reactions are performed [312]. The same is true for CNTs. They are generally obtained by arc discharge, laser ablation, chemical vapor deposition (CVD), and high-pressure carbon monoxide disproportionation, but often come together with large amounts of amorphous carbon. The pronounced tendency of CNTs toward aggregation defines the need for debundling by, for example, wrapping them up in a shell of polymers [313–316]. Mixtures of metallic and semiconducting CNTs also require separation, which can be achieved either by chromatography or by making use of their different reactivities [317–319].

A related case is that of graphene, a one-atom-thick monolayer (see Scheme 1.43). Stimulated by the pioneering research of Geim, Novoselov, and coworkers [103, 320–322], it is often described as a wonder material. Indeed, the world of 1D conjugated polymers must warmly welcome 2D graphene with its unique band structure and remarkable electronic [322], magnetic [323], and mechanical [324] properties. Although these superlatives create a rich playground for theory and physics, the multitude of chemical challenges should not be ignored. Interestingly, graphenes can be obtained by many different methods. Among those, the two following ones highlight a fundamental difference: exfoliation from graphite stands for a top-down and chemical synthesis for a bottom-up approach [103]. Regarding the first protocol, how



Scheme 1.43 Fundamentally different ways to obtain graphene.

can one strictly peel off layer by layer from graphite? A mechanical assistance may be described as not requiring much chemistry, but an electrochemical exfoliation raises many mechanistic and experimental questions. Thus, one must consider the intercalation of electrolytes in-between the layers and the oxidative formation of radicals from electrolyte anions [325]. The latter can either chemically attack the carbon network or form gas bubbles, both processes weakening the adhesion between graphene layers. The solvent is also critical, for example, to prevent reaggregation of separate sheets after exfoliation [325]. The exfoliation can also be driven by harsher chemical oxidation, yielding yellow dispersions of graphene oxide (GO). The diverse oxygen functions must then be removed by chemical or thermal reduction to reestablish the targeted graphene. This technique has been appealing to many research groups because GO could be purchased and easily deposited into films [326–329]. GO can, indeed, be regarded as a processable precursor material for graphene. However, as described for the case of PPV, quantitative transformation of the precursor is essential, and GO treatment is far from meeting this requirement. There are remaining oxygen functions and, more severe, reduction is accompanied by loss of carbon fragments yielding a defect-rich material [103]. The bottom-up approach can utilize CVD where, for example, C2-fragments from various sources are fused on copper surfaces. Alternatively, PAHs, which can be viewed as molecular cutouts from the graphene lattice, can be made larger and larger [301]. The advantage of the controlled synthesis is not so much the graphene fabrication, but that of providing access to new semiconductors such as graphene nanoribbons (GNRs), as shown in Scheme 1.41. GNRs represent a kind of intermediate π-system between conjugated polymers and graphene [304]. They have assumed special importance because of a characteristic feature of graphene: although it displays extremely high charge carrier mobilities, certainly a desirable property in a transistor, it possesses a vanishing band gap. As a consequence, the current in the device will never be “off.” One way of opening the band gap and enabling an “on–off behavior” is a geometric confinement in the π-system such as that provided in a GNR [302]. They have therefore been sought, for example, by lithographic techniques and by unzipping of CNTs, but these methods lack the structural precision to achieve control over the aspect ratio of the ribbons and, in particular, their edge structure [301, 302, 306, 330–332]. GNRs, as a new family of semiconductors with distinct advantages over classical conjugated polymers, are thus another convincing case to support the role of synthesis for advancing electronic materials [19].

1.5 Conclusions

Toward the end, the reader may – or not – agree to our claim that precision synthesis is an indispensible tool in providing structurally defined, soluble, and pure conjugated polymers for device fabrication. As always, arguments should not be overstretched because in an interdisciplinary field like polymer electronics, synthesis cannot be looked at as self-sufficient. It is rather the starting point of a whole series of events. There is also a trivial need of practicality: not only must the monomer be available without multistep synthesis but also must the synthesis be simple and straightforward enough to provide samples in sufficient quantities. Otherwise, optimizing deposition techniques and testing devices under various circumstances would remain unreliable. Of course, when building devices, one cannot set aside the issue of performance. Although conceptual novelty in organic electronics could be fueled by, both, chemistry and physics, chasing records in performance should not become the main motivation and belongs more to engineering. Even more so, as metrics alone such as the charge carrier mobility of an FET sometimes appear as the only criterion without ever including the issues of shelf-life and operational stability. This again emphasizes the need for sufficient quantities in tedious device optimization. Perhaps one might best discriminate between "synthesis" and "preparation" in which the former includes the creative search for novel structures and methods and the latter includes more routine aspects such as scaling up and securing reproducibility. Tuning the solubility could be part of such a more technical approach whereby already the use of a halogenated solvent might appear as prohibitive. Further, if conjugated polymers and solution processing should be elements of a low-end electronics, costs must play an essential role.

We might come back to the beginning in iterating that conjugated polymers offer an unbelievable breadth of structural and functional opportunities. Admittedly, the material basis of the field has seen trends and fashions, but always has there been a close interplay between targeted physical function and the availability of a material. The rise and decline of the search for organic NLO (nonlinear optical) chromophores might serve as an instructive example [333–335]. Although herein we have mostly concentrated on the three most common cases of (opto)electronic devices, new concepts such as memory and spintronics devices or single-molecule electronics will undoubtedly continue to define new challenges for polymer synthesis.

There is the danger of researchers focusing their attention too much on oligomers and polymers as active components of devices. Although electrodes and substrates have already been mentioned as additional ingredients, approaches toward sensing or medical diagnostics require additional measures regarding encapsulation, self-healing, and biocompatibility. May this chapter and this book help the reader enjoy the undiminished vivacity of his or her field – but to never set aside chemistry.

Acknowledgments

The authors are greatly indebted to all the present and former group members and collaboration partners who have made this text possible.

References

1 McCullough, R.D. (1998). The chemistry of conducting polythiophenes. *Advanced Materials* 10 (2): 93–116.

2 Tyler McQuade, D., Pullen, A.E., and Swager, T.M. (2000). Conjugated polymer-based chemical sensors. *Chemical Reviews* 100 (7): 2537–2574.

3 Roncali, J. (1992). Conjugated poly(thiophenes): synthesis, functionalization, and applications. *Chemical Reviews* 92 (4): 711–738.

4 Roncali, J. (1997). Synthetic principles for bandgap control in linear π-conjugated systems. *Chemical Reviews* 97 (1): 173–206.

5 Akcelrud, L. (2003). Electroluminescent polymers. *Progress in Polymer Science* 28 (6): 875–962.

6 Koßmehl, G. (1979). Semiconductive conjugated polymers. *Berichte der Bunsengesellschaft für Physikalische Chemie* 83 (4): 417–426.

7 Grimsdale, A.C. and Müllen, K. (2006). Polyphenylene-type emissive materials: poly(para-phenylene)s, polyfluorenes, and ladder polymers. *Advances in Polymer Science* 199 (February): 1–82.

8 Chung, H. and Diao, Y. (2016). Polymorphism as an emerging design strategy for high performance organic electronics. *Journal of Materials Chemistry C* 4 (18): 3915–3933.

9 Roth, S. and Filzmoser, M. (1990). Conducting polymers – thirteen years of polyacetylene doping. *Advanced Materials* 2 (8): 356–360.

10 Le, T.-H., Kim, Y., and Yoon, H. (2017). Electrical and electrochemical properties of conducting polymers. *Polymers (Basel)* 9 (12): 150.

11 Jain, V. and Kokil, A. (2015). *Optical Properties of Functional Polymers and Nano Engineering Applications*. CRC Press.

12 Conradie, J. (2015). A Frontier orbital energy approach to redox potentials. *Journal of Physics Conference Series* 633 (1): 12045.

13 D'Andrade, B.W., Datta, S., Forrest, S.R. et al. (2005). Relationship between the ionization and oxidation potentials of molecular organic semiconductors. *Organic Electronics* 6 (1): 11–20.

14 Chiang, C.K., Fincher, C.R., Park, Y.W. et al. (1977). Electrical conductivity in doped polyacetylene. *Physical Review Letters* 39 (17): 1098–1101.

15 Sun, Y., MacDiarmid, A.G., and Epstein, A.J. (1990). Polyaniline: synthesis and characterization of pernigraniline base. *Journal of the Chemical Society, Chemical Communications* (7): 529.

16 Chiang, C.K., Druy, M.A., Gau, S.C. et al. (1978). Synthesis of highly conducting films of derivatives of polyacetylene, (CH)x. *Journal of the American Chemical Society* 100 (3): 1013–1015.

17 MacDiarmid, A.G. (2001). "Synthetic metals": a novel role for organic polymers. *Angewandte Chemie International Edition* 40 (14): 2581–2590.

18 Will, F.G. and McKee, D.W. (1983). Thermal oxidation of polyacetylene. *Journal of Polymer Science, Polymer Chemistry Edition* 21 (12): 3479–3492.

19 Müllen, K., Reynolds, J.R., and Masuda, T. (2013). *Conjugated Polymers: A Practical Guide to Synthesis*. Royal Society of Chemistry.

20 Saxman, A.M., Liepins, R., and Aldissi, M. (1985). Polyacetylene: its synthesis, doping and structure. *Progress in Polymer Science* 11 (1–2): 57–89.

21 Rozenberg, B.A. and Tenne, R. (2008). Polymer-assisted fabrication of nanoparticles and nanocomposites. *Progress in Polymer Science* 33 (1): 40–112.

