A Polymer Lost in the Shuffle: The Perspective of Poly(para)phenylenes

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During 1990s, poly(para)phenylenes (PPPs) are one of the most prominent and hyped classes of conjugated polymers. Even though they have been heavily investigated for different applications, they are now eking out a rather niche existence. It is believed that this decline of interest partly has come from the early obstacle of synthesizing high-molecular weight, processable, and defect-free PPPs. Early examples of PPPs are not only rather oligomers than polymers but also contain many regiochemical and structural defects. Furthermore, early unsubstituted materials are infusible and insoluble, which have made their practical application almost impossible. Another reason for the decline of research interest in PPPs may be their underperformance in early applications, particularly in organic light-emitting diodes (OLEDs), which ultimately lead to a lack of follow-up publications. However, over the last two decades not only more precise and advanced synthesis methods have arisen but also a more profound understanding of those applications has been achieved within which new technological approaches have emerged. It is believed that PPPs would benefit from this development. Accordingly, in this perspective, the synthesis, structures, properties, and applications of PPPs reported so far as well as their potential in future technologies are discussed.

1. Introduction

Poly(para)phenylenes, also known as PPPs, are a well-known polymer class with remarkable properties. Poly(para)phenylenes are so-called conjugated polymers consisting of directly 1,4-linked benzene units. Due to the sp²-hybridization of carbon atoms composing the polymer backbone, PPPs possess a large, delocalized π-electron system, which gives rise to unique properties, unknown for nonconjugated commodity polymers. Among

these unique characteristics are the intrinsic conductivity after doping as well as electro- and photoluminescence.[1] Furthermore, defect-free PPPs are considered as rigid-rod polymers, the feature that often enables liquid-crystalline behavior and brings certain advantages in mechanical properties.[2]

Beginning with the hype around "synthetic metals" and conjugated polymers in the late 1970s, also PPPs got much attention. Back then, the predominant material was unsubstituted PPP, synthesized by various approaches which will be briefly discussed later on. It became evident that those methods were limited, and the synthesis of PPPs was proving to be difficult. The main issue was to obtain high molecular weight and defect-free PPPs. In fact, most of the first synthesis examples of PPPs yielded rather short-chained oligomers with high amount of structural and chemical defects.[3] Besides, the processability and applicability also proved to be difficult as unsubstituted PPPs are infusible and insoluble in conventional solvents with a degree of polymerization (DP) larger than 8.[4] The poor solubility and the defects were widely believed to be the main challenge in the synthesis and application of PPPs.[4] This assertion resulted in the development of substituted PPPs with sidechains that increase the solubility of the resulting polymer tremendously by interrupting the π-stacking of macromolecules. Substituted PPPs obtained in the first experiments of the Yamamoto group and in the works of Schlüter, Wegner, and Rehahn in the 1980s and 1990s were solution-processable and defect-free, but their molecular weight was still limited.[5]

Today, the most common methods for synthesizing prevalent substituted PPPs are cross-coupling-based polymerizations. In this context, the most prominent examples are the Suzuki polycondensation (SPC) and the Kumada-catalyst transfer polymerization (KCTP or GRIM-polymerization). With these new modern synthesis possibilities, substituted PPPs were tested for several applications. They were considered especially promising in the field of optoelectronics because of their deep-blue photoluminescence. Other applications aimed at their mechanic properties, using PPPs in high-performance blends or as a comonomer, as well as at their redox properties, utilizing PPPs as anode material in batteries. Furthermore, with the new synthesis methods of substituted PPPs, various functional groups like sulfones, alcohols, PEG, etc. could be incorporated into the polymer structure,

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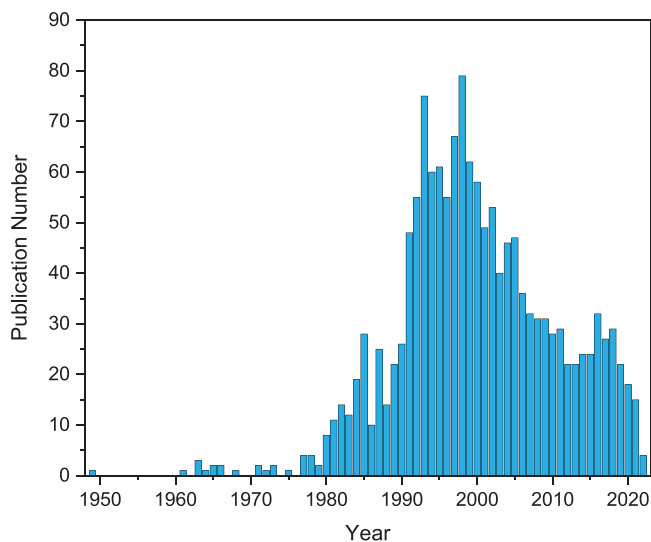E-mail: rieger@tum.de

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Figure 1. Number of publications mentioning PPPs either in the title, abstract or keywords during the last decades. Search conducted via Web of Science.

Scheme 1. Prominent examples of early polymerization attempts toward PPPs.

making PPPs potentially interesting, e.g., as polymer electrolytes in batteries, proton-exchange membrane in fuel-cells, etc.

When we started to work in this field, we found contradictory conclusions in literature. While some papers awarded PPPs in preliminary application tests for "having interesting application potential" other publications found PPPs failed to live up to the expectations in preliminary trials. In the organic light-emitting diode (OLED) field PPPs were replaced by structurally similar polymers like polyfluorenes and ladder-type polymers. Over the years, the research interest in PPPs declined (cf. **Figure 1**), resulting in their niche existence nowadays. Was the insufficient performance of these polymers in various applications just a matter of synthesis and device optimization? In this respect, we wonder if the modern synthesis methods of PPPs together with the currently existing and quickly developing technological know-how can contribute to a revival of the interest in this polymer class. In other words: would it be worth to screen PPPs once again for different applications by taking the knowledge gained over the last two to three decades into account? For example, in the field of light-emitting diodes (LEDs), much knowledge was achieved especially regarding the multilayer setup to facilitate the charge-carrier mobility and in the understanding of structure–behavior relationship of emissive materials.

This perspective will shortly discuss typical synthesis methods of PPPs. Subsequently, different applications of PPPs will be discussed to illuminate further investigation potential as well as to present optimization approaches for using PPPs in these applications.

2. Synthesis

2.1. Early Synthesis Attempts

Many excellent reviews of research in this area were published and therefore we just briefly mention the main achievements.[6–11]
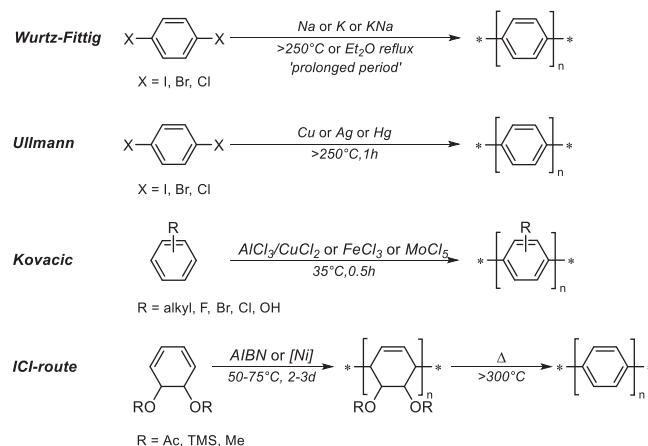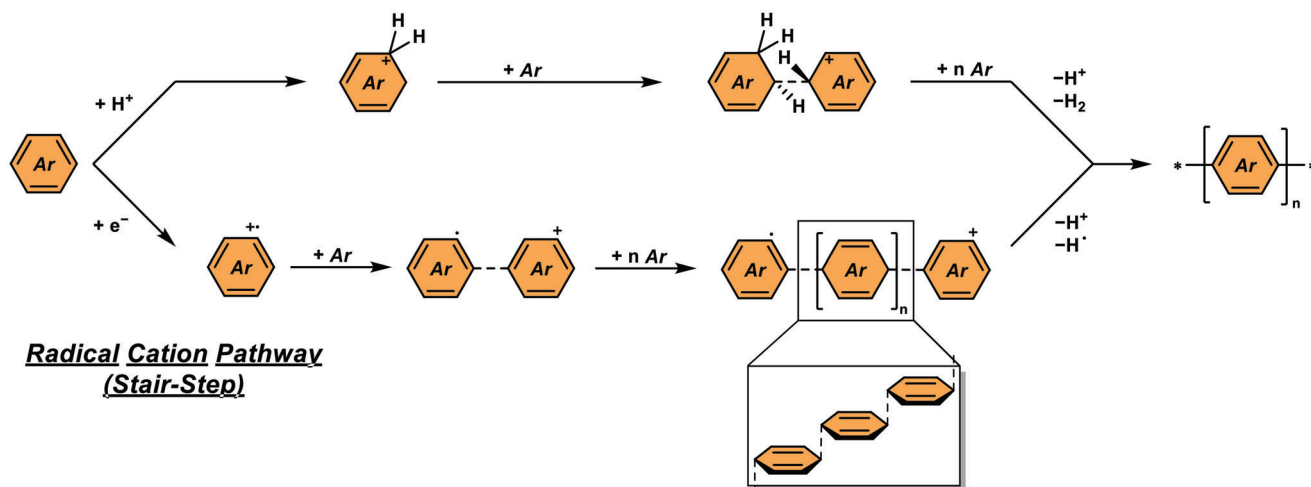
2.1.1. Wurtz–Fittig Reaction

One of the first reported syntheses of PPPs was probably published in 1872 by F. Riese, describing the reaction of elemental sodium on 1,4-dibromobenzene (cf. **Scheme 1**).[10,12] Today, we know this reaction under the name Wurtz–Fittig reaction. It is believed that this Wurtz–Fittig coupling proceeds via a carbanion, generated by the reaction of elemental sodium with an aryl halide.[6] Subsequently, this carbanion reacts with another aryl halide and generates the corresponding diaryl with the sodium halogenide as a by-product. Accordingly, using aryl halides with two halogen moieties leads to poly-coupled products—hence polymers. However, the harsh reaction conditions, the need of high amounts of sodium, as well as the high amount of side products which are difficult-to-separate making this reaction unpractical. Furthermore, the resulting polyaryl is rather a branched oligomer with considerable structural defects.[6]

2.1.2. Ullmann Coupling

One of the most popular synthesis strategies of unsubstituted polyaryls in the early 20th century was the polymerization utilizing the Ullmann reaction.[4,6] In this approach, the aryl halides are heated with elemental copper or silver up to 200–300 °C, forming the corresponding polyaryl (cf. Scheme 1).[6] Back then, the Ullmann reaction was mainly used in the context of defined di- or terphenyls, however, there are literature examples where poly(para)phenylenes were also synthesized via the Ullmann condensation.[8] The advantage over the Wurtz–Fittig reaction is that the Ullmann condensation of phenyl halides often results in polyphenylenes with higher molecular weight and fewer side products.[8] Furthermore, it is possible to synthesize nitro-, fluoro- or methyl-substituted PPPs with the Ullmann approach.[13] However, the Ullmann condensation has similar problems as the Wurtz–Fittig polymerization concerning the polymer purification, molecular weight, and structural defects.[6]

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Scheme 2. Possible polymerization mechanism of the Kovacic approach.[7,17]

2.1.3. Kovacic Method

One milestone in the direct synthesis of poly(para)phenylenes was achieved by the Kovacic group already in the 1960s.[14,15] Their strategy proceeds via dehydrocoupling of benzenes utilizing a catalyst-oxidant system either consisting of a binary mixture of a Lewis acid and an oxidant or of a single reagent with both properties (cf. Scheme 1). This method falls into the domain of the Scholl-reaction.[7] The primary advantage of the method is the mild reaction conditions. For example, for the binary system of aluminum chloride and cupric chloride, a polymerization occurs already at 30–37 °C and only take 15 to 30 min to full conversion.[6,14] During the 1970s and 1980s, much effort was put into the investigation of the mechanism and kinetics of the polymerization.[7] One accepted mechanism proposed by the Kovacic-group is the so-called "stair-step" mechanism or "radical cation mechanism." This stair-step mechanism suggests that in the first step a benzene radical is formed which then functions as a coordination site for other benzene nuclei. Those benzenes arrange in such a way that they appear as stair steps. In a subsequent step, covalent bond formation probably proceeds via a proton abstraction at the sigma-terminus as well as an electron and hydrogen abstraction at the other terminus.[7] Another mechanism is the so-called "arenium cation mechanism."[16,17] Both mechanisms are depicted in **Scheme 2**.

