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 (λ_{abs}) and emission (λ_{em}) maxima, and fluorescence quantum yields (Φ_F) are summarized in Tables 1.1–1.3, respectively. However, it should be noted

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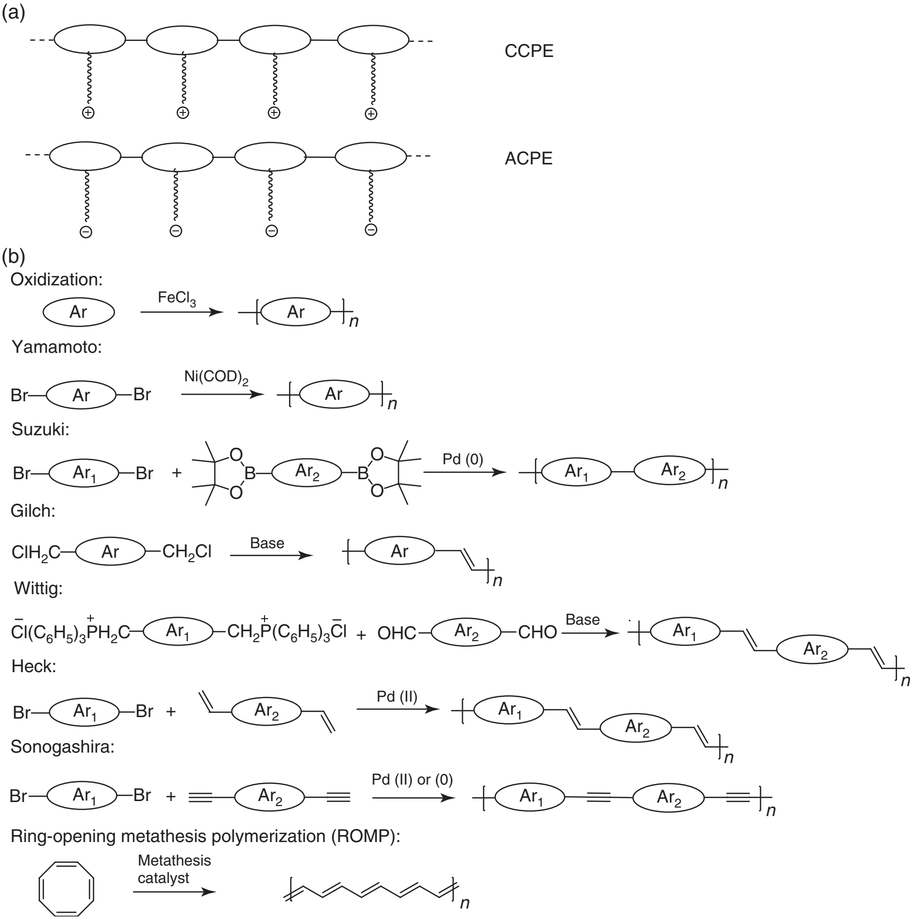


Scheme 1.1 (a) Illustration of typical structures for CCPE and ACPE. (b) Examples of most widely used polymerization methods; Ar, Ar_1, and Ar_2 represent aromatic structures.

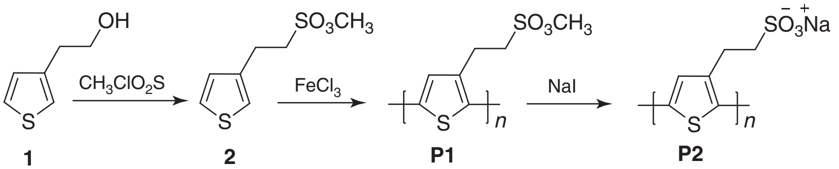
that these properties can be dependent on purification method, molecular weight, and polymer concentration.

1.2
Poly(arylene)s

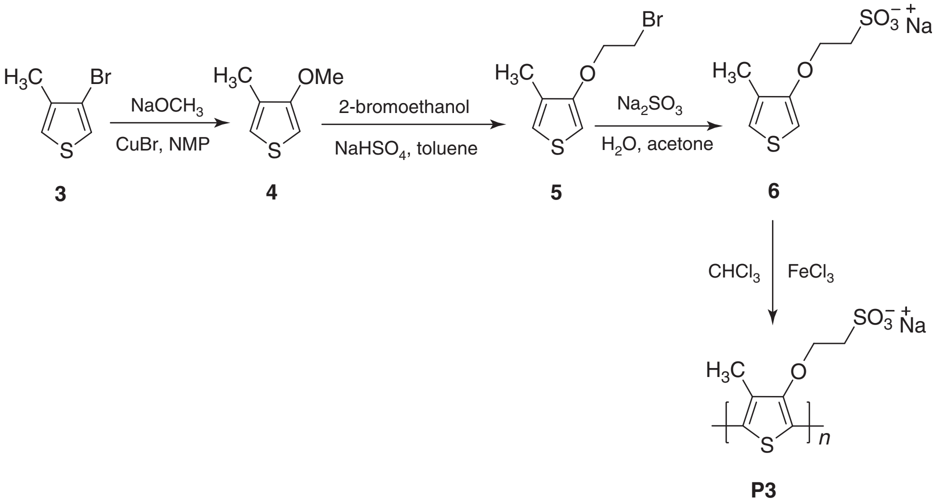
1.2.1
Polythiophenes

1.2.1.1 Anionic Polythiophenes

The first sulfonated polythiophene was synthesized by Wudl and coworkers [84] in 1987. A neutral polythiophene (**P1**, Scheme 1.2) was first synthesized from methyl 2-(thiophen-3-yl)ethanesulfonate (**2**). Subsequent treatment of



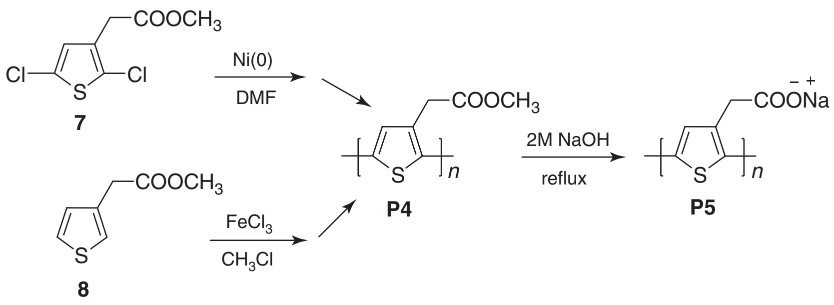
Scheme 1.2 Synthesis of a sulfonated polythiophene (**P2**).



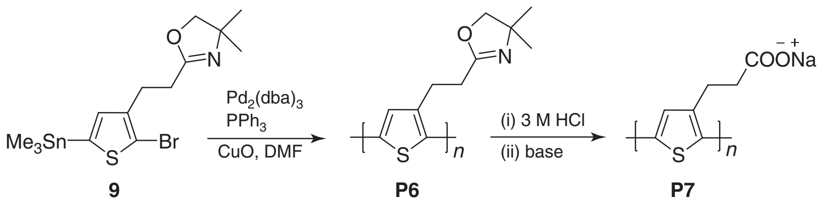
Scheme 1.3 Synthesis of a sulfonated polythiophene (**P3**).

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 $FeCl_3$-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], $FeCl_3$-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



Scheme 1.4 Synthesis of a carboxylated polythiophene (**P5**).



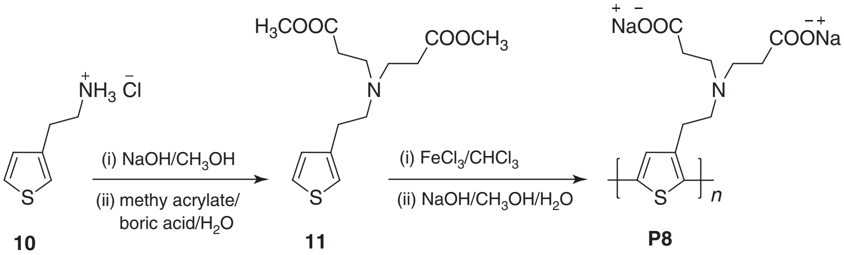
Scheme 1.5 Synthesis of a carboxylated polythiophene (**P7**).

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.

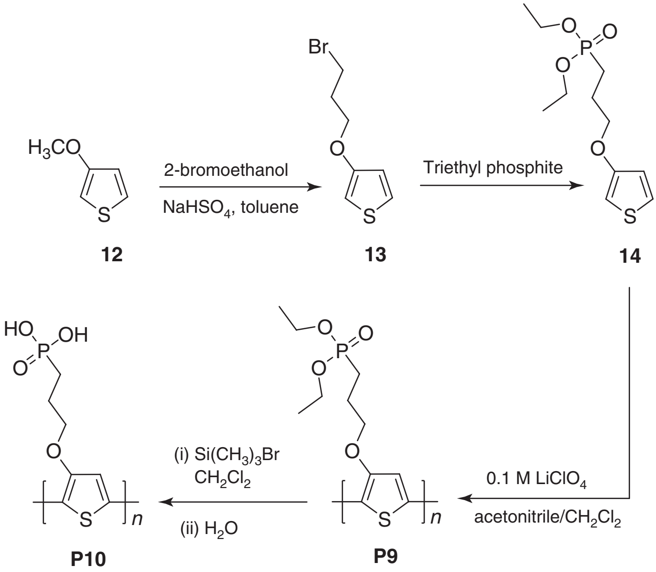
Recently, Wang's group also synthesized a carboxylated polythiophene (**P8**) [6]. As shown in Scheme 1.6, the key monomer **11** was prepared by reacting the salt of 2-(3-thienyl)ethylamine (**10**) with methyl acrylate in the presence of boric acid. **P8** was obtained through oxidative polymerization 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 $LiClO_4$/acetonitrile/CH_2Cl_2 yielded **P9**, which after silyl dealkylation and hydrolysis gave poly(3-(3′-thienyloxy)propanephosphonate) (**P10**).

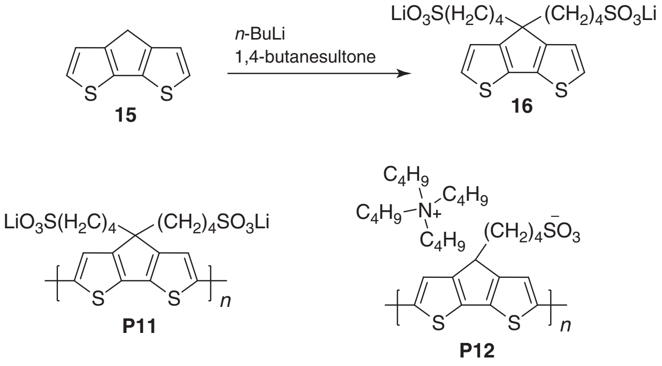
An important series of polythiophene derivatives, poly(cyclopentadithiophene)s, were developed by Zotti's group [7, 90]. As shown in Scheme 1.8, the key anionic monomer **16** was prepared from a one-pot reaction between 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (**15**) and 1,4-butanesultone in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



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-1*H*-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 Bu_4NCl 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

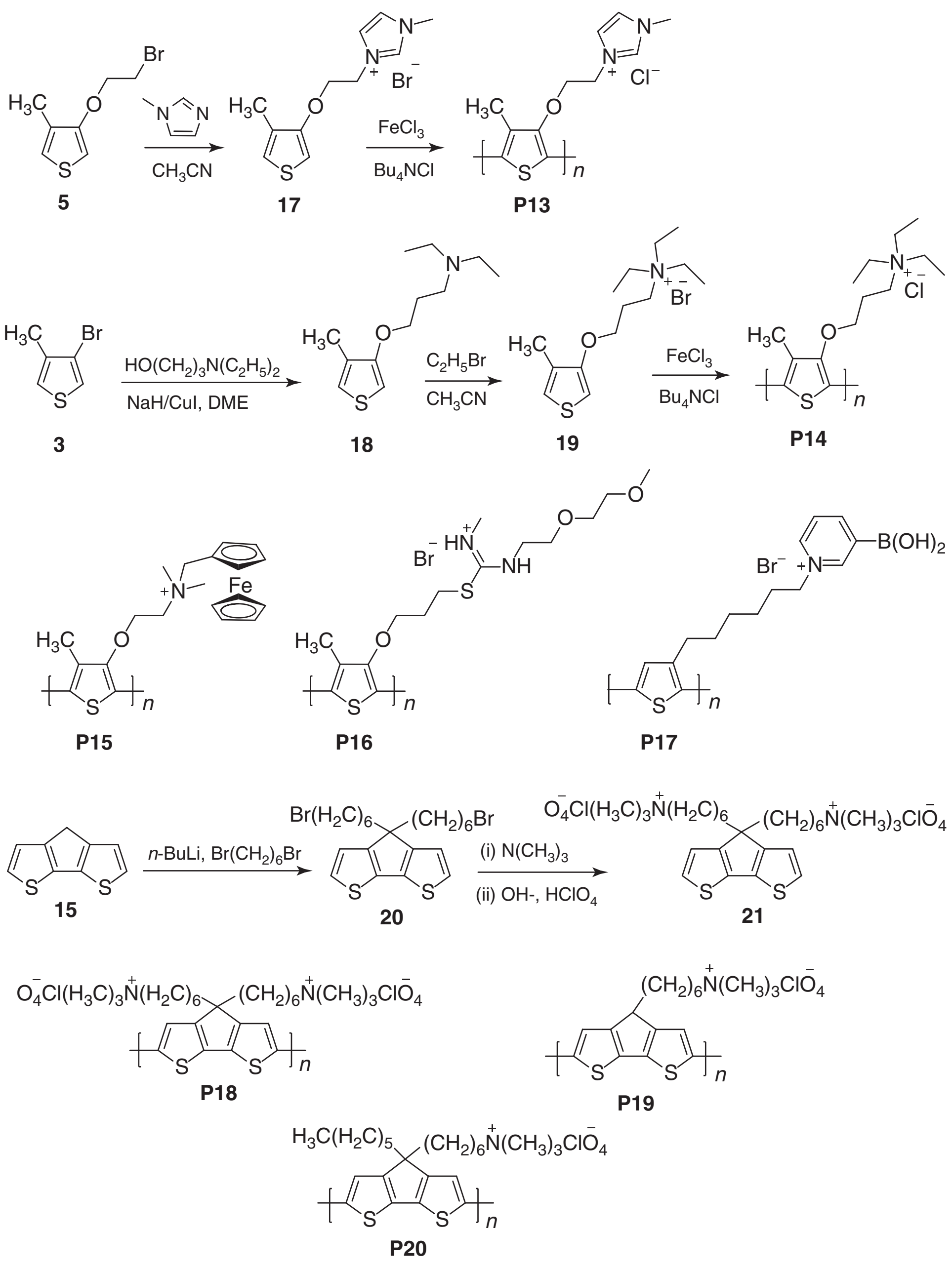
Zwitterionic CPEs contain side groups with anionic and cationic functionalities that are covalently bound to each other. Zwitterionic polythiophenes have been synthesized by Inganäs' group [12, 13]. As shown in Scheme 1.10, **1** was brominated with NBS and tosylated to yield a thiophene derivative **22**. 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 CH_2Cl_2, the salt counterpart of **24** was directly polymerized in $CHCl_3$ using anhydrous $FeCl_3$ 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

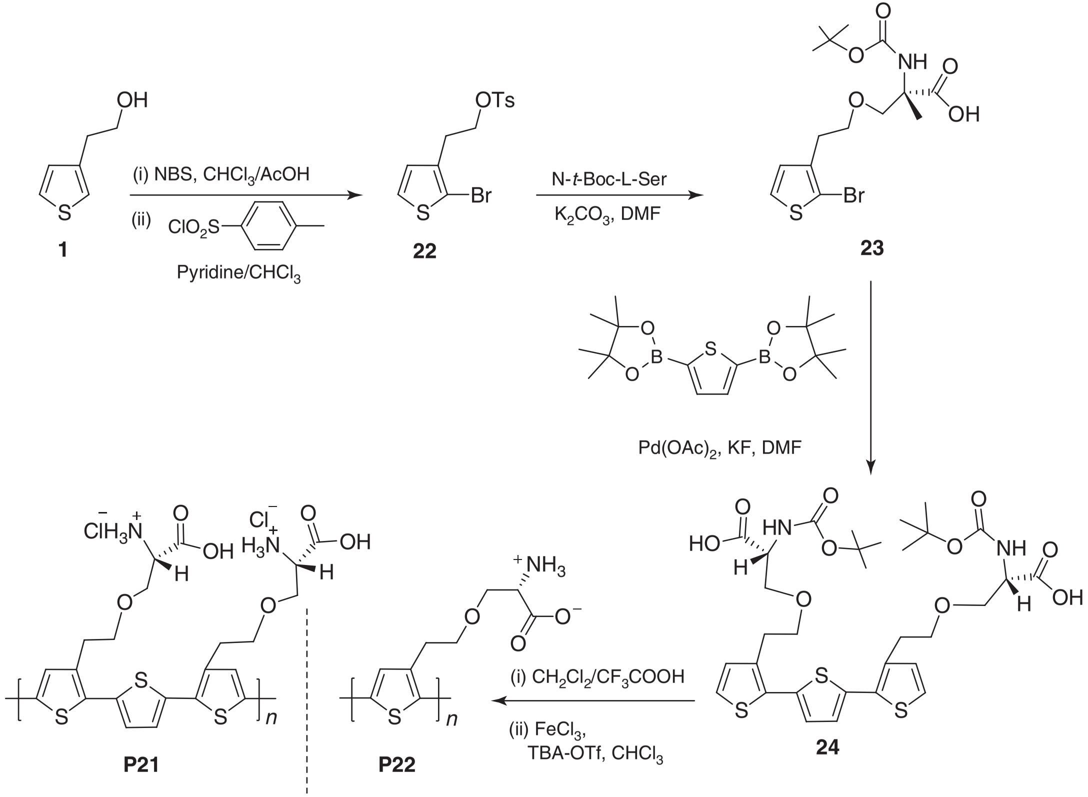
1.2.2.1 Anionic Poly(*p*-phenylene)s

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].