22 Nathanael, A.J., Han, S.S., and Oh, T.H. (2013). Polymer-assisted hydrothermal synthesis of hierarchically arranged hydroxyapatite nanoceramic. *Journal of Nanomaterials* 2013: 1–8.

23 Liu, K., Nie, Z., Zhao, N. et al. (2010). Step-growth polymerization of inorganic nanoparticles. *Science* 329 (5988): 197–200.

24 Arrebola, J.C., Caballero, A., Cruz, M. et al. (2006). Crystallinity control of a nanostructured $LiNi_{0.5}Mn_{1.5}O_4$ spinel via polymer-assisted synthesis: a method for improving its rate capability and performance in 5 V lithium batteries. *Advanced Functional Materials* 16 (14): 1904–1912.

25 Wang, Y.D., Djerdj, I., Antonietti, M., and Smarsly, B. (2008). Polymer-assisted generation of antimony-doped SnO_2 nanoparticles with high crystallinity for application in gas sensors. *Small* 4 (10): 1656–1660.

26 Aimable, A., Buscaglia, M.T., Buscaglia, V., and Bowen, P. (2010). Polymer-assisted precipitation of ZnO nanoparticles with narrow particle size distribution. *Journal of the European Ceramic Society* 30 (2): 591–598.

27 Venditti, I. (2017). Gold nanoparticles in photonic crystals applications: a review. *Materials (Basel)* 10 (12): 97.

28 Sönnichsen, C., Franzl, T., Wilk, T. et al. (2002). Plasmon resonances in large noble-metal clusters. *New Journal of Physics* 4: 93.

29 Pelton, M., Aizpurua, J., and Bryant, G. (2008). Metal-nanoparticle plasmonics. *Laser and Photonics Reviews* 2 (3): 136–159.

30 Anatoly, V.Z. and Igor, I.S. (2003). Near-field photonics: surface plasmon polaritons and localized surface plasmons. *Journal of Optics A: Pure and Applied Optics* 5 (4): S16.

31 Liao, H., Nehl, C.L., and Hafner, J.H. (2006). Biomedical applications of plasmon resonant metal nanoparticles. *Nanomedicine* 1 (2): 201–208.

32 Wöll, C. (2009). *Organic Electronics: Structural and Electronic Properties of OFETs*. Wiley-VCH.

33 Shi, W., Liu, C., and Lei, A. (2011). Transition-metal catalyzed oxidative cross-coupling reactions to form C—C bonds involving organometallic reagents as nucleophiles. *Chemical Society Reviews* 40 (5): 2761.

34 Suzuki, A. (2011). Cross-coupling reactions of organoboranes: an easy way to construct C—C bonds (Nobel Lecture). *Angewandte Chemie International Edition* 50 (30): 6723–6733.

35 Suzuki, A. (1999). Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *Journal of Organometallic Chemistry* 576 (1–2): 147–168.

36 Negishi, E., King, A.O., and Okukado, N. (1977). Selective carbon–carbon bond formation via transition metal catalysis. 3. A highly selective synthesis of unsymmetrical biaryls and diarylmethanes by the nickel- or palladium-catalyzed reaction of aryl- and benzylzinc derivatives with aryl halides. *Journal of Organic Chemistry* 42 (10): 1821–1823.

37 Negishi, E. (1982). Palladium- or nickel-catalyzed cross coupling. A new selective method for carbon–carbon bond formation. *Accounts of Chemical Research* 15 (11): 340–348.

38 Cho, S.H., Kim, J.Y., Kwak, J., and Chang, S. (2011). Recent advances in the transition metal-catalyzed twofold oxidative C—H bond activation strategy for C—C and C—N bond formation. *Chemical Society Reviews* 40 (10): 5068.

39 Stille, J.K. (1986). The palladium-catalyzed cross-coupling reactions of organotin reagents with organic electrophiles. *Angewandte Chemie (International Edition in English)* 25: 508–524.

40 Alberico, D., Scott, M.E., and Lautens, M. (2007). Aryl-aryl bond formation by transition-metal-catalyzed direct arylation. *Chemical Reviews* 107 (1): 174–238.

41 Petrone, D.A., Ye, J., and Lautens, M. (2016). Modern transition-metal-catalyzed carbon–halogen bond formation. *Chemical Reviews* 116 (14): 8003–8104.

42 Nuyken, O. and Pask, S.D. (2013). Ring-opening polymerization – an introductory review. *Polymers (Basel)* 5 (2): 361–403.

43 Kamber, N.E., Jeong, W., Waymouth, R.M. et al. (2007). Organocatalytic ring-opening polymerization. *Chemical Reviews* 107 (12): 5813–5840.

44 Albertsson, A.C. and Varma, I.K. (2003). Recent developments in ring opening polymerization of lactones for biomedical applications. *Biomacromolecules* 4 (6): 1466–1486.

45 Sutthasupa, S., Shiotsuki, M., and Sanda, F. (2010). Recent advances in ring-opening metathesis polymerization, and application to synthesis of functional materials. *Polymer Journal* 42 (12): 905–915.

46 Bielawski, C.W. and Grubbs, R.H. (2007). Living ring-opening metathesis polymerization. *Progress in Polymer Science* 32 (1): 1–29.

47 Rahman, A. and Choudhary, M.I. (2015). *Applications of NMR Spectroscopy*, vol. 3. Bentham Science Publishers.

48 Ardenkjaer-Larsen, J.H., Fridlund, B., Gram, A. et al. (2003). Increase in signal-to-noise ratio of >10,000 times in liquid-state NMR. *Proceedings of the National Academy of Sciences* 100 (18): 10158–10163.

49 Darbeau, R.W. (2006). Nuclear magnetic resonance (NMR) spectroscopy: a review and a look at its use as a probative tool in deamination chemistry. *Applied Spectroscopy Reviews* 41 (4): 401–425.

50 Wind, M., Saalwächter, K., Wiesler, U.M. et al. (2002). Solid-state NMR investigations of molecular dynamics in polyphenylene dendrimers: evidence of dense-shell packing. *Macromolecules* 35 (27): 10071–10086.

51 Brown, S.P. and Spiess, H.W. (2001). Advanced solid-state NMR methods for the elucidation of structure and dynamics of molecular, macromolecular, and supramolecular systems. *Chemical Reviews* 101 (12): 4125–4156.

52 Sakurai, S. (2017). Recent developments in polymer applications of synchrotron small-angle X-ray scattering. *Polymer International* 66 (2): 237–249.

53 Pregl, F. (1930). *Die Quantitative Organische Mikroanalyse*. Berlin Heidelberg: Springer-Verlag.

54 Hubbell, J.H., Trehan, P.N., Singh, N. et al. (1994). A review, bibliography, and tabulation of K, L, and higher atomic shell X-ray fluorescence yields. *Journal of Physical and Chemical Reference Data* 23 (2): 339–364.

55 Bambynek, W., Crasemann, B., Fink, R.W. et al. (1972). X-ray fluorescence yields, Auger, and Coster–Kronig transition probabilities. *Reviews of Modern Physics* 44 (4): 716–813.

56 Farkov, P.M., Il'icheva, L.N., and Finkel'shtein, A.L. (2005). X-ray fluorescence determination of carbon, nitrogen, and oxygen in fish and plant samples. *Journal of Analytical Chemistry* 60 (5): 426–430.

57 Greenham, N.C., Moratti, S.C., Bradley, D.D.C. et al. (1993). Efficient light-emitting diodes based on polymers with high electron affinities. *Nature* 365 (6447): 628–630.

58 Burroughes, J.H., Bradley, D.D.C., Brown, A.R. et al. (1990). Light-emitting diodes based on conjugated polymers. *Nature* 347 (6293): 539–541.

59 Braun, D. and Heeger, A.J. (1991). Visible light emission from semiconducting polymer diodes. *Applied Physics Letters* 58 (18): 1982–1984.

60 Dimitrakopoulos, C.D. and Malenfant, P.R.L. (2002). Organic thin film transistors for large area electronics. *Advanced Materials* 14 (2): 99–117.

61 McCullough, R.D. and Lowe, R.D. (1992). Enhanced electrical conductivity in regioselectively synthesized poly(3-alkylthiophenes). *Journal of the Chemical Society, Chemical Communications* (1): 70.

62 Sirringhaus, H. (2014). 25th anniversary article: organic field-effect transistors: the path beyond amorphous silicon. *Advanced Materials* 26 (9): 1319–1335.

63 Sariciftci, N.S., Smilowitz, L., Heeger, A.J., and Wudl, F. (1992). Photoinduced electron transfer from a conducting polymer to Buckminsterfullerene. *Science* 258 (5087): 1474–1476.

64 Chamberlain, G.A.A. (1983). Organic solar cells: a review. *Sol Cells* 8 (1): 47–83.

65 Ho, C.L., Wong, W.Y., Gao, Z.Q. et al. (2008). Red-light-emitting iridium complexes with hole-transporting 9-arylcarbazole moieties for electrophosphorescence efficiency/color purity trade-off optimization. *Advanced Functional Materials* 18 (2): 319–331.

66 Yook, K.S. and Lee, J.Y. (2014). Small molecule host materials for solution processed phosphorescent organic light-emitting diodes. *Advanced Materials* 26 (25): 4218–4233.

67 Duan, L., Hou, L., Lee, T.-W. et al. (2010). Solution processable small molecules for organic light-emitting diodes. *Journal of Materials Chemistry* 20 (31): 6392.

68 Karabunarliev, S., Baumgarten, M., and Mu, K. (2000). Adiabatic one- and two-photon excited states in phenylene-based conjugated oligomers: a quantum-chemical study. *The Journal of Physical Chemistry A* 104 (35): 8236–8243.