However, although this was one of the first synthesis methods where poly(para)phenylenes were synthesized in a more controlled and defined way, the resulting polymers were also rather short-chained (DP usually around 15).[3,4] Furthermore, PPPs synthesized by the Kovacic method often showed high amounts of oxygen, chlorine, and catalyst residues besides other structural defects which render dark color to the material.[7,8] It was assumed that one of the main reasons for low molecular weights was the insolubility of the resulting polymers, which caused a premature precipitation of the polymer from the reaction solution.[3] Follow-up publications trying to circumvent this problem showed ambiguous results: using ionic liquids with benzene increased the molecular weight significantly.[18] However, attaching soluble alkyl sidechains to

the monomer did not increase the DP of the resulting polymer substantially.[19]

2.1.4. ICI-Route

In order to address the insolubility and thus the challenging processability, as well as the low molecular weights resulting from the above synthetic approaches toward the unsubstituted PPPs, the ICI-route, was developed.[20] The idea—originated from the Marvel method[21]—was to synthesize a high-molecular weight, soluble precursor-polymer which can be easily processed and is then, subsequently converted to the corresponding poly(para)phenylene via, e.g., thermal treatment of the precursor polymer (cf. Scheme 1). As precursor polymer poly(5,6-diacetoxycyclohexa-1,3-diene) was often used, which was obtained by radical polymerization with usually high-molecular weights. This precursor showed good solubility, and low chemical defects but in the early examples ≈10% ortho-linkages.[3,22] The subsequent aromatization was then accomplished by thermal cleavage of two acetic acid molecules. Through the years, several improvements were implemented in this route. This included new synthesis methods toward the monomer (5,6-functionalized 1,3-cyclohexadienes) as early reports often involved many challenging reaction steps and difficult-to-purify intermediates.[9] Other improvements comprised the polymerization itself to reduce the number of ortho-linkages as well as the optimization of the aromatization-step by using different leaving groups.[22]

Although with this method high-molecular weight, processed PPPs were accessible, indirect polymerization methods like the ICI-route have in common that postpolymerization steps like the aromatization often do not proceed quantitatively and therefore lead to chemical defects along the polymer's backbone interrupting the conjugation.[4,23] However, because of the low number of competing side-reactions, low amount of branching, good processability of the precursor, and high molecular weights, this method was a major accomplishment and until the 1980s one of the best approaches toward the synthesis of high-molecular weight PPPs.
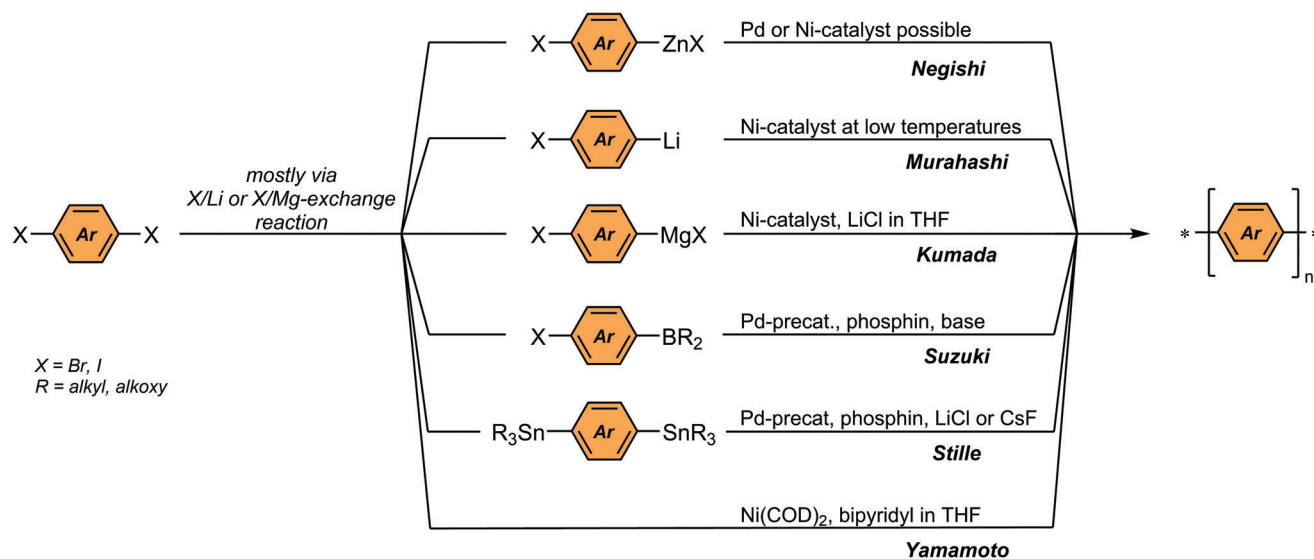
Scheme 3. Different prominent polymerization routes toward substituted PPPs based on modern cross-coupling reactions.

2.1.5. Other Polymerization Methods

Besides the above-mentioned early synthesis routes of PPPs, there were also several other less frequently used polymerization methods. Among these are the Diels–Alder polymerization,[24] electrochemical polymerization[11,25] as well as surface-aided polymerization methods.[26] Each method was developed to address some of the limitations of the aforementioned polymerization methods. However, all those approaches were either very difficult to accomplish, resulted in low molecular weights, tended to form structural or chemical defects, or required very harsh reaction conditions.
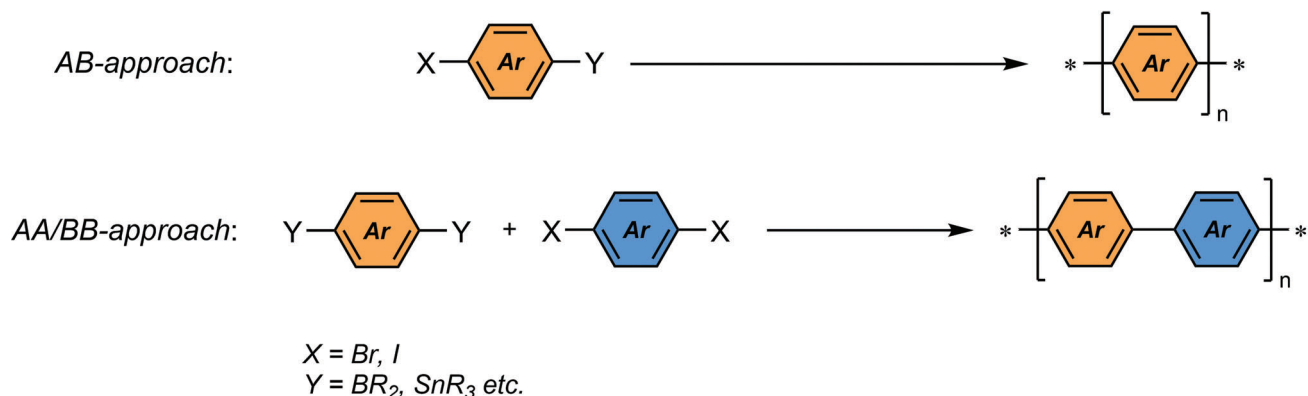
2.2. Yamamoto Coupling

The next major milestone in the synthesis of structurally defined, defect-free poly(para)phenylenes in the 20th century was accomplished by the group of Yamamoto in the 1970s.[27] Motivated by the lack of synthesis methods for PPPs, Yamamoto investigated the coupling of aryl halides with nickel catalysts in the presence of reducing metals as zinc, magnesium, etc. (cf. **Scheme 3**).[28] These investigations resulted in the first synthesis of structurally regular, defect-free unsubstituted PPPs.[4,29] It quickly became evident that the main advantage of the Yamamoto polycondensation is that this method shows no branching, no polynuclear regions, and no chemical as well as no meta- or ortho-linkage upon very mild reaction conditions.[4] Furthermore, it is possible to introduce side-groups to synthesize substituted PPPs without sacrificing the regioregularity as opposed to the Kovacic method for example.[5] Over the years, the catalysis mechanism was investigated, and great efforts have been made regarding the optimization of the polymerization toward high molecular weights, as especially early results were limited to DPs between 8 and 20 accompanied with high polydispersities while using stoichiometric amounts of expensive nickel reagents.[4,22,30]

Today, the Yamamoto polycondensation is still used and may be even advantageous over other approaches toward conjugated substituted polymers that are based on organometallic reactions. Especially, it benefits from practical simplicity, mild reaction conditions, and defect-free products. As an example of the method's utility, benzoyl-substituted PPPs representing high-performance polymers were commercially offered till recently and were synthesized by a Yamamoto route.[31] However, the molecular weights of materials from Yamamoto polymerization remain rather limited compared to the modern and powerful polymerization methods based on Suzuki- and Kumada-cross-coupling reactions, particularly when soluble conjugated polymers are targeted.[22,32]

2.3. Cross-Coupling Based Polymerizations

2.3.1. Suzuki Polycondensation

Initially intrigued by the results of Yamamoto, Wegner and co-workers started research on the investigation and optimization of the Yamamoto coupling and eventually developed a polymerization based on another organometallic cross-coupling reaction: the Suzuki polycondensation (SPC also known as SCTP or Suzuki–Miyaura polymerization, cf. Scheme 3).[4,29,33] This Suzuki cross-coupling polymerization was the first method which could outperform the Yamamoto route.[4,29] The polymerization of alkyl-substituted, boron, and bromine-functionalized monomers resulted in high-molecular weight soluble PPPs with no structural or chemical defects.[4,33] This breakthrough opened new possibilities for application of PPPs, for example, by introducing new functionalities and properties through the attached sidechains that are tolerated under the mild reaction conditions of Suzuki cross-coupling. For instance, incorporation of ion-conducting sidechains led to PPP-based polymer electrolytes for batteries or to proton-exchange membranes for fuel cells.[29] PPP–dendrimers were synthesized for biomedical applications

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AB-approach:

AA/BB-approach:

X = Br, I
Y = BR_2, SnR_3 etc.

Scheme 4. The *AB* and *AA/BB*-approach.

as well as for investigating the aggregation behavior of such structures.[29,34]

The SPC proceeds via a polycondensation between a boron functionality and halogen moiety using a Pd-precatalyst, which is converted with a suitable phosphine ligand in situ into the corresponding active Pd(0)-catalyst. The boron-functionality (e.g., boronic acid or boronic ester) and halide can be attached to a single monomer molecule (*AB*-approach) or can be split into two different comonomers, one bearing two boron-functionalities and the other possessing two halide groups (*AA/BB*-approach) (cf. **Scheme 4**). The first approach is especially advantageous for yielding high molecular weight homopolymers. This is because in the case the polycondensation occurs via a step-growth mechanism, ideal stoichiometry, and thus high conversions, which is needed for achieving high molecular weights is realized in an *AB*-monomer (cf. Carother's equation). However, chain-growth mechanism has also been suggested to occur upon Suzuki-polymerization of *AB*-monomers giving rise to high molecular weights, which is not possible for *AA/BB*-monomers. Nevertheless, the latter method is especially advantageous for synthesizing alternating copolymers where an *AA*-comonomer can have functionalities and properties different from those of a *BB*-comonomer. Whereas the boron-monomers (here *AA*) are synthesized via Grignard or lithium reagents, which among others do not tolerate electrophilic or protic functional groups in the monomer precursor's structure, the dihalo-comonomers (*BB*) can be "equipped" with a broad range of functional groups that are not reactive under mild conditions of SPC. The *AA/BB*-SPC approach made it possible to synthesize many functional substituted polymers used especially in ion-conducting applications. Nowadays, the SPC is still in use for the synthesis of conjugated polymers bearing functionalities in the sidechains, and much effort was made to optimize and even broaden its scope further. Many excellent reviews of research in this area were published and therefore we just briefly mention the main achievements.[4,22,29,32,35]
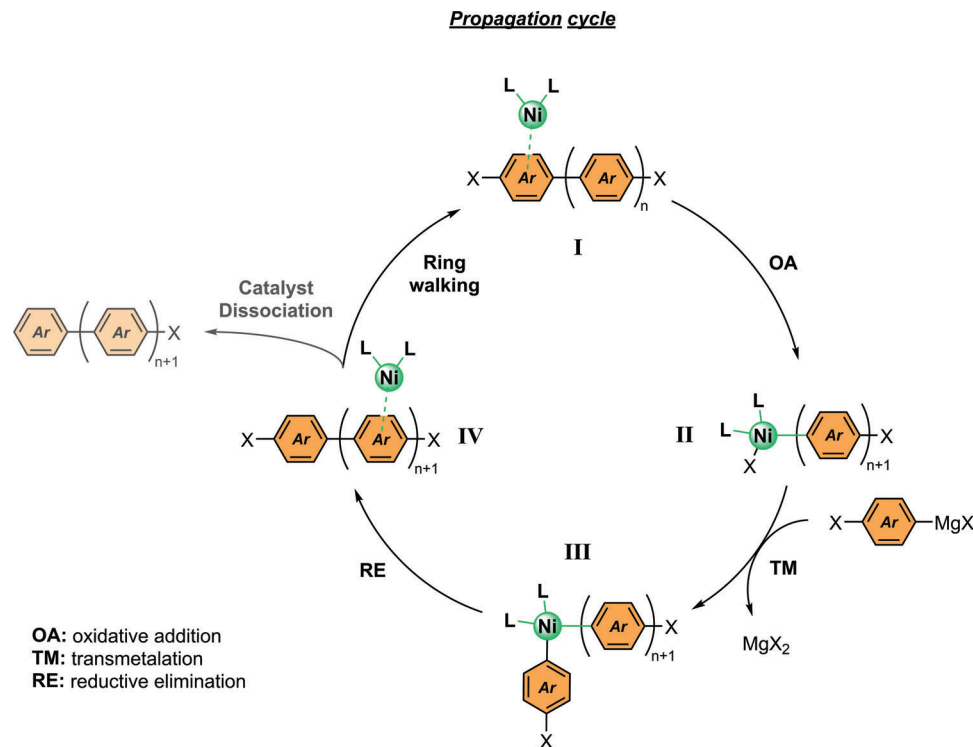
In this context, new catalyst systems, different bases, solvents, and reaction conditions were screened, and effort was put into finding new synthetic approaches toward boron-based monomers. The latter was necessary as the synthesis, purification, and stability of boron-based functional groups proved to be difficult and was one of the main reasons for yielding low

molecular weight polymers for a long time.[22,29] Further, the establishment of Buchwald-ligands made low catalyst loadings in SPC possible.[4,35] This is a very important issue because the high amounts of Pd catalyst which were required in the early polymerization protocols tend to remain in the polymer and deteriorate the material properties.[35]

Therefore, parallel to optimization of the SPC, researchers sought for alternative polymerization methods which do not rely on palladium as a catalyst. Nowadays—at least for some conjugated polymers like polythiophenes—the SPC is not the state-of-the-art synthesis route anymore.