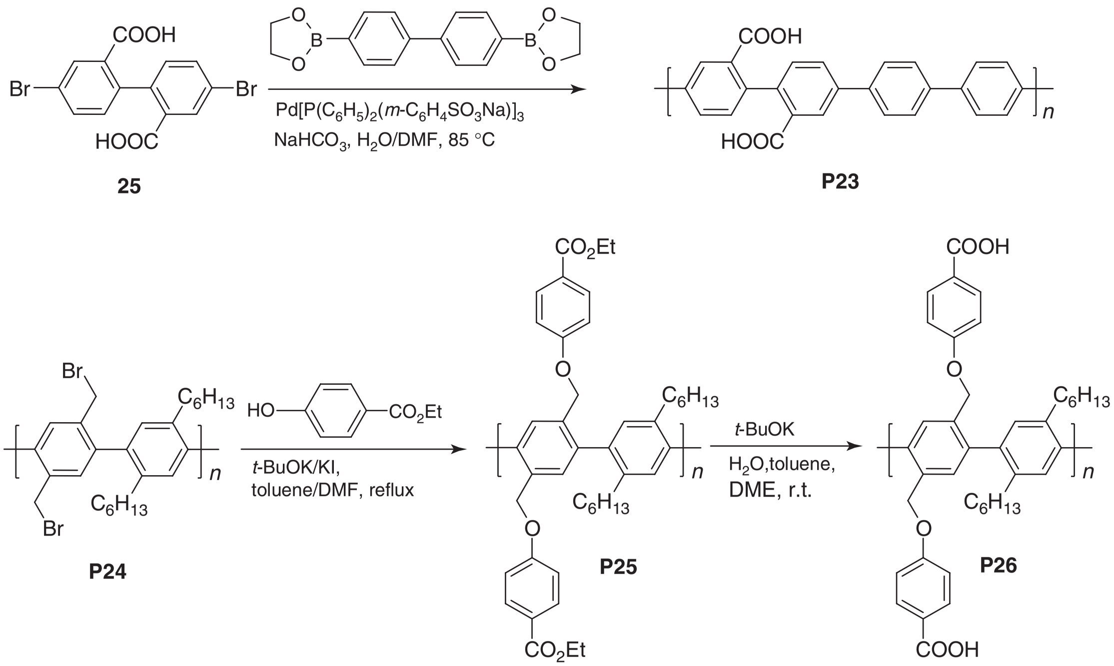
The first sulfonated poly(*p*-phenylene) **P28** was designed and synthesized by Wegner's group through a postpolymerization method (Scheme 1.12) [100].



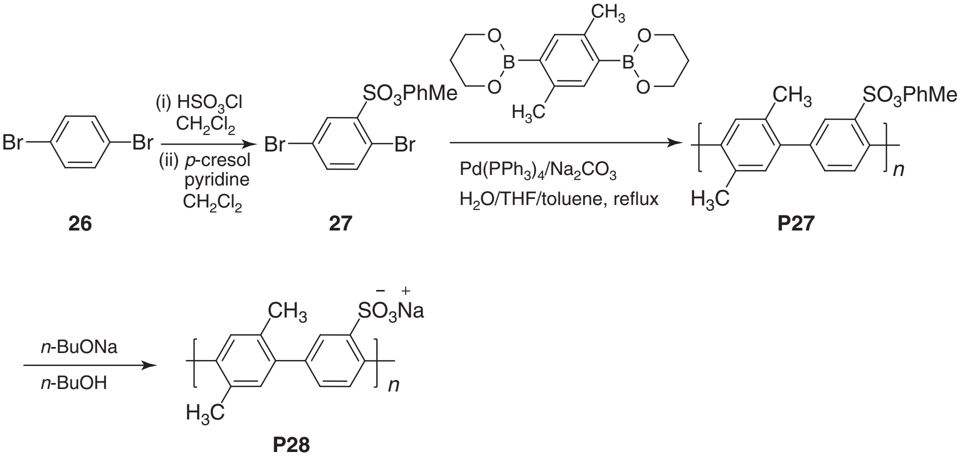
Scheme 1.9 Synthesis of cationic polythiophenes and poly(cyclopentadithiophene)s (**P13**–**P20**).



Scheme 1.10 Synthesis of zwitterionic polythiophenes (**P21**) and (**P22**).



Scheme 1.11 Synthesis of carboxylated poly(*p*-phenylene)s (**P23**) and (**P26**).



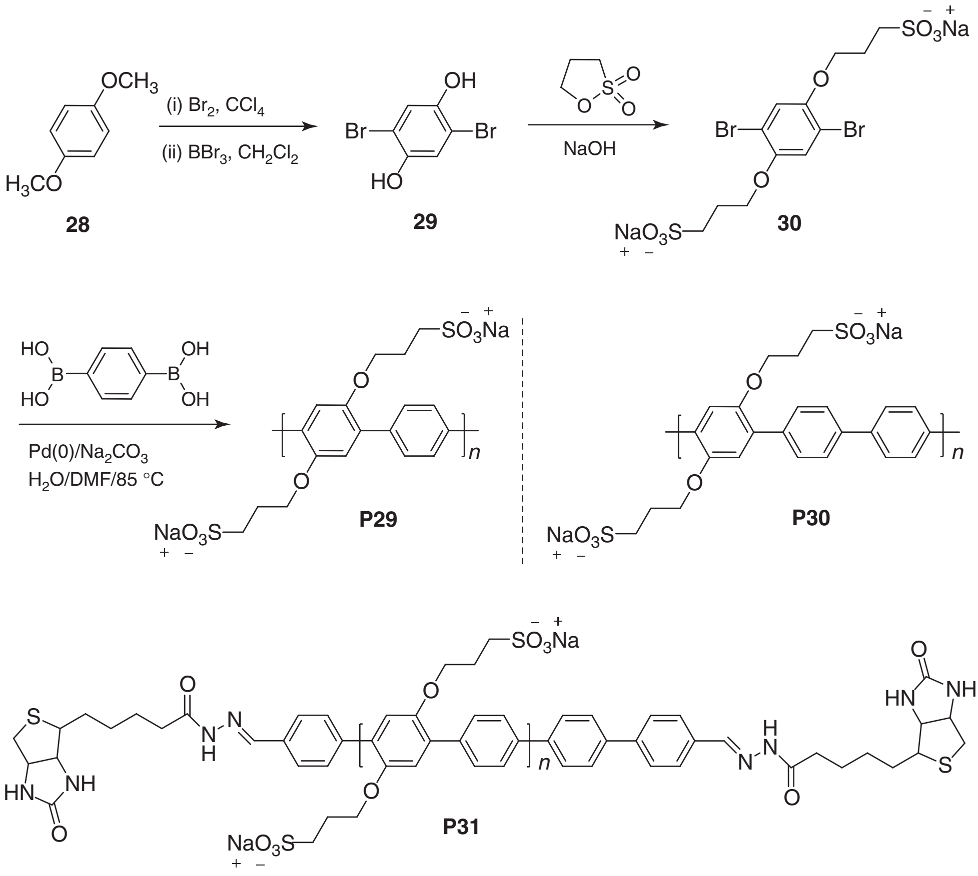
Scheme 1.12 Synthesis of a sulfonated poly(*p*-phenylene) (**P28**).

The key monomer **27** was synthesized via chlorosulfonation of 1,4-dibromo benzene (**26**) with chlorosulfonic acid, followed by treatment with *p*-cresol in the presence of pyridine. The Suzuki coupling between **27** and 2,2′-(2,5-dimethyl-1,4-phenylene)-bis(1,3,2-dioxaborinane) afforded **P27**. Saponification of **P27** by BuONa in *n*-BuOH led to **P28**, which is soluble in DMSO.

A direct approach to sulfonated poly(*p*-phenylene)s was reported by Reynold's group [14]. The key sulfonate monomer **30** was prepared by treating 2,5-dibromobenzene-1,4-diol (**29**) with propane sultone under basic condition (Scheme 1.13). The Suzuki polymerization between **30** and 1,4-phenyldiboronic acid yielded **P29** and, similarly, between **30** and 4,4′-biphenyldiboronic acid ester yielded **P30** [15]. To endow **P29** with biorecognition ability, endcapping reaction was carried out by adding 4-bromobenzaldehyde at the end of the Suzuki polymerization to afford a polymer with aldehyde end groups. The biotin-attached polymer **P31** was obtained through hydrazone formation (−CH=N=NH−) between the aldehyde groups and biotin hydrazide in aqueous solution [16].

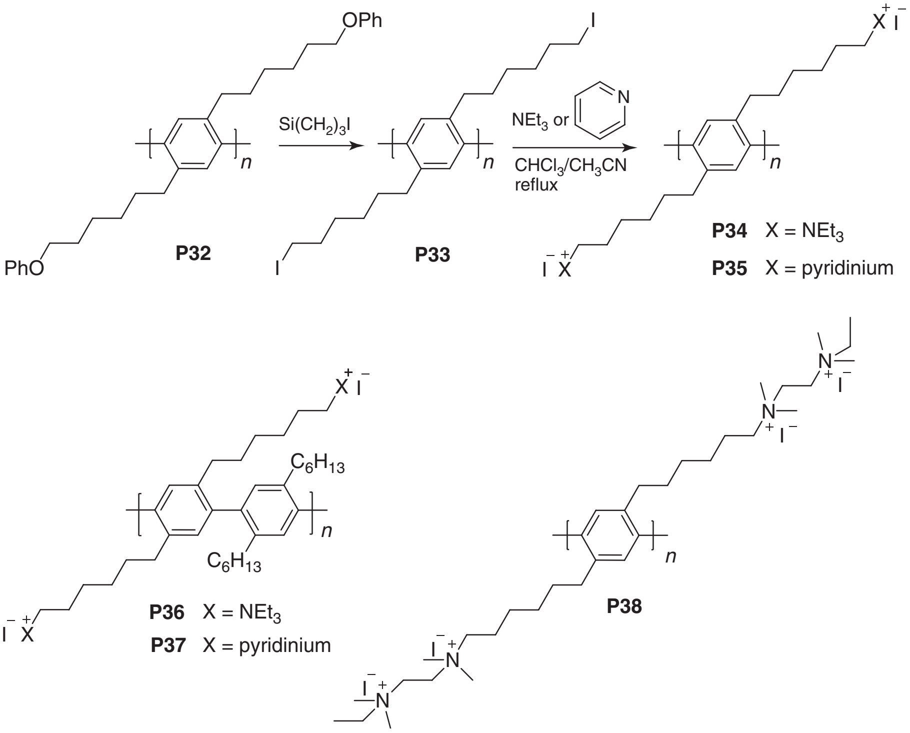
1.2.2.2 Cationic Poly(*p*-phenylene)s

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 **P32** with trimethylsilyl iodide, **P33** was obtained with alkyl iodide side chains. Subsequent reaction with triethylamine (NEt_3) or pyridine gave the cationic poly(*p*-phenylene)s (**P34** and **P35**) with nearly 100% degree of quaternization. **P36**–**P38** were synthesized via the same postpolymerization strategy. Particularly, **P38** with four cationic charges per repeat unit was prepared from consecutive quaternization of **P33** with tetramethylethylenediamine and iodoethane [102].



Scheme 1.13 Synthesis of sulfonated poly(*p*-phenylene)s (**P29**–**P31**).

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 dibromohydroquinone (**29**) in the presence of 2-chloroethyldiethylamine 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 $PdCl_2(PPh_3)_2$ as the catalyst gave the neutral polymer, which on treatment with bromoethane yielded **P41**.

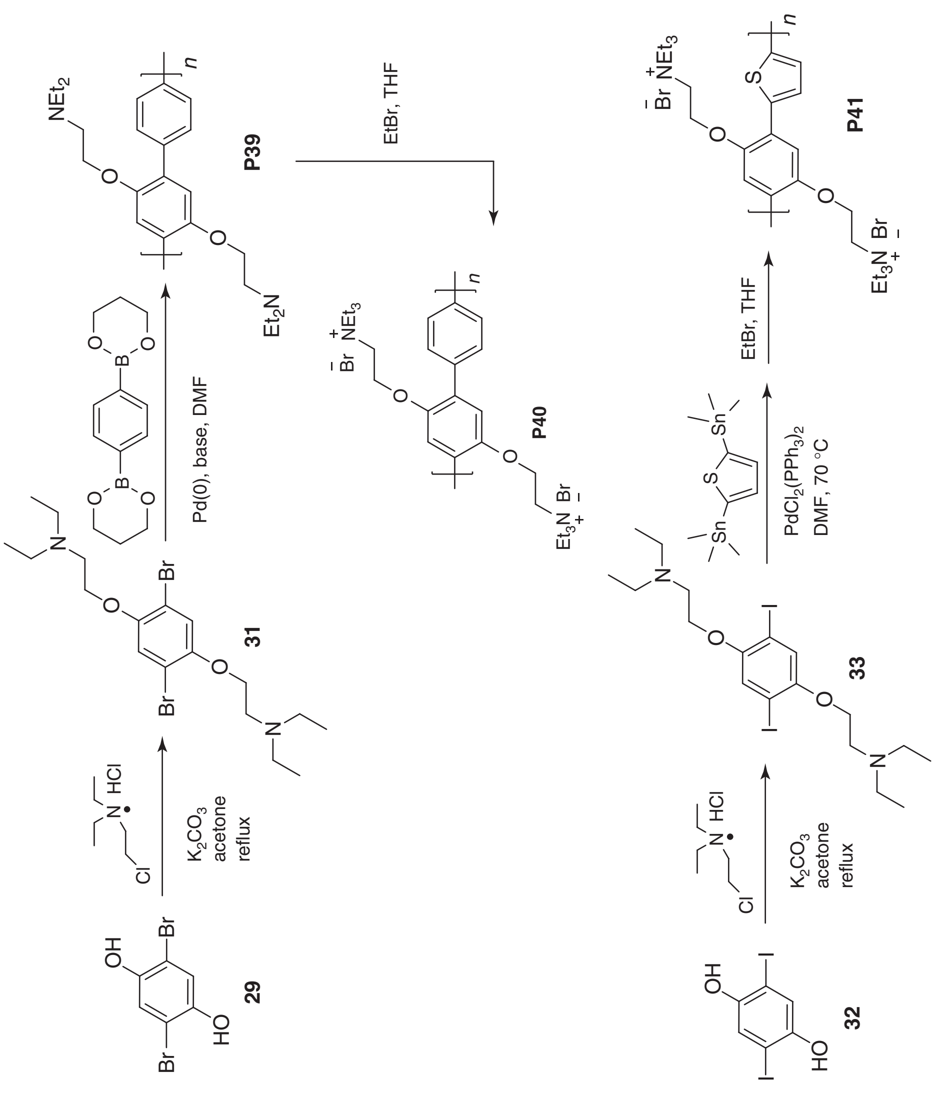


Scheme 1.14 Synthesis of cationic poly(*p*-phenylene)s (**P34**–**P38**).

