1 Design and Synthesis of Conjugated Polyelectrolytes

Kan-Yi Pu, Guan Wang, and Bin Liu

1.1 Introduction

Conjugated polyelectrolytes (CPEs) are a kind of π-conjugated polymers (CPs) containing side chains with ionic functionality [1]. CPEs can be divided into two categories according to the charge of their side chains: cationic conjugated polyelectrolytes (CCPEs) and anionic conjugated polyelectrolytes (ACPEs). Typical cationic groups of CCPEs include quaternary ammonium (NR$_3^+$) and pyridinium, while anionic groups of ACPEs include carboxylate (CO$_2^-$), phosphonate (PO$_3^{2-}$), and sulfonate (SO$_3^-$). The solubility of CPEs in polar solvents (e.g., water and methanol) is not only dependent on the ionic side groups but also affected by the hydrophobic aromatic backbones [2].

During the past 20 years, a variety of CPEs have been synthesized, most typically via carbon–carbon bond-forming reactions using organometallic catalysts. The most widely used polymerization methods are shown in Scheme 1.1, which include FeCl$_3$-catalyzed or electrochemical oxidization; the Yamamoto and Suzuki coupling reactions for poly(arylene)s [3]; the Wittig, Gilch, Wessling, and Heck reactions for poly(arylene vinylene)s [4]; and the Sonogashira coupling reactions for poly(arylene ethynylene)s [5]. Through these well-established reactions, CPEs can be obtained directly or via postpolymerization strategy. Another example is the ring-opening metathesis polymerization of cyclooctatetraenes, which is described in more detail in Chapter 3. Among these reactions, palladium-catalyzed coupling methods (the Suzuki, Heck, and Sonogashira methods) are the most popular ones because of their tolerance to various functional groups, mild reaction conditions, and capability to produce different backbone structures.

This chapter summarizes the design and synthesis of various CPEs. The sections are organized according to the backbone structures of CPEs. The chapter starts with poly(arylene)s, which is followed by poly(arylene ethynylene)s and poly(arylene vinylene)s. In addition, reported physical properties of CPEs including solubility, absorption ($\lambda_{\text{abs}}$) and emission ($\lambda_{\text{em}}$) maxima, and fluorescence quantum yields ($\Phi_F$) are summarized in Tables 1.1–1.3, respectively. However, it should be noted...
that these properties can be dependent on purification method, molecular weight, and polymer concentration.

1.2 Poly(arylene)s

1.2.1 Polythiophenes

1.2.1.1 Anionic Polythiophenes

The first sulfonated polythiophene was synthesized by Wudl and coworkers [84] in 1987. A neutral polythiophene \( (P_1, \text{Scheme 1.2}) \) was first synthesized from methyl 2-(thiophen-3-yl)ethanesulfonate (2). Subsequent treatment of
1.2 Poly(arylene)s

Scheme 1.2 Synthesis of a sulfonated polythiophene (P2).

Scheme 1.3 Synthesis of a sulfonated polythiophene (P3).

P1 with NaI in acetone yielded the sulfonated polymer (P2, Scheme 1.2). Later, Leclerc’s group [85] reported the synthesis of sulfonated polythiophene (P3, Scheme 1.3) via direct polymerization of a sulfonated monomer. In the first step, 3-methoxy-4-methylthiophene (4) was synthesized from 3-bromo-4-methylthiophene (3) with sodium methoxide and CuBr in N-methyl-2-pyrrolidone (NMP). The methoxy substituent was subsequently reacted with 2-bromoethanol in toluene with sodium hydrogen sulfite to yield 3-(2-bromoethoxy)-4-methylthiophene (5). Treatment of 5 with sodium sulfite in water/acetone mixture yielded sodium 2-(4-methyl-3-thienyl-1-oxy)ethanesulfonate (6), which underwent FeCl₃-catalyzed oxidative polymerization to afford polymer P3. By changing 2-bromoethanol to other alcohols bearing different functionalities, such as halogens, carboxylic acids, and amines, various polythiophene-based CPEs have been synthesized [85].

Carboxylated polythiophenes were synthesized using the Ni(0)-catalyzed Yamamoto coupling polymerization [86], FeCl₃-catalyzed oxidative polymerization [87], or the Stille coupling polymerization [88]. As shown in Scheme 1.4, both the Yamamoto polymerization of methyl 2-(2,5-dichlorothiophen-3-yl)acetate (7) and oxidative polymerization of methyl 2-(thiophen-3-yl)acetate (8) yielded
poly(methyl thiophene-3-carboxylate) (P4). Hydrolysis of P4 with NaOH led to poly(sodium thiophene-3-carboxylate) (P5). In addition, a CuO-modified Stille coupling polymerization was performed for 9 to give poly(4,5-dihydro-4,4-dimethyl-2-(2-(thiophen-3-yl)ethyl)oxazole) (P6, Scheme 1.5) [88], which after acid-assisted hydrolysis and base treatment yielded the carboxylated polymer P7. These polymers showed pH-dependent conformational and optical changes.

Recently, Wang’s group also synthesized a carboxylated polythiophene (P8) [6]. As shown in Scheme 1.6, the key monomer 11 was prepared by reacting the salt of 2-(3-thienyl)ethylamine (10) with methyl acrylate in the presence of boric acid. P8 was obtained through oxidative polymerization of 11 in chloroform, followed by hydrolysis in NaOH aqueous solution.

In addition, phosphonated polythiophene was synthesized as shown in Scheme 1.7. 13 was synthesized in a way similar to that of 5 and the key monomer, 3-(3′-thienyloxy)propanephosphonic acid diethyl ester (14), was synthesized by treatment of 13 with triethyl phosphite [89]. Electropolymerization of 14 in LiClO₄/acetonitrile/CH₂Cl₂ yielded P9, which after silyl dealkylation and hydrolysis gave poly(3-(3′-thienyloxy)propanephosphonate) (P10).

An important series of polythiophene derivatives, poly(cyclopentadithiophene)s, were developed by Zotti’s group [7, 90]. As shown in Scheme 1.8, the key anionic monomer 16 was prepared from a one-pot reaction between 4H-cyclopenta[2,1-b:3,4-b′]-dithiophene (15) and 1,4-butanedisulfone in the presence of n-BuLi. Electropolymerization of 16 led to polymer P11. P12 was prepared using the same strategy.
1.2 Poly(arylene)s

Scheme 1.6  Synthesis of a carboxylated polythiophene (P8).

Scheme 1.7  Synthesis of a phosphonated polythiophene (P10).

Scheme 1.8  Synthesis of sulfonated poly(cyclopentadithiophene)s (P11) and (P12).
1.2.1.2 Cationic Polythiophenes

Cationic polythiophenes were synthesized by Leclerc’s group [8] on direct oxidation of cationic thiophene monomers. The cationic monomer 17 was synthesized on quaternization of 5 with 1-methyl-1H-imidazole (Scheme 1.9). The cationic monomer 19 was synthesized from the Williamson reaction between 3-bromo-4-methylthiophene and 3-(diethylamino)propanol, followed by quaternization with bromoethane. Oxidative polymerization of 17 and 19 in the presence of Bu₄NCl led to P13 and P14, respectively, with chloride counterions [8, 9, 91, 92]. P15–P17 (Scheme 1.9) were synthesized based on a similar approach [10, 11, 93].