69 Meier, H., Stalmach, U., and Kolshorn, H. (1997). Effective conjugation length and UV/vis spectra of oligomers. *Acta Polymerica* 48 (9): 379–384.

70 Talipov, M.R., Boddeda, A., Timerghazin, Q.K., and Rathore, R. (2014). Key role of end-capping groups in optoelectronic properties of poly-*p*-phenylene cation radicals. *Journal of Physical Chemistry. C, Nanomaterials and Interfaces* 118 (37): 21400–21408.

71 Eslamian, M. (2017). Inorganic and organic solution-processed thin film devices. *Nano-Micro Letters* 9 (1): 1–23.

72 Mercier, J.P. (1990). Nucleation in polymer crystallization: a physical or a chemical mechanism? *Polymer Engineering and Science* 30 (5): 270–278.

73 Tanaka, F. (1996). Phase formation of associating polymers: gelation, phase separation and microphase formation. *Advances in Colloid and Interface Science* 63 (1995): 23–40.

74 Wilkes, G.L. (1981). An overview of the basic rheological behavior of polymer fluids with an emphasis on polymer melts. *Journal of Chemical Education* 58 (11): 880.

75 Xu, L., Yang, L., and Lei, S. (2012). Self-assembly of conjugated oligomers and polymers at the interface: structure and properties. *Nanoscale* 4 (15): 4399.

76 Fichou, D., Horowitz, G., Xu, B., and Garnier, F. (1990). Stoichiometric control of the successive generation of the radical cation and dication of extended α-conjugated oligothiophenes: a quantitative model for doped polythiophene. *Synthetic Metals* 39 (2): 243–259.

77 Garnier, F., Horowitz, G., Peng, X.Z., and Fichou, D. (1991). Structural basis for high carrier mobility in conjugated oligomers. *Synthetic Metals* 45 (2): 163–171.

78 Garnier, F., Horowitz, G., Peng, X., and Fichou, D. (1990). An all-organic "soft" thin film transistor with very high carrier mobility. *Advanced Materials* 2 (12): 592–594.

79 Tourillon, G. and GF. (1983). Stability of conducting polythiophene and derivatives. *Journal of the Electrochemical Society* 130 (10): 2042.

80 Garnier, F., Horowitz, G., Fichou, D., and Yassar, A. (1997). Role of mesoscopic molecular organization in organic-based thin film transistors. *Supramolecular Science* 4 (1–2, 162): 155.

81 Kagan, J., Arora, K., and S. (1983). The synthesis of alpha-thiophene oligomers by oxidative coupling of 2-lithiothiophenes. *Heterocycles* 20 (10): 1937.

82 Fichou, D., Horowitz, G.F., Garnier, F. (1991). Applicant: Centre Nat Rech Scient. Patent number FR2648140 (B1).

83 Roncali, J., Garnier, F., Lemaire, M., and Garreau, R. (1986). Poly mono-, bi- and trithiophene: effect of oligomer chain length on the polymer properties. *Synthetic Metals* 15 (4): 323–331.

84 Jurchescu, O.D., Baas, J., and Palstra, T.T.M. (2004). Effect of impurities on the mobility of single crystal pentacene. *Applied Physics Letters* 84 (16): 3061–3063.

85 Bao, Z. and Locklin, J. (2007). *Organic Field-effect Transistors*. CRC Press.

86 Coropceanu, V., Cornil, J., da Silva Filho, D.A. et al. (2007). Charge transport in organic semiconductors. *Chemical Reviews* 107 (4): 926–952.

87 Berg, O., Chronister, E.L., Yamashita, T. et al. (1999). *s*-Dipentacene: structure, spectroscopy, and temperature- and pressure-dependent photochemistry. *Journal of Physical Chemistry A* 103 (14): 2451–2459.

88 Yamada, M., Ikemoto, I., and Kuroda, H. (1988). Photooxidation of the evaporated films of polycyclic aromatic hydrocarbons studied by X-ray photoelectron spectroscopy. *Bulletin of the Chemical Society of Japan* 61 (4): 1057–1062.

89 Reddy, A.R. and Bendikov, M. (2006). Diels–Alder reaction of acenes with singlet and triplet oxygen – theoretical study of two-state reactivity. *Chemical Communications* (11): 1179.

90 Swager, T.M. (2017). 50th anniversary perspective: conducting/semiconducting conjugated polymers. A personal perspective on the past and the future. *Macromolecules* 50 (13): 4867–4886.

91 Heeger, A.J., Kivelson, S., Schrieffer, J.R., and Su, W.-P. (1988). Solitons in conducting polymers. *Reviews of Modern Physics* 60 (3): 781–850.

92 Basescu, N., Liu, Z.-X., Moses, D. et al. (1987). High electrical conductivity in doped polyacetylene. *Nature* 327 (6121): 403–405.

93 Fabretto, M.V., Evans, D.R., Mueller, M. et al. (2012). Polymeric material with metal-like conductivity for next generation organic electronic devices. *Chemistry of Materials* 24 (20): 3998–4003.

94 Naarmann, H. and Theophilou, N. (1987). New process for the production of metal-like, stable polyacetylene. *Synthetic Metals* 22 (1): 1–8.

95 Park, Y.W., Yoon, C.O., Lee, C.H. et al. (1989). Conductivity and thermoelectric power of the newly processed polyacetylene. *Synthetic Metals* 28 (3): 27–34.

96 Saitō, R., Dresselhaus, G., and Dresselhaus, M.S. (1998). *Physical Properties of Carbon Nanotubes*. Imperial College Press.

97 Thostenson, E.T., Ren, Z., and Chou, T.-W. (2001). Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology* 61 (13): 1899–1912.

98 Donaldson, K., Aitken, R., Tran, L. et al. (2006). Carbon nanotubes: a review of their properties in relation to pulmonary toxicology and workplace safety. *Toxicological Sciences* 92 (1): 5–22.

99 Han, Z. and Fina, A. (2011). Thermal conductivity of carbon nanotubes and their polymer nanocomposites: a review. *Progress in Polymer Science* 36 (7): 914–944.

100 Ma, P.C., Siddiqui, N.A., Marom, G., and Kim, J.K. (2010). Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. *Composites. Part A, Applied Science and Manufacturing* 41 (10): 1345–1367.

101 Ying, L.S., Bin Mohd Salleh, M.A., Mohamed Yusoff, H.B. et al. (2011). Continuous production of carbon nanotubes – a review. *Journal of Industrial and Engineering Chemistry* 17 (3): 367–376.

102 Geckeler, K. and Samal, S. (1999). Syntheses and properties of macromolecular fullerenes, a review. *Polymer International* 757: 743–757.

103 Novoselov, K.S., Fal'Ko, V.I., Colombo, L. et al. (2012). A roadmap for graphene. *Nature* 490 (7419): 192–200.

104 Choi, W., Lahiri, I., Seelaboyina, R., and Kang, Y.S. (2010). Synthesis of graphene and its applications: a review. *Critical Reviews in Solid State and Materials Sciences* 35 (1): 52–71.

105 Kroto, H.W., Heath, J.R., O'Brien, S.C. et al. (1985). C60: Buckminsterfullerene. *Nature* 318 (6042): 162–163.

106 Mark, H. (1948). Purity and identity of polymers. *Analytical Chemistry* 20 (2): 104–110.

107 Usluer, Ö., Abbas, M., Wantz, G. et al. (2014). Metal residues in semiconducting polymers: impact on the performance of organic electronic devices. *ACS Macro Letters* 3 (11): 1134–1138.

108 Sorrell, T.N. (2006). *Organic Chemistry*. University Science Books.

109 Enkelmann, V. (1982). Photoelectronic properties of crystals of polymers with conjugated main chains. *Macromolecular Materials and Engineering* 109 (1): 253–265.

110 Lorcy, D., Bellec, N., Fourmigué, M., and Avarvari, N. (2009). Tetrathiafulvalene-based group XV ligands: synthesis, coordination chemistry and radical cation salts. *Coordination Chemistry Reviews* 253 (9–10): 1398–1438.

111 Torrance, J.B., Scott, B.A., Welber, B. et al. (1979). Optical properties of the radical cation tetrathiafulvalenium (TT F+) in its mixed-valence and monovalence halide salts. *Physical Review B* 19 (2): 730–741.

112 Heckmann, A. and Lambert, C. (2012). Organic mixed-valence compounds: a playground for electrons and holes. *Angewandte Chemie International Edition* 51 (2): 326–392.

113 Geiser, U. and Schlueter, J.A. (2004). Conducting organic radical cation salts with organic and organometallic anions. *Chemical Reviews* 104 (11): 5203–5241.

114 Rieger, R., Enkelmann, V., and Müllen, K. (2010). Charge-transfer controlled crystallization of a model oligomer for donor–acceptor-polythiophenes. *Materials (Basel)* 3 (3): 1904–1912.

115 Raible, C., Gmeiner, J., Winter, H. et al. (1993). Magnetic properties of the new conducting radical cation salt (trans-1,2-bis(2-naphthyl)ethene)SbF6. *Synthetic Metals* 59 (1): 71–80.

116 Sachs, G., Dormann, E., and Schwoerer, M. (1985). One-dimensionality of the organic conductor (FA)+{·}2PF-6. *Solid State Communications* 53 (1): 73–76.

117 Schütz, W., Gmeiner, J., Schilder, A. et al. (1996). Characterization of the mixed fullerene radical-anion salt $[PPh_4{}^+]_2\ C_{60}{}^-Cl_{1-x}{}^-I_x{}^-$. *Chemical Communications* (13): 1571.