2.3.2. Kumada-Catalyst-Transfer Polycondensation (KCTP, GRIM-Polymerization)

For the synthesis of high-molecular weight polythiophenes and also partly for other conjugated polyarenes, the KCTP (Kumada catalyst-transfer polycondensation, also known as GRIM-polymerization) is predominately used.[36] The KCTP is a polymerization method based on the nickel-catalyzed cross-coupling reaction between a Grignard reagent and an aryl halide. The polymerization proceeds via a controlled step-growth mechanism and for some monomers (e.g., polythiophenes) via a living polymerization.[37] The typical KCTP starts with the generation of the *AB*-monomer by a halogen-magnesium exchange reaction of a dihalide-monomer precursor. The generated *AB*-monomer is then polymerized without further purification or isolation as Grignard reagents are highly air- and moisture sensitive and are subject to the Schlenk equilibrium, which makes most purification methods unsuitable. Hence, a quantitative halogen-magnesium exchange reaction of the precursor to the monomer is crucial for achieving high molecular weights and yields.[38] Also, possible side products generated during this exchange reaction may influence the polymerization results. In this regard, many studies aimed to improve the halogen-magnesium exchange reaction of dihalobenzenes. In this process, especially the works of the Knochel group who introduced the so-called turbo-Grignard reagents set a milestone in improving the KCTP.[39] Turbo-Grignard reagents are complex-solutions of Grignard reagents with lithium chloride which are particularly

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Scheme 5. Most accepted mechanism for the KCTP.

reactive for the halogen–magnesium exchange and may also accelerate the polymerization itself.[40]

Over the last two decades, many studies regarding the investigation and optimization of the KCTP were published. Especially, a lot of research has been done concerning the mechanistics, catalyst, and monomer design as well as optimization of the KCTP. However, it should be noted that those investigations and optimizations were almost exclusively done for polythiophenes. It is widely accepted that the polymerization in KCTP proceeds via a chain growth mechanism involving the so-called ring-walking which is an intramolecular reoxidative addition of the catalyst to the terminal benzene–halide bond.[41] This is shown in **Scheme 5**.

With this knowledge, many new catalyst systems were introduced replacing the well-established nickel–diphosphine complexes.[42,43] Nowadays, the KCTP is the state-of-the-art polymerization technique for many conjugated polyarenes. The KCTP is favored for high-molecular weights, defect-free polyarenes with Grignard-tolerable side chains. The often-observed controlled chain-growth polymerization in KCTP allows the synthesis of polymers with precise molecular weights and small polydispersities as well as the synthesis of block-copolymers.[42,44]

Despite the many positive features, the KCTP is not suitable for polymerizing monomers bearing sidechains that are not compatible with Grignard reagents or for polymerizing electronegative monomers. This somewhat limits the scope of the KCTP compared to the SPC. Furthermore, it should be noted that most of those investigations and optimization studies were conducted with polythiophenes. Surprisingly, KCTP toward PPPs was only

occasionally applied, resulting in moderate to low molecular weights, until the very recent investigations could show that this type of polymerization can be optimized to obtain substituted PPPs with a DP of up to 260.[38]

2.3.3. Other Cross-Coupling Based Polymerizations: Stille-Polycondensation and Negishi-Catalyst-Transfer Polycondensation (NCTP)

Besides the KCTP and SPC, which are used by the vast majority of researchers to polymerize substituted conjugated PPPs, there are also a few examples of other cross-coupling-based polymerizations. The most prominent examples are the Stille and the Negishi cross-coupling-based polymerization. The Negishi CTP (NCTP) is a nickel or palladium catalyzed polymerization using either _AA/BB_ or _AB_-monomers where a zinc moiety reacts with a halogen functionality.[45,46] The NCTP somewhat fills the gap between the KCTP and the SCP: organozinc compounds are more moisture- and air sensitive but also more reactive than the boron-based functionality. On the other hand, Negishi monomers are less reactive than Gringard reagents while tolerating more functional groups in the monomer's sidechains.[47] Similar to the boron-based functional groups, organozinc compounds are synthesized via the corresponding lithium or Grignard reagents. Additionally, the zinc-containing monomers can be synthesized using either the highly reactive Rieke zinc or via zincate complexes.[48] Usually, the NCTP proceeds similarly to the KCTP via a controlled chain-growth polymerization when _AB_-monomers are used.[46,49]

The Stille polycondensation reaction is one of the mildest polymerizations toward π-conjugated polyarenes known so far and quite similar to the Suzuki polycondensation: the Stille-type polymerization proceeds either via a step-growth mechanism between a ditin- and dihalide-monomer (*AA/BB*-approach) using a palladium precatalyst and a phosphine ligand or via a chain-growth mechanism of an *AB*-monomer.[50] The tin-monomer is typically synthesized by using highly toxic tin trialkylstannanes and organolithium reagents.[51] The Stille methodology is especially advantageous in the context of functional group compatibility as the tin moieties show an even higher functional group tolerance than the boron-based moieties of Suzuki monomers.[47,51] However, the Stille polycondensation shows similar limitations like the Suzuki-based polymerization (SPC): in case of the *AA/BB*-approach a very precise stoichiometric balance of the monomers is crucial for high-molecular weights. Since Stille monomers are laborious to purify and they tend to undergo homocoupling, the control of stoichiometry is difficult. Furthermore, polymers produced by Stille polycondensation may contain palladium colloids as well as difficult-to-remove tin impurities, which not only have an influence on the optical and electronic properties but also pose a serious health risk.[51]

3. Applications of Poly(para)phenylenes

3.1. Light-Emitting Diode (LED, OLED)

Undoubtedly, one of the most prominent applications of conjugated polymers in general and PPPs in particular are based on their ability to emit light upon electrical current (electroluminescence, EL). Here, especially the utilization of PPPs as active layer for OLEDs was heavily investigated as PPPs emit light in the blue region because of their unique wide bandgap. In order to understand their potential and perspective in this field, one has to look at the history and the recent progress of OLEDs. The following section aims to illuminate the recent developments of the display market, the superior operating principle of OLEDs over conventional liquid crystal displays (LCDs) as well as the need and approaches to achieve stable, efficient, and long lifetime deep-blue OLEDs. Regarding the latter, we recommend comprehensive reviews in this area published earlier elsewhere.[22,32,52–56]

In the recent years the display market changed arguably. The commonly used LCDs were steadily replaced by the new panel technology based on self-emitting OLEDs. For instance, over 80% of 5G-compatible smartphones (equivalent to the mid-range and high-end smartphone sector) are utilizing OLED screens nowadays.[57] In case of TVs, the picture is similar: 42% of the 2021 sold mid-range to high-end TVs (retail price above 1500$) are using OLED-panels. Even though the market share for TVs is somewhat smaller compared to smartphones, as the panel size and price are still impeding the transition, the trend is clear: in both sectors OLEDs are taking over.[58] By contrast, the vast majority of laptops and computer monitors are still relying on LCD screens. One of the main reasons why the implementation of OLEDs is lingering in this case, is that the current OLEDs are still suffering from an increased risk of burn-in—especially in the context of static pictures. However, in the field of smartphones and TVs the advantages by far outweigh those disadvantages. Among the advantages of OLEDs are the significantly higher contrast ratios with a true black color, the superior color volume, fast response times, and low input-lag as well as the good viewing-angles and the higher energy efficiency compared to LCD screens. These can mainly be attributed to the different functional principles of OLEDs and LCDs.[59]

Contrary to LCD requiring the so-called backlight throughout the device operation, OLED-pixels (smallest units which can be addressed by the graphics adapter) only emit light upon applying an electric current to them. This emission proceeds via a radiative relaxation of the nascent excitons upon electron and electron hole recombination in the emissive layer.[60] In a typical OLED assembly, the active emissive layer is placed between a transparent anode (e.g., ITO substrate) and an opaque cathode. Usually, modern OLED devices are using multilayer setups where charge-inject- and charge-transport-facilitating layers are incorporated between the emissive active layer and the electrodes (cf. **Figure 2**). These layers increase the device's efficiency significantly but also complicate the device fabrication, increase their thickness, and may have a negative impact on the driving voltage.[22]

Until now, especially blue OLEDs are still expensive, difficult-to-manufacture, often lack high efficiencies and suffer from short lifetimes.[55] The blue pixels in displays are mainly responsible for the occurrence of burn-in, and the average lifetime of a blue OLED is significantly lower compared to green or red OLEDs.[55] This is partly attributed to the high bandgap, which is necessary for producing deep blue light ($\approx$460 nm or "Commission Internationale de l'Eclairage (CIE$_y$)" "y" coordinate of 0.05 which corresponds to $\approx$2.8 eV).[52] The required high excitation energies can lead to bond rupture and degradation of the conjugated polymer. Recently, Wang et al. discussed different degradation mechanisms in blue OLEDs.[61] They concluded that especially heat generation may be responsible for blue OLED degradation as well as bond dissociations caused by exciton–exciton interaction or simply due to the high-energy excited states. The heat is created either by joule heat or nonradiative relaxation processes. Furthermore, impurities, traces of oxygen or manufacturing contaminations can cause premature OLED degradation. Over the last years several approaches to achieve higher efficiencies and lifetimes were introduced and tested, however, especially in the context of inexpensive, commercially applicable blue OLEDs there is still a need for research.

Often referred to as first-generation OLEDs are emitters that are based on fluorescence (cf. **Figure 3**).[53] Fluorescence-based OLEDs (F-OLEDs) are especially advantageous for blue emission as excited singlet states (S_n) usually have a higher energy than triplet states (T_n; cf. Hund law). Therefore, many easy-to-synthesize substances with suitable S_1–S_0 transitions, high thermal stability, and good charge transfer properties were found swiftly. By contrast, molecules where radiative relaxations from the excited triplet state (T_1) to the ground state S_0 (known as phosphorescence) produce blue light, often require more complicated molecular designs. This is attributed to the fact that such high triplet states are rather uncommon. Furthermore, as fluorescence is spin-allowed and thus singlet excited states have only low lifetimes of few ns resulting in a very low probability of exciton–exciton interactions as for example singlet–singlet annihilation.[61]

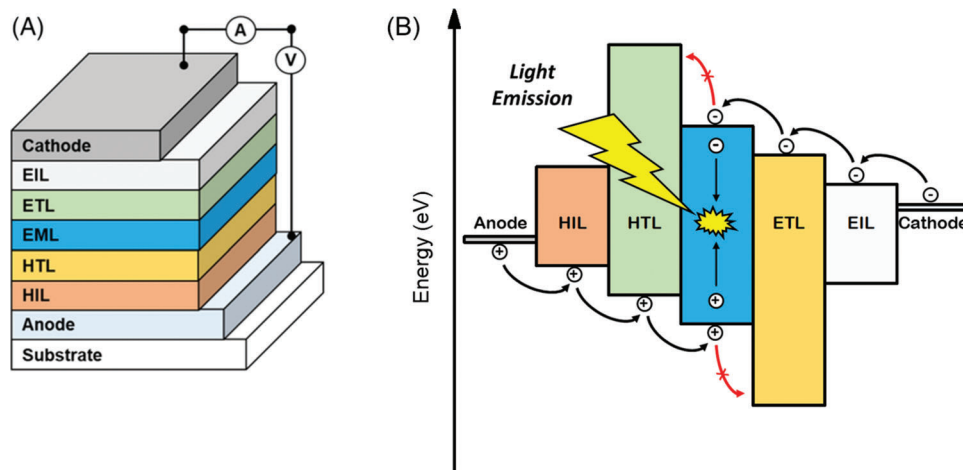However, due to spin statistics, only 25% of singlet excitons are formed upon the recombination of electron–holes and

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Figure 2. a) Typical multilayer OLED setup comprising injection and transmission facilitating layers for the electron holes and electrons generated by the transparent anode and cathode, respectively. b) Function principle shown with a flat energy band structure. HIL, HTL, EML, ETL, and EIL refers to hole injection layer, hole transmission layer, emission layer, electron transmission layer, and electron injection layer, respectively. Adapted with permission.[60] Copyright 2021, Wiley.
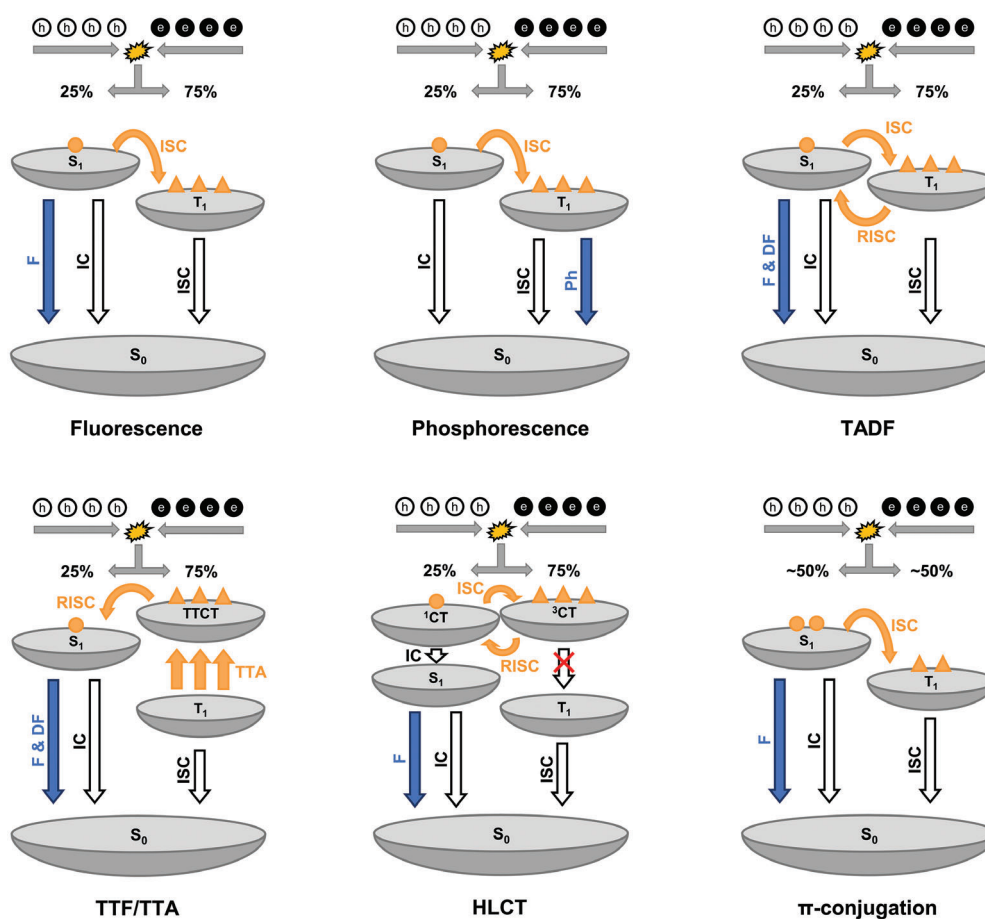