As also shown in Scheme 1.9, a series of cationic poly(cyclopentadithiophene)s were also synthesized. 20 was prepared through alkylation of 15 with 1,6-dibromohexane in the presence of n-BuLi. Further quaternization of 20 with trimethylamine, followed by ion exchange afforded the cationic monomer 21 with perchlorate counterion. Electropolymerization of 21 led to cationic polymers P18. P19 and P20 were prepared using the same strategy [7, 94].

1.2.1.3 Zwitterionic Polythiophenes

Zwitterionic CPEs contain side groups with anionic and cationic functionalities that are covalently bound to each other. Zwitterionic polythiophenes have been synthesized by Inganäs’ group [12, 13]. As shown in Scheme 1.10, 1 was brominated with NBS and tosylated to yield a thiophene derivative 22. Displacing the tosyl group of 22 by a Boc-protected amino acid, N-t-Boc-l-Ser, yielded the key monomer 23. Palladium-catalyzed cross-coupling between 23 and thiophene-2,5-bispinacolboronate gave the regioregular terthiophene (24). After removing the Boc groups by trifluoroacetic acid treatment in CH₂Cl₂, the salt counterpart of 24 was directly polymerized in CHCl₃ using anhydrous FeCl₃ as the catalyst in the presence of tetrabutylammonium (TBA-OTf) to afford P21. The homopolymer P22 with the same thiophene unit was also synthesized using a similar strategy [95–97].

1.2.2 Poly(p-phenylene)s

1.2.2.1 Anionic Poly(p-phenylene)

The first carboxylated poly(p-phenylene), poly(p-quaterphenylene-2,2′-dicarboxylic acid) (P23, Scheme 1.11), was synthesized by Novak’s group using the Suzuki cross-coupling between 2,2′-bis-(4,4′-biphenyl)-1,3,2-dioxaborolane and aryl halide 25 [98]. P23 is insoluble in water and organic solvents but is soluble in dilute aqueous hydroxide solution. A postpolymerization method was also used to synthesize a carboxylated poly(p-phenylene) P25 (Scheme 1.11) via the Williamson reaction between P24 and ethyl p-hydroxybenzoate. After hydrolysis of the ester groups, P26 was obtained and exhibited solubility in polar organic solvents [99].

The first sulfonated poly(p-phenylene) P28 was designed and synthesized by Wegner’s group through a postpolymerization method (Scheme 1.12) [100].
Scheme 1.9  Synthesis of cationic polythiophenes and poly(cyclopentadithiophene)s (P13–P20).
Scheme 1.10 Synthesis of zwitterionic polythiophenes (P21) and (P22).
Scheme 1.11 Synthesis of carboxylated poly(p-phenylene)s (P23) and (P26).
1.2.2.2 Cationic Poly(p-phenylene)s

The first cationic poly(p-phenylene) was synthesized by Baullauff and Rehahn [101] through a postpolymerization method. As shown in Scheme 1.14, the cationic poly(p-phenylene)s were synthesized from neutral precursors with phenoxy-substituted alkyl chains. After cleaving the phenoxy groups of \( P_{32} \) with trimethylsilyl iodide, \( P_{33} \) was obtained with alkyl iodide side chains. Subsequent reaction with triethylamine (NEt₃) or pyridine gave the cationic poly(p-phenylene)s (\( P_{34} \) and \( P_{35} \)) with nearly 100% degree of quaternization. \( P_{36} - P_{38} \) were synthesized via the same postpolymerization strategy. Particularly, \( P_{38} \) with four cationic charges per repeat unit was prepared from consecutive quaternization of \( P_{33} \) with tetramethylethylenediamine and iodoethane [102].
A more efficient and universal approach toward cationic poly(p-phenylene)s is shown in Scheme 1.15 [17]. The key monomer, 2,5-bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-dibromobenzene (31), was synthesized via etherification of dibromo-hydroquinone (29) in the presence of 2-chloroethylamine hydrochloride [18]. The Suzuki polymerization between 31 and 1,4-bisphenyl-(1,3,2-dioxaborinane) afforded P39. Reaction between the tertiary amine groups and bromoethane yielded the cationic polymer P40 with good water solubility. In addition, the Stille coupling was also used to synthesize cationic poly(p-phenylene)s containing thiophene units [19]. As shown in Scheme 1.15, 2,5-bis(3-[N,N-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (33) was synthesized similarly to that of 31. Copolymerization between 33 and 2,5-bis(trimethylstannyl)thiophene in anhydrous DMF using PdCl2(PPh3)2 as the catalyst gave the neutral polymer, which on treatment with bromoethane yielded P41.
1.2.3 Poly(fluorene)s

1.2.3.1 Cationic Poly(fluorene)

The first cationic poly(fluorene) was based on the key monomer of 2,5-bis[3-(N,N-dimethylamino)-1-oxapropyl]-1,4-dibromobenzene (34) [20]. As shown in Scheme 1.16, 34 was synthesized via etherification of dibromohydroquinone (29) with 2-chlorotrimethylamine hydrochloride and potassium carbonate in acetone. Subsequently, the Suzuki polymerization between 34 and 2,7-bis-9,9′-dihexylfluorenyl-(1,3,2-dioxaborinane) gave the neutral polymer P42. Treatment of P42 with bromoethane in DMSO/THF mixture led to P43 with a quaternization degree of ~80%. In an analogous way, P44 was synthesized from 31 [103]. The quaternization degree of P45 could be adjusted from 25 to 80% by varying the amount of bromoethane and the reaction time. P45a has a quaternization degree of 25%, which is almost not soluble in any solvent. However, polymers with quaternization degrees of 60% (P45b) or 80% (P45c) are soluble in DMSO and methanol, and P45c has also shown limited solubility in hot water.
Scheme 1.15 Synthesis of cationic poly(\(p\)-phenylene)s (P40) and (P41).
To improve water solubility of polyfluorenes, Bazan and coworkers [21] attached charged side chains to fluorene rather than phenylene. The key monomer, 2,7-dibromo-9,9′-bis(6-(N,N-dimethylamino)hexyl)fluorene (37), was synthesized in two steps as shown in Scheme 1.17. Under basic condition, 2,7-dibromofluorene (35) was reacted with 1,6-dibromohexane to afford 2,7-dibromo-9,9-bis(6-bromohexyl)fluorene (36). Treatment of 36 with dimethylamine (Me₂NH) in THF led to 37. The Suzuki polymerization between 37 and 1,4-phenyldiboronic acid gave the neutral polymer P46, which on treatment with iodomethane yielded P47.

On the basis of 2,7-dibromo-9,9-bis[3-(N,N-dimethylamino)propyl]fluorene (38), Cao and coworkers [22] reported a series of cationic polymers P48–P53 (Scheme 1.18). The key monomer 38 was synthesized by reacting 2,7-dibromofluorene with 3-dimethylaminopropylchloride hydrochloride in a water/DMSO
1.2 Poly(arylene)s

Scheme 1.17 Synthesis of a cationic polyfluorene (P47).

mixture in the presence of excess NaOH. The Suzuki copolymerization between 38 and different diboronate monomers followed by treatment with bromoethane led to blue-fluorescent alternating polyfluorenes (P48 and P49). To fine-tune the polymer emission, random copolymerization between 38, 2,2′-(9,9-diocyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), and other dibromide monomers such as 2,1,3-benzothiazole, 2,1,3-benzoselenadiazole, 4,7-di-2-thienyl-2,1,3-benzothiadiazole, and the Ir(ppy)₃ complex afforded green-to-yellow-emissive P50 [104], orange-to-red-emissive P51 [105], red-emissive P52 [106], and orange-red-emissive P53 [107], respectively. These materials are designed for device applications as discussed in Chapter 11.