118 Zarras, P. and Irvin, J. (2007). Electrically active polymers. In: *Encyclopedia of Polymer Science and Technology, Concise* (ed. H.F. Mark), 351. Hoboken, NJ: Wiley.

119 Kovacic, P. and Jones, M.B. (1987). Dehydro coupling of aromatic nuclei by catalyst-oxidant systems: poly(*p*-phenylene). *Chemical Reviews* 87 (2): 357–379.

120 Kovacic, P. and Kyriakis, A. (1962). Polymerization of benzene to -polyphenyl. *Tetrahedron Letters* 3 (11): 467–469.

121 Leclerc, M., Diaz, F.M., and Wegner, G. (1989). Structural analysis of poly(3-alkylthiophene)s. *Die Makromol Chemie* 190 (12): 3105–3116.

122 Stein, P.C., Botta, C., Bolognesi, A., and Catellani, M. (1995). NMR study of the structural defects in poly(3-alkylthiophene)s: influence of the polymerization method. *Synthetic Metals* 69: 305–306.

123 Sengodu, P. and Deshmukh, A.D. (2015). Conducting polymers and their inorganic composites for advanced Li-ion batteries: a review. *RSC Advances* 5 (52): 42109–42130.

124 Lin, J.W.-P. and Dudek, L.P. (2002). Synthesis and properties of poly(2,5-thienylene). *Journal of Polymer Science, Polymer Chemistry Edition* 18 (9): 2869–2873.

125 Yamamoto, T., Sanechika, K., and Yamamoto, A. (1980). Preparation of thermostable and electric-conducting poly(2,5-thienylene). *Journal of Polymer Science, Polymer Letters Edition* 18 (1): 9–12.

126 Sato, M., Tanaka, S., and Kaeriyama, K. (1986). Electrochemical preparation of conducting poly(3-methylthiophene): comparison with polythiophene and poly(3-ethylthiophene). *Synthetic Metals* 14 (4): 279–288.

127 Klapper, M. and Müllen, K. (1995). New methods of C—C and C—O bond formation in the synthesis of conjugated polymers. *Macromolecular Symposia* 98 (1): 233–246.

128 Li, C., Liu, M., Pschirer, N.G. et al. (2010). Polyphenylene-based materials for organic photovoltaics. *Chemical Reviews* 110 (11): 6817–6855.

129 Rehahn, M., Schlüter, A.-D., Wegner, G., and Feast, W.J. (1989). Soluble poly(para-phenylene)s. 1. Extension of the Yamamoto synthesis to dibromobenzenes substituted with flexible side chains. *Polymer (Guildf)* 30 (6): 1054–1059.

130 Vahlenkamp, T. and Wegner, G. (1994). Poly(2,5-dialkoxy-*p*-phenylene)s – synthesis and properties. *Macromolecular Chemistry and Physics* 952: 1933–1952.

131 Ullmann, F. and Bielecki, J. (1901). Über synthesen in der biphenylreihe. *Berichte der Dtsch Chem Gesellschaft* 34 (2): 2174–2185.

132 Grignard, V. (1900). *Sur quelques nouvelles combinaisons organométalliques du magnèsium et leur application à des synthèses d'alcools et d'hydrocarbures*, 1322–1324. Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences.

133 Yamamoto, T., Hayashi, Y., and Yamamoto, A. (1978). A novel type of polycondensation utilizing transition metal-catalyzed C–C coupling. I. Preparation of thermostable polyphenylene type polymers. *Bulletin of the Chemical Society of Japan* 51 (7): 2091–2097.

134 Elsom, L.F. and Alexander McKillop, E.C.T. (1976). 4,4′-Dimethyl-1,1′-biphenyl. *Organic Syntheses* 55: 48.

135 Yamamoto, T. and Yamamoto, A. (1977). A novel type of polycondensation of polyhalogenated organic aromatic compounds producing thermostable polyphenylene type polymers promoted by nickel complexes. *Chemistry Letters* 6 (4): 353–356.

136 Yamamoto, T., Morita, A., Maruyama, T. et al. (1990). New method for the preparation of poly(2,5-thienylene), poly(*p*-phenylene), and related polymers. *Polymer Journal* 22: 187–190.

137 Tamao, K. (2002). Discovery of the cross-coupling reaction between Grignard reagents and C(sp2) halides catalyzed by nickel-phosphine complexes. *Journal of Organometallic Chemistry* 653 (1–2): 23–26.

138 Schlüter, A.-D. and Wegner, G. (1993). Palladium and nickel catalyzed polycondensation – the key to structurally defined polyarylenes and other aromatic polymers. *Acta Polymerica* 44 (2): 59–69.

139 Nojima, M., Ohta, Y., and Yokozawa, T. (2014). Investigation of catalyst-transfer condensation polymerization for synthesis of poly(*p*-phenylenevinylene). *Journal of Polymer Science, Part A: Polymer Chemistry* 52 (18): 2643–2653.

140 Koltzenburg, S., Maskos, M., and Nuyken, O. (2014). Polymer: synthesis. *Eigenschaften und Anwendungen.* https://doi.org/10.1007/978-3-642-34773-3.

141 Liu, C., Zhang, H., Shi, W., and Lei, A. (2011). Bond formations between two nucleophiles: transition metal catalyzed oxidative cross-coupling reactions. *Chemical Reviews* 111 (3): 1780–1824.

142 Han, F.-S. (2013). Transition-metal-catalyzed Suzuki–Miyaura cross-coupling reactions: a remarkable advance from palladium to nickel catalysts. *Chemical Society Reviews* 42 (12): 5270.

143 Astruc, D. (2010). The 2010 chemistry nobel prize to R.F. Heck, E. Negishi, and A. Suzuki for palladium-catalyzed cross-coupling reactions. *Analytical and Bioanalytical Chemistry* 399 (5): 1811–1814.

144 de Meijere, A. and Meyer, F.E. (1995). Fine feathers make fine birds: the Heck reaction in modern Garb. *Angewandte Chemie (International Edition in English)* 33 (23–24): 2379–2411.

145 Heck, K.F. and Nolley, J.P. (1972). Palladium-catalyzed vinylic hydrogen substitution reactions with aryl, benzyl, and styryl halides. *Journal of Organic Chemistry* 37 (14): 2320–2322.

146 Beletskaya, I.P. and Cheprakov, A.V. (2000). Heck reaction as a sharpening stone of palladium catalysis. *Chemical Reviews* 100 (8): 3009–3066.

147 Martin, R. and Buchwald, S.L. (2008). Palladium-catalyzed Suzuki–Miyaura cross-coupling reactions employing dialkylbiaryl phosphine ligands. *Accounts of Chemical Research* 41 (11): 1461–1473.

148 Chatterjee, A. and Ward, T.R. (2016). Recent advances in the palladium catalyzed Suzuki–Miyaura cross-coupling reaction in water. *Catalysis Letters* 146 (4): 820–840.

149 Haas, D., Hammann, J.M., Greiner, R., and Knochel, P. (2016). Recent developments in Negishi cross-coupling reactions. *ACS Catalysis* 6 (3): 1540–1552.

150 Nicolaou, K.C., Bulger, P.G., and Sarlah, D. (2005). Palladium-catalyzed cross-coupling reactions in total synthesis. *Angewandte Chemie International Edition* 44 (29): 4442–4489.

151 Jana, R., Pathak, T.P., and Sigman, M.S. (2011). Advances in transition metal (Pd,Ni,Fe)-catalyzed cross-coupling reactions using alkyl-organometallics as reaction partners. *Chemical Reviews* 111 (3): 1417–1492.

152 Kissel, P., Erni, R., Schweizer, W.B. et al. (2012). A two-dimensional polymer prepared by organic synthesis. *Nature Chemistry* 4 (4): 287–291.

153 Lennox, A.J.J. and Lloyd-Jones, G.C. (2014). Selection of boron reagents for Suzuki–Miyaura coupling. *Chemical Society Reviews* 43 (1): 412–443.

154 Ingham, R.K., Rosenberg, S.D., and Gilman, H. (1960). Organotin compounds. *Chemical Reviews* 60 (5): 459–539.

155 Zhou, J. and Fu, G.C. (2003). Palladium-catalyzed Negishi cross-coupling reactions of unactivated alkyl iodides, bromides, chlorides, and tosylates. *Journal of the American Chemical Society* 125 (41): 12527–12530.

156 van Mullekom, H. (2001). Developments in the chemistry and band gap engineering of donor–acceptor substituted conjugated polymers. *Materials Science & Engineering R: Reports* 32 (1): 1–40.

157 Marszalek, T., Li, M., and Pisula, W. (2016). Design directed self-assembly of donor–acceptor polymers. *Chemical Communications* 52 (73): 10938–10947.

158 Todd, A.D. and Bielawski, C.W. (2015). Controlled synthesis of an alternating donor–acceptor conjugated polymer via Kumada catalyst-transfer polycondensation. *ACS Macro Letters* 4 (11): 1254–1258.

159 Kang, T.E., Choi, J., Cho, H.H. et al. (2016). Donor–acceptor random versus alternating copolymers for efficient polymer solar cells: importance of optimal composition in random copolymers. *Macromolecules* 49 (6): 2096–2105.

160 Yan, H., Chen, Z., Zheng, Y. et al. (2009). A high-mobility electron-transporting polymer for printed transistors. *Nature* 457 (7230): 679–686.

161 Hendriks, K.H., Li, W., Heintges, G.H.L. et al. (2014). Homocoupling defects in diketopyrrolopyrrole-based copolymers and their effect on photovoltaic performance. *Journal of the American Chemical Society* 136 (31): 11128–11133.