Figure 3. Different approaches to achieve blue-emitting OLEDs. F, DF, Ph, ISC, IC denote fluorescence, delayed fluorescence, phosphorescence, inter-system crossing, and internal conversion, respectively. Figure redrawn from Xu et al.[54]

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electrons.[54] The other 75% are usually triplet excitons. Therefore, only a maximum internal quantum efficiency (IQE) of 25% for fluorescence-based emitters can be yielded. Without further optimization (e.g., of light outcoupling), those 25% IQE correspond to an external quantum efficiency (EQE) of typically 5%.[53] This upper limit of the IQE is not only problematic for producing efficient F-OLEDs but also has a negative effect on the OLEDs' lifetime as the triplet excitons relax via nonradiative processes leading to heat production.

The second-generation OLEDs correspond to phosphorescence-based emitters, i.e., utilizing the spin-forbidden T_1–S_0 transition (Ph-OLEDs, cf. Figure 3).[53] Although, this approach increases the upper limit of the IQE to 75% (by efficient intersystem crossing (ISC) from S_1 to T_1 even 100% is possible), some disadvantages go alongside hampering their industrial use. Phosphorescence is a spin-forbidden radiative process and therefore rather slow. Consequently, the excited triplet states have a significantly longer lifetime (∼μs) compared to singlet excited sates (few ns) and thus exciton–exciton interactions, e.g., triplet–triplet-annihilation (TTA) or exciton–polaron interactions are more likely. Such effects are also known as efficiency roll-off.[61] However, these processes do not only reduce the Ph-OLEDs efficiency but are also one of the main reasons for short lifetimes of blue Ph-OLEDs. In fact, TTA, for example, is a process where two triplet excitons fuse into a higher excited level forming so-called hot excitons. Those hot excited states typically lie above the bond dissociation energy and thus cause a bond rupture resulting in the degradation of the emissive active material.[61] Furthermore, Ph-OLEDs mainly rely on expensive metal-based complexes like iridium and palladium. Such metals do not only increase the manufacturing costs of the OLEDs and pose an environmental challenge but also contribute to shorter lifetimes of the OLEDs. The latter is mainly caused by small potential energy barriers between metal-to-ligand charge transfer states (MLCT-states) and nonluminescent metal center states (^{3}MC-states) of those complexes, which then can result in dissociation of the corresponding ligand.[61]

Over the recent years many other approaches aiming to increase the internal quantum efficiency up to 100% were presented. Those approaches are also often called singlet or triplet harvesting, respectively. Among the most promising ones are emitters based on thermally activated delayed fluorescence, emitters using the interaction of two low-lying triplet states forming a high-energy singlet exciton (TTA- or also known as TTF-OLED), hybrid local and charge-transfer emitters (HLCT-OLEDs), and aggregation-induced emission (cf. Figure 3).[54] Correspondingly, those approaches are often referred to as third, fourth generation of OLEDs, etc. Although, a lot of progress was made in the field and OLEDs, where EQE of up to 30% was achieved, most of those OLED setups a very expensive and challenging to manufacture due to the use of difficult-to-synthesize and complex organic molecules, expensive metal-based complexes, and relying on complicated layer structures. Furthermore, most of the established structures still suffer from high efficiency roll-offs and short lifetimes.[52]

Another possibility of increasing the internal quantum efficiency, is the usage of π-conjugated structures. It was found by Heeger and co-workers that weak electron–hole binding molecules, as for example π-conjugated polymers, show a higher singlet exciton formation which eventually led to IQEs up to 50%.[62] This is where PPPs could come into play. Actually, phenylene-based conjugated polymers were especially actively tested as blue light emitting materials in optoelectronic devices between the early 1990s and the early 2000s, but the interest in them faded away upon the development of blue OLEDs newer generations relying on other materials (cf. Figure 3). A short historical excurses will help to understand this trend.

The first examples of poly(para)phenylenes in OLEDs were published in 1992 by Grem et al.[63] They used a monolayer setup consisting of ITO as anode, unsubstituted PPP as emitting layer and aluminum as cathode. Due to the high energy barrier between ITO and cathode they only achieved low EQEs and had to apply very high turn-on voltages (>12 V) to operate their OLEDs. As mentioned in the previous section, beside the high turn-on voltage and low EQEs, pristine, defect-free, high-molecular weight unsubstituted PPPs were rather difficult to synthesize and to process. Furthermore, unsubstituted PPPs tend to a show red-shifted emission spectrum due to the formation of aggregates.[22] In fact, PPPs deposited as Langmuir–Blodgett (LB) film often show a yellow emission (≈530 nm).[22] Soon, first groups tried to incorporate several substituted PPPs which were prepared via the aforementioned cross-coupling polymerizations. Those substituted PPPs were used as spin-coated film, which is in general not as prone to form aggregates as LB films.[22] It could be shown that bulky sidechains are advantageous regarding the EQE and narrow emission bandwidth by probably preventing exciton migration and nonradiative decay through steric shielding in the solid-state polymer.[56] It quickly became evident that the sidechains do not only increase solubility but also prevent aggregation through their disruption of the π-stacking and steric shielding. Unfortunately, the sidechains do not only show these positive effects but also induce a torsion into PPPs backbone due to van der Waals repulsion. This torsion significantly reduces the effective conjugation length of the polymer, which results in a hypsochromic shift (blue-shift) of the emission maxima and leads to lower EQEs.

To circumvent this torsion of the benzene rings in the polymer's backbone and to prevent the unfavored blue-shift without sacrificing the good solubility of substituted PPPs, polymers with covalently tethered adjacent benzene-rings via alkyl bridges were synthesized. The most prominent examples are ladder-type poly(para)phenylenes (LPPPs) and the stepladder-type polyfluorenes (cf. **Figure 4**).

That said, LPPP using unsubstituted methine or ethene-bridges show 0° twist, whereas 20° torsion is usual upon tethering via an ethane-bridge.[22,64] Therefore, a control of the optical properties by varying the tethering bridges is possible. The classical synthesis of a methine-tethered ladder-type PPP (Me-LPPP) is shown in **Scheme 6**. Expectedly, the extent of the conversion in the polymer-analogue reaction steps defines the amount of structural defects and thus has an impact on the emission spectrum. Polyfluorenes, on the other hand, are synthesized without any postpolymerization functionalization: a fluorene monomer bearing suitable groups at 2,7-positions is polymerized via Yamamoto coupling or SPC. More often, 9,9-dialkyl derivatives are used to impart to the resulting polymer the higher chemical stability and solubility.
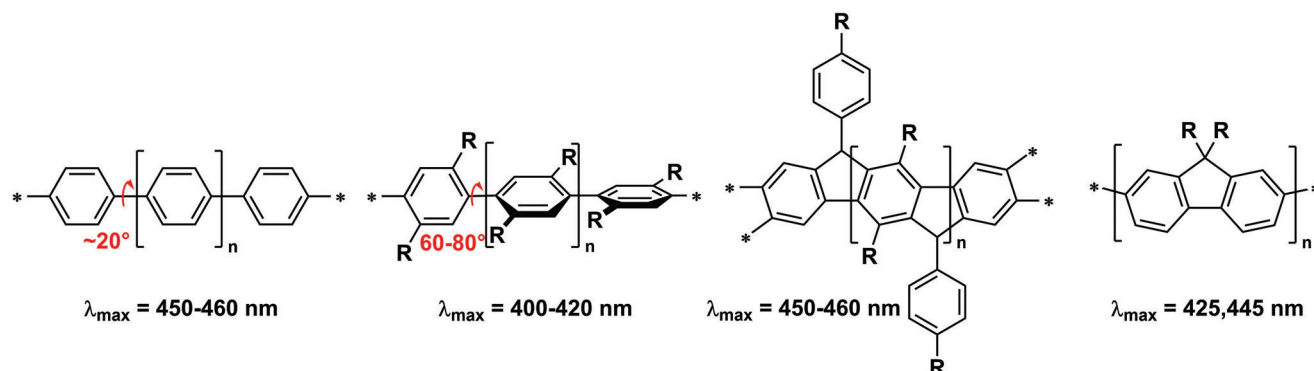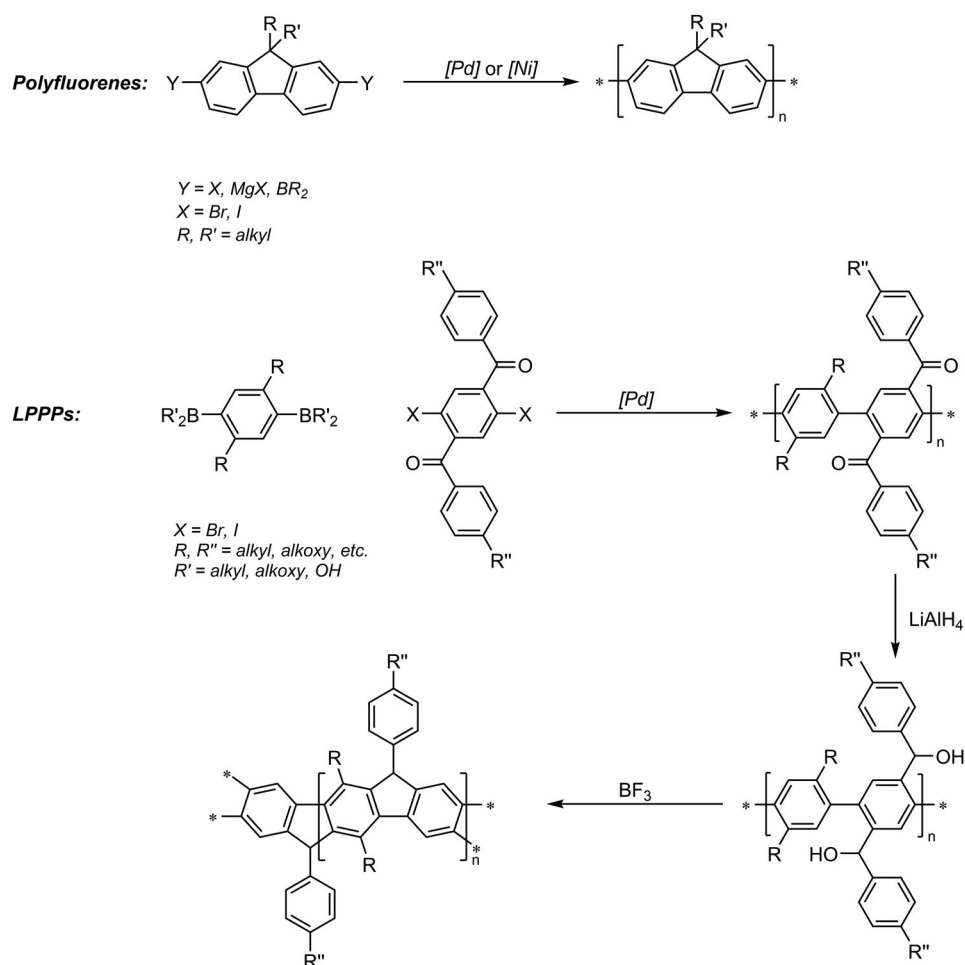
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Figure 4. Different PPP-type polymers and their typical emission maxima.[22]

Scheme 6. Schematic synthesis of polyfluorenes and LPPPs.[22]

Both polymer-classes exhibit emission maxima between 420 and 460 nm depending on their exact chemical structure.[22] Furthermore, polyfluorenes and LPPPs show high photoluminescence quantum efficiency of up to 90%.[22] In fact, nowadays research is using predominantly polyfluorenes or LPPPs as blue-emitting conjugated polymers in the context of OLEDs (cf. **Figure 5**).[22]

Although both polymer-classes are state-of-the-art and displaced substituted PPPs nowadays, they suffer from short lifetimes and poor color stability—one of the reasons why the overall interest in blue-emitting conjugated polymers in OLEDs decreased over the last decade.