To obtain cationic polyfluorene homopolymers, the dioxaborolane monomer, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-bis[3-(N,N-dimethylamino)propyl]fluorene (39), was synthesized by reacting 38 with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in the presence of n-BuLi (Scheme 1.19) [23]. The Suzuki polymerization between 38 and 39 and subsequent treatment with bromoethane led to the cationic homopolymer P54 with good water solubility. On the basis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-bis[3′-(N,N-dimethylamino)hexyl]fluorene (40), a cationic polyfluorene copolymer containing oxadiazole units P55 was synthesized to serve as a hole-transporting material in light-emitting devices (Scheme 1.19) [108]. In addition, the boronic acid monomer 41 was synthesized to obtain cationic cross-conjugated P56 [24].

To solve the problem of incomplete quaternization for polymers containing side chains with terminal tertiary amine, a new postpolymerization method was
Scheme 1.18 Synthesis of cationic polyfluorenes (P48–P53).
Scheme 1.19  Synthesis of cationic polyfluorenes (P54–P56).
developed based on highly efficient reaction between alkyl bromide and trimethylamine [25]. In the first step, a neutral polymer was synthesized via the Suzuki coupling reaction between \(36\) and 1,4-phenyldiboronic acid (Scheme 1.20). This was followed by trimethylamine treatment to afford P57 with >95% degree of quaternization. Poly(fluorene-co-phenylene)s (P57a–f) with different amount of meta-phenyl units have been synthesized to adapt to the secondary structure of biomolecules. Cationic poly(fluorene-co-thiophene) (P58) was synthesized similarly from 9,9-bis(6-bromohexyl)-2,7-diiodofluorene (42) and 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene followed by trimethylamine treatment [26].

To further facilitate the synthesis of cationic polyfluorene derivatives, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9’-bis(di(bromoalkyl))fluorene (43) was synthesized by reacting 36 with excess 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1.21) [27]. The Suzuki coupling between 43 and substituted dibromophenylene, followed by trimethylamine treatment, afforded polymers P59a–d with tunable energy levels of 5.6 ± 0.2 eV for the highest occupied molecular orbital and 2.7 ± 0.1 eV for the lowest unoccupied molecular orbitals.

---

**Scheme 1.20** Synthesis of cationic poly(fluorene-co-phenylene)s (P57a–f) and a poly(fluorene-co-thiophene) (P58).
Scheme 1.21 Synthesis of cationic polyfluorenes (P59a–d).
orbital, respectively. These CPEs have been used for sensor applications as described in Chapter 6.

The availability of 43 allows the facile synthesis of a series of cationic polyfluorenes with different side chains [28, 109]. Different cationic polyfluorenes (P60 and P62a–c) were obtained via the Suzuki polymerization between 43 and dibromomonomers, such as 36 and 44a–c (Scheme 1.22), followed by trimethylamine treatment. Subsequent ion exchange of P60 afforded P61 with different counterions [110].

Apart from blue-emitting polyfluorenes, a new class of polyfluorene copolymers were synthesized via the Suzuki polymerization between dioxaborolane monomer 43 and 4,7-dibromo-2,1,3-benzothiadiazole (45), which was followed
by quaternization with trimethylamine to yield cationic poly(fluorene-co-benzothiadiazole) (P63, Scheme 1.23) [29, 30]. Polymers with the same backbone but different counteranions (P64a–e) were also synthesized via ion-exchange reactions [111]. To improve water solubility of P63, 2,2′-(9,9-bis(2-(2-bromoethoxy)ethoxy)ethyl)-9H-fluorene-2,7-diyl)biss(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (46)
was synthesized via the Miyaura reaction by heating a mixture of 44a and bis(pinacolato)diborane with KOAc in anhydrous dioxane [31]. The Suzuki coupling between 45 and 46, followed by trimethylamine treatment, led to P65.

Random copolymers (P66–P69, Scheme 1.24) have also been synthesized by the Suzuki polymerization of the dioxaborolane monomer (43 or 46) with 45 and other dibromo monomers, followed by quaternization [32–35]. The benzothiadiazole content was adjusted by changing the feed ratio of monomers for polymerization. To increase the benzothiadiazole content and maintain good water solubility, P67a and P67b were synthesized with short side chains on the fluorene monomers and high charge densities for the final polymers. By attaching cationic oligo(ethylene oxide) side chains to the fluorene units, P68 and P69 were synthesized to have 20 mol% benzothiadiazole content with high water solubility. Similar polymer structures with bromide or tetrafluoroborate as the counteranion have also been reported by Friend et al. [112].

Cationic polyfluorenes with dendritic or bulky water-soluble side chains were also synthesized [36, 113]. As shown in Scheme 1.25, the polymers were synthesized by coupling Boc-protected dendritic fluorene monomers (47 or 49), Boc-protected fluorene (48) with 1,4-bisphenyl-(5,5-dimethyl-1,3,2-dioxaborinane) at a feed ratio of 1 : 1 : 2 in K2CO3/Pd(dppf)Cl2/toluene solution, followed by trifluoroacetic acid treatment to yield P70 and P71, respectively.

In addition, a spiro(anthracene-9,9′-fluorene)-based cationic polyfluorene containing an anthracenyl “molecular bumper” has also been reported [37]. As shown in Scheme 1.26, the Suzuki polymerization between 10,10′-bis(6-bromohexyl)-10H-spiro(anthracene-9,9′-(2′,7′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene)) (50) and 1,4-bis(6-bromohexyloxy)-2,5-dibromobenzene (51) afforded the neutral polymer, which on quaternization yielded P72.

Hyperbranched cationic polyfluorene derivatives have been developed by Liu’s group [38–40]. As shown in Scheme 1.27, the diyne monomer, 9,9′-bis(6-bromohexyl)-2,7-diethynylfluorene (52), was synthesized from 36 via the Sonagashira coupling reaction in two steps. Homopolycyclotrimerization of 52 under UV irradiation with CpCo(CO)2 as catalyst yielded P73, which after treatment with trimethylamine gave cationic polymer P74. Similarly, homopolycyclotrimerization of 56 afforded P75, which on quaternization yielded P76.