162 Ku, S.Y., Brady, M.A., Treat, N.D. et al. (2012). A modular strategy for fully conjugated donor–acceptor block copolymers. *Journal of the American Chemical Society* 134 (38): 16040–16046.

163 Lee, J.H., Lee, D.H., Kim, H.J. et al. (2017). Ambipolar charge transport in a donor–acceptor–donor-type conjugated block copolymer and its gate-voltage-controlled thin film transistor memory. *Journal of Polymer Science, Part A: Polymer Chemistry* 55 (19): 3223–3235.

164 Nakabayashi, K. and Mori, H. (2014). Donor–acceptor block copolymers: synthesis and solar cell applications. *Materials (Basel)* 7 (4): 3274–3290.

165 Iovu, M.C., Sheina, E.E., Gil, R.R., and McCullough, R.D. (2005). Experimental evidence for the quasi-“living” nature of the grignard metathesis method for the synthesis of regioregular poly(S-alkylthiophenes). *Macromolecules* 38 (21): 8649–8656.

166 Sheina, E.E., Liu, J., Lovu, M.C. et al. (2004). Chain growth mechanism for regioregular nickel-initiated cross-coupling polymerizations. *Macromolecules* 37 (10): 3526–3528.

167 Miyakoshi, R., Yokoyama, A., and Yokozawa, T. (2005). Catalyst-transfer polycondensation. Mechanism of Ni-catalyzed chain-growth polymerization leading to well-defined poly(3-hexylthiophene). *Journal of the American Chemical Society* 127 (49): 17542–17547.

168 Yokoyama, A., Miyakoshi, R., and Yokozawa, T. (2004). Chain-growth polymerization for poly(3-hexylthiophene) with a defined molecular weight and a low polydispersity. *Macromolecules* 37 (4): 1169–1171.

169 Cheng, Y.-J., Yang, S.-H., and Hsu, C.-S. (2009). Synthesis of conjugated polymers for organic solar cell applications. *Chemical Reviews* 109 (11): 5868–5923.

170 Heo, J., Kim, Y.J., Seo, M. et al. (2012). Photoinduced reversible transmittance modulation of rod–coil type diblock copolymers containing azobenzene in the main chain. *Chemical Communications* 48 (27): 3351.

171 Vanhee, S., Rulkens, R., Lehmann, U. et al. (1996). Synthesis and characterization of rigid rod poly(*p*-phenylenes). *Macromolecules* 29 (96): 5136–5142.

172 Scherf, U., Adamczyk, S., Gutacker, A., and Koenen, N. (2009). All-conjugated, rod–rod block copolymers-generation and self-assembly properties. *Macromolecular Rapid Communications* 30 (13): 1059–1065.

173 Yokozawa, T. and Ohta, Y. (2016). Transformation of step-growth polymerization into living chain-growth polymerization. *Chemical Reviews* 116 (4): 1950–1958.

174 Yokoyama, A., Suzuki, H., Kubota, Y. et al. (2007). Chain-growth polymerization for the synthesis of polyfluorene via Suzuki Miyaura coupling reaction from an externally added initiator unit. *Journal of the American Chemical Society* 129 (23): 7236–7237.

175 Yokozawa, T., Kohno, H., Ohta, Y., and Yokoyama, A. (2010). Catalyst-transfer Suzuki–Miyaura coupling polymerization for precision synthesis of poly(*p*-phenylene). *Macromolecules* 43 (17): 7095–7100.

176 Scherf, U. and List, E.J.W. (2002). Semiconducting polyfluorenes – towards reliable structure-property relationships. *Advanced Materials* 14 (7): 477–487.

177 Berresheim, A.J., Müller, M., and Müllen, K. (1999). Polyphenylene nanostructures. *Chemical Reviews* 99 (7): 1747–1785.

178 Scherf, U. and Müllen, K. (1991). Polyarylenes and poly(arylenevinylenes), 7. A soluble ladder polymer via bridging of functionalized poly(*p*-phenylene)-precursors. *Die Makromolekulare Chemie. Rapid Communications* 12 (8): 489–497.

179 Greiner, A. (2005). A commentary on "Polyarylenes and poly(arylenevinylenes), 7. A soluble ladder polymer via bridging of functionalized poly(*p*-phenylene)-precursors" by U. Scherf, K. Müllen (Makromol. Chem., Rapid Commun. 1991, 12, 489–497). *Macromolecular Rapid Communications* 26 (17): 1361–1370.

180 Jiang, W.F., Wang, H.L., Wang, A.G., and Li, Z.Q. (2008). Simple and efficient method for obtaining fluorene and spirobifluorene bromide derivatives. *Synthetic Communications* 38 (12): 1888–1895.

181 Mansø, M., Koole, M., Mulder, M. et al. (2016). Synthesis and single-molecule conductances of neutral and cationic indenofluorene-extended tetrathiafulvalenes: Kondo effect molecules. *Journal of Organic Chemistry* 81 (18): 8406–8414.

182 Hadizad, T., Zhang, J., Wang, Z.Y. et al. (2005). A general synthetic route to indenofluorene derivatives as new organic semiconductors. *Organic Letters* 7 (5): 795–797.

183 Setayesh, S., Grimsdale, A.C., Weil, T. et al. (2001). Polyfluorenes with polyphenylene dendron side chains: toward non-aggregating, light-emitting polymers. *Journal of the American Chemical Society* 123 (5): 946–953.

184 Setayesh, S., Marsitzky, D., and Müllen, K. (2000). Bridging the gap between polyfluorene and ladder-poly-*p*-phenylene: synthesis and characterization of poly-2,8-indenofluorene. *Macromolecules* 33 (6): 2016–2020.

185 Reisch, H., Wiesler, U., Scherf, U., and Tuytuylkov, N. (1996). Poly(indenofluorene) (PIF), a novel low band gap polyhydrocarbon. *Macromolecules* 29 (25): 8204–8210.

186 Bernius, B.M.T., Inbasekaran, M., Brien, J.O., and Wu, W. (2000). Progress with light-emitting polymers. *Advanced Materials* 12 (23): 1737–1750.

187 Li, S.-S., Qin, L., and Dong, L. (2016). Rhodium-catalyzed C–C coupling reactions via double C–H activation. *Organic & Biomolecular Chemistry* 14 (20): 4554–4570.

188 Hussain, I. and Singh, T. (2014). Synthesis of biaryls through aromatic C—H bond activation: a review of recent developments. *Advanced Synthesis and Catalysis* 356 (8): 1661–1696.

189 Li, B. and Dixneuf, P.H. (2013). sp^2 C—H bond activation in water and catalytic cross-coupling reactions. *Chemical Society Reviews* 42 (13): 5744.

190 Chen, X., Engle, K.M., Wang, D.H., and Jin-Quan, Y. (2009). Palladium(II)-catalyzed C–H activation/C–C cross-coupling reactions: versatility and practicality. *Angewandte Chemie International Edition* 48 (28): 5094–5115.

191 Yi, H., Zhang, G., Wang, H. et al. (2017). Recent advances in radical C–H activation/radical cross-coupling. *Chemical Reviews* 117 (13): 9016–9085.

192 Majchrzak, M., Grzelak, M., and Marciniec, B. (2016). Synthesis of novel styryl-*N*-isopropyl-9H-carbazoles for designing trans-conjugated regular silicon hybrid materials. *Organic & Biomolecular Chemistry* 14 (39): 9406–9415.

193 Dierschke, F., Grimsdale, A.C., and Müllen, K. (2003). Efficient synthesis of 2,7-dibromocarbazoles as components for electroactive materials. *Synthesis (Stuttg)* 16: 2470–2472.

194 Vollmann, H., Becker, H., Corell, M., and Streeck, H. (1937). Pyrene and its derivatives. *European Journal of Organic Chemistry* 531 (1): 1–159.

195 Figueira-Duarte, T.M., Del Rosso, P.G., Trattnig, R. et al. (2010). Designed suppression of aggregation in polypyrene: toward high-performance blue-light-emitting diodes. *Advanced Materials* 22 (9): 990–993.

196 Miura, Y., Yamano, E., Tanaka, A., and Yamauchi, J. (1994). Generation, isolation, and characterization of *N*-(arylthio)-7-tert-butyl- and *N*-(arylthio)-2,7-di-tert-butyl-1-pyrenylaminyl radicals. *Journal of Organic Chemistry* 59 (12): 3294–3300.

197 Coventry, D.N., Batsanov, A.S., Goeta, A.E. et al. (2005). Selective Ir-catalysed borylation of polycyclic aromatic hydrocarbons: structures of naphthalene-2,6-bis(boronate), pyrene-2,7-bis(boronate) and perylene-2,5,8,11-tetra(boronate) esters. *Chemical Communications* (16): 2172.

198 Hall, D.G. (2006). Structure, properties, and preparation of boronic acid derivatives. Overview of their reactions and applications. In: *Boronic AcidsWiley-VCH Verlag*, 1–99. Weinheim, FRG.

199 Coffin, R.C., Peet, J., Rogers, J., and Bazan, G.C. (2009). Streamlined microwave-assisted preparation of narrow-bandgap conjugated polymers for high-performance bulk heterojunction solar cells. *Nature Chemistry* 1 (8): 657–661.

200 Li, Y., Zou, J., Yip, H.L. et al. (2013). Side-chain effect on cyclopentadithiophene/fluorobenzothiadiazole-based low band gap polymers and their applications for polymer solar cells. *Macromolecules* 46 (14): 5497–5503.

201 Albrecht, S., Janietz, S., Schindler, W. et al. (2012). Fluorinated copolymer PCPDTBT with enhanced open-circuit voltage and reduced recombination for highly efficient polymer solar cells. *Journal of the American Chemical Society* 134 (36): 14932–14944.