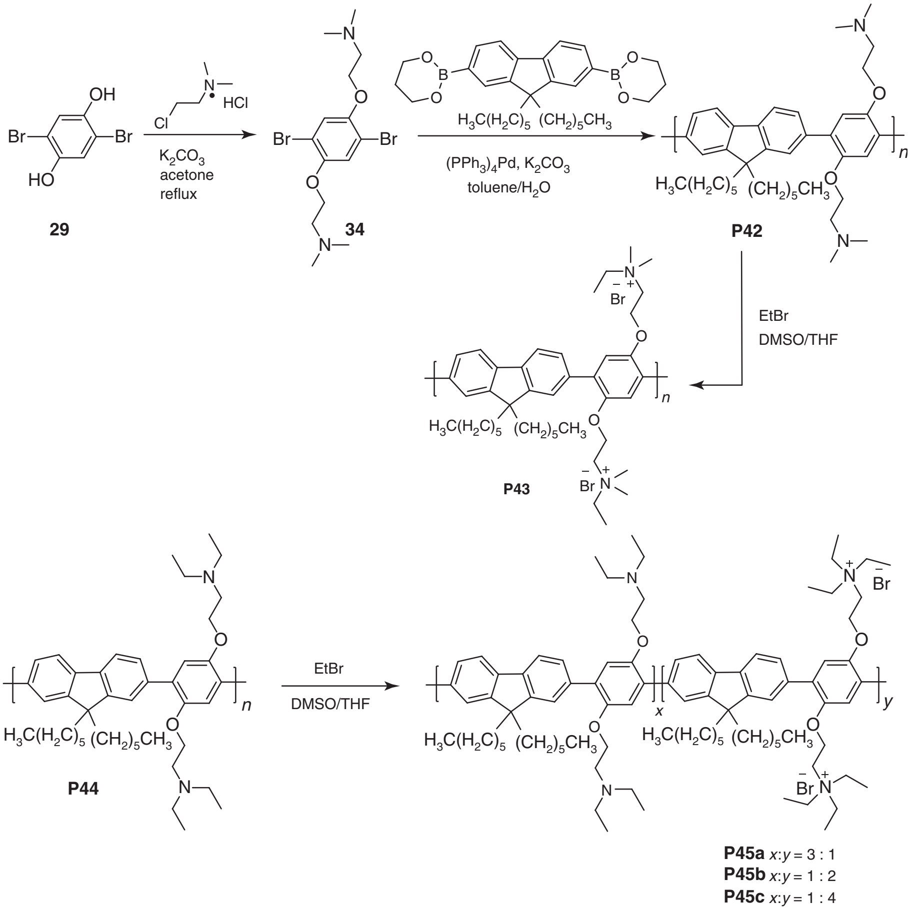
1.2.3
Poly(fluorene)s

1.2.3.1 Cationic Poly(fluorene)s

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.



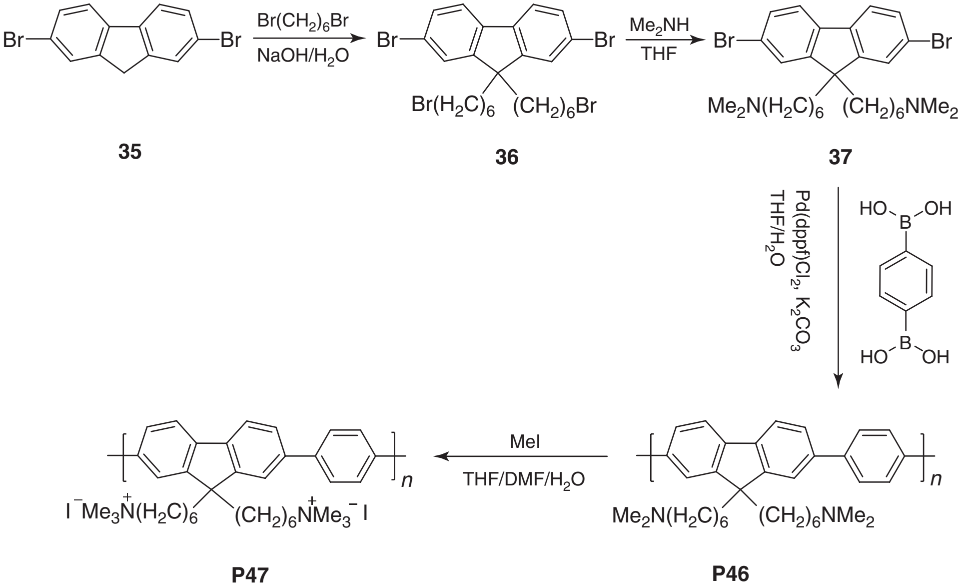
Scheme 1.15 Synthesis of cationic poly(*p*-phenylene)s (**P40**) and (**P41**).



Scheme 1.16 Synthesis of cationic polyfluorenes (**P43**) and (**P45a**–**c**).

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 (Me_2NH) 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

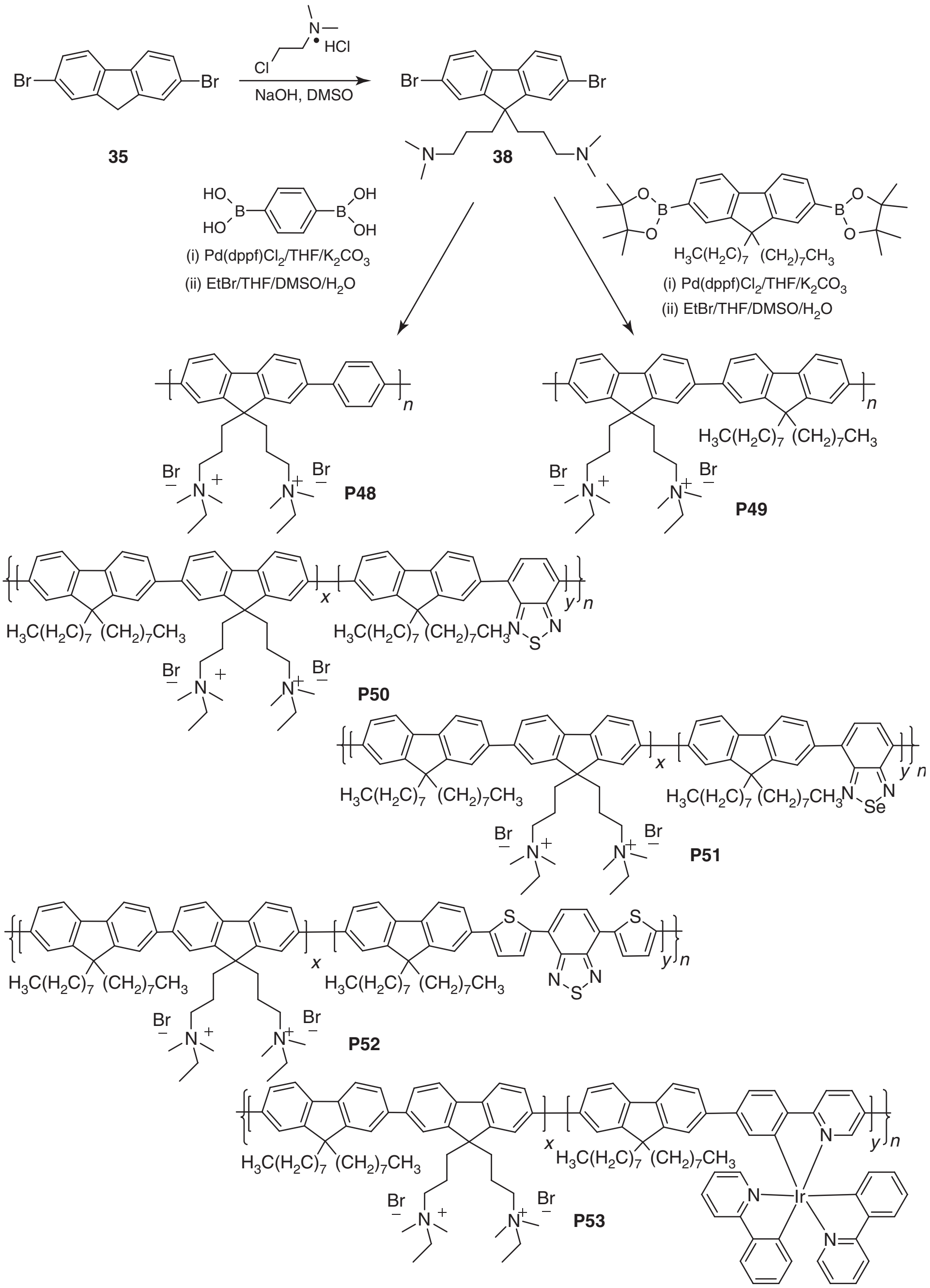


Scheme 1.17 Synthesis of a cationic polyfluorene (**P47**).

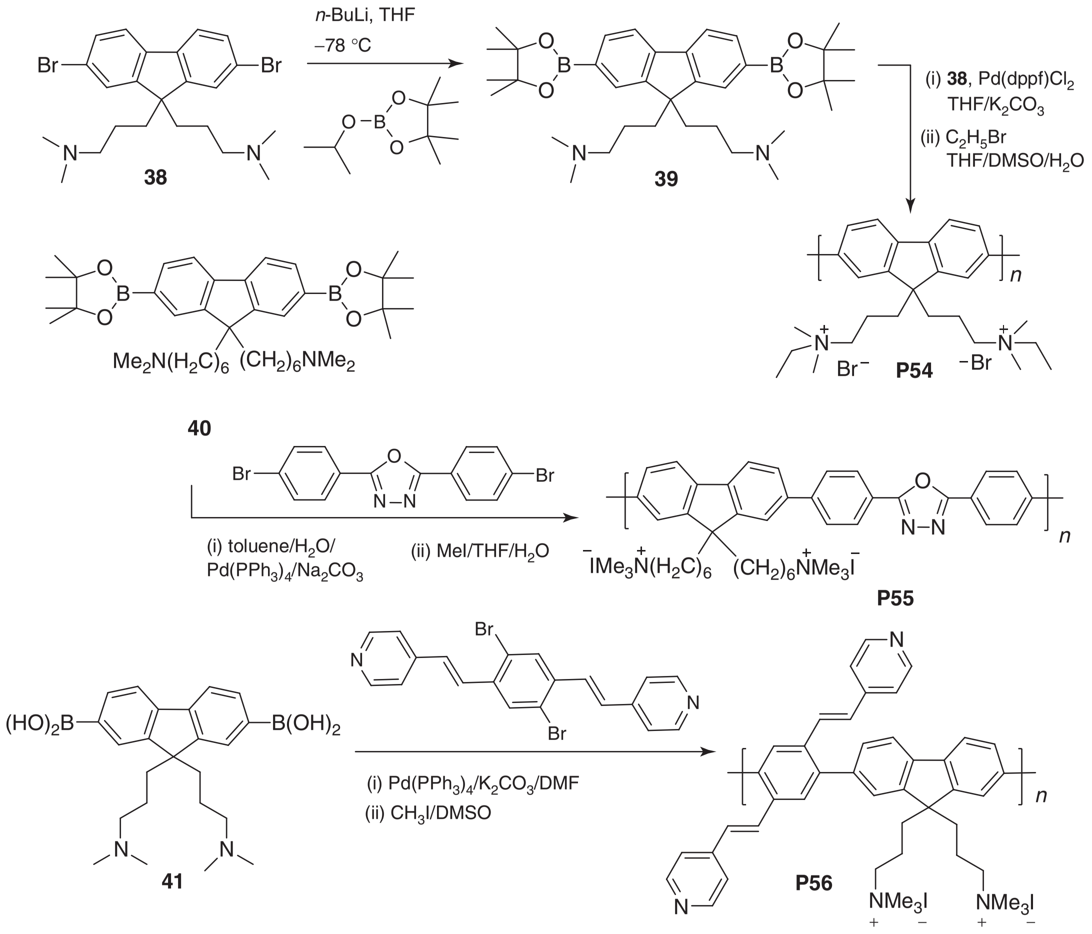
mixture in the presence of excess NaOH. The Suzuki copolymerization between **38** and different diboronate monomers followed by treatment with bromoethane led to blue-fluorescent alternating polyfluorenes (**P48** and **P49**). To fine-tune the polymer emission, random copolymerization between **38**, 2,2′-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), and other dibromide monomers such as 2,1,3-benzothiadiazole, 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].

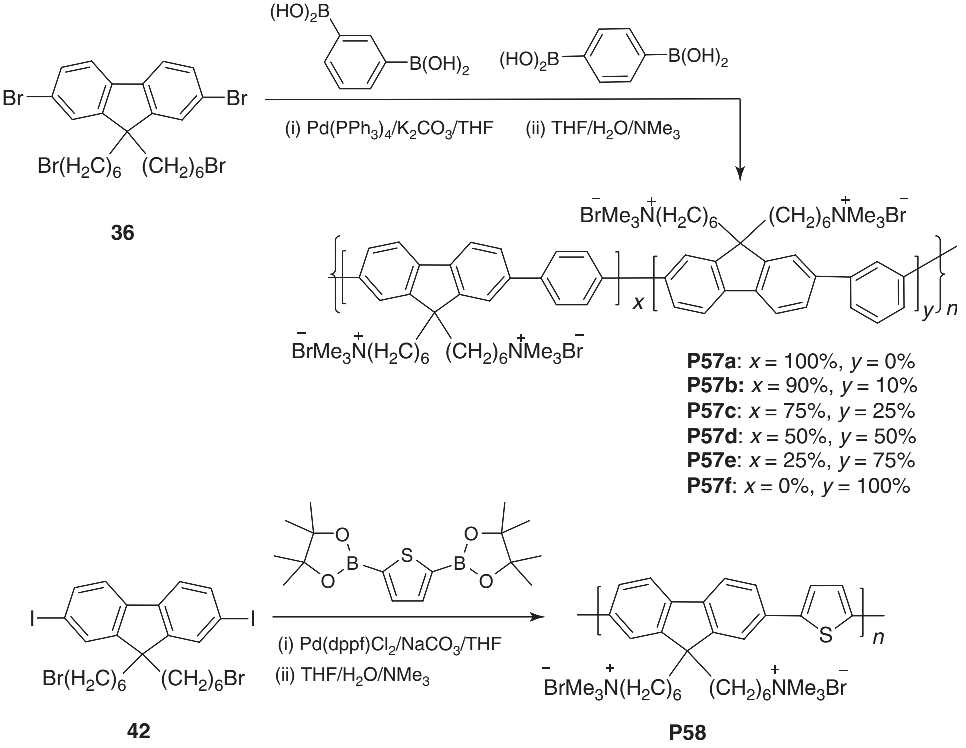
To solve the problem of incomplete quaternization for polymers containing side chains with terminal tertiary amine, a new postpolymerization method was



Scheme 1.18 Synthesis of cationic polyfluorenes (**P48**–**P53**).