Whereas diluted solutions of polyfluorenes or LPPP showed a deep-blue emission, thin films of those polymers produced a
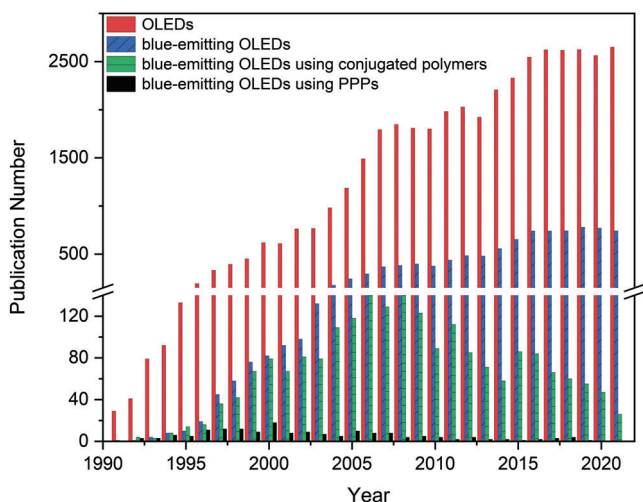
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Figure 5. Number of publications during the last three decades regarding OLEDs (red), blue-emitting OLEDs (blue), blue-emitting OLEDs which used conjugated polymers as emitting layer (green) and blue-emitting OLEDs which used PPPs as emitting layer (black). Retrieved via Web of Science.

significant band in the yellow region ($\approx$600 nm). Initially, it was assumed that this featureless yellow band is due to the formation of aggregates or excimers.[22] This was also supported by several experiments where polyfluorenes or LPPPs where blended with other polymers and by the observation that this yellow band appeared after several minutes. It was believed that this delay is due to the formation of joule heat which would promote excimers or aggregates.[64] However, over the time evidence arose that the yellow emission of LPPP and polyfluorenes comes from chemical defects in the backbone. This was supported by theoretical and experimental studies where fluorenone units produced emission in the yellow region.[22,64] It was assumed that the fluorenone units are formed due to oxidation or side-reactions during the postfunctionalization toward LPPP. In following studies, it could be shown that substituting the hydrogen atom of methine bridge with alkyl substituents could to a certain extent increase the polymers stability against oxidation, but the emission of the corresponding polymer is red-shifted with a λ_{max} of 460–490 nm.[22,64] Nevertheless, such LPPPs or polyfluorenes are still suffering from a low color stability and even small amounts of oxygen (e.g., $\approx$0.5 ppm inside of a glove box) led to an oxidation upon annealing.[22] Further studies suggested that elimination of oligomers as well as reducing the polymer's chain end mobility by cross-linking could contribute to a more stable emission.[65] This is because oligomers and flexible chain ends might facilitate exciton migration to the defect sides. It was proven that purification, blending, and cross-linking of PPPs, LPPPs or polyfluorenes led to stable blue emission.[22,66] Further source of the defect emission, particularly the bands in the region of 600–650 nm corresponding to phosphorescence, is the polymer-bound palladium which was used as catalyst in the synthesis.[22,64]

Another attempt to reduce the backbone torsion of substituted poly(para)phenylenes was the synthesis of amphiphilic PPPs. In particular, the group of Valiyaveettil could show that the addition of metal salts to hydroxylated amphiphilic PPPs (C_6PPPOH,

C_{12}PPPOH, and C_{18}PPPOH) led to a coordination of the polymer chain to the metal centers which resulted in a bathochromic shift.[67] By using different metal salts, the shift and torsion of the corresponding PPP could be controlled resulting in doped PPPs with emission maxima ranging from sky-blue to green. Although, this first example of the emission tunability of PPPs via coordination or self-organization seemed to be promising, the applicability was hampered by low molecular weight, and a difficult polymer synthesis. While this example was an important finding for tuning the emission of substituted PPPs, no follow-up papers utilizing such PPPs in OLEDs were published to our knowledge.

Here we see an application potential for PPPs since they have a higher chemical stability and do not show oxidation-based defect emission. They are also much easier to synthesize compared to LPPP and polyfluorenes. The recently developed KCTP synthesis protocols can be helpful in achieving high-molecular weight defect-free PPPs including those with amphiphilic properties. In fact, our group recently published a PEGylated PPP with a molecular weight of 30 kg mol^{-1}. By doping such PPPs with metal salts and tuning the chelating sidechains, PPPs with a precise emission band could be achievable. Drawing parallels to the findings on polyfluorenes and LPPPs regarding the effective reduction of aggregation and exciton migration, design of PPPs with high stability and deep-blue emission is not illusive anymore. We also anticipate that chelating or self-organizing PPPs can unfold advantageous features also in OLED field. Soluble and tunable PPPs clearly have the potential to replace the difficult-to-synthesize, expensive, metal-based, and therefore environmentally problematic small molecules which are currently used to produce blue-emitting OLEDs and give birth to a next generation of long lifetime deep blue OLEDs.

3.2. PPPs in Energy Storage Technologies

Over the past hundred years, electricity has become a major part of our lifestyle. Today electricity is ubiquitous and our civilization as we know would not function without it. Ever since we rely on this technology, the generation and especially the storage of electrical energy has been a major focus of chemical and technical research.

Nowadays the global challenges such as climate change, the impending shortage of resources, dependency on fossil energy sources, etc., require novel, efficient and sustainable technological solutions. Batteries, fuel-cells, and redox-flow batteries are a hot topic in research as improvement regarding higher power and energy densities, longer lifetimes, and a higher efficiency in those technologies is still needed.

From this point of view and due to their excellent mechanical and electrochemical properties, as well as the possibility to functionalize the rigid-rod-type backbone with ion-conducting side chains, PPPs were discussed as promising materials for proton-exchange membranes in fuel-cells, as electrodes for secondary batteries, and as solid polymer electrolyte for all-solid-state batteries.

3.2.1. PPPs in Batteries

For supplying portable devices with energy or storing electrical currents in a small scale, secondary batteries have been proven
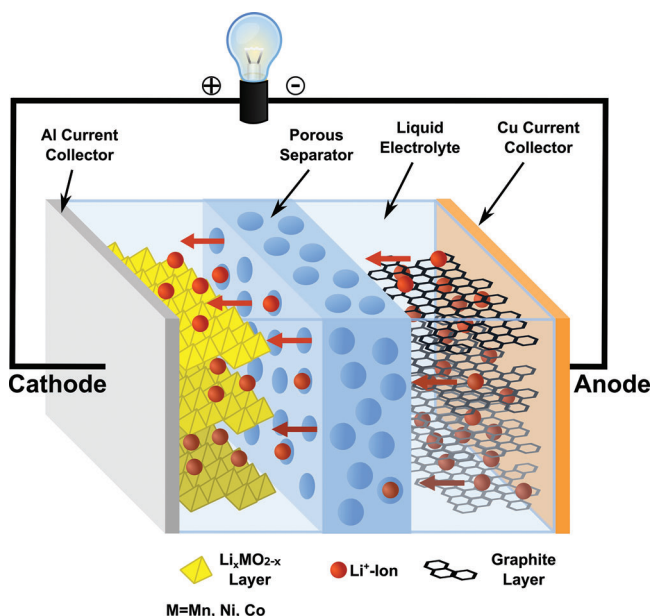
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Figure 6. Schematic structure of a conventional lithium-ion battery consisting of a lithium-intercalating graphite anode and a metal oxide as cathode, divided by a porous separator to prevent short-circuits. To facilitate the ion-transport between the electrodes, the vast majority of commercial LIBs are still using liquid electrolytes. In this drawing the discharge is depicted.

particularly suitable. Modern lithium-based batteries are of distinct interest due to their comparable high energy and power density as well as high efficiency. Today, the most common secondary battery is certainly the lithium-ion battery (LIB).

Generally, commercial lithium-ion batteries consist of a graphite anode, and a metal oxide as cathode (e.g., lithium cobalt oxide) surrounded by a liquid electrolyte solution (e.g., lithium hexafluorophosphate) and divided by a porous separator to prevent short-circuits (cf. **Figure 6**). Such a common LIB-setup has a maximum possible specific capacity of 370 mAh g^{-1} for the anode, but the value is usually limited by the capacity of the metal oxide cathode.[68]

Over the last two decades, new electrode materials, electrolytes, and cell setups were tested to not only increase the energy and power density but also to reduce manufacturing costs and to make LIBs more sustainable.

In this context, PPPs were tested both as anode and as cathode material. For example, in the early 1980s the group of Baughman published several studies about the usage of PPPs as electrode material.[69] They synthesized unsubstituted PPPs via the Kovacic approach and pressed them into pellets for use as electrodes. By a brief exposure of the pressed pellets with dopants like AsF$_6$ and NOBF$_4$ they increased the conductivity of the pellets above 10^{-6} S cm^{-1}. This predoping was conducted to facilitate the electrochemical doping of the electrodes later. The acceptor doping (cathode) was then conducted with PF$_6^-$ at a positive potential whereas donor doping (anode) was performed by exposing the predoped PPP-pellet to a lithium electrode in a lithium perchlorate-THF solution. Eventually, they produced a battery which consisted of the n- and p-doped PPP

surrounded by a propylene carbonate electrolyte and yielded an open circuit voltage of 3.3 V. They concluded that PPPs exhibited a promising application potential as their doped PPPs showed many features of an ideal electrode: high electronic conductivity, high ionic mobility, insolubility, structural integrity, and high voltage. However, they noted that this preliminary test had also few limitations like anode stability and solvent compatibility.
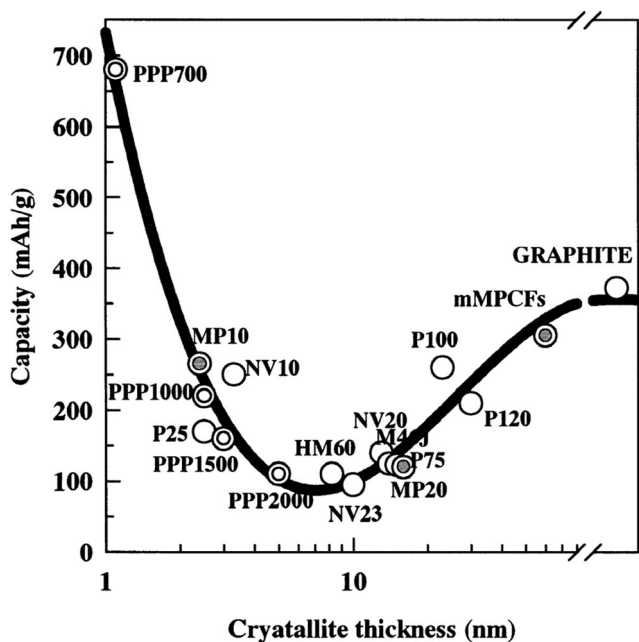
Twenty years later, Zhu et al. published a similar study where they incorporated n- and p-doped PPPs into a battery.[70] As electrolyte they used LiPF$_6$ in an 1:1:1 EC–DMC–EMC (ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate) mixture. They received a 3.0 V battery with a "considerably high capacity and cycling stability" concluding that doped PPPs could serve as alternative to conventional transition metals-based batteries. However, even though PPPs showed promising properties such as a comparable easy synthesis and processability as well as decent electrochemical performances as electrode material, conjugated polymers suffer from several limitations which hamper their applicability as electrodes in LIBs as for example Baughman have found.

Especially when used as cathode-material (i.e., p-doped) PPPs show a limited cycling stability particularly at high cutoff-voltages due to overoxidation and chemical side-reactions.[71] Furthermore, p-doped PPPs suffer from a low theoretical capacity ($\approx$141 mAh g^{-1}) due to low maximum doping levels, low coulombic efficiencies, and a relatively high self-discharge.[71]

By contrast, when using PPPs as anode material (i.e., n-doped PPPs), they show much higher capacities and coulombic efficiencies. For example, Zhu et al. achieved a reversible capacity for n-doped PPPs of $\approx$600 mAh g^{-1} with an efficiency of 98% and high cycling stability.[70] Studies which investigated the effect of the structure as well as the effect of the heat treatment of PPP-anodes on their battery performance could clearly show that the heat-treatment temperature had a significant effect on the charge capacity of PPP-anode based batteries. In fact, n-doped PPPs which were previously treated at 700 °C showed charge capacities up to 680 mAh g^{-1} exceeding those of conventional graphite-based LIBs (370 mAh g^{-1}). PPPs treated with 1000, 1500 or 2000 °C respectively yielded only charge capacities between 100 and 200 mAh g^{-1} (cf. **Figure 7**).[72,73]

Also, the synthesis procedure proved to be a crucial parameter for a high charge capacity. Kim et al., for example, could observe that Kovacic polymerized heat-treated PPPs showed much higher charge capacities as Yamamoto-polymerized, heat-treated PPPs.[74] They assumed—by investigating their manufactured electrodes via SEM and XRD—that this difference might be due to quinoid defects and the disordered carbon structure of the Kovacic-polymerized PPPs resulting additionally in a more porous anode material compared to the linear, defect-free PPP chains yielded via the Yamamoto approach. These effects were partly attributed to the different lithium-ion intercalation mechanisms which were found to occur in PPP-based anodes in contrast to graphite-based anodes.[74,75]

Thus, easy-to-synthesize PPPs are a very promising application candidate as intercalatable anode material which may pose an alternative to graphite-based anodes. In another recent example, Lobo et al. produced anodes based on hyperbranched-polyphenylene mixed with multiwalled carbon nanotubes.[76]

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Figure 7. Effect of heat treatment temperature during PPP-anode manufacturing on the crystallite thickness and theoretical capacity. Reproduced with permission.[73] Copyright 2020, Elsevier.

They yielded an LIB with a good electrochemical performance (stable reversible specific capacity of 450 mAh g^{-1} at 100 mA g^{-1}) as well as a good cycling stability. This recent paper clearly highlights the potential of phenylene-based anode materials.