202 Zhang, M., Tsao, H.N., Pisula, W. et al. (2007). Field-effect transistors based on a benzothiadiazole–cyclopentadithiophene copolymer. *Journal of the American Chemical Society* 129 (12): 3472–3473.

203 Hinkel, F., Cho, D., Pisula, W. et al. (2015). Alternating donor–acceptor arrays from hexa-perihexabenzocoronene and benzothiadiazole: synthesis, optical properties, and self-assembly. *Chemistry – A European Journal* 21 (1): 86–90.

204 Tan, S.E. and Sarjadi, M.S. (2017). The recent development of carbazole-, benzothiadiazole-, and isoindigo-based copolymers for solar cells application: a review. *Polymer Science, Series B* 59 (5): 479–496.

205 Wang, Y. and Michinobu, T. (2016). Benzothiadiazole and its π-extended, heteroannulated derivatives: useful acceptor building blocks for high-performance donor–acceptor polymers in organic electronics. *Journal of Materials Chemistry C* 4 (26): 6200–6214.

206 Blouin, N., Michaud, A., and Leclerc, M. (2007). A low-bandgap poly(2,7-carbazole) derivative for use in high-performance solar cells. *Advanced Materials* 19 (17): 2295–2300.

207 Ding, X., Chen, L., Honsho, Y. et al. (2011). An *n*-channel two-dimensional covalent organic framework. *Journal of the American Chemical Society* 133 (37): 14510–14513.

208 Perumattam, J., Shao, C., and Confer, W.L. (1994). Studies on the alkylation and chlorination of fluorenes: preparation of 9-(2-hydroxyethyl)fluorene and 2,7-dichloro-9-(2-hydroxyethyl)fluorene. *Synthesis (Stuttg)* 1994 (11): 1181–1184.

209 Romaner, L., Pogantsch, A., De Freitas, P.S. et al. (2003). The origin of green emission in polyfluorene-based conjugated polymers: on-chain defect fluorescence. *Advanced Functional Materials* 13 (8): 597–601.

210 Olivier, Y., Niedzialek, D., Lemaur, V. et al. (2014). 25th anniversary article: high-mobility hole and electron transport conjugated polymers: how structure defines function. *Advanced Materials* 26 (14): 2119–2136.

211 Markiewicz, J.T. and Wudl, F. (2015). Perylene, oligorylenes, and aza-analogs. *ACS Applied Materials and Interfaces* 7 (51): 28063–28085.

212 Lee, J., Kalin, A.J., Yuan, T. et al. (2017). Fully conjugated ladder polymers. *Chemical Science* 8 (4): 2503–2521.

213 Hörhold, H.-H., Gottschaldt, J., and Opfermann, J. (1977). Studies on poly(arylenevinylene)s. XVII. Poly(1,4-phenylene-1,2-diphenylvinylene). *Advanced Synthesis and Catalysis* 319 (4): 611–621.

214 Babudri, F., Cicco, S.R., Farinola, G.M. et al. (1996). Synthesis, characterization and properties of a soluble polymer with a poly(phenylenevinylene) structure. *Macromolecular Rapid Communications* 17 (12): 905–911.

215 Pfeiffer, S. and Hörhold, H. (1999). Synthesis of soluble dialkoxy-substituted poly(phenylene alkenylidene)s by applying the Horner-reaction for condensation polymerization. *Macromolecular Chemistry and Physics* 200 (8): 1870–1878.

216 Hsieh, B.R., Wan, W.C., Yu, Y. et al. (1998). Synthesis of highly phenylated poly(*p*-phenylenevinylenes) via a chlorine precursor route. *Macromolecules* 31 (3): 631–636.

217 Schwalm, T. and Rehahn, M. (2007). Toward controlled Gilch synthesis of poly(*p*-phenylenevinylenes): synthesis and thermally induced polymerization of α-bromo-*p*-quinodimethanes. *Macromolecules* 40 (11): 3921–3928.

218 Cosemans, I., Hontis, L., Van Den Berghe, D. et al. (2011). Discovery of an anionic polymerization mechanism for high molecular weight PPV derivatives via the sulfinyl precursor route. *Macromolecules* 44 (19): 7610–7616.

219 Hontis, L., Van Der Borght, M., Vanderzande, D., and Gelan, J. (1999). Radical as well as anionic polymerisation mechanisms in the synthesis of poly(p-arylene vinylene) precursors. *Polymer (Guildf)* 40 (23): 6615–6617.

220 Wessling, R.A. (1985). The polymerization of xylylene bisdialkyl sulfonium salts. *Journal of Polymer Science Polymer Symposium* 72: 55–66.

221 Wise, D.L., Wnek, G.E., Trantolo, D.J. et al. (1998). *Photonic Polymer Systems: Fundamentals, Methods and Applications*. CRC Press.

222 Sun, S.-S. and Dalton, L.R. (2008). *Introduction to Organic Electronic and Optoelectronic Materials and Devices*. CRC Press.

223 Stenger-Smith, J.D., Lenz, R.W., and Wegner, G. (1989). Orientation during the conversion of precursor polymer films to poly(arylenevinylene) films. *Makromolekulare Chemie* 190: 3005–3011.

224 Becker, H., Spreitzer, H., Ibrom, K., and Kreuder, W. (1999). New insights into the microstructure of GILCH-polymerized PPVs. *Macromolecules* 32 (15): 4925–4932.

225 Grimsdale, A.C. and Müllen, K. (2011). Molecular and supramolecular conjugated polymers for electronic applications. In: *Macromolecular Engineering*, 2225–2262. Weinheim, Germany: Wiley-VCH Verlag.

226 Abdulkarim, A., Hinkel, F., Jänsch, D. et al. (2016). A new solution to an old problem: synthesis of unsubstituted poly(para-phenylene). *Journal of the American Chemical Society* 138 (50): 16208–16211.

227 Jasti, R., Bhattacharjee, J., Neaton, J.B., and Bertozzi, C.R. (2008). Synthesis, characterization, and theory of [9]-, [12]-, and [18]cycloparaphenylene: carbon nanohoop structures. *Journal of the American Chemical Society* 130 (52): 17646–17647.

228 Takaba, H., Omachi, H., Yamamoto, Y. et al. (2009). Selective synthesis of [12]cycloparaphenylene. *Angewandte Chemie International Edition* 48 (33): 6112–6116.

229 Golling, F.E., Quernheim, M., Wagner, M. et al. (2014). Concise synthesis of 3D π-extended polyphenylene cylinders. *Angewandte Chemie International Edition* 53 (6): 1525–1528.

230 Quernheim, M., Golling, F.E., Zhang, W. et al. (2015). The precise synthesis of phenylene-extended cyclic hexa-peri-hexabenzocoronenes from polyarylated [*n*]cycloparaphenylenes by the Scholl reaction. *Angewandte Chemie International Edition* 54 (35): 10341–10346.

231 Lee, J., Rajeeva, B.B., Yuan, T. et al. (2016). Thermodynamic synthesis of solution processable ladder polymers. *Chemical Science* 7 (2): 881–889.

232 Edwards, J.H. and Feast, W.J. (1980). A new synthesis of poly(acetylene). *Polymer (Guildf)* 21 (6): 595–596.

233 Mark, H.F. (2013). *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons.

234 Townsend, R.H.F., Bradley, D.D.C., and D, P. (1987). Photo-excitation in conjugated polymers. *Journal of Physics D: Applied Physics* 20 (11): 1367.

235 Dragutan, V. and Streck, R. (2000). *Catalytic Polymerization of Cycloolefins: Ionic, Ziegler–Natta, and Ring-opening Metathesis Polymerization*. Elsevier.

236 Chen, Z., Mercer, J.A.M., Zhu, X. et al. (2017). Mechanochemical unzipping of insulating polyladderene to semiconducting polyacetylene. *Science* 357 (6350): 475–479.

237 Zen, A., Pflaum, J., Hirschmann, S. et al. (2004). Effect of molecular weight and annealing of poly(3-hexylthiophene)s on the performance of organic field-effect transistors. *Advanced Functional Materials* 14 (8): 757–764.

238 Pomerantz, M., Tseng, J.J., Zhu, H. et al. (1991). Processable polymers and copolymers of 3-alkylthiophenes and their blends. *Synthetic Metals* 41 (3): 825–830.

239 Stepto, R.F.T. (2009). Dispersity in polymer science (IUPAC Recommendations 2009). *Pure and Applied Chemistry* 81 (2): 351–353.

240 Tierney, S., Heeney, M., and McCulloch, L. (2005). Microwave-assisted synthesis of polythiophenes via the Stille coupling. *Synthetic Metals* 148 (2): 195–198.

241 Trznadel, M., Pron, A., Zagorska, M. et al. (1998). Effect of molecular weight on spectroscopic and spectroelectrochemical properties of regioregular poly(3-hexylthiophene). *Macromolecules* 31 (15): 5051–5058.

242 Moore, J.C. (1964). Gel permeation chromatography. I. A new method for molecular weight distribution of high polymers. *Journal of Polymer Science, Part A: General Papers* 2 (2): 835–843.

243 Tseng, H.R., Phan, H., Luo, C. et al. (2014). High-mobility field-effect transistors fabricated with macroscopic aligned semiconducting polymers. *Advanced Materials* 26 (19): 2993–2998.

244 Lv, M., Li, S., Jasieniak, J.J. et al. (2013). A hyperbranched conjugated polymer as the cathode interlayer for high-performance polymer solar cells. *Advanced Materials* 25 (47): 6889–6894.