Scheme 1.19 Synthesis of cationic polyfluorenes (**P54**–**P56**).

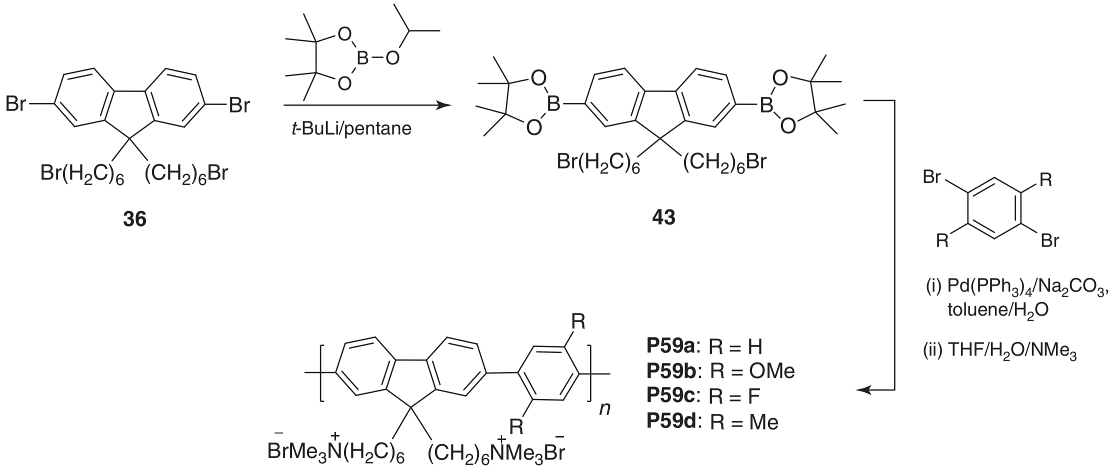


P57a: $x = 100\%$, $y = 0\%$
P57b: $x = 90\%$, $y = 10\%$
P57c: $x = 75\%$, $y = 25\%$
P57d: $x = 50\%$, $y = 50\%$
P57e: $x = 25\%$, $y = 75\%$
P57f: $x = 0\%$, $y = 100\%$

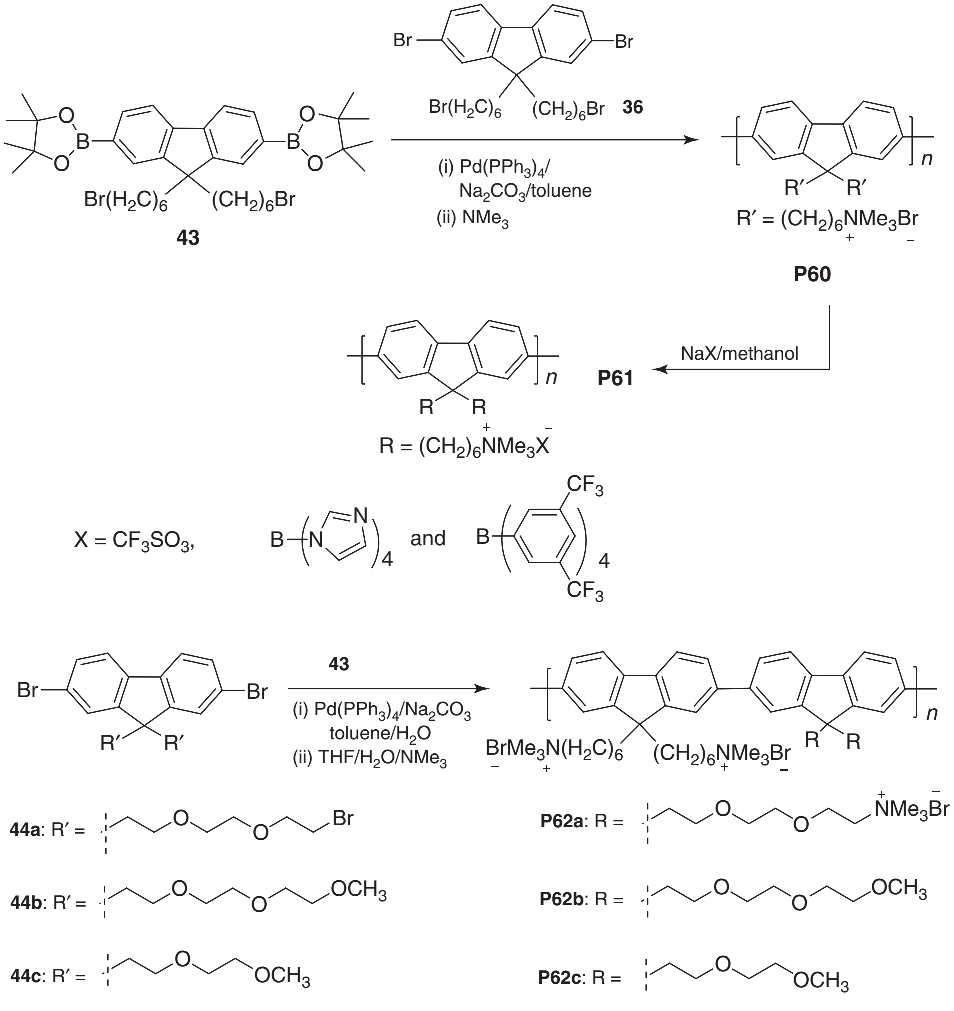
Scheme 1.20 Synthesis of cationic poly(fluorene-*co*-phenylene)s (**P57a–f**) and a poly(fluorene-*co*-thiophene) (**P58**).

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



Scheme 1.21 Synthesis of cationic polyfluorenes (**P59a–d**).

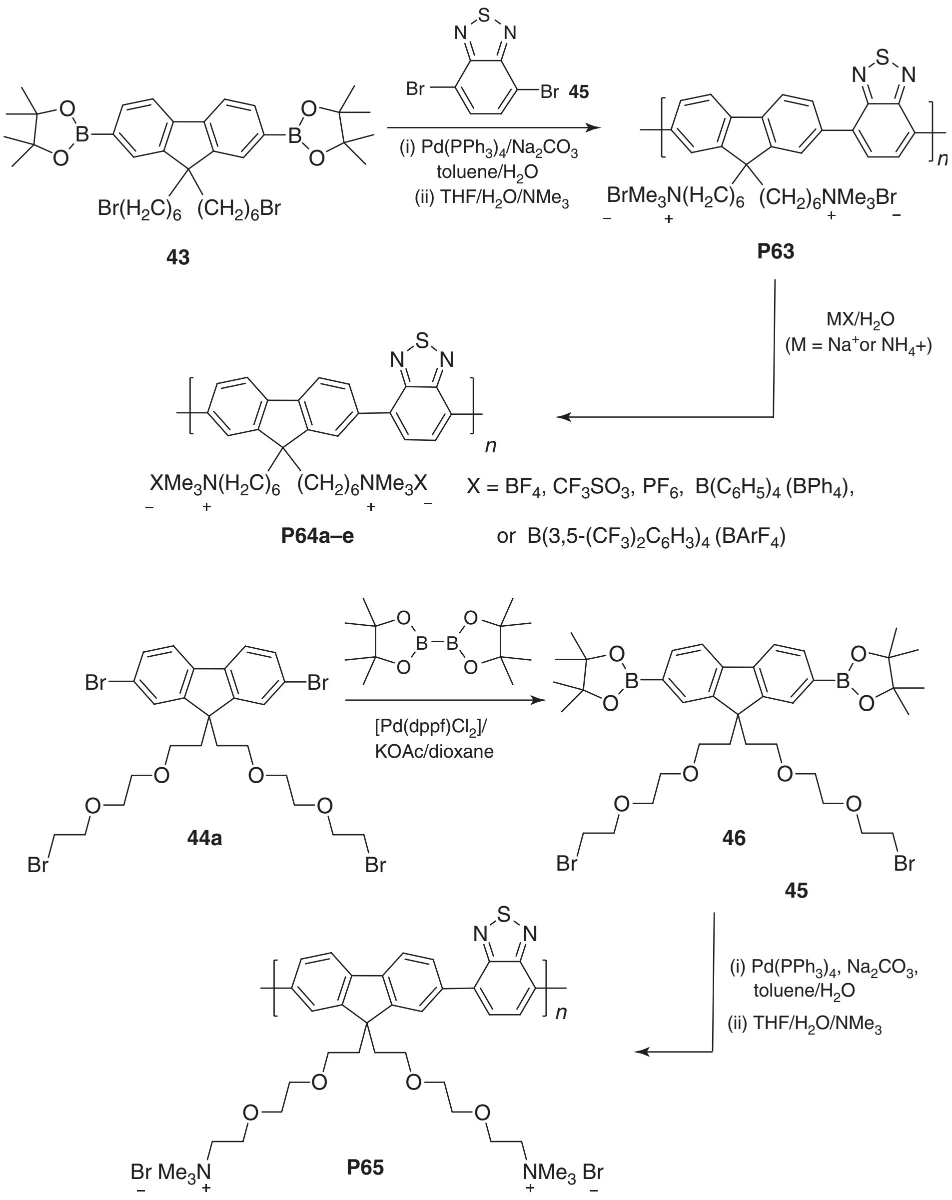


Scheme 1.22 Synthesis of cationic polyfluorenes (**P60**), (**P61**), and (**P62a**–**c**).

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



Scheme 1.23 Synthesis of cationic polyfluorenes (**P63**), (**P64a–e**), and (**P65**).

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-(2-bromoethoxy)ethoxy)ethyl)-9*H*-fluorene-2,7-diyl)bis(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].

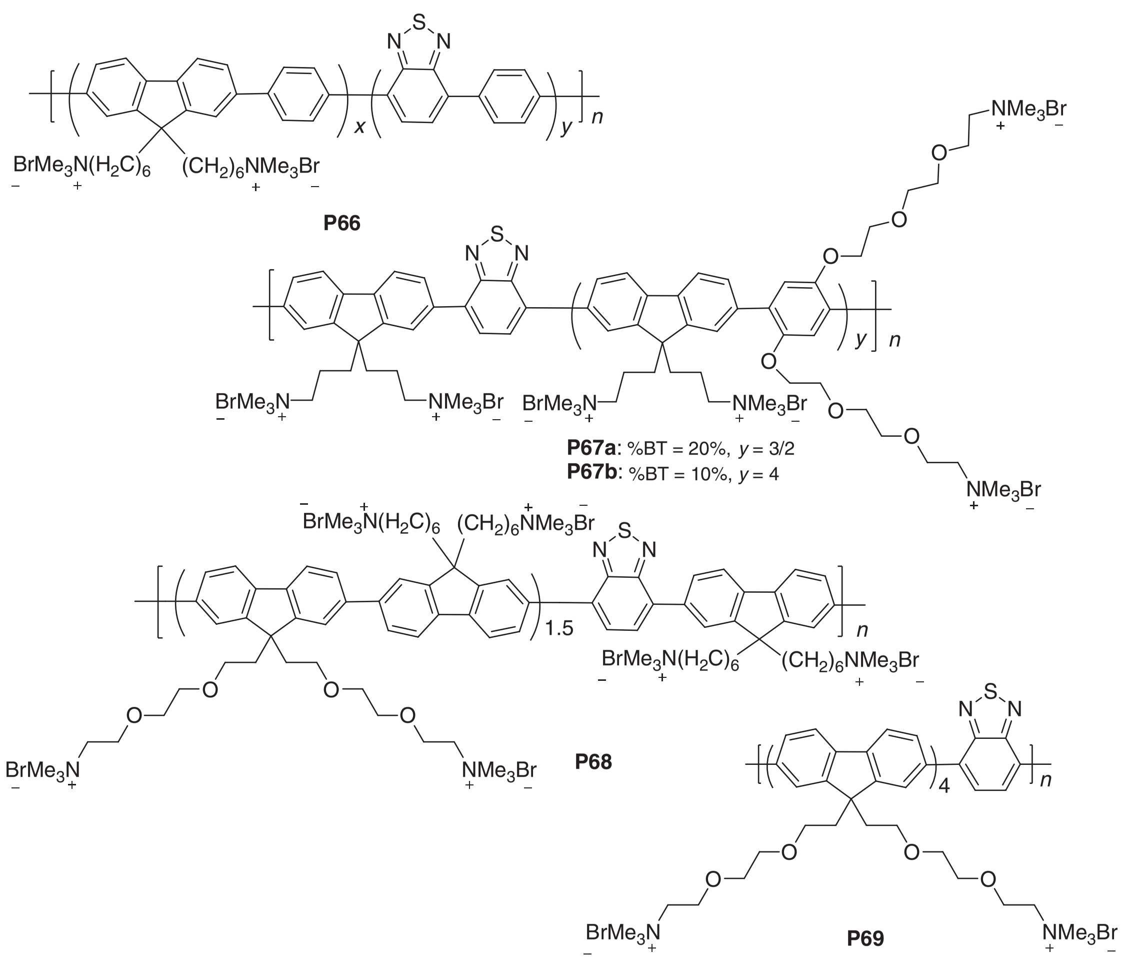
Cationic polyfluorenes with dendritic or bulky water-soluble side chains were also synthesized [36, 113]. As shown in Scheme 1.25, the polymers were synthesized by coupling Boc-protected dendritic fluorene monomers (**47** or **49**), Boc-protected fluorene (**48**) with 1,4-bisphenyl-(5,5-dimethyl-1,3,2-dioxaborinane) at a feed ratio of 1 : 1 : 2 in K_2CO_3/Pd(dppf)Cl_2/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)-10*H*-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**.