Unsubstituted PPPs were also utilized as electrodes beyond LIBs. For example, Zhang et al. used PPPs as bulk anode material in potassium-ion batteries.[71] They observed that PPPs undergo a much lower volume expansion upon intercalation with potassium ions and possess higher specific capacity compared to other materials like the commonly used graphite, manganese oxide, etc. In this study, PPPs as anode material show a low diffusion barrier and therefore good rapid-charge capabilities.

Furthermore, unsubstituted PPPs were used as cathode material for aluminum-ion batteries.[77] Due to their larger lateral distance (4.53 Å) compared to graphite (3.34 Å) tetrachloroaluminate anions can intercalate much faster into PPPs than graphite. Using this electrode material, the researchers prepared a rechargeable aluminum-ion battery with an excellent rate performance, a high working voltage of 1.4 V, rapid charge and discharge capabilities as well as a high stability.

Other groups, for example Chen et al., followed a different strategy.[78] They did not use PPPs as anode material but rather tried to take advantage of the PPPs excellent lithium conductivity and used unsubstituted PPPs as bulk material for embedding silicon nanoparticles. The latter possesses an exceptionally high theoretical Li-storage capacity of 4200 mAh g^{-1} while also having a good lithiation potential but suffer from a poor cycling stability.[78] This is mainly due to huge volumetric changes dur-

ing lithium insertion/extraction leading to degradation as well as to fractures and pulverization of the Si particles over time. To circumvent this limitation, Chen et al. used PPPs as host material to embed those Si particles. This approach not only led to an increased dimensional and mechanical integrity of those Si particles but also shielded the particles from the electrolyte which increased the cycling stability further. A follow-up publications used a similar approach and showed that unsubstituted PPPs are a very suitable host material for such silicon particles.[78,79]

Besides the utilization of unsubstituted PPPs as electrode material, some publications used the reversible dopeability of PPPs for creating LIB separators with overcharge protection. For example, a paper published by Xiao et al. utilized unsubstituted PPPs blended with polyaniline (PAn) as current shunt when the battery is overcharged.[80] The idea is that when the charging voltage exceeds a certain value (>4.3 V), which would lead to a harmful overcharging of the battery the conjugated polymer which is used as separator is oxidized from its insulating neutral to its highly conductive p-doped state and thus causing a short-circuit. In this context, PAn is used to prevent n-doping of PPP and thus a short-circuit at low potentials (i.e., during operation).

Sidechain-substituted PPPs exhibit considerably lower performances as electrode or intercalating material but maintain the superior mechanical and electrochemical stability known for unsubstituted PPPs. PPPs with ion-conductive sidechains synthesized via modern cross-coupling based polymerization methods can be utilized as solid polymer electrolytes (SPEs). Solid-state electrolytes (SSEs) have gained much attention lately as they prevent dendritic growth when metallic lithium is used as anode and thus provide the way to achieve all-solid-state batteries with higher specific energy. Such batteries are safer, are applicable with more versatility, show higher cycling stability, and are easier to recycle.[81]

Until now, the wide utilization of SSEs is hampered by their low ionic conductivities and slow ion transport between electrolyte and electrode, in part due to a lower contact area in comparison to liquid electrolytes. Nevertheless, over the last year particularly solid polymer electrolytes gained much attention, as they are cheaper, more flexible, show a better interconnection of the solid–solid electrode–electrolyte interface and allow higher specific energy densities compared to their inorganic counterpart (inorganic solid electrolytes; ISEs).[81] At the same time, SPEs are prone to suffer from lower cycling stabilities since most polymers have a generally lower compressional strength than inorganic solids. Thus, SPEs cannot sufficiently prevent dendritic lithium growth upon recharging.[81,82] From this point of view, PPP-based SPEs might be a promising alternative to the commonly used SPEs, as PPPs are known to have very good mechanical properties. According to Mississippi Polymer Technologies, Inc., an American company which manufactured benzoyl-substituted PPPs under the trademark Parmax, PPPs have a five times higher compressive strength compared to the high-performance polymers PEEK, PSSU, and PC (polyether ether ketone, polyphenylene sulfone, and polycarbonate, respectively).[83] Other mechanical properties like tensile strength, flexural strength, and flexural modulus are also significantly higher compared to the aforementioned polymers. Furthermore, PPPs have a very high chemical stability and heat resistance. These superior mechanical prop-
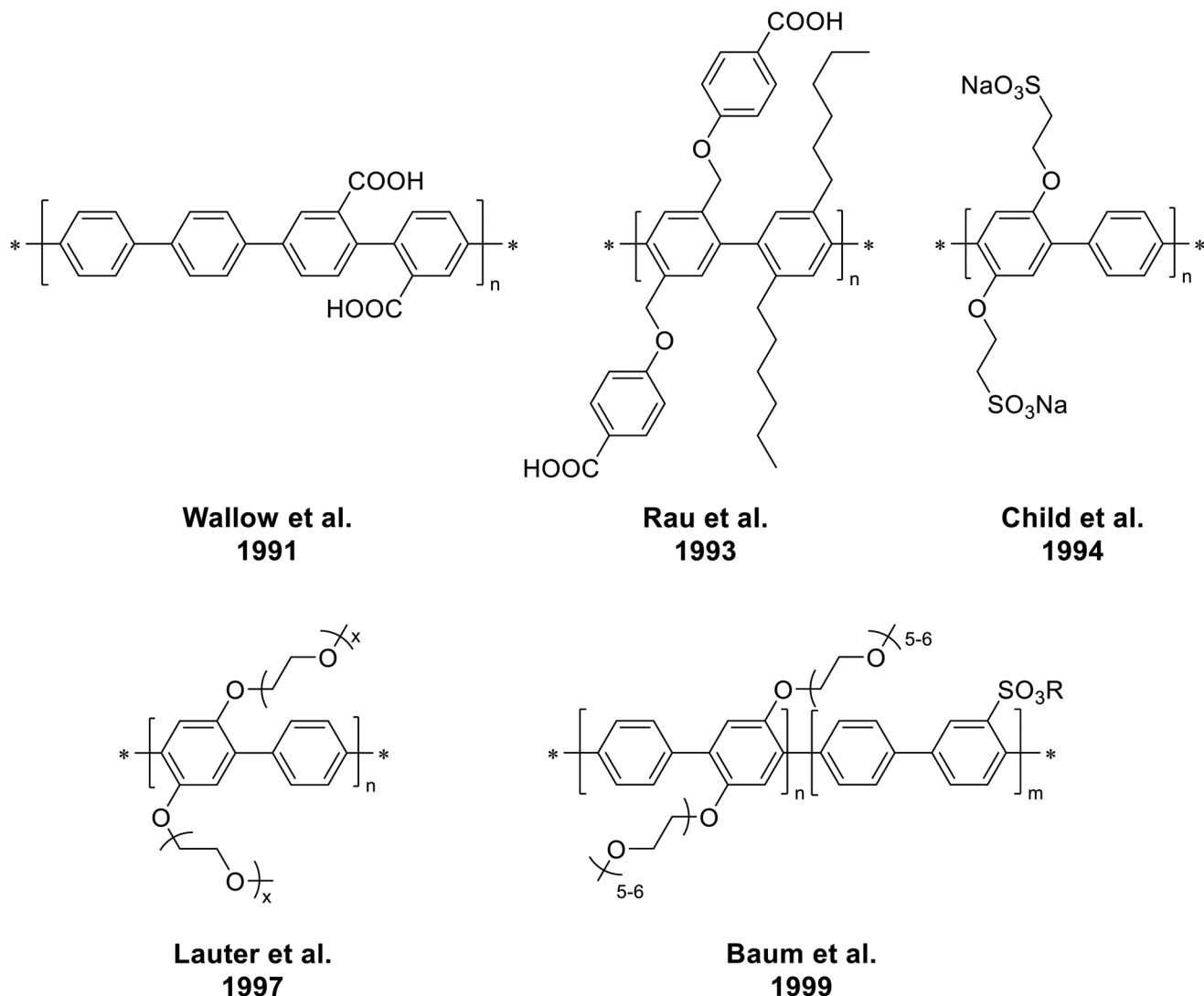
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Figure 8. Selected examples of early PPP-based cation conductors applicable as solid polymer electrolyte synthesized mostly via Suzuki-based polymerizations.[84–88,91]

erties depend on the structure of the sidechains, but even 2,5-functionalized PPPs are expected to show mechanical properties exceeding those of aliphatic, coil-type polymers commonly used as SPEs.

One of the first examples of PPP-based electrolytes was published by the group of Novak who synthesized a PPP bearing carboxylic acid moieties.[84] Subsequently, Rau et al., Child et al., and Lauter et al. reported PPPs bearing carboxy–phenoxy–methylene, sulfonatoalkoxy, and oligo-ethylene glycol-sidechains, respectively (**Figure 8**).[85–88] All researchers observed extraordinary mechanical properties due to the hairy-rod-type structures of those polymers. Furthermore, Lauter et al. found an attractive ion-conductivity of more than 10^{-6} S cm^{-1} in their material at ambient temperature.[87] In this context it has to be noted that conventional biionic electrolytes (i.e., solid-state electrolytes where Li-ion and counterions are mobile) have the inconvenience of producing concentration gradients in the cell as cations are normally less mobile than their counterions which results in accu-

mulation, concentration gradients and polarization in the cell and hence in a poor cell performance.[89,90]

With those single Li-ion conducting solid polymer electrolytes (SLIC-SPEs) such concentration gradients do not occur. Furthermore, SLIC-SPEs are also known for reducing dendritic growth of the metallic lithium electrode significantly.[89,90] It could also be shown that SLIC-SPEs with lithium transference numbers near to one show a performance comparable to an ambipolar electrolyte with a ten-times higher ion-conductivity.[89] Following this, Baum et al. synthesized a novel ion conductor based on PPPs bearing sulfone and oligo-ethylene glycol sidechains alternately (cf. Figure 8).[91] As expected, the conductivity of this polymeric electrolyte was some magnitude lower compared to biionic-SPEs. They also showed that the ion-conductivities of such PPP-based SLIC-SPEs are highly dependable on the ratio of sulfone- to oligo-ethylene glycol moiety. Furthermore, by adding an ethylene-glycol plasticizer a lithium transference number of one and conductivities comparable to ambipolar electrolytes
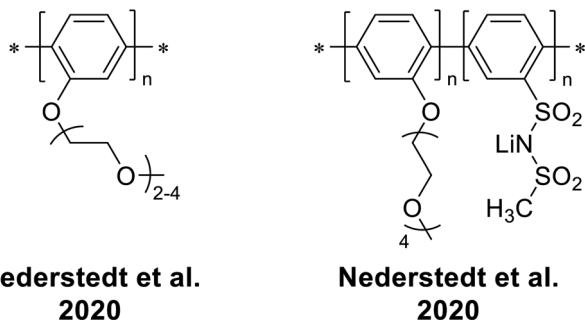
Figure 9. Two recent examples of PPP-based cation conductors synthesized by the Jannasch group.[90,92]

could be achieved.[87] Later the group of Jannasch synthesized a similar block-copolymer (cf. **Figure 9**).[90,92] They realized a PPP-based electrolyte with sufficient ion conductivities while also maintaining good mechanical and thermal properties.

However, it should be noted, that only few of the abovementioned publications tested PPPs in actual battery setups. Especially publications which utilized PPPs as SPEs, tested their polymers only in ex situ experiments so far. The progress of knowledge encompassing modern battery technologies may justify reassessment and utilization of these and related materials in prototype devices. For a further read into poly(para)phenylene-based electrolytes the following section is recommended.[93]

3.2.2. PPP as Ion-Exchange Membrane

Over the last decades, researchers sought to find energy storage technologies beyond secondary batteries. Particularly, in the context of finding large-scale energy storage technologies or operating lager vehicles and devices, secondary batteries are not optimally suitable due to high costs and a low sustainability.[68] Furthermore, the access to metal recourses is currently either limited or restricted by socioenvironmental concerns and might not be sufficient to satisfy the soaring demand for electrical energy storage.[94] From this point of view, redox flow batteries and fuel-cells became very popular in research.[95] The applicability of such technologies is still partly hampered by the lack of stable, durable, inexpensive, and disposable/recyclable ion-exchange membranes.[68,96] Especially proton-exchange membranes (PEMs) necessary, for instance, in vanadium redox flow batteries and in PEM-fuel (cf. **Figure 10**) cells are still a subject of research.[96,97] The latter technology is essential for using green hydrogen—the energy source which is currently pushed by many industry- and government-initiatives.