245 Imin, P., Cheng, F.Y., and Adronov, A. (2011). The effect of molecular weight on the supramolecular interaction between a conjugated polymer and single-walled carbon nanotubes. *Polymer Chemistry* 2 (6): 1404–1408.

246 Wu, S., Bu, L., Huang, L. et al. (2009). Synthesis and characterization of phenylene-thiophene all-conjugated diblock copolymers. *Polymer (Guildf)* 50 (26): 6245–6251.

247 Moroni, M., Le Moigne, J., and Luzzati, S. (1994). Rigid rod conjugated polymers for nonlinear optics. 1. Characterization and linear optical properties of poly(aryleneethynylene) derivatives. *Macromolecules* 27 (2): 562–571.

248 Axelson, D.E. and Russell, K.E. (1985). Characterization of polymers by means of 13C NMR spectroscopy. *Progress in Polymer Science* 11 (3): 221–282.

249 Przybilla, L., Brand, J.-D., Yoshimura, K. et al. (2000). MALDI-TOF mass spectrometry of insoluble giant polycyclic aromatic hydrocarbons by a new method of sample preparation. *Analytical Chemistry* 72 (19): 4591–4597.

250 Byrd, H.C.M. and McEwen, C.N. (2000). The limitations of MALDI-TOF mass spectrometry in the analysis of wide polydisperse polymers. *Analytical Chemistry* 72 (19): 4568–4576.

251 Trimpin, S., Grimsdale, A.C., Räder, H.J., and Müllen, K. (2002). Characterization of an insoluble poly(9,9-diphenyl-2,7-fluorene) by solvent-free sample preparation for MALDI-TOF mass spectrometry. *Analytical Chemistry* 74 (15): 3777–3782.

252 Schärtl, W. (2007). *Light Scattering from Polymer Solutions and Nanoparticle Dispersions*. Springer.

253 Hermans, T.M., Broeren, M.A.C., Gomopoulos, N. et al. (2009). Self-assembly of soft nanoparticles with tunable patchiness. *Nature Nanotechnology* 4 (11): 721–726.

254 Schilinsky, P., Asawapirom, U., Scherf, U. et al. (2005). Influence of the molecular weight of poly(3-hexylthiophene) on the performance of bulk heterojunction solar cells. *Chemistry of Materials* 17 (8): 2175–2180.

255 Kline, R.J., McGehee, M.D., Kadnikova, E.N. et al. (2003). Controlling the field-effect mobility of regioregular polythiophene by changing the molecular weight. *Advanced Materials* 15 (18): 1519–1522.

256 Kline, R.J., McGehee, M.D., Kadnikova, E.N. et al. (2005). Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight. *Macromolecules* 38 (8): 3312–3319.

257 Facchetti, A. (2011). π-Conjugated polymers for organic electronics and photovoltaic cell applications. *Chemistry of Materials* 23 (3): 733–758.

258 Hamilton, R., Bailey, C., Duffy, W. et al. (2006). The influence of molecular weight on the microstructure and thin film transistor characteristics of pBTTT polymers. *Proceedings of SPIE* 6336 (2006): 633611.

259 McCulloch, I., Heeney, M., Bailey, C. et al. (2006). Liquid-crystalline semiconducting polymers with high charge-carrier mobility. *Nature Materials* 5 (4): 328–333.

260 Shaked, S., Tal, S., and Roichman, Y. (2003). Charge density and film morphology dependence of charge mobility in polymer field effect transistors. *Advanced Materials* (11): 913–916.

261 Liu, J., Tanaka, T., Sivula, K. et al. (2004). Employing end-functional polythiophene to control the morphology of nanocrystal – polymer composites in hybrid solar cells. *Journal of the American Chemical Society* 126 (21): 6550–6551.

262 Koldemir, U., Puniredd, S.R., Wagner, M. et al. (2015). End capping does matter: enhanced order and charge transport in conjugated donor–acceptor polymers. *Macromolecules* 48 (18): 6369–6377.

263 Malika, J.E.L., Sauvé, G., and McCullough, R.D. (2004). In-situ end-group functionalization of regioregular poly(3-alkylthiophene) using the grignard metathesis polymerization method. *Advanced Materials* 16 (12): 1017–1019.

264 Jeffries-El, M., Sauvé, G., and McCullough, R.D. (2005). Facile synthesis of end-functionalized regioregular poly(3-alkylthiophene)s via modified Grignard metathesis reaction. *Macromolecules* 38 (25): 10346–10352.

265 Svensson, M., Zhang, F., Veenstra, S.C. et al. (2003). High-performance polymer solar cells of an alternating polyfluorene copolymer and a fullerene derivative. *Advanced Materials* 15 (12): 988–991.

266 Andersson, M.R., Selse, D., Berggren, M. et al. (1994). Regioselective polymerization of 3-(4-octylphenyl)thiophene with $FeCl_3$. *Macromolecules* 27 (22): 6503–6506.

267 Olle, I., Fengling, Z., and Andersson, M.R. (2009). Alternating polyfluorenes collect solar light in polymer photovoltaics. *Accounts of Chemical Research* 42 (11): 1731–1739.

268 Sato, M.A. and Morii, H. (1991). Nuclear magnetic resonance studies on electrochemically prepared poly(3-dodecylthiophene). *Macromolecules* 24 (5): 1196–1200.

269 Troshin, P.A., Susarova, D.K., Moskvin, Y.L. et al. (2010). Impedance measurements as a simple tool to control the quality of conjugated polymers designed for photovoltaic applications. *Advanced Functional Materials* 20 (24): 4351–4357.

270 De Haas, M.P. and Warman, J.M. (1982). Photon-induced molecular charge separation studied by nanosecond time-resolved microwave conductivity. *Chemical Physics* 73 (1–2): 35–53.

271 Nikiforov, M.P., Lai, B., Chen, W. et al. (2013). Detection and role of trace impurities in high-performance organic solar cells. *Energy & Environmental Science* 6 (5): 1513.

272 Abdou, M.S.A., Lu, X., Xie, Z.W. et al. (1995). Nature of impurities in π-conjugated polymers prepared by ferric chloride and their effect on the electrical properties of metal-insulator-semiconductor structures. *Chemistry of Materials* 7 (4): 631–641.

273 Grand, C. and Reynolds, J.R. (2015). The interplay between structure, processing, and properties in organic photovoltaic devices: how to translate recent laboratory-scale developments to modules. *MRS Communications* 5 (2): 155–167.

274 Kouijzer, S., Michels, J.J., Van Den Berg, M. et al. (2013). Predicting morphologies of solution processed polymer: Fullerene blends. *Journal of the American Chemical Society* 135 (32): 12057–12067.

275 Kim, C.S., Lee, S., Gomez, E.D. et al. (2008). Solvent-dependent electrical characteristics and stability of organic thin-film transistors with drop cast bis(triisopropylsilylethynyl) pentacene. *Applied Physics Letters* 93 (10): 1–4.

276 Gericke, A., Simon-Kutscher, J., and Hühnerfuss, H. (1993). Influence of the spreading solvent on the properties of monolayers at the air/water interface. *Langmuir* 9 (8): 2119–2127.

277 Thompson, D.C., Cha, Y.N., and Trush, M.A. (1986). *The Peroxidative Activation of Butylated Hydroxytoluene to BHT-Quinone Methide and Stilbenequinone*, 301–309. Boston, MA: Springer.

278 Na, P.S., Kim, H., So, H.-M. et al. (2005). Investigation of the humidity effect on the electrical properties of single-walled carbon nanotube transistors. *Applied Physics Letters* 87 (9): 93101.

279 Kim, W., Javey, A., Vermesh, O. et al. (2003). Hysteresis caused by water molecules in carbon nanotube field-effect transistors. *Nano Letters* 3 (2): 193–198.

280 Rinkiö, M., Zavodchikova, M.Y., Törmä, P., and Johansson, A. (2008). Effect of humidity on the hysteresis of single walled carbon nanotube field-effect transistors. *Physica Status Solidi* 245 (10): 2315–2318.

281 Nicolai, H.T., Kuik, M., Wetzelaer, G.A.H. et al. (2012). Unification of trap-limited electron transport in semiconducting polymers. *Nature Materials* 11 (10): 882–887.

282 Tseng, H.-E., Peng, K.-Y., and Chen, S.-A. (2003). Molecular oxygen and moisture as traps in poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene]: locations and detrapping by chain relaxation. *Applied Physics Letters* 82 (23): 4086–4088.

283 Aguirre, C.M., Levesque, P.L., Paillet, M. et al. (2009). The role of the oxygen/water redox couple in suppressing electron conduction in field-effect transistors. *Advanced Materials* 21 (30): 3087–3091.

284 Sung, D., Hong, S., Kim, Y.-H. et al. (2006). *Ab initio* study of the effect of water adsorption on the carbon nanotube field-effect transistor. *Applied Physics Letters* 89 (24): 243110.

285 Chang, C.-Y., Huang, Y.-C., Tsao, C.-S. et al. (2017). Quantitative correlation of the effects of crystallinity and additives on nanomorphology and solar cell performance of isoindigo-based copolymers. *Physical Chemistry Chemical Physics* 19 (34): 23515–23523.

286 Liao, H.C., Ho, C.C., Chang, C.Y. et al. (2013). Additives for morphology control in high-efficiency organic solar cells. *Materials Today* 16 (9): 326–336.

287 Dao, Q.D., Hori, T., Fukumura, K. et al. (2013). Effects of processing additives on nanoscale phase separation, crystallization and photovoltaic performance of solar cells based on mesogenic phthalocyanine. *Organic Electronics* 14 (10): 2628–2634.

288 Krissinel, E. and Henrick, K. (2007). Inference of macromolecular assemblies from crystalline state. *Journal of Molecular Biology* 372 (3): 774–797.