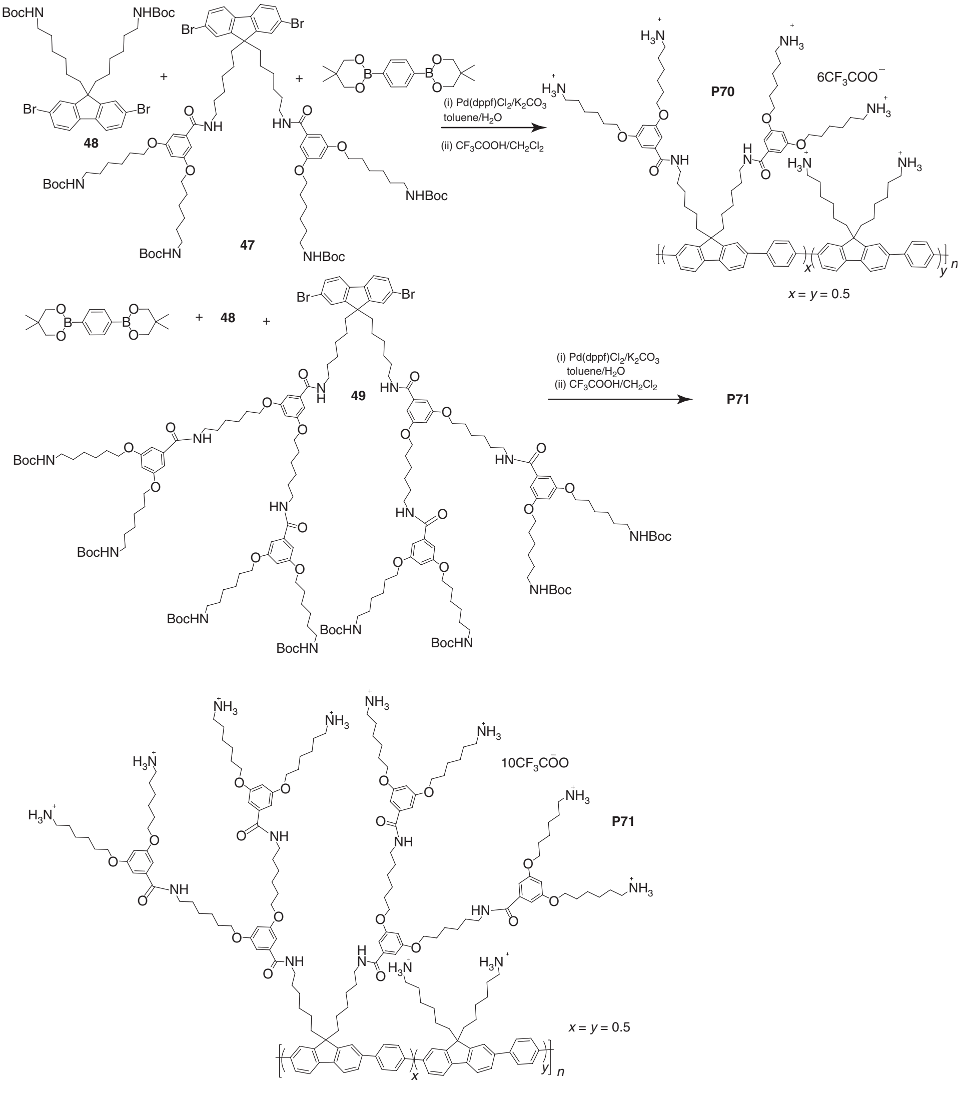
Hyperbranched cationic polyfluorene derivatives have been developed by Liu’s group [38–40]. As shown in Scheme 1.27, the diyne monomer, 9,9′-bis(6-bromohexyl)-2,7-diethynylfluorene (**52**), was synthesized from **36** via the Sonagashira coupling reaction in two steps. Homopolycyclotrimerization of **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)s

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].

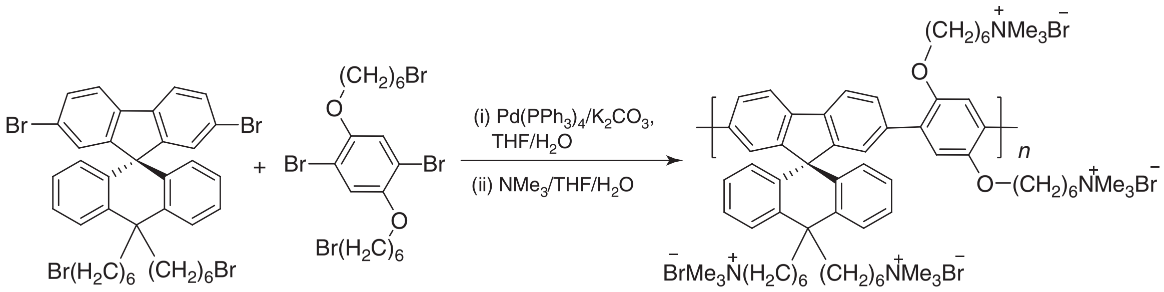


Scheme 1.24 Structures of cationic polyfluorenes (**P66**–**P69**).



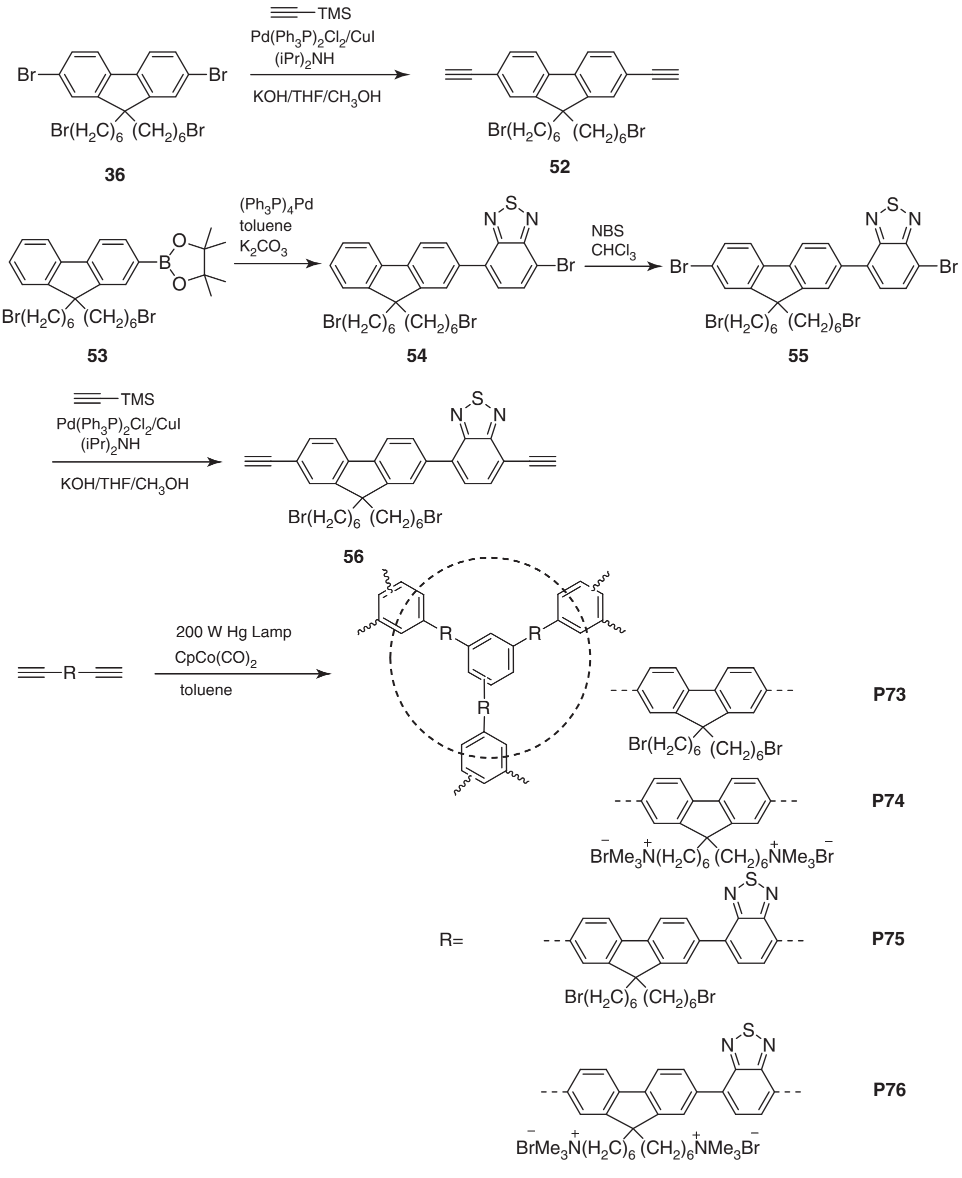
Scheme 1.25 Synthesis of cationic polyfluorenes (**P70**) and (**P71**).

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-butane sultone 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.



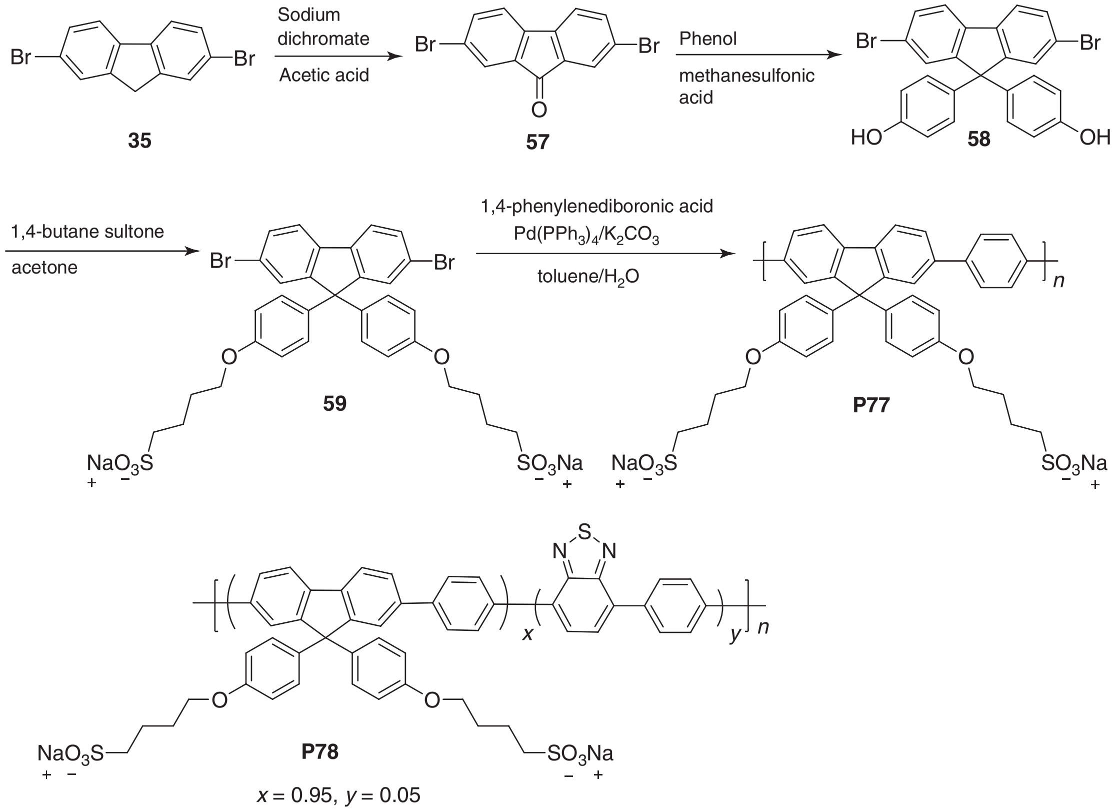
50 **51** **P72**

Scheme 1.26 Synthesis of a cationic polyfluorene (**P72**).

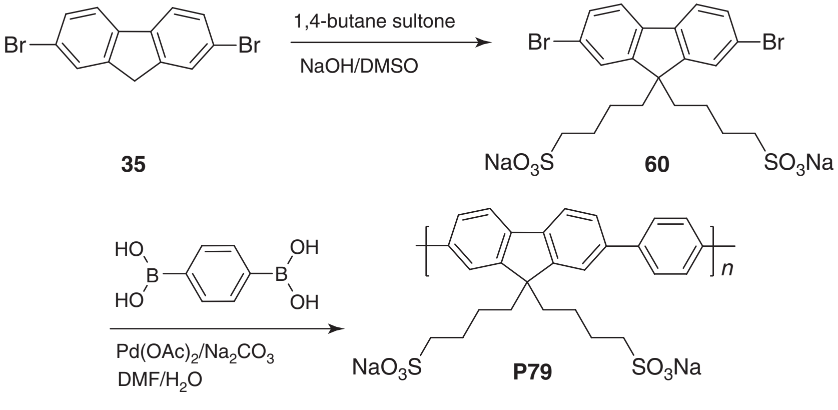


Scheme 1.27 Synthesis of hyperbranched cationic polyfluorenes (**P74**) and (**P76**).

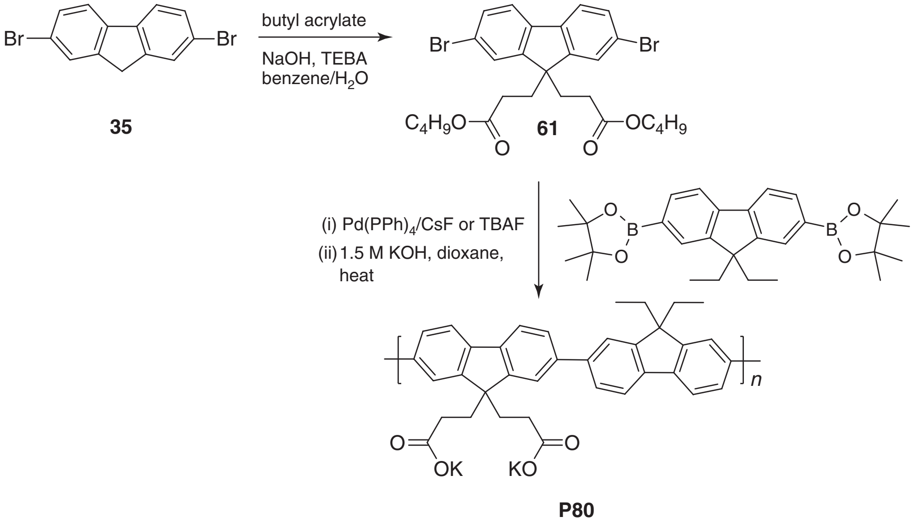
A carboxylated polyfluorene was synthesized by Reynolds' group [44]. The key monomer, 2,7-dibromofluorene-9,9-dipropanoic acid-dibutylester (**61**), was synthesized from 2,7-dibromofluorene (**35**) via the Michael addition of the bridge carbon with butyl acrylate (Scheme 1.30) in the presence of triethylbenzyl ammonium chloride (TEBA). **61** was copolymerized with 2,2′-(9,9-diethyl-



Scheme 1.28 Synthesis of anionic polyfluorenes (**P77**) and (**P78**).



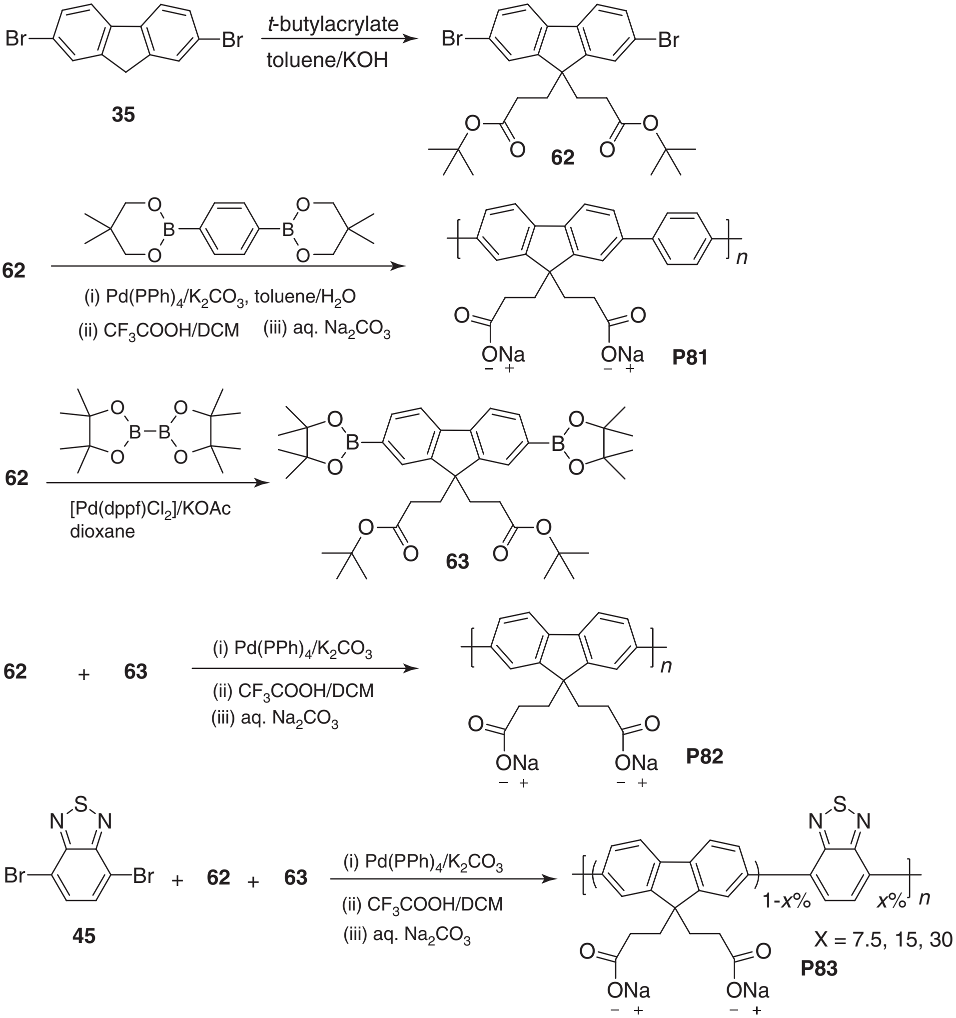
Scheme 1.29 Synthesis of a sulfonated polyfluorene (**P79**).