1.2.3.2 Anionic Poly(fluorene)
The first anionic polyfluorene was synthesized by Scherf’s group based on the key monomer 2,7-dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene (59, Scheme 1.28) [41]. 2,7-Dibromofluorene (35) was oxidized with sodium dichromate in acetic acid to yield 57, which reacted with phenol/methanesulfonic acid to give 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene (58). Etherification of 58 with 1,4-butane sultone led to 59. The Suzuki polymerization between 59 and 1,4-phenyldiboronic acid yielded P77. Similarly, a benzothiadiazole-containing random copolymer (P78) was also synthesized in a similar way [42].
Scheme 1.24 Structures of cationic polyfluorenes (P66–P69).
Another approach to yield sulfonated polyfluorenes was demonstrated by Cao’s group [43]. The key monomer 2,7-dibromo-9,9-bis(4-sulfonatobutyl)-fluorene disodium (60) was directly prepared from 2,7-dibromofluorene (35) and 1,4-butanesultone in the presence of excess NaOH aqueous solution (Scheme 1.29). Polymerization between 60 and 1,4-phenyldiboronic acid in the presence of Pd(OAc)$_2$ and NaCO$_3$ in DMF/water yielded P79 with good water solubility.
Scheme 1.26 Synthesis of a cationic polyfluorene (P72).
A carboxylated polyfluorene was synthesized by Reynolds’ group [44]. The key monomer, 2,7-dibromofluorene-9,9-dipropanoic acid-dibutylester (61), was synthesized from 2,7-dibromofluorene (35) via the Michael addition of the bridge carbon with butyl acrylate (Scheme 1.30) in the presence of triethylbenzyl ammonium chloride (TEBA). 61 was copolymerized with 2,2′-(9,9-diethyl-
Scheme 1.28 Synthesis of anionic polyfluorenes (P77) and (P78).
fluorene-2,7-diyl)-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) under modified Suzuki reaction conditions using cesium fluoride (CsF) and tetrabutylammonium fluoride (TBAF) as the base to yield a neutral polymer, which was followed by hydrolysis to afford P80.

Carboxylated polyfluorenes [45, 46, 114] were also synthesized from 2,7-dibromo-9,9-bis(3′-(tert-butyl propanoate))fluorene (62), which was synthesized via direct alkylation of 2,7-dibromofluorene (35) with tert-butylacrylate in a mixture of toluene and aqueous KOH (Scheme 1.31). Polymerization between 62 and 1,4-bisphenyl-(5,5-dimethyl-1,3,2-dioxaborinane) was conducted under
the standard Suzuki coupling condition, which was followed by hydrolysis in CF$_3$COOH/CH$_2$Cl$_2$ to yield P81, which is soluble in water, DMSO, and methanol. The diboronate ester 63 was synthesized under the Miyaura reaction conditions. The availability of this key monomer facilitates the synthesis of the homopolymer P82 and benzothiadiazole-containing polymer P83.

Starting from a similar carboxyl-acid-functionalized dibromofluorene, Wang’s group synthesized an amino-acid-functionalized polyfluorene (P84, Scheme 1.32) [47]. The key monomer 65 was synthesized by reacting 64 with l-aspartic acid dimethyl ester hydrochloride in the presence of
Scheme 1.32 Synthesis of an anionic amino-acid-functionalized polyfluorene (P84).
1.3 Poly(arylene ethynylene)s

1.3.1 Poly(phenylene ethynylene)s

1.3.1.1 Anionic Poly(phenylene ethynylene)s

Poly(phenylene ethynylene)s are typically synthesized via the Pd-catalyzed Sonogashira reaction. Copolymerization between acetylene and 3,5-diiodobenzoic acid (73) in aqueous solution using Pd(0) and CuI as the catalyst directly resulted in carboxylated poly(phenylene ethynylene) (P91) [116]. Another carboxylated poly(phenylene ethynylene) (P92) was synthesized via the Sonogashira reaction between 74 and 75 (Scheme 1.37) [51].
Scheme 1.33 Synthesis of a phosphonated polyfluorene (P85).
Schanze’s group synthesized P94 in an analogous way (Scheme 1.38) [52]. The ester-protected diiodo monomer (77) was synthesized in two steps from 32. Then, 77 was reacted with trimethylsilyl acetylene in the presence of (Ph₃P)₂PdCl₂/CuI, which was followed by trimethylsilyl deprotection in a basic solution to afford the diacetylene monomer 78. Copolymerization between 77 and 78 under the Sonagashira reaction conditions yielded the neutral precursor P93, which underwent hydrolysis to give P94. Copolymerization between 77 and other diacetylene monomers followed by base treatment yielded the alternating carboxylated poly(phenylene ethynylene)s P95–P97 [53, 117].

Bunz’s group also synthesized a series of carboxylated poly(phenylene ethynylene)s (Scheme 1.39). The homopolymer P94 was synthesized via the Sonogashira reaction between 79 and 80 [118]. Different from Schanze’s method, the diiodo monomer 79 was synthesized directly from 32 with ethyl 2-bromoacetate. Using the diacetylene monomer 80, alternating carboxylated poly(phenylene ethynylene)s (P98–P101) were synthesized [54–56, 119].