In both applications, commercially available membranes are commonly based on Nafion, a sulfonated perfluoropolymer (cf. **Figure 11**).[96,97] However, such fluorinated polymers are not only expensive and difficult to manufacture in big scale but also pose a serious health and environmental risk.[96] Until now, perfluorinated polymers suitable for proton-exchange membranes are very difficult to dispose and recyclability is still not possible for such materials. Thinking of deploying such membranes in the by 2050 predicted millions of fuel cells, will arguably cause a serious environmental hazard, and will thus collide with the idea of having a sustainable nonpolluting green energy source/storage
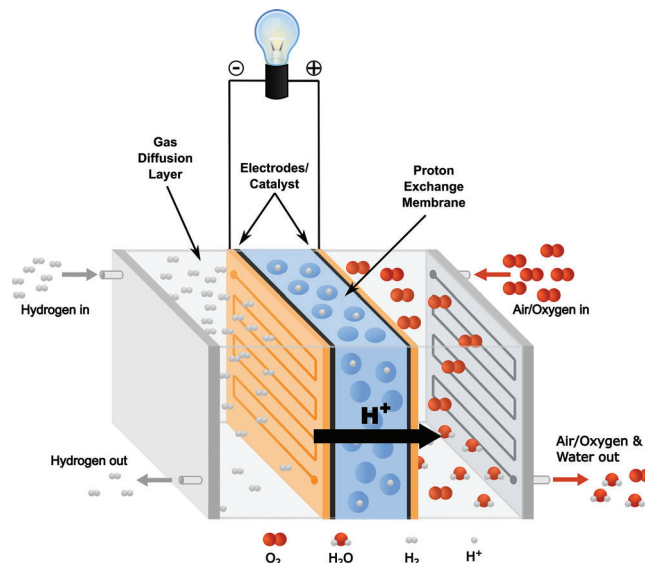

Figure 10. Simplified schematic structure of a proton-exchange membrane fuel cell (PEMFC). At the anode side hydrogen is oxidized to protons which migrate through a proton-exchange membrane to form water at the cathode side upon the reduction of air.
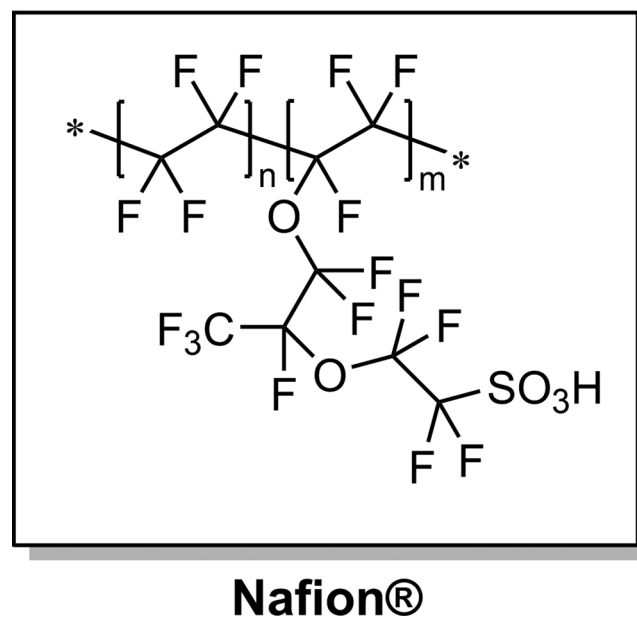

Figure 11. Chemical structure of Nafion.

device.[96] Consequently, other polymeric proton-exchange membranes need to be found.

Following this, especially sulfonated polyaromatics showed a high potential rendering superior mechanical properties, heat resistance as well as low reactant gas permeability while showing similar proton conductivities like Nafion. In this context, research placed special emphasis on polyphenylene-based sulfonated polyaromatics.[96,97] Recently, a very comprehensive review article published by Adamski et al. illuminated this field.[96] Therefore, only crucial insights will be summarized here.
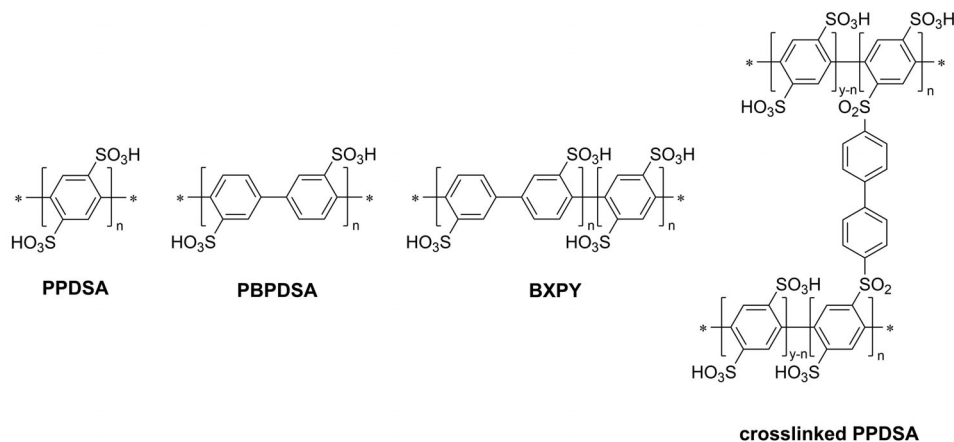
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Figure 12. Some examples of linear sulfonated PPPs synthesized by Litt and co-workers via Ullmann coupling.[98–101]

For designing a suitable membrane various parameters have to be taken into account. Among the most important ones are the membrane's morphology, proton conductivity, ion exchange capability (IEC), water uptake, gas permeability, and mechanical stability. Some of these properties are closely linked with each other and have to be controlled holistically.[96] With increasing water uptake, more water channels are formed and consequently the IEC and the proton conductivity increase. However, with increasing water uptake also the membrane swells which has a negative impact on the membrane's mechanical properties and deteriorates the durability and the dimensional integrity of the fuel cell. Furthermore, morphology and gas permeability of the membrane have to be controlled precisely to avoid reactant gas transport through the membrane, which is reducing the cell efficiency and accelerating their degradation while simultaneously maintaining water transport through the membrane.[96]

All these aspects make the manufacturing of PEMs quite difficult. Polyphenylene-based membranes have the advantage of very good mechanical properties increasing the membrane's durability, chemical stability as well as heat resistance. Functionalization of polyphenylene-based polymers with sulfone moieties may provide proton conductivities and IECs comparable to Nafion.[96]

The review by Adamski et al. divided the materials into different classes: linear sulfonated PPPs with sulfone groups directly attached to their backbone; kinked sulfonated PPPs consisting of a backbone with linear sulfonated para-phenylene and nonlinear nonsulfonated meta-phenylene units; sidechain-sulfonated PPPs as well as sulfo-phenylated polyphenylenes synthesized either by pre- or postsulfonation.[96]

The first class resembles unsubstituted PPPs in terms of extraordinary mechanical properties, high crystallinity, and additionally exhibits very attractive IECs and proton-conductivity. Due to the low polymer chain flexibility, linear sulfonated PPPs show a high volumetric expansion upon water uptake. Unfortunately, polymers like PBPDSA and PPDSA (cf. **Figure 12**), synthesized and investigated by Litt and co-workers, lost their mechanical stability at high relative humidity (RH) levels and were also partially soluble in water.[98–101] Modification (e.g., alkylation) of the sulfone group resulted in a nonpolymerizable monomer. It should be noted that Litt and co-workers utilized the Ullmann

coupling as polymerization method, which is known for having a small monomer scope, harsh reaction conditions, and for producing low molecular weights as well as being prone to introducing defects. Apparently, no other direct synthesis method could yield such linear sulfonated PPPs. However, by copolymerizing or crosslinking the sulfone-bearing phenyl-monomers, Litt and co-workers achieved membranes with sufficient mechanical stability.[98–101] In ex situ conductivity and in situ power density test, such structures typically achieved 400–900 mS cm^{-1} and 0.43 W cm^{-2}, respectively.[96] Furthermore, linear sulfonated PPPs showed one of the highest ion exchange capabilities known in literature with values above 8 meq. g^{-1} exceeding those of Nafion ($\approx$1 meq. g^{-1}).

Nevertheless, due to the poor mechanical characteristics at a high relative humidity, their high swelling (up to 120 vol%) and their difficult synthesis, linear sulfonated PPPs lost partly their attractiveness in this research field. For a further insight into linear sulfonated PPPs the review by Litt and Wycisk is recommended.[95]

Sidechain-sulfonated PPPs on the other hand, exhibit very good mechanical properties also at high relative humidity levels. This is true especially for presulfonated benzoyl-substituted PPPs either as homopolymer or as copolymerized with, e.g., alkylbenzoyl substituted monomers.[96] For instance, polymers synthesized by the group of Whangi Kim (cf. **Figure 13**) showed IECs of 2.3–2.5 meq. g^{-1}, moderate water uptakes of 78–105 wt%, and in situ power densities of $\approx$0.6–0.7 W cm^{-1} which is comparable to the power density of Nafion (0.7 W cm^{-1}).[96,102–105]

Unfortunately, Kim and co-workers did not study their mechanical properties, but stated that only small dimensional changes were observed upon 5–15%.[102,103] Another advantage of sidechain sulfonated PPPs is that they are accessible via facile cross-coupling-based polymerization methods (e.g., the Yamamoto coupling), making the synthesis of those PPPs more precise and controllable,. Furthermore, sidechain-sulfonated PPPs can be manufactured via the post- or presulfonation routes which leave them a sufficient scope of synthesis. The disadvantage of postsulfonation, a postpolymerization procedure, is the difficulty in precise adjustment of active sulfone-moieties—their amount and location in the polymer. It is also known to introduce chemical defects.[96,107]
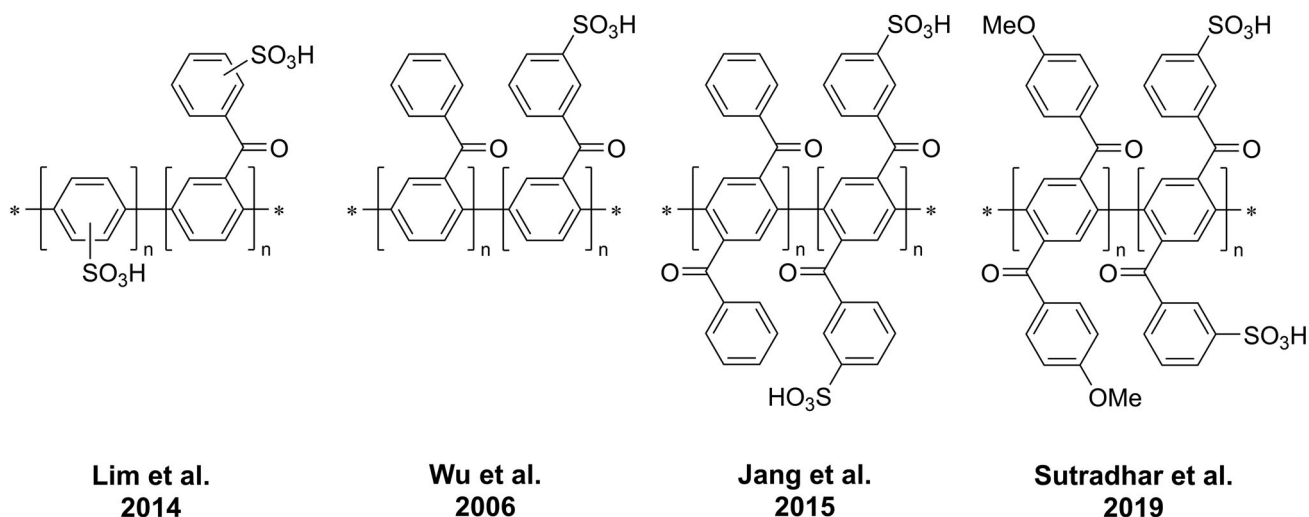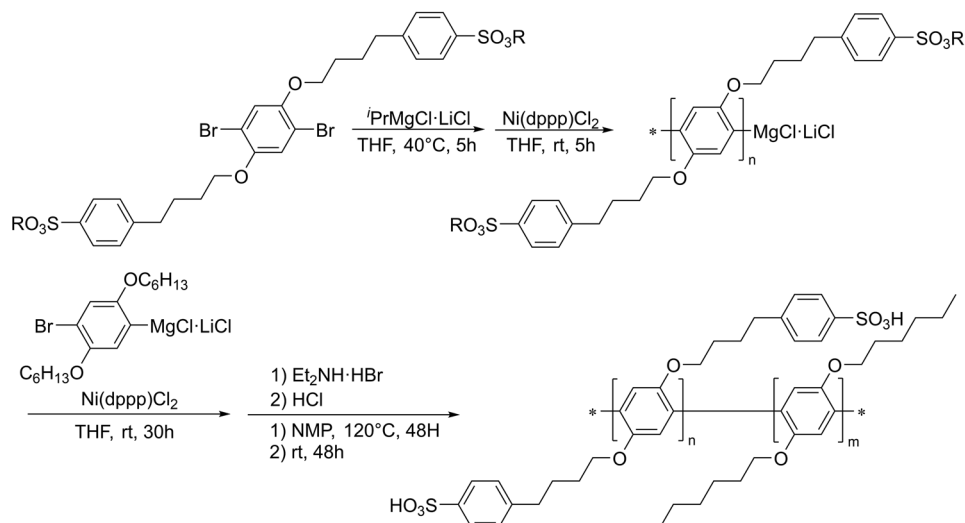
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Figure 13. Selected examples of sidechain sulfonated PPPs synthesized by Kim and co-workers and Wu et al.[102–106]
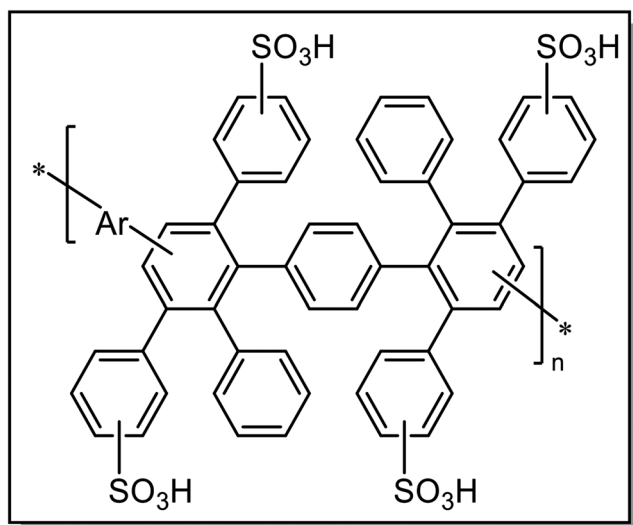

Scheme 7. Kumada-polymerized sidechain sulfonated diblock-PPP by Umezawa et al.[108,109]

Another approach was published by the group of Rikukawa. They prepared diblock-copolymers (in which one block was sulfonated and the other was hydrophobic) via the highly controllable Kumada-CTP.[108,109] Normally, Grignard reagents which are necessary for the synthesis are not compatible with sulfonic acid-moieties. However, Umezawa et al. protected these groups by alkylation and the resulting sulfonic ester moieties tolerated the corresponding Mg/Br-exchange reaction using a turbo-Grignard reagent (cf. **Scheme 7**).