Scheme 1.30 Synthesis of a carboxylated polyfluorene (**P80**).

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**.

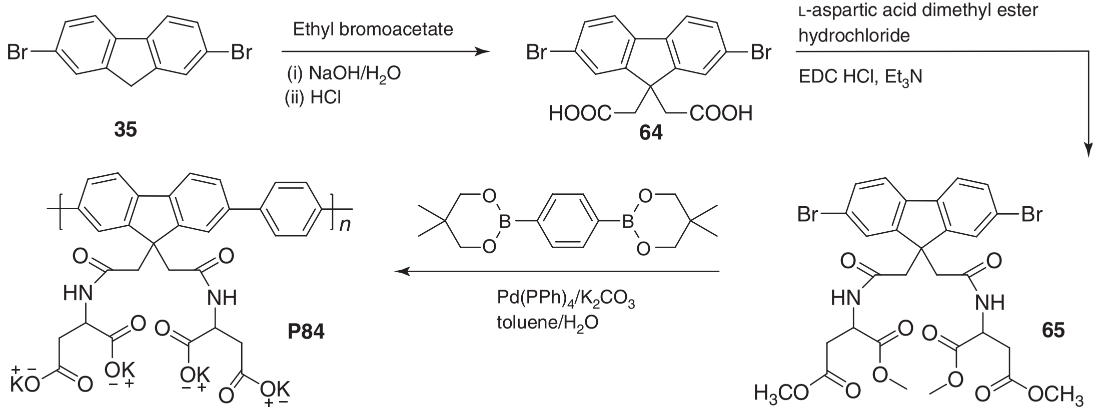
Carboxylated polyfluorenes [45, 46, 114] were also synthesized from 2,7-dibromo-9,9-bis(3′-(*tert*-butyl propanoate))fluorene (**62**), which was synthesized via direct alkylation of 2,7-dibromofluorene (**35**) with *tert*-butylacrylate in a mixture of toluene and aqueous KOH (Scheme 1.31). Polymerization between **62** and 1,4-bisphenyl-(5,5-dimethyl-1,3,2-dioxaborinane) was conducted under



Scheme 1.31 Synthesis of carboxylated polyfluorenes (**P81**–**P83**).

the standard Suzuki coupling condition, which was followed by hydrolysis in CF_3COOH/CH_2Cl_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-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC · HCl) in dry dichloromethane. The Suzuki polymerization between **65** and 1,4-bisphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) yielded **P84** directly because of *in situ* hydrolysis of the carboxylic esters during polymerization.

A phosphonated polyfluorene was also synthesized [48]. The key monomer, 2,7-dibromo-9,9-bis(3-diethoxylphosphorylpropyl)fluorene (**67**), was synthesized from 2,7-dibromo-9,9-bis(3′-bromopropyl)-fluorene (**66**) (Scheme 1.33) [115]. Treatment of **67** with trimethylsilyl bromide and subsequently methanol yielded 2,7-dibromo-9,9-bis(3′-phosphonic acid propyl)fluorene (**68**). The Suzuki copolymerization between **68** and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene with Pd(dppf)Cl_2 as catalyst in DMF and Na_2CO_3 aqueous solution gave **P85** as yellow powder.

1.2.3.3 Zwitterionic Poly(fluorene)s

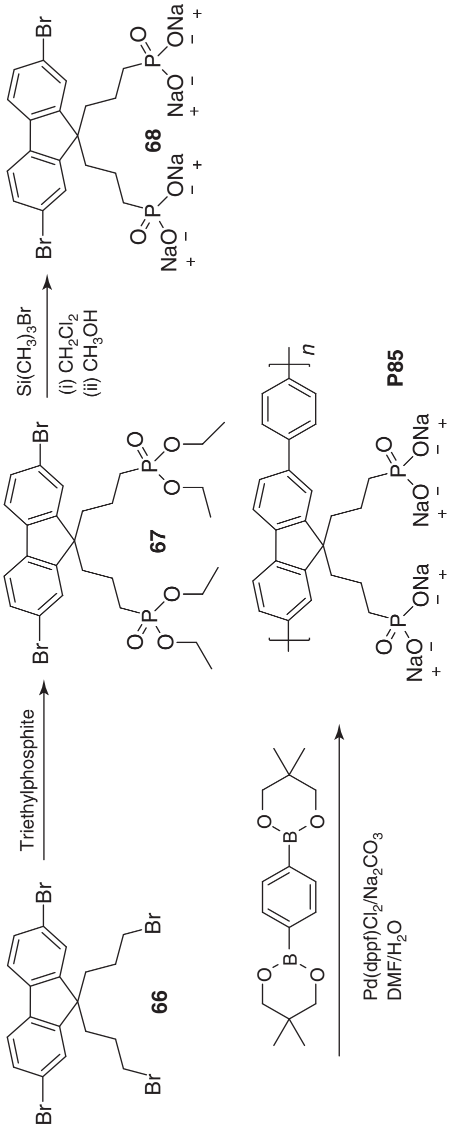
As compared to cationic and anionic polyfluorenes, zwitterionic polyfluorenes have been less developed. However, they have been found useful as electron-transporting/injecting materials in organic light-emitting diodes (OLEDs) [49, 50]. Huck's group synthesized **P87** of which the repeat unit contains a zwitterionic fluorene and a neutral fluorene (Scheme 1.34). The Suzuki polymerization between 2,7-dibromo-9,9-bis((*N,N*-dimethylamino)ethyl)fluorene (**69**) and 2,7-bis-(1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene led to the neutral polymer **P86** with terminal tertiary amine. Quaternization of **P86** with 1,4-butane sultone in THF/methanol mixture yielded **P87**, which was soluble in methanol and DMSO. Meanwhile, Huang's group also synthesized a zwitterionic polyfluorene homopolymer (**P89**, Scheme 1.35) using a similar postpolymerization strategy. Different from **P87** and **P89** with zwitterions on the same structural unit, **P90** was synthesized to have both cationic and anionic structural units (Scheme 1.36). **P90** is soluble in water and partially soluble in DMF and DMSO [24]. The physical properties of poly(arylene)-based CPEs are summarized in Table 1.1.

1.3
Poly(arylene ethynylene)s

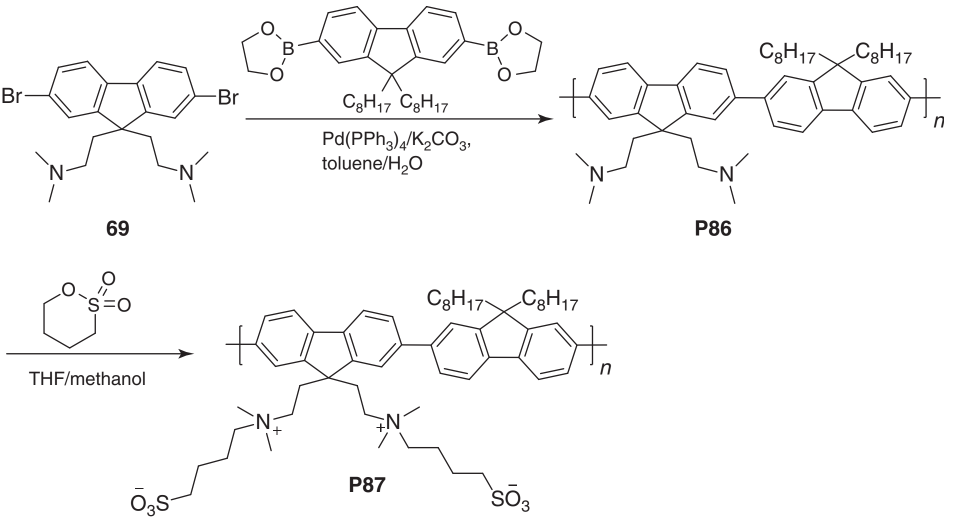
1.3.1
Poly(phenylene ethynylene)s

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-dioidobenzoic 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**).

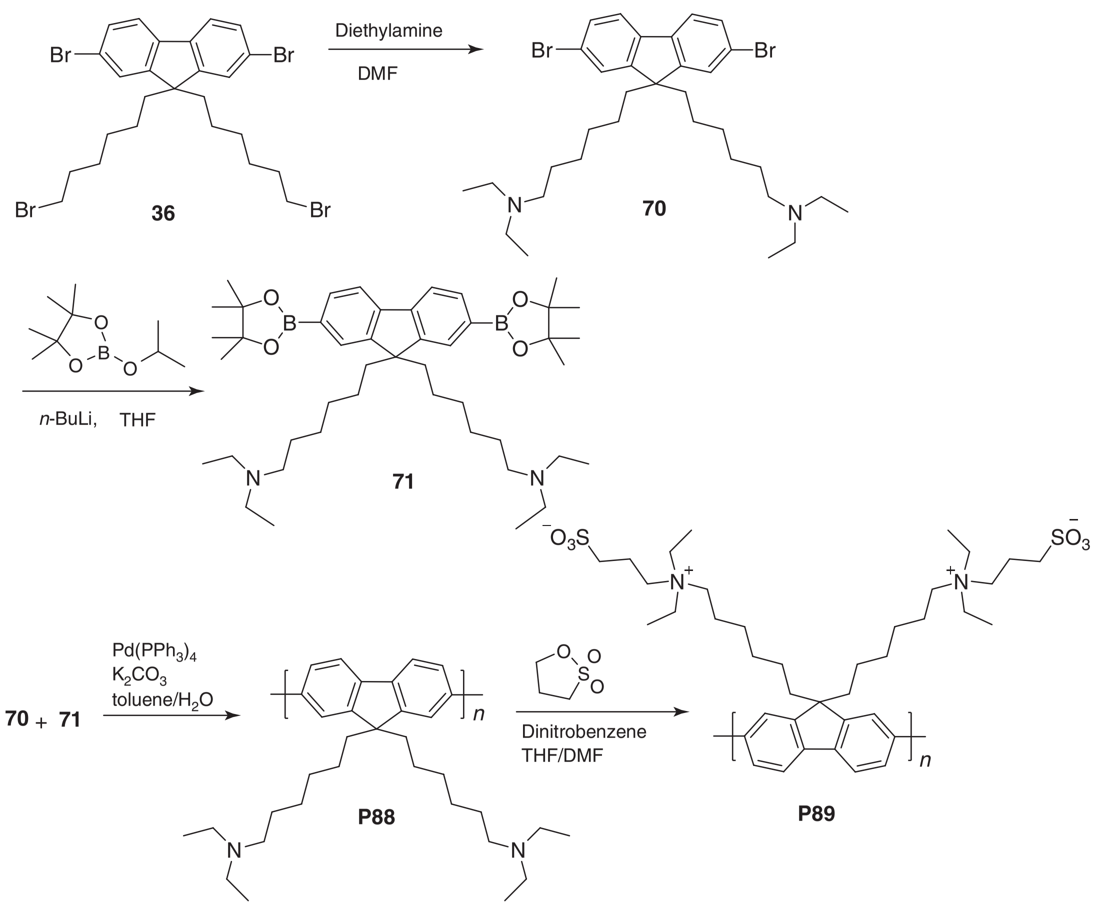


Scheme 1.34 Synthesis of a zwitterionic polyfluorene (**P87**).

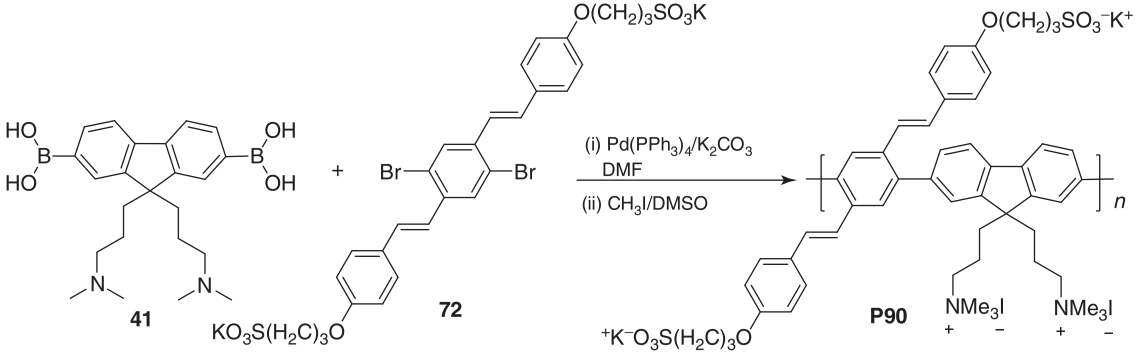
Schanze's group synthesized **P94** in an analogous way (Scheme 1.38) [52]. The ester-protected diiodo monomer (**77**) was synthesized in two steps from **32**. Then, **77** was reacted with trimethylsilyl acetylene in the presence of $(Ph_3P)_2PdCl_2$/CuI, which was followed by trimethylsilyl deprotection 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**).

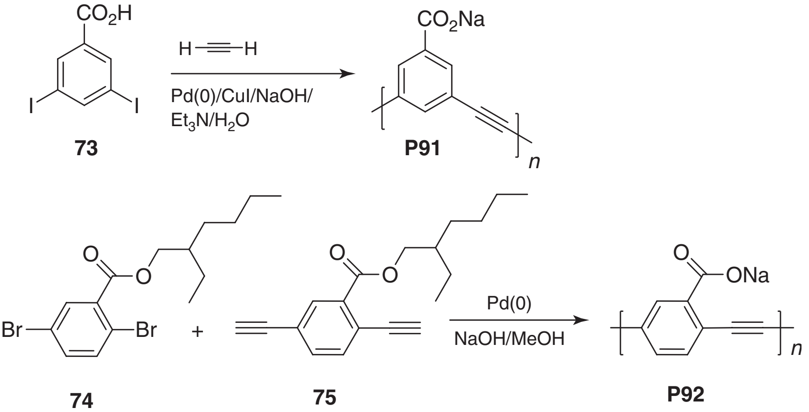
Table 1.1 Physical properties of poly(arylene)-based CPEs.[a]

Entry	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_F (%)	References
P8	Water	410	561	4.8	[6]
P12	Water	540	—	—	[7]
P13	Water[b]	397	530	3.0	[8]
P14	Water	400	536	—	[9]
P16	Water	438	546	1.2	[10]
P17	Water	410	560	2.1	[11]
P21	Water	434	555	—	[12]
P22	Water	438	540	—	[13]
P29	Water	339	410	~55	[14, 15]
P30	Water	352	—	—	[15]
P31	Water	338	417	—	[16]
P40	Water	330	408	—	[17, 18]
P41	Water	411	494	—	[19]
P43	Water	343	409	25	[20]
P47	Water	369	417	32	[21]
P48	Water	386	416	—	[22]
P49	Methanol	388	416	—	[22]
P54	Water	—	417	44	[23]
P56	Water	359	407	—	[24]
P57a	Water	335	369	51	[25]
P57f	Water	384	417	42	[25]
P58	Water	425	478	—	[26]
P59a	Water	385	415	24	[27]
P59b	Water	363	410	32	[27]
P59c	Water	369	414	29	[27]
P60	Water	395	426	46	[28]
P62a	Water	389	426	50	[28]
P62b	Water	382	421	50	[28]
P63	Water	330, 455	590	7.0	[29, 30]
P65	Water	320, 455	598	0.4	[31]
P66	Water	—	410, 550	—	[32, 33]
P67	Water	352, 430	412	5	[34]
P68	Water	375	415	—	[35]
P70	Water	384	422	7.2	[36]
P71	Water	385	420	7.2	[36]
P72	Water	~355	~410	39	[37]
P74	Water	355	409	40	[38]
P76	Water	309, 410	598	3	[39, 40]
P77	Water	381	424	10	[41]
P78	Water	—	415	—	[42]
P79	Water	365	420	90	[43]
P80	Methanol	385	—	—	[44]
P81	Water	380	434	21	[45]
P82	Water	390	434	25	[46]
P84	Water	365	409	89	[47]

Table 1.1 (*continued*)

Entry	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_F (%)	References
P85	Water	364	410	75	[48]
P87	Water	~390	~410	—	[49]
P88	Methanol	395	419, 443	—	[50]
P90	Water	326	454	—	[24]

[a] λ_{abs} and λ_{em} are the maximum absorption and emission wavelengths, respectively; Φ_F is the fluorescence quantum yield.
[b] At a temperature of 55 °C.