Apart from carboxylated poly(phenylene ethynylene)s, a series of sulfonated poly(phenylene ethynylene)s were also developed by Schanze’s group based on the key monomer 81 (Scheme 1.40), which was synthesized analogously as 30 [57]. The Sonogashira coupling between 81 and different diacetylene monomers in aqueous media afforded sulfonated poly(phenylene ethynylene)s (P102–P107) [58, 59]. A diacetylene monomer with four oligo(ethylene glycol) was used by Kim’s group to copolymerize with 81 to afford P108. In addition, a meta-linked sulfonated poly(phenylene ethynylene) (P109, Scheme 1.41) was also synthesized from 83, which was prepared on treatment of 3,5-diiodophenol (82) with 1,3-propanesultone.
Scheme 1.35 Synthesis of a zwitterionic polyfluorene (P89).
Scheme 1.36 Synthesis of a zwitterionic polyfluorene (P90).
### Table 1.1 Physical properties of poly(arylene)-based CPEs.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>( \lambda_{\text{abs}} ) (nm)</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>( \Phi_F ) (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P8</td>
<td>Water</td>
<td>410</td>
<td>561</td>
<td>4.8</td>
<td>[6]</td>
</tr>
<tr>
<td>P12</td>
<td>Water</td>
<td>540</td>
<td>—</td>
<td>—</td>
<td>[7]</td>
</tr>
<tr>
<td>P13</td>
<td>Water</td>
<td>397</td>
<td>530</td>
<td>3.0</td>
<td>[8]</td>
</tr>
<tr>
<td>P14</td>
<td>Water</td>
<td>400</td>
<td>536</td>
<td>—</td>
<td>[9]</td>
</tr>
<tr>
<td>P16</td>
<td>Water</td>
<td>438</td>
<td>546</td>
<td>1.2</td>
<td>[10]</td>
</tr>
<tr>
<td>P21</td>
<td>Water</td>
<td>434</td>
<td>555</td>
<td>—</td>
<td>[12]</td>
</tr>
<tr>
<td>P22</td>
<td>Water</td>
<td>438</td>
<td>540</td>
<td>—</td>
<td>[13]</td>
</tr>
<tr>
<td>P29</td>
<td>Water</td>
<td>339</td>
<td>410</td>
<td>( \sim ) 55</td>
<td>[14, 15]</td>
</tr>
<tr>
<td>P30</td>
<td>Water</td>
<td>352</td>
<td>—</td>
<td>—</td>
<td>[15]</td>
</tr>
<tr>
<td>P31</td>
<td>Water</td>
<td>338</td>
<td>417</td>
<td>—</td>
<td>[16]</td>
</tr>
<tr>
<td>P40</td>
<td>Water</td>
<td>330</td>
<td>408</td>
<td>—</td>
<td>[17, 18]</td>
</tr>
<tr>
<td>P41</td>
<td>Water</td>
<td>411</td>
<td>494</td>
<td>—</td>
<td>[19]</td>
</tr>
<tr>
<td>P43</td>
<td>Water</td>
<td>343</td>
<td>409</td>
<td>25</td>
<td>[20]</td>
</tr>
<tr>
<td>P47</td>
<td>Water</td>
<td>369</td>
<td>417</td>
<td>32</td>
<td>[21]</td>
</tr>
<tr>
<td>P48</td>
<td>Water</td>
<td>386</td>
<td>416</td>
<td>—</td>
<td>[22]</td>
</tr>
<tr>
<td>P49</td>
<td>Methanol</td>
<td>388</td>
<td>416</td>
<td>—</td>
<td>[22]</td>
</tr>
<tr>
<td>P54</td>
<td>Water</td>
<td>—</td>
<td>417</td>
<td>44</td>
<td>[23]</td>
</tr>
<tr>
<td>P56</td>
<td>Water</td>
<td>359</td>
<td>407</td>
<td>—</td>
<td>[24]</td>
</tr>
<tr>
<td>P57a</td>
<td>Water</td>
<td>335</td>
<td>369</td>
<td>51</td>
<td>[25]</td>
</tr>
<tr>
<td>P57f</td>
<td>Water</td>
<td>384</td>
<td>417</td>
<td>42</td>
<td>[25]</td>
</tr>
<tr>
<td>P58</td>
<td>Water</td>
<td>425</td>
<td>478</td>
<td>—</td>
<td>[26]</td>
</tr>
<tr>
<td>P59a</td>
<td>Water</td>
<td>385</td>
<td>415</td>
<td>24</td>
<td>[27]</td>
</tr>
<tr>
<td>P59b</td>
<td>Water</td>
<td>363</td>
<td>410</td>
<td>32</td>
<td>[27]</td>
</tr>
<tr>
<td>P59c</td>
<td>Water</td>
<td>369</td>
<td>414</td>
<td>29</td>
<td>[27]</td>
</tr>
<tr>
<td>P60</td>
<td>Water</td>
<td>395</td>
<td>426</td>
<td>46</td>
<td>[28]</td>
</tr>
<tr>
<td>P62a</td>
<td>Water</td>
<td>389</td>
<td>426</td>
<td>50</td>
<td>[28]</td>
</tr>
<tr>
<td>P62b</td>
<td>Water</td>
<td>382</td>
<td>421</td>
<td>50</td>
<td>[28]</td>
</tr>
<tr>
<td>P63</td>
<td>Water</td>
<td>330, 455</td>
<td>590</td>
<td>7.0</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>P65</td>
<td>Water</td>
<td>320, 455</td>
<td>598</td>
<td>0.4</td>
<td>[31]</td>
</tr>
<tr>
<td>P66</td>
<td>Water</td>
<td>—</td>
<td>410, 550</td>
<td>—</td>
<td>[32, 33]</td>
</tr>
<tr>
<td>P67</td>
<td>Water</td>
<td>352, 430</td>
<td>412</td>
<td>5</td>
<td>[34]</td>
</tr>
<tr>
<td>P68</td>
<td>Water</td>
<td>375</td>
<td>415</td>
<td>—</td>
<td>[35]</td>
</tr>
<tr>
<td>P70</td>
<td>Water</td>
<td>384</td>
<td>422</td>
<td>7.2</td>
<td>[36]</td>
</tr>
<tr>
<td>P71</td>
<td>Water</td>
<td>385</td>
<td>420</td>
<td>7.2</td>
<td>[36]</td>
</tr>
<tr>
<td>P72</td>
<td>Water</td>
<td>( \sim ) 355</td>
<td>( \sim ) 410</td>
<td>39</td>
<td>[37]</td>
</tr>
<tr>
<td>P74</td>
<td>Water</td>
<td>355</td>
<td>409</td>
<td>40</td>
<td>[38]</td>
</tr>
<tr>
<td>P76</td>
<td>Water</td>
<td>309, 410</td>
<td>598</td>
<td>3</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>P77</td>
<td>Water</td>
<td>381</td>
<td>424</td>
<td>10</td>
<td>[41]</td>
</tr>
<tr>
<td>P78</td>
<td>Water</td>
<td>—</td>
<td>415</td>
<td>—</td>
<td>[42]</td>
</tr>
<tr>
<td>P79</td>
<td>Water</td>
<td>365</td>
<td>420</td>
<td>90</td>
<td>[43]</td>
</tr>
<tr>
<td>P80</td>
<td>Methanol</td>
<td>385</td>
<td>—</td>
<td>—</td>
<td>[44]</td>
</tr>
<tr>
<td>P81</td>
<td>Water</td>
<td>380</td>
<td>434</td>
<td>21</td>
<td>[45]</td>
</tr>
<tr>
<td>P82</td>
<td>Water</td>
<td>390</td>
<td>434</td>
<td>25</td>
<td>[46]</td>
</tr>
<tr>
<td>P84</td>
<td>Water</td>
<td>365</td>
<td>409</td>
<td>89</td>
<td>[47]</td>
</tr>
</tbody>
</table>
1.3 Poly(arylene ethynylene)s

Table 1.1 (continued)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi_F$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P85</td>
<td>Water</td>
<td>364</td>
<td>410</td>
<td>75</td>
<td>[48]</td>
</tr>
<tr>
<td>P87</td>
<td>Water</td>
<td>$\sim390$</td>
<td>$\sim410$</td>
<td>—</td>
<td>[49]</td>
</tr>
<tr>
<td>P88</td>
<td>Methanol</td>
<td>395</td>
<td>419, 443</td>
<td>—</td>
<td>[50]</td>
</tr>
<tr>
<td>P90</td>
<td>Water</td>
<td>326</td>
<td>454</td>
<td>—</td>
<td>[24]</td>
</tr>
</tbody>
</table>

$a\lambda_{\text{abs}}$ and $\lambda_{\text{em}}$ are the maximum absorption and emission wavelengths, respectively; $\Phi_F$ is the fluorescence quantum yield.

$^b$At a temperature of 55°C.

Scheme 1.37 Synthesis of carboxylated poly(phenylene ethynylene)s (P91) and (P92).

in the presence of NaOH. P109 was reported to self-assemble into a helical structure in aqueous solution [60].

Phosphonated poly(phenylene ethynylene)s constitute the third type of anionic poly(phenylene ethynylene)s. P110 was synthesized by Schanze’s group through a postpolymerization method (Scheme 1.42) [61]. The key monomer 87 was obtained from 2,2’-(1,4-phenylenebis(oxy))diethanol (84) in three steps. Copolymerization between the dibutylphosphonate monomer 87 and 1,4-diethynylbenzene under the Sonogashira reaction conditions, followed by trimethylsilyl-bromide-promoted hydrolysis, yielded the anionic poly(phenylene ethynylene) (P110).