During the Kumada-CTP, which is known to proceed via a controlled chain-growth polymerization mechanism, Umezawa et al. added a second nonsulfonated Grignard-monomer to yield a diblock-polymer. By changing the ratio of the second monomer to the catalyst the length of the second block could be varied. By increasing the sulfonate-containing block they did not only achieve membranes with a higher IECs (up to

2.20 meq. g^{-1}) and higher proton conductivities but also good tensile strengths (up to 20 MPa at room temperature and 50% RH).[108,109]

Even though the above studies still lack in-depth investigations regarding the mechanical behavior, morphology and in situ application, sidechain sulfonated PPPs could demonstrate their attractive application potential as PEM.[96] Due to their sidechains, they possess a higher flexibility and better mechanical properties at high relative humidity levels as well as better processability and solubility in organic solvents than unsubstituted sulfonated PPPs. Furthermore, in the preliminary tests sidechain sulfonated PPPs showed IEC values and proton conductivities which matched or exceeded those of Nafion.[96] By varying the sidechain structures, the electrochemical and mechanical characteristics can also be precisely tuned which renders them widely applicable.

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Figure 14. Representative Markush structure of the sulfo-phenylated polyphenylene produced by Ionomr Innovations, Inc. distributed under the trademark Pemion.[96]

Another approach to achieve sulfonated PPPs suitable for PEM fuel cells is to copolymerize sulfonated PPP-monomers with kinked building units.[110] The idea behind this approach is that the kinked monomer decreases the persistence length of the resulting polymers, which leads to a higher flexibility as well as increased entanglement of the polymer chains. This would help to make tougher membranes.[96,110] Indeed, the kinked sulfonated PPP-copolymer SSP-QP synthesized via Yamamoto coupling by Miyake et al. showed very promising properties such as a high IEC (2.6 meq. g^{-1}), very good mechanical properties (34 MPa at 80 °C and 60% RH; 68% elongation break; 1.3 GPa Young's modulus) as well as very good oxidative stability and wet-dry cycling durability.[110] For example, a two-hour treatment of SSP-QP with the highly oxidative Fenton's reagent, which is known to decompose other common polyether-, polysulfone- or polyketone-based proton-exchange membranes, showed no negative impact on the SSP-QP polymer. Furthermore, the SSP-QP-based membranes allowed to double the lifetime of the fuel cells compared to those Nafion-based.[96,111] For a more detailed insight into kinked sulfonated PPPs, the recent publications by the group of Miyatake are recommended.[112]

The evolution of sulfonated PPPs as proton exchange membranes could show that research is on the right path toward a suitable Nafion-alternative for sustainable, nontoxic and inexpensive fuel-cells. Especially with their studies on the sidechain sulfonated diblock-polymer the group of Rikukawa could impressively demonstrate the potential of combining new synthesis methods of substituted PPPs and the knowledge we gained on the structure–morphology relationship and on PEM fuel cells. We believe that further research in this area may pave the way for a wide commercialization of sulfonated PPPs as Nafion-alternative. A good example in this context is a presulfonated phenylated polyphenylene, which was already commercialized under the trademark Pemion (**Figure 14**).[96]

In our view, additional mean for the improvement of PPP-based PEMs may arise from considering, targeting, and controlling molecular arrangement and self-assembly within these materials.

3.3. Organic Photovoltaic

As mentioned before, our energy sector is in transformation as we are facing challenges like climate change, the impending shortage of fossil energy sources as well as problematic energy import dependencies. Currently, many countries enacted legislations which aim to increase the share of renewable energy sources.

In this respect, use of organic photovoltaic (OPV) might be promising. The advantages of organic photovoltaic over conventional silicon based photovoltaic cells are that they are flexible, solution processable as well as semitransparent. Even though OPVs are significantly less efficient compared to their silicon-based counterpart, they possess the advantage of being applicable on basically every surface.

We recommend many comprehensive reviews on organic photovoltaics published earlier elsewhere.[113a,b,114,115,116]

A typical organic photovoltaic cell employs photoactive material which can be a conjugated polymer. When choosing/designing a suitable polymer to use as donor material in OPVs, particular focus must be placed on the polymer's optical bandgap. The reason for this is an inherent trade-off between lifetime, photocurrent and photovoltage.[115] For example, low-bandgap molecules are known to absorb much more light, as photons with an equal or greater energy compared to the polymer's optical bandgap are absorbed and thus producing large photocurrents.[116] However, if the energy of the absorbed photons is exceeding the polymer's bandgap, nonradiative decays occur which are known to produce heat. Those losses are also known as thermalization which can lead to the degradation.[115] On the contrary, high bandgap polymers (>1.8 eV) show low thermalization losses while producing high photovoltages. However, high bandgap polymers only absorb a narrow part of the sunlight emission spectrum which is resulting in low photocurrents.[115] With including the efficiency loss associated with the exciton dissociation, an optimal bandgap was predicted between ≈1.4 and 1.6 eV.[117] Further investigation revealed that the ionization potential (IP; approx. HOMO level) should also be higher than 5.4 eV to maintain good air-stability.[114,115] Consequently, a polymer with a LUMO level of ≈−3.8 eV and a HOMO level of −5.4 eV would be ideal.

Currently, poly(para)phenylenes play a rather minor role in OPVs. This is mainly attributed to two reasons: in case of unsubstituted PPPs, their defect-free synthesis and processability is challenging and limited which makes big-scale applicability difficult. However, when using solution-processable sidechain-substituted PPPs, their absorption of the sunlight emission spectrum is limited only to UV-region due to their torsion of the backbone. Therefore, planarized polyphenylene-based materials such as polyfluorenes, polycarbazoles, and LPPPs were used to produce copolymer materials. For a more profound insight into polyphenylene-based OPVs the comprehensive review of Li et al. is recommended.[114]

3.4. Other Applications

So far, we have considered the most prominent applications of PPPs. In the following, we address other less common utilizations to demonstrate the potential of these materials.

3.4.1. As Sensor

One rather recent application of conjugated polymers in general and poly(para)phenylenes in particular is the utilization as photoluminescent microspheres. Photoluminescent microspheres are from particular interest in the field of biomedical imaging and labeling as well as to sensor, for example, drinking water purity.[118] Currently, commercially available microspheres are manufactured by dye entrapment in nonconjugated polymers like polystyrene. However, such microspheres suffer from low maximum fluorescence through concentration quenching of the entrapped dye or low solubility of the dye in the polymer. Recently, the group of Meldrum has demonstrated the advantages of microspheres composed of conjugated polymers.[118,119] They produced polyphenylene-based microspheres by carefully pumping a chloroform-polymer solution into a water/1-propanol/PVA mixture. They yielded brightly emitting photoluminescent microspheres with a narrow size distribution. By blending them with other conjugated polymers they were also able to tune the color as well as creating Janus particles, platelets, and core–shell structures.[118,119]

Beside those microspheres there are also other publications which use PPPs as sensor material but rely on other properties of PPPs. For instance, the group of Sirivat used doped PPPs embedded in zeolites for sensing SO_2 and ammonia based on relative electrical conductivity response.[120] Mehrdad and Ahangari used PPPs as gate material to manufacture a CMOS compatible junctionless FinFET-based multigas sensor, which was capable to differentiate between methanol, isopropanol, and chloroform.[121]

Other publications utilized substituted PPPs with functional sidechains for sensing different compounds. For example, the group of Korri-Youssoufi synthesized several redox conjugated PPPs bearing ferrocenes and carboxylic acids which were applied for simultaneous electrochemical sensing of dopamine, ascorbic acid, and uric acid in human serum samples as well as for DNA.[122] Namgung et al. synthesized a PPP bearing rhodamine 6G derivatives for sensing iron(III) salts in organic or aqueous media relying on an FRET-based detection mechanism.[123] Harrison et al. synthesized a PPP-based polycation for the detection of anionic fluorescence quenchers like $Ru(phen')^{4-}$ and $FE(CN)_6^{4-}$.[124] Tang et al. used changes in the fluorescence of oligo(ethylene glycol) functionalized PPPs for monitoring the pH-value and enzyme activity.[125] A similar polymer was synthesized by Yuksel et al. who used poly(para)phenylene-*g*-poly(ethylene glycol) carbon nanotube conjugates for targeted cell imaging.[126]

3.4.2. For Catalysis

Several other publications utilized PPPs for catalysis. For instance, the group of McCulla conducted several studies on PPPs in the utilization for light-driven catalysis. They photocatalytically reduced aryl aldehydes[127] and promoted the aryl halide pinacol coupling[128] as well as dehalogenated aryl halides[129] by using PPPs. Li et al. synthesized ionic-liquid-grafted rigid poly(para)phenylene microspheres which they utilized for heterogeneous catalysis by metal immobilization. For instance, they used their microspheres to efficiently absorb palladium nanoparticles and were able to perform Suzuki-cross-coupling with those microspheres. This is especially interesting as palladium-catalyzed reactions are known to be contaminated by difficult-to-remove palladium traces.[130]

Sprick et al. and Prentice et al. demonstrated the potential of PPPs in the photocatalytic hydrogen evolution.[131,132] They showed that unsubstituted PPPs as homopolymer already has an attractive hydrogen evolution potential in the presence of sacrificial electron donors. Sprick et al. also showed that by rigidification of PPPs the hydrogen evolution potential can be substantially increased. For example PPPs as copolymers in the combination of planarized polyphenylene-based copolymers like dibenzo[*b,d*]thiophene sulfones and dibenzo[*b,d*]thiophenes showed hydrogen evolution rates 10- to 20-fold higher compared to the PPP-homopolymer.[131] We can expect that the potential of this polymer-type in the reaction is not fully exploited yet.

3.4.3. Application Utilizing the Superior Mechanical Properties of PPPs

Several other publications on poly(para)phenylenes tried to make use of their excellent mechanic properties. For example, the group of Frick used phenyl-substituted PPPs as orthopedic biomaterial.[133,134] They not only demonstrated that PPPs have superior mechanical properties to other high performance polymers including PEEK, UHMWPE, PU, PCL, PMMA but also that bone plates manufactured from PPPs are not cytotoxic and only show a negligible effect of soaking the polymer in a phosphate buffered saline over a month.[133–135]

Xu et al. used PPP-based copolymers to produce high-performance electrospun nanofiber belts which might be useful as filtration media or as separator in batteries and supercapacitors.[136] Studies conducted by Friedrich and Almajid investigated scratch and wear resistance, and mechanical behavior of extrusion and injection molded PPP-copolymers.[137] They found that those polymers showed mechanical properties being equal or superior compared to other high-performance polymers like PEEK. Ikizier et al. recently published a method to achieve an inexpensive and easy method to produce carbon fibers from PPPs.[138] Instead of producing carbon fibers via the conventional route by the conversion of polyacrylnitrile, which is known to be complicated and costly, they synthesized PPPs-fibers via a microbial precursor route (ICI-route) and carbonized them at different temperatures. They achieved carbon fibers with similar properties compared to conventional manufactured carbon fibers while demonstrating the ease of the preparation.

3.4.4. Further Applications

Other applications of PPPs comprise the utilization as electrochromic films,[139] the storage of hydrogen,[140] the utilization

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of PPPs blends as electroactive polymer,[141] or in the biomedical field. Among the latter are amino-functionalized PPPs which were bioconjugated with anti-HER2 antibodies and utilized for cell imagining and for radiotherapeutic experiments. Geyik et al. found that such PPP-based polymers are particular promising for cancertherapeutic applications as they show a good intrinsic fluorescence, radiosensitizer properties as well as a good target or drug immobilization behavior via the amino functionalities.[142] In a previous study the same group found that PPPs grafted with both PEG and amino functionalities are especially suitable for a controlled drug release in the cancer therapy. In this process, they demonstrated that with the use of PPP-NH2-*g*-PEG/cysteine bioconjugates the doses of the anticancer drug doxorubicin could be significantly reduced while still inhibiting cell proliferation of cervix adenocarcinoma cells efficiently.[143] Barlas et al. synthesized gold nanoparticle conjugated PPP-*co*-*β*-cyclodextrin-*g*-PEG copolymer which also found application in the field of cancer theranostics.[144] Other examples of the group of Timur and Yagci comprise following studies.[145] One of the main reasons for the wide interest in PPPs in the field of biomedical application is their unique combination of useful features like their photoluminescence, the good mechanic, and intrinsic electronic properties as well as a low cytotoxicity.

4. Conclusion

The research on sulfonated PPPs as proton-exchange membrane remarkably demonstrated the potential of taking PPP-research to the 21st century and combining modern polymerization approaches with the recently gained knowledge in material science as well as in the device engineering. We believe that by the analogy to the aforementioned example other application-fields of PPPs will also show comparable progress once they are reconsidered. Indeed, PPPs possess a unique set of features, among them their comparable simple and highly controllable synthesis, their broad functionalizability, their unique electronic as well as their extraordinary mechanical property tunability.

Despite it was not discussed in this perspective, a lot has been done toward self-organization of PPP-based materials which might offer a new strategy to improve their performance in the herein described applications.

We are certain that there is still room for improvement toward the application of PPPs in the field of inexpensive, easy-to-manufacture deep-blue OLEDs; efficient energy storage; sensing; biomedical applications or simply in the field of high-performance polymer among others.

Conflict of Interest

The authors declare no conflict of interest.

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