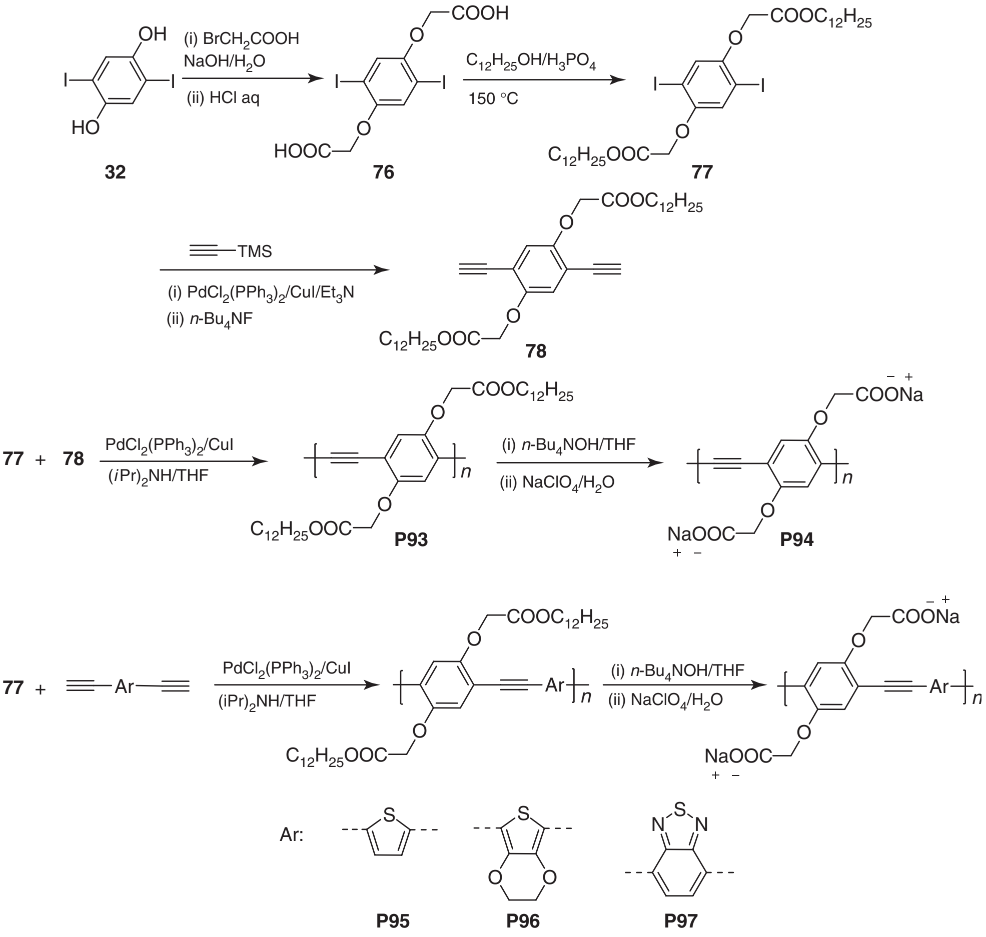
Scheme 1.37 Synthesis of carboxylated poly(phenylene ethynylene)s (**P91**) and (**P92**).

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**

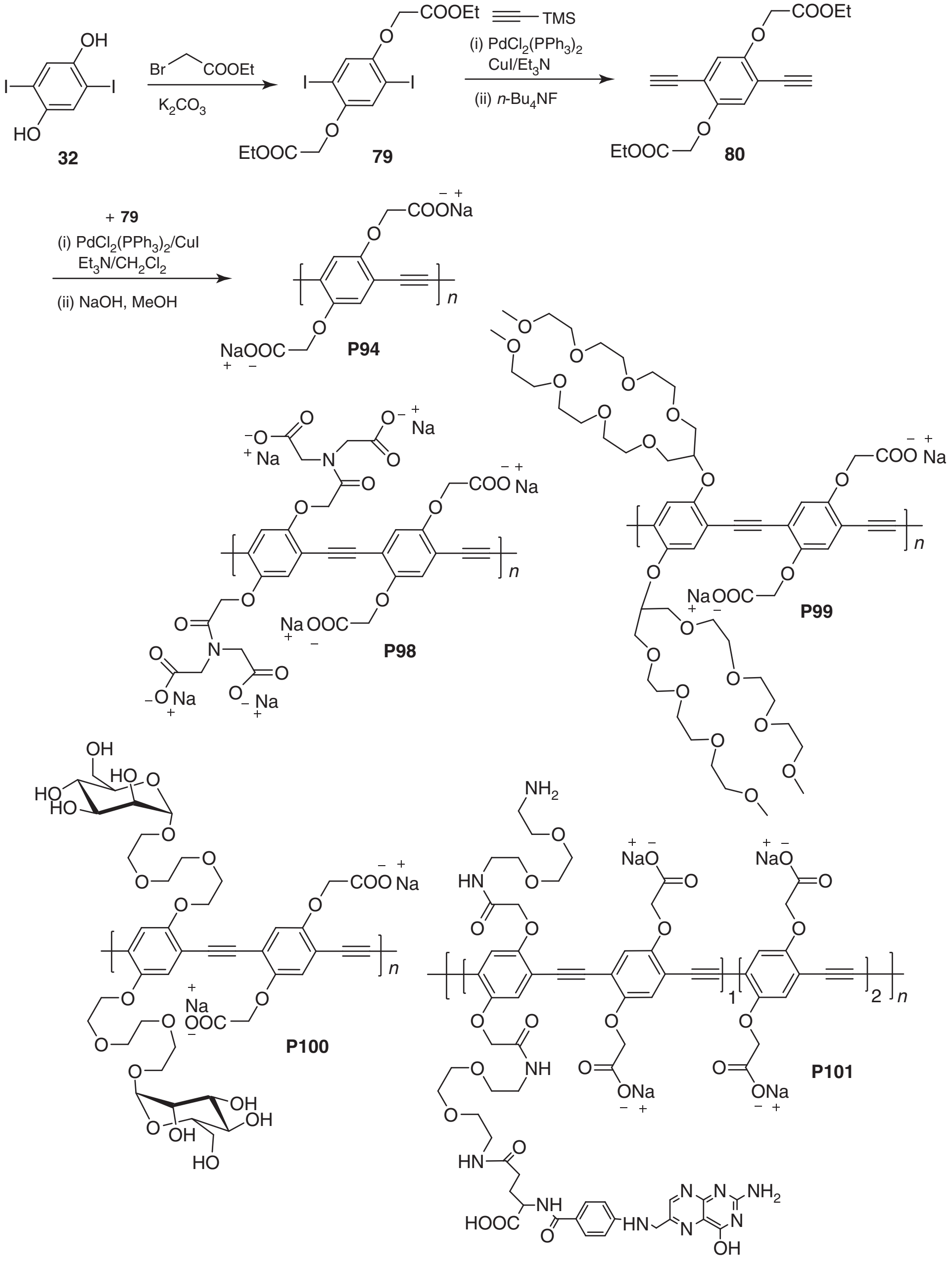
Swager's group synthesized a cationic poly(phenylene ethynylene) (**P111**, Scheme 1.43) by reaction between **89** and **90** in DMF/Et_3N/water using



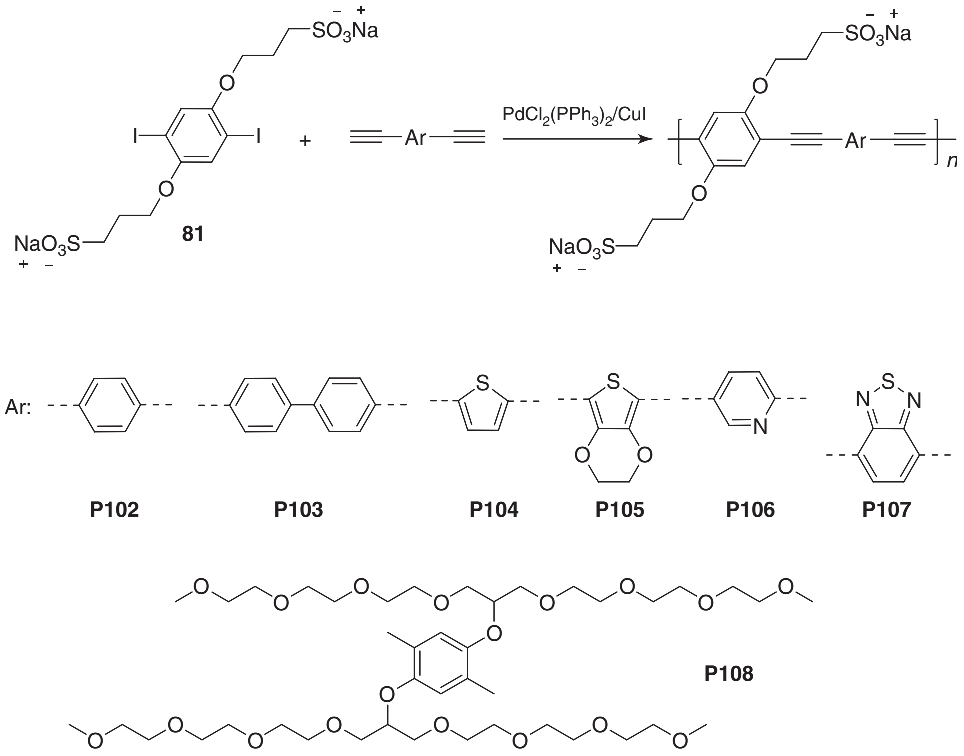
Scheme 1.38 Synthesis of carboxylated poly(phenylene ethynylene)s (**P94**–**P97**).

$Pd(PPh_3)_4/CuI$ 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 quanternization.

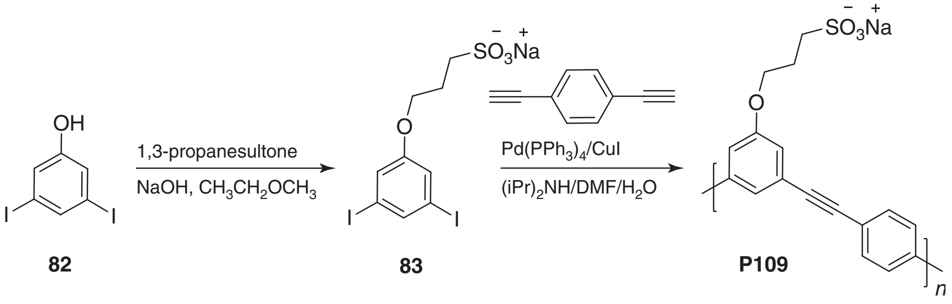
A series of bis(dialkylammonium) substituted poly(phenylene ethynylene)s with different backbones were synthesized by Schanze's group (Scheme 1.45)



Scheme 1.39 Synthesis of carboxylated poly(phenylene ethynylene)s (**P94**) and (**P98–P101**).

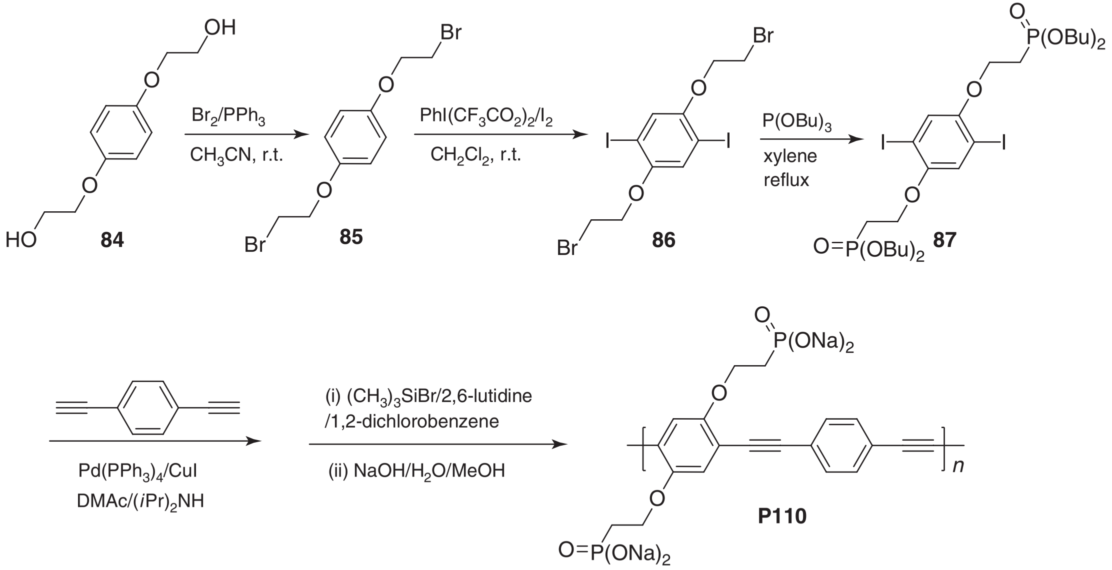


Scheme 1.40 Synthesis of sulfonated poly(phenylene ethynylene)s (**P102**–**P108**).

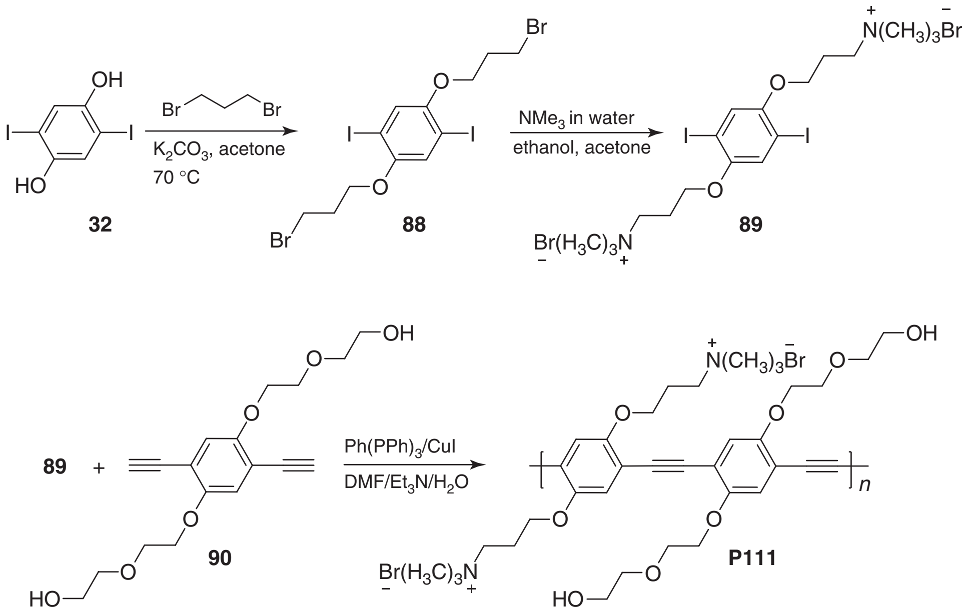


Scheme 1.41 Synthesis of a sulfonated poly(phenylene ethynylene) (**P109**).