1.3.1.2 Cationic Poly(phenylene ethynylene)s

Swager’s group synthesized a cationic poly(phenylene ethynylene) (P111, Scheme 1.43) by reaction between 89 and 90 in DMF/Et$_3$N/water using
Pd(PPh$_3$)$_4$/CuI as the catalyst [120]. The key monomer 89 was obtained from etherification of 32 with 1,3-dibromopropane, followed by quaternization with trimethylamine. Huang’s group also synthesized a cationic poly(phenylene ethynylene) (P113, Scheme 1.44) [62]. The key monomer 91 was obtained by reacting between 31 and trimethylsilyl acetylene under the Sonagashira reaction conditions, followed by trimethylsilyl deprotection in basic solution. Copolymerization between 91 and 31 led to the neutral polymer P112, which on treatment with bromoethane gave P113 with 45% degree of quaternization.

A series of bis(dialkylammonium) substituted poly(phenylene ethynylene)s with different backbones were synthesized by Schanze’s group (Scheme 1.45).
Scheme 1.39  Synthesis of carboxylated poly(phenylene ethynylene)s (P94) and (P98–P101).
Scheme 1.40  Synthesis of sulfonated poly(phenylene ethynylene)s \( (P_{102}–P_{108}) \).

[63]. The key monomer \( (92) \) was synthesized on quaternization of \( 86 \) with 1-hexyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide. Copolymerization between \( 92 \) and different diacetylene monomers led to \( P_{114}–P_{118} \), which have four cationic charges per repeat unit.
Scheme 1.42 Synthesis of a phosphonated poly(phenylene ethynylene) (P110).
1.3.2 Poly(fluorene ethynylene)s

1.3.2.1 Cationic Poly(fluorene ethynylene)s

A series of cationic poly(fluorene ethynylene)s were reported in 2007 to study solvent-induced self-assembly [64, 65]. The synthetic route to poly(fluorene ethynylene)s with different meta-phenylene contents is described in Scheme 1.46. The neutral poly(fluorene ethynylene)s were prepared by heating \( p\)- and \( m\)-diiodobenzene with 2,7-diethynyl-9,9-bis\(^{\prime}\)(N,N-diethyl)hexyl)fluorene (96) using Pd(PPh\(_3\))\(_4\)/CuI as the catalyst. Treatment of neutral poly(fluorene ethynylene)s with iodo-methane in THF/DMF mixture afforded P119–P122 with 70–80% degree of quaternization.

To simplify the synthesis of cationic poly(fluorene ethynylene)s, the key monomer 52 (Scheme 1.47) was prepared directly by treatment of 36 with trimethylsilyl acetylene under the Sonogashira coupling conditions, followed by deprotection in the presence of KOH in THF/CH\(_3\)OH solution [66]. Subsequent polymerization between 52 and 1,4-diiodobenzene in diisopropylamine/toluene mixture, followed by NMe\(_3\) treatment in THF/water solution, afforded P123. Benzothiadiazole-containing poly(fluorene ethynylene) (P124) was also synthesized by copolymerization between 99 and 4,7-diethylnylbenzothiadiazole [67].
1.3 Poly(arylene ethynylene)s

Scheme 1.44 Synthesis of a cationic poly(phenylene ethynylene) (P113).

(1) PdCl₂(PPh₃)₂/CuI
(2) (iPr)₂NH
(3) KOH, MeOH
(4) HCl, MeOH
(5) K₂CO₃
(6) EtBr, THF

50 °C

TMS

91:45, 55

P112

P113
Scheme 1.45 Synthesis of cationic poly(phenylene ethynylene)s (P114–P118).
1.3 Poly(arylene ethynylene)s

1.3.2.2 Anionic Poly(fluorene ethynylene)s

Wang’s group reported an organometallic poly(fluorene ethynylene) (P125, Scheme 1.48) with phosphorescence properties [68]. The diacetylene monomer (100) was synthesized from 65 via the Sonogashira coupling reaction. Polymerization between 100 and [Pt(PMe3)2Cl2], followed by hydrolysis of the
Scheme 1.47 Synthesis of cationic poly(fluorene ethynylene)s (P123) and (P124).
carboxylic esters under basic condition, led to \( \text{P125} \). Another anionic poly(fluorene ethynylene) (\( \text{P126} \), Scheme 1.49) was synthesized through direct coupling reaction between sulfonated monomer \( 60 \) and 4,7-diethynylbenzothiadiazole [67]. The physical properties of poly(arylene ethynylene)-based CPEs are summarized in Table 1.2.
Table 1.2 Physical properties of poly(arylene ethynylene)-based CPEs.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi_F$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P92</td>
<td>Water</td>
<td>404</td>
<td>426</td>
<td>—</td>
<td>[51]</td>
</tr>
<tr>
<td>P94</td>
<td>Water</td>
<td>317</td>
<td>470</td>
<td>6.3</td>
<td>[52]</td>
</tr>
<tr>
<td>P95</td>
<td>Methanol</td>
<td>435</td>
<td>476</td>
<td>13</td>
<td>[53]</td>
</tr>
<tr>
<td>P96</td>
<td>Methanol</td>
<td>457</td>
<td>497</td>
<td>9.0</td>
<td>[53]</td>
</tr>
<tr>
<td>P97</td>
<td>Methanol</td>
<td>495</td>
<td>642</td>
<td>0.20</td>
<td>[53]</td>
</tr>
<tr>
<td>P98</td>
<td>Water\textsuperscript{b}</td>
<td>419</td>
<td>465</td>
<td>8.0</td>
<td>[54]</td>
</tr>
<tr>
<td>P99</td>
<td>Water\textsuperscript{b}</td>
<td>425</td>
<td>466</td>
<td>33</td>
<td>[54]</td>
</tr>
<tr>
<td>P100</td>
<td>Water</td>
<td>$\sim$419</td>
<td>$\sim$465</td>
<td>8.0</td>
<td>[55]</td>
</tr>
<tr>
<td>P101</td>
<td>Water</td>
<td>421</td>
<td>460</td>
<td>2.0</td>
<td>[56]</td>
</tr>
<tr>
<td>P102</td>
<td>Water</td>
<td>446</td>
<td>547</td>
<td>1.0</td>
<td>[57]</td>
</tr>
<tr>
<td>P103</td>
<td>Water</td>
<td>419</td>
<td>503</td>
<td>—</td>
<td>[58]</td>
</tr>
<tr>
<td>P104</td>
<td>Water</td>
<td>484</td>
<td>478</td>
<td>3.6</td>
<td>[57]</td>
</tr>
<tr>
<td>P105</td>
<td>Water</td>
<td>506</td>
<td>—</td>
<td>—</td>
<td>[57]</td>
</tr>
<tr>
<td>P106</td>
<td>Water</td>
<td>455</td>
<td>532</td>
<td>18.7</td>
<td>[57]</td>
</tr>
<tr>
<td>P107</td>
<td>Water</td>
<td>549</td>
<td>634</td>
<td>0.34</td>
<td>[57]</td>
</tr>
<tr>
<td>P108</td>
<td>Water</td>
<td>425</td>
<td>460</td>
<td>53</td>
<td>[59]</td>
</tr>
<tr>
<td>P109</td>
<td>Water</td>
<td>325</td>
<td>445</td>
<td>—</td>
<td>[60]</td>
</tr>
<tr>
<td>P110</td>
<td>Water</td>
<td>444</td>
<td>518</td>
<td>3.0</td>
<td>[61]</td>
</tr>
<tr>
<td>P111</td>
<td>Water</td>
<td>378</td>
<td>444</td>
<td>—</td>
<td>[62]</td>
</tr>
<tr>
<td>P112</td>
<td>Water</td>
<td>394</td>
<td>436</td>
<td>4.7</td>
<td>[63]</td>
</tr>
<tr>
<td>P113</td>
<td>Water</td>
<td>429</td>
<td>478</td>
<td>7.1</td>
<td>[63]</td>
</tr>
<tr>
<td>P114</td>
<td>Water</td>
<td>455</td>
<td>496</td>
<td>1.1</td>
<td>[63]</td>
</tr>
<tr>
<td>P115</td>
<td>Water</td>
<td>426</td>
<td>508</td>
<td>0.8</td>
<td>[63]</td>
</tr>
<tr>
<td>P116</td>
<td>Water</td>
<td>520</td>
<td>630</td>
<td>0.06</td>
<td>[63]</td>
</tr>
<tr>
<td>P117</td>
<td>Water</td>
<td>403</td>
<td>436</td>
<td>—</td>
<td>[64]</td>
</tr>
<tr>
<td>P118</td>
<td>Water</td>
<td>418</td>
<td>431</td>
<td>—</td>
<td>[64]</td>
</tr>
<tr>
<td>P119</td>
<td>Water</td>
<td>415</td>
<td>431</td>
<td>—</td>
<td>[64]</td>
</tr>
<tr>
<td>P120</td>
<td>Water</td>
<td>364</td>
<td>428</td>
<td>—</td>
<td>[65]</td>
</tr>
<tr>
<td>P121</td>
<td>Water</td>
<td>389</td>
<td>425</td>
<td>22</td>
<td>[66]</td>
</tr>
<tr>
<td>P122</td>
<td>Water</td>
<td>339</td>
<td>450</td>
<td>1.1</td>
<td>[67]</td>
</tr>
<tr>
<td>P123</td>
<td>Water</td>
<td>390</td>
<td>405</td>
<td>0.23</td>
<td>[68]</td>
</tr>
<tr>
<td>P124</td>
<td>Water</td>
<td>339</td>
<td>450</td>
<td>0.9</td>
<td>[67]</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\lambda_{\text{abs}}$ and $\lambda_{\text{em}}$ are the maximum absorption and emission wavelengths, respectively; $\Phi_F$ is the fluorescence quantum yield.