289 Muramatsu, Y., Yamamoto, T., Hayakawa, T., and Koinuma, H. (2002). Combinatorial synthesis and screening for blue luminescent π-conjugated polymer thin film. *Applied Surface Science* 189 (3–4): 319.

290 Wang, B., Watt, S., Hong, M. et al. (2008). Synthesis, properties, and tunable supramolecular architecture of regioregular poly(3-alkylthiophene)s with alternating alkyl and semifluoroalkyl substituents. *Macromolecules* 41 (14): 5156–5165.

291 Tour, J.M. (1996). Conjugated macromolecules of precise length and constitution. Organic synthesis for the construction of nanoarchitectures. *Chemical Reviews* 96 (1): 537–554.

292 Goseki, R., Ito, S., Matsuo, Y. et al. (2017). Precise synthesis of macromolecular architectures by novel iterative methodology combining living anionic polymerization with specially designed linking chemistry. *Polymers (Basel)* 9 (12): 470.

293 Matyjaszewski, K. (2005). Macromolecular engineering: from rational design through precise macromolecular synthesis and processing to targeted macroscopic material properties. *Progress in Polymer Science* 30 (8–9): 858–875.

294 Hsu, C.H. and Cheng, S.Z.D. (2018). The deconstruction of supramolecular structures based on modular precise macromolecules. *Macromolecular Chemistry and Physics* 219 (3): 1–8.

295 Wieghold, S., Li, J., Simon, P. et al. (2016). Photoresponse of supramolecular self-assembled networks on graphene-diamond interfaces. *Nature Communications* 7: 1–8.

296 Lutz, J.-F., Lehn, J.-M., Meijer, E.W., and Matyjaszewski, K. (2016). From precision polymers to complex materials and systems. *Nature Reviews Materials* 1 (5): 16024.

297 Wu, J., Pisula, W., and Müllen, K. (2007). Graphenes as potential material for electronics. *Chemical Reviews* 107 (3): 718–747.

298 Lee, C.-H., Lai, Y.-Y., Hsu, J.-Y. et al. (2017). Side-chain modulation of dithienofluorene-based copolymers to achieve high field-effect mobilities. *Chemical Science* 8 (4): 2942–2951.

299 Ong, B.S., Wu, Y., Liu, P., and Gardner, S. (2004). High-performance semiconducting polythiophenes for organic thin-film transistors. *Journal of the American Chemical Society* 126 (11): 3378–3379.

300 Kastler, M., Pisula, W., Laquai, F. et al. (2006). Organization of charge-carrier pathways for organic electronics. *Advanced Materials* 18 (17): 2255–2259.

301 Talirz, L., Söde, H., Dumslaff, T. et al. (2017). On-surface synthesis and characterization of 9-atom wide armchair graphene nanoribbons. *ACS Nano* 11 (2): 1380–1388.

302 Llinas, J.P., Fairbrother, A., Borin Barin, G. et al. (2017). Short-channel field-effect transistors with 9-atom and 13-atom wide graphene nanoribbons. *Nature Communications* 8 (1): 8–13.

303 Chang, S.-J., Liu, X., Lu, T.-T. et al. (2017). Ladder-type poly(indenofluorene-co-benzothiadiazole)s as efficient gain media for organic lasers: design, synthesis, optical gain properties, and stabilized lasing properties. *Journal of Materials Chemistry C* 5 (26): 6629–6639.

304 Zhao, S., Borin Barin, G., Rondin, L. et al. (2017). Optical investigation of on-surface synthesized armchair graphene nanoribbons. *Physica Status Solidi Basic Res* 254 (11): 1–5.

305 Chen, Y.C., De Oteyza, D.G., Pedramrazi, Z. et al. (2013). Tuning the band gap of graphene nanoribbons synthesized from molecular precursors. *ACS Nano* 7 (7): 6123–6128.

306 Cai, J., Ruffieux, P., Jaafar, R. et al. (2010). Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* 466 (7305): 470–473.

307 Cooper, D.R., D'Anjou, B., Ghattamaneni, N. et al. (2012). Experimental review of graphene. *ISRN Condensed Matter Physics* 2012: 1–56.

308 Rao, C.N.R., Voggu, R., and Govindaraj, A. (2009). Selective generation of single-walled carbon nanotubes with metallic, semiconducting and other unique electronic properties. *Nanoscale* 1 (1): 96.

309 Ziegler, K., Holzkamp, E., Breil, H., and Martin, H. (1955). Polymerization of ethylene and other olefins. *Angewandte Chemie* 67 (16): 426–426.

310 Natta, G. (1964). From stereospecific polymerization to the asymmetric autocatalytic synthesis of macromolecules. *Angewandte Chemie* 76 (13): 553–566.

311 Villalpando-Paez, F., Muramatsu, H., Kim, Y.A. et al. (2010). Wall-to-wall stress induced in (6,5) semiconducting nanotubes by encapsulation in metallic outer tubes of different diameters: a resonance Raman study of individual C60-derived double-wall carbon nanotubes. *Nanoscale* 2 (3): 406–411.

312 Kanungo, M., Lu, H., Malliaras, G.G., and Blanchet, G.B. (2009). Suppression of metallic conductivity of single-walled carbon nanotubes by cycloaddition reactions. *Science* 323 (5911): 234–237.

313 Meng, L., Fu, C., and Lu, Q. (2009). Advanced technology for functionalization of carbon nanotubes. *Progress in Natural Science* 19 (7): 801–810.

314 Ntim, S.A., Sae-Khow, O., Witzmann, F.A., and Mitra, S. (2011). Effects of polymer wrapping and covalent functionalization on the stability of MWCNT in aqueous dispersions. *Journal of Colloid and Interface Science* 355 (2): 383–388.

315 Fujigaya, T. and Nakashima, N. (2015). Non-covalent polymer wrapping of carbon nanotubes and the role of wrapped polymers as functional dispersants. *Science and Technology of Advanced Materials* 16 (2): 24802.

316 Szleifer, I. and Yerushalmi-Rozen, R. (2005). Polymers and carbon nanotubes – dimensionality, interactions and nanotechnology. *Polymer (Guildf)* 46 (19): 7803–7818.

317 Komatsu, N. and Wang, F. (2010). A comprehensive review on separation methods and techniques for single-walled carbon nanotubes. *Materials (Basel)* 3 (7): 3818–3844.

318 Saridara, C. and Mitra, S. (2005). Chromatography on self-assembled carbon nanotubes. *Analytical Chemistry* 77 (21): 7094–7097.

319 Lustig, S.R., Jagota, A., Khripin, C., and Zheng, M. (2005). Theory of structure-based carbon nanotube separations by ion-exchange chromatography of DNA/CNT hybrids. *Journal of Physical Chemistry B* 109 (7): 2559–2566.

320 Novoselov, K.S., Jiang, D., Schedin, F. et al. (2005). Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences* 102 (30): 10451–10453.

321 Pisana, S., Lazzeri, M., Casiraghi, C. et al. (2007). Breakdown of the adiabatic Born–Oppenheimer approximation in graphene. *Nature Materials* 6 (3): 198–201.

322 Castro Neto, A.H., Guinea, F., Peres, N.M.R. et al. (2009). The electronic properties of graphene. *Reviews of Modern Physics* 81 (1): 109–162.

323 Nigar, S., Zhou, Z., Wang, H., and Imtiaz, M. (2017). Modulating the electronic and magnetic properties of graphene. *RSC Advances* 7 (81): 51546–51580.

324 Akinwande, D., Brennan, C.J., Bunch, J.S. et al. (2017). A review on mechanics and mechanical properties of 2D materials – graphene and beyond. *Extreme Mechanics Letters* 13: 42–77.

325 Li, X., Yu, J., Wageh, S. et al. (2016). Graphene in photocatalysis: a review. *Small* 12 (48): 6640–6696.

326 Coleman, J.N. (2013). Liquid exfoliation of defect-free graphene. *Accounts of Chemical Research* 46 (1): 14–22.

327 Paton, K.R., Varrla, E., Backes, C. et al. (2014). Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nature Materials* 13 (6): 624–630.

328 Liu, S., Zeng, T.H., Hofmann, M. et al. (2011). Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress. *ACS Nano* 5 (9): 6971–6980.

329 Liu, S., Hu, M., Zeng, T.H. et al. (2012). Lateral dimension dependent antibacterial activity of graphene oxide sheets. *Langmuir* 28: 12364–12372.

330 Li, X., Wang, X., Zhang, L. et al. (2008). Chemically derived, ultrasmooth graphene nanoribbon semiconductors. *Science* 319 (5867): 1229–1232.

331 Ritter, K.A. and Lyding, J.W. (2009). The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. *Nature Materials* 8 (3): 235–242.

332 Han, M.Y., Özyilmaz, B., Zhang, Y., and Kim, P. (2007). Energy band-gap engineering of graphene nanoribbons. *Physical Review Letters* 98 (20): 1–4.

333 Yesodha, S.K., Sadashiva Pillai, C.K., and Tsutsumi, N. (2004). Stable polymeric materials for nonlinear optics: a review based on azobenzene systems. *Progress in Polymer Science* 29 (1): 45–74.

334 Ma, X., Ma, F., Zhao, Z. et al. (2009). Synthesis and properties of NLO chromophores with fine-tuned gradient electronic structures. *Journal of Materials Chemistry* 19 (19): 2975.

335 Marder, S.R., Kippelen, B., Jen, A.K.Y., and Peyghambarian, N. (1997). Design and synthesis of chromophores and polymers for electro-optic and photorefractive applications. *Nature* 388 (6645): 845–851.