\textsuperscript{b}At pH = 7.

1.4

Poly(arylene vinylene)s

1.4.1

Poly(phenylene vinylene)s

1.4.1.1 Anionic Poly(phenylene vinylene)s

The first anionic poly(phenylene vinylene) was synthesized by Wudl’s group via the Wessling route (Scheme 1.50) [69]. Homopolymerization of 101 under
basic condition afforded the sulfonium precursor P127. Further hydrolysis followed by base- or acid-assisted elimination yielded the sulfonated poly(phenylene vinylene) (P129). The Wittig and Gilch reactions were also used to synthesize sulfonated alternating poly(phenylene vinylene)s [70, 71]. As shown in Scheme 1.51, the key monomer (104) was synthesized in three steps. Potassium 3-(4-methoxyphenoxy)propanesulfonate (103) was obtained via reaction between potassium 4-methoxyphenolate and 1,3-propanesultone in anhydrous ethanol. 5-Methoxy-2-(3-sulfonatopropoxy)-1,4-xylene-α,α′-dichloride (104) was prepared by chloromethylation of 103 in aqueous solution at 40 °C. Dehydrohalogenation polymerization of 104 using potassium tert-butoxide as the catalyst gave P129. The monomer 105 was obtained by reacting 104 with PPh3. The Wittig polymerization between 105 and terephthalaldehyde with potassium tert-butoxide as the catalyst led to the poly(phenylene vinylene) P130.

In addition to the above-mentioned base-catalyzed polymerization methods, the Pd-catalyzed Heck reaction [72] also led to sulfonated poly(phenylene vinylene)s. As shown in Scheme 1.52, the divinyl monomers (106 and 107) were, respectively, copolymerized with the sulfonated monomer 81 using Pd(OAc)2 and tri-o-tolylphosphine [P(o-Tol)3] as the catalyst in NEt3/DMSO to yield P131 and P132.

Carboxylated poly(phenylene vinylene)s were also synthesized via the Heck [73] and Gilch reactions [121, 122]. Copolymerization between 108 and 109 catalyzed by Pd(OAc)2/P(o-Tol)3 in DMF led to the neutral polymer (P133, Scheme 1.53). Hydrolysis and acidification of P133 yielded the carboxylated poly(phenylene vinylene) P134. P134 is soluble in DMSO and aqueous solution but is not soluble in common organic solvents. Similarly, carboxylated poly(phenylene vinylene) (P135, Scheme 1.54) was synthesized from 111 in the presence of t-BuOK.
1.4.1.2 Cationic Poly(phenylene vinylene)s

A series of cationic poly(phenylene vinylene)s with tertiary amine side chains were also synthesized through the Gilch and Wittig reactions (Scheme 1.55) [74, 75]. Palladium-catalyzed aryl–aryl coupling between 112 and 113 afforded 114, which was converted to the key monomer 115 through acid-assisted deprotection and chlorification with thionyl chloride. The Gilch reaction of 115 with t-BuOK in THF gave the neutral polymer (P136). Further treatment of P136 with bromoethane yielded the cationic poly(phenylene vinylene) (P137). On the other hand, reaction of 115 with PPh₃ yielded 116, a key monomer for the Wittig reaction. The availability of 116 allows the synthesis of alternating cationic poly(phenylene vinylene)s (P138–P142) through copolymerization with different dialdehyde monomers. The homopolymer (P137) is primarily of trans-vinyl while the alternating polymers (P138–P142) are of ∼81% cis-vinyl conformation.

The Heck reaction has also been used to synthesize cationic poly(phenylene vinylene)s. It relies on monomers that are easier to synthesize as compared to
Scheme 1.52 Synthesis of sulfonated poly(phenylene vinylene)s (P131) and (P132).
Scheme 1.53 Synthesis of a carboxylated poly(phenylene vinylene) (P134).
1.4 Poly(arylene vinylene)s

those for the Gilch and Wittig reactions. As shown in Scheme 1.57, polymerization between 33 and 1,4-divinylbenzene catalyzed by Pd(OAc)2/P(o-Tol)3 in tri-n-butyramine/DMF, followed by quaternization yielded P145 [77].

1.4.2 Poly(fluorene vinylene)s

1.4.2.1 Cationic Poly(fluorene vinylene)s

Poly(fluorene vinylene)-based CPEs are commonly synthesized by the Heck coupling and the Wittig–Horner reactions. Mikroyannidis and Barberis [78] first designed and synthesized cationic poly(fluorene vinylene) and poly(phenylene vinylene-alt-fluorenevinylene) derivatives. Divinylfluorene monomer (122, Scheme 1.58) was prepared via the Stille coupling reaction between 121 and tributylvinyltin catalyzed by PdCl2(PPh3)2 in toluene. The neutral polymer P146 was obtained by the Heck coupling between monomers 121 and 122 catalyzed by Pd(OAc)2/P(o-Tol)3 in DMF. P147 was obtained with 60% degree of quaternization by treatment of P146 with excess bromoethane in THF. P148 and P149 were synthesized using a similar method [123].

Recently, Liu’s group [79] designed and synthesized poly[9,9-bis(6′-(N,N,N-trimethylammonium)hexyl)fluorenyldivinylene-alt-4,7-(2,1,3-benzothiadiazole) dibromide] (P150, Scheme 1.59). The neutral divinyl monomer 125 was synthesized via a Pd(OAc)2/2,6-di-tert-butylphenol-catalyzed Stille coupling reaction on heating the mixture of 36 and tributylvinyltin in toluene. Treatment of 125 with excess trimethylamine in THF led to cationic monomer 126. Coupling between 126 and 4,7-dibromo-2,1,3-benzothiadiazole (45) in DMF/H2O/Et3N using Pd(OAc)2/P(o-tolyl)3 as the catalyst afforded P150. Similarly, P151 was synthesized via polymerization between 126 and 1,4-dibromobenzene [80].

Wang’s group [81] synthesized a cationic poly(fluorene vinylene) via the Wittig–Horner reaction (Scheme 1.60). 36 was reacted with morpholine-4-carbaldehyde in the presence of n-BuLi to afford 9,9-bis(6-bromohexyl)-fluorene-2,7-dicarbaldehyde (127) that was then reacted with (1,3-dioxolan-2-yl-methyl)-triphenylphosphonium bromide in the presence of t-BuOK by the Wittig condensation followed by HCl treatment to give 9,9-bis(6-bromohexyl)-fluorene-2,7-diacylaldehyde (128). Coupling reaction between 128 and 1,4-bis(diethoxyphosphinyl methyl)benzene in the presence of t-BuOK led to the neutral polymer P152, which on NMe3 treatment yielded P153. Similarly, P151 was synthesized from 127.
Scheme 1.55  Synthesis of cationic poly(phenylene vinylene)s (P137–P142).
Scheme 1.56 Synthesis of a cationic poly(phenylene vinylene) (P144).
Scheme 1.57  Synthesis of a cationic poly(phenylene vinylene) (P145).

Scheme 1.58  Synthesis of a cationic poly(fluorene vinylene) (P147) and poly(phenylenevinylene-alt-fluorenevinylene)s (P149).
Scheme 1.59 Synthesis of cationic poly(fluorene vinylene) derivatives (P150 and P151).
and 1,4-bis(diethoxyphosphinylmethyl)benzene (Scheme 1.60) [124]. However, it should be noted that P151 obtained from the Heck reaction has a trans-CH=CH configuration, while the polymer obtained from the Wittig–Horner reaction has a random configuration.

1.4.2.2 Anionic Poly(fluorene vinylene)s

Sulfonated poly(fluorene vinylene)s were also synthesized based on the anionic fluorene monomer 60 (Scheme 1.61) [82, 83]. 9,9-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2,7-divinylfluorene (129) was synthesized from 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethoxy)-ethyl)fluorene (44b) via the Stille coupling reaction. Copolymerization between 60 and 129 under the standard Heck reaction conditions directly led to P154. Random copolymerization between 60, 129, and 4,7-dibromo-2,1,3-benzothiadiazole afforded the multicolor polymer (P155) that
1.5 Conclusion

This chapter has summarized a myriad of CPEs with different molecular structures, which have been synthesized via well-established polymerization methods, most commonly by palladium-catalyzed reactions. These CPEs show different solubility

showed fluorescent color variation from green to red upon aggregation [83]. The physical properties of poly(arylene vinylene)-based CPEs are summarized in Table 1.3.

Scheme 1.61 Synthesis of sulfonated poly(fluorene vinylene) s (P154) and (P155).
Table 1.3 Physical properties of poly(arylene vinylene)-based CPEs.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi_F$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P129</td>
<td>Water</td>
<td>425</td>
<td>535</td>
<td>5.0</td>
<td>[69, 70]</td>
</tr>
<tr>
<td>P130</td>
<td>Water</td>
<td>378</td>
<td>480</td>
<td>52</td>
<td>[71]</td>
</tr>
<tr>
<td>P131</td>
<td>Water</td>
<td>426</td>
<td>530</td>
<td>28</td>
<td>[72]</td>
</tr>
<tr>
<td>P132</td>
<td>Water</td>
<td>402</td>
<td>515</td>
<td>54</td>
<td>[72]</td>
</tr>
<tr>
<td>P134</td>
<td>Water</td>
<td>484</td>
<td>593</td>
<td>4.2</td>
<td>[73]</td>
</tr>
<tr>
<td>P137</td>
<td>Water</td>
<td>412</td>
<td>483</td>
<td>18</td>
<td>[74]</td>
</tr>
<tr>
<td>P138</td>
<td>Methanol</td>
<td>370</td>
<td>483</td>
<td>28</td>
<td>[74]</td>
</tr>
<tr>
<td>P139</td>
<td>Water</td>
<td>368</td>
<td>481</td>
<td>15</td>
<td>[74]</td>
</tr>
<tr>
<td>P140</td>
<td>Methanol</td>
<td>404</td>
<td>508</td>
<td>18</td>
<td>[75]</td>
</tr>
<tr>
<td>P141</td>
<td>Methanol</td>
<td>449</td>
<td>551</td>
<td>1.0</td>
<td>[75]</td>
</tr>
<tr>
<td>P142</td>
<td>Methanol</td>
<td>413</td>
<td>470</td>
<td>35</td>
<td>[75]</td>
</tr>
<tr>
<td>P144</td>
<td>Water</td>
<td>449</td>
<td>520</td>
<td>—</td>
<td>[76]</td>
</tr>
<tr>
<td>P145</td>
<td>Water</td>
<td>412</td>
<td>520</td>
<td>—</td>
<td>[77]</td>
</tr>
<tr>
<td>P149</td>
<td>Ethanol</td>
<td>371</td>
<td>488</td>
<td>32</td>
<td>[78]</td>
</tr>
<tr>
<td>P150</td>
<td>Water</td>
<td>385, 515</td>
<td>685</td>
<td>0.50</td>
<td>[79]</td>
</tr>
<tr>
<td>P151</td>
<td>Water</td>
<td>452</td>
<td>515</td>
<td>—</td>
<td>[80]</td>
</tr>
<tr>
<td>P153</td>
<td>Water</td>
<td>459</td>
<td>515</td>
<td>1</td>
<td>[81]</td>
</tr>
<tr>
<td>P154</td>
<td>Water</td>
<td>428</td>
<td>475</td>
<td>56</td>
<td>[82]</td>
</tr>
<tr>
<td>P155</td>
<td>Water</td>
<td>430</td>
<td>472</td>
<td>17</td>
<td>[83]</td>
</tr>
</tbody>
</table>

$^a\lambda_{\text{abs}}$ and $\lambda_{\text{em}}$ are the maximum absorption and emission wavelengths, respectively; $\Phi_F$ is the fluorescence quantum yield.

and optical properties dependent on both side chains and backbones, among which polyfluorene-based CPEs have grown to be the most versatile class. In future, improved molecular design strategy is highly desired to yield new CPEs, especially red-emissive CPEs with high fluorescence quantum yield.

References