[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 **P114**–**P118**, which have four cationic charges per repeat unit.



Scheme 1.42 Synthesis of a phosphonated poly(phenylene ethynylene) (**P110**).



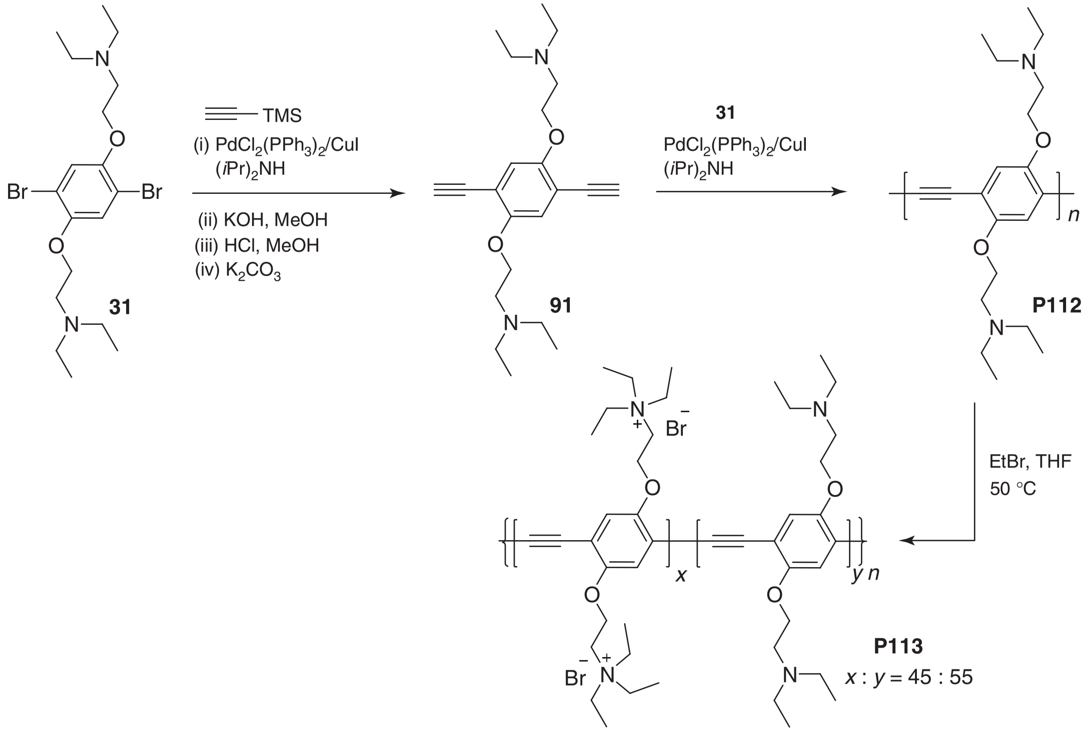
Scheme 1.43 Synthesis of a cationic poly(phenylene ethynylene) (**P111**).

1.3.2
Poly(fluorene ethynylene)s

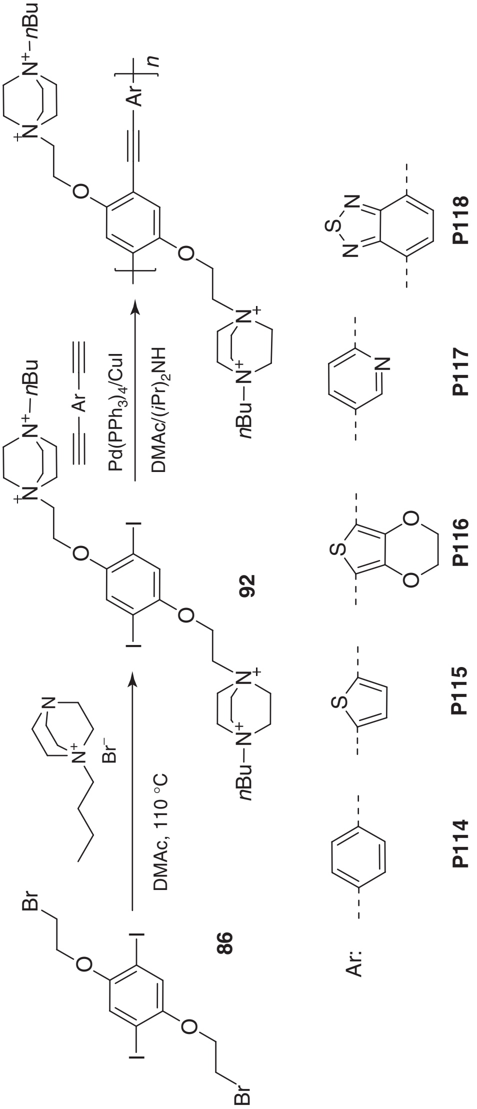
1.3.2.1 Cationic Poly(fluorene ethynylene)s

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[6′-(*N*,*N*-diethyl)hexyl]fluorene (**96**) using $Pd(PPh_3)_4/CuI$ as the catalyst. Treatment of neutral poly(fluorene ethynylene)s with iodomethane in THF/DMF mixture afforded **P119**–**P122** with 70–80% degree of quaternization.

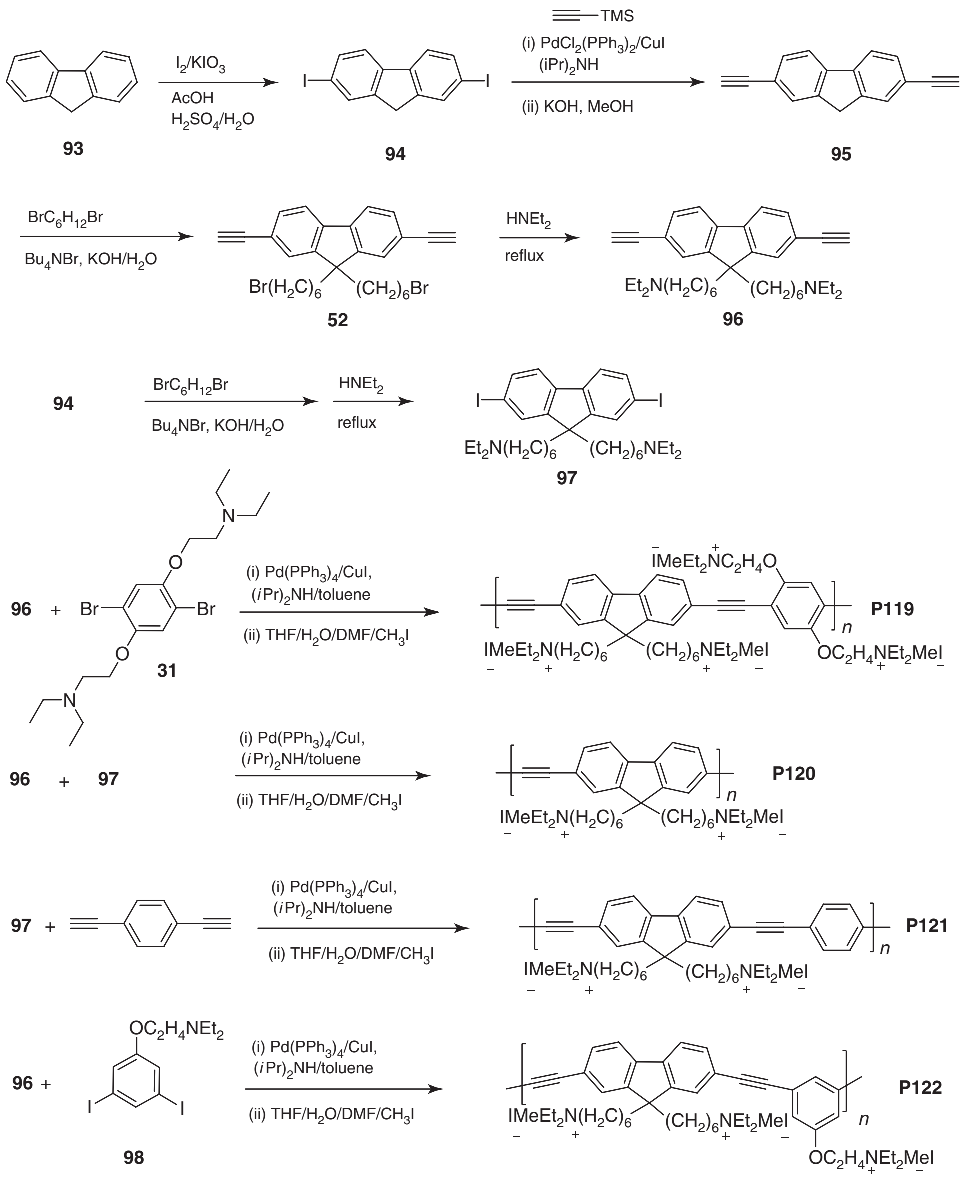
To simplify the synthesis of cationic poly(fluorene ethynylene)s, the key monomer **52** (Scheme 1.47) was prepared directly by treatment of **36** with trimethylsilyl acetylene under the Sonogashira coupling conditions, followed by deprotection in the presence of KOH in THF/CH_3OH solution [66]. Subsequent 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-diethynylbenzothiadiazole [67].



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



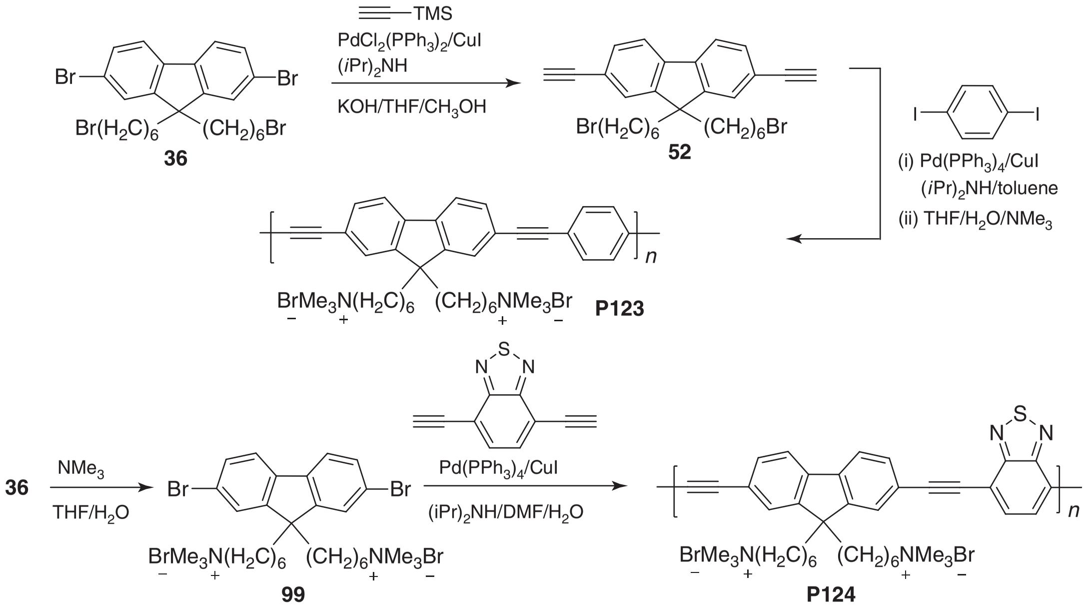
Scheme 1.45 Synthesis of cationic poly(phenylene ethynylene)s (**P114–P118**).



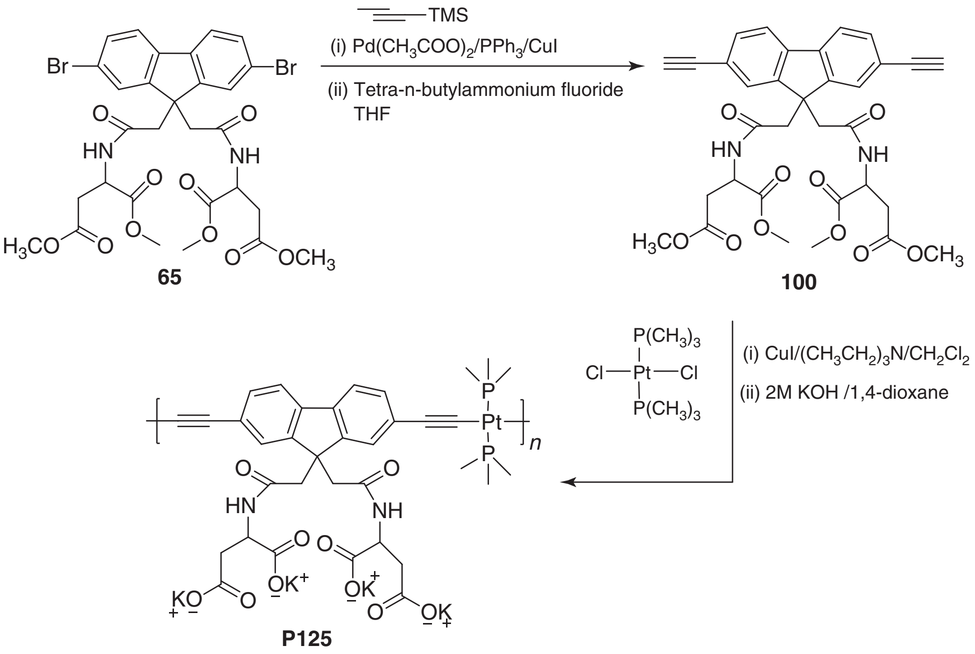
Scheme 1.46 Synthesis of cationic poly(fluorene ethynylene)s (**P119**–**P122**).

1.3.2.2 Anionic Poly(fluorene ethynylene)s

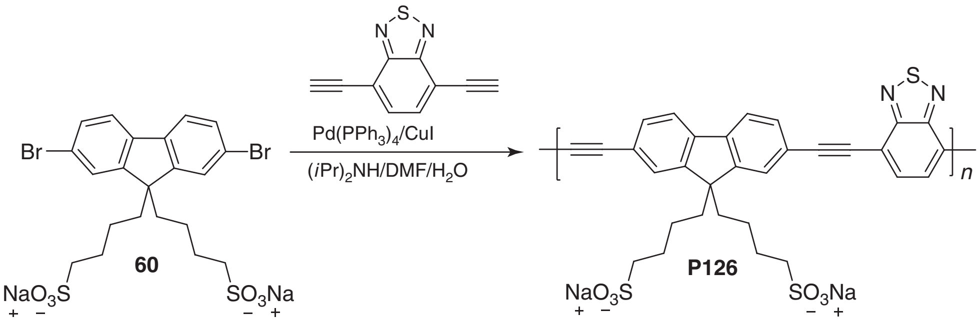
Wang's group reported an organometallic poly(fluorene ethynylene) (**P125**, Scheme 1.48) with phosphorescence properties [68]. The diacetylene monomer (**100**) was synthesized from **65** via the Sonogashira coupling reaction. Polymerization between **100** and [Pt(PMe_3)$_2$$Cl_2$], followed by hydrolysis of the



Scheme 1.47 Synthesis of cationic poly(fluorene ethynylene)s (**P123**) and (**P124**).



Scheme 1.48 Synthesis of a carboxylated poly(fluorene ethynylene) (**P125**).



Scheme 1.49 Synthesis of a sulfonated poly(fluorene ethynylene) (**P126**).

carboxylic esters under basic condition, led to **P125**. Another anionic poly(fluorene ethynylene) (**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.[a]

Entry	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_F (%)	References
P92	Water	404	426	—	[51]
P94	Water	317	470	6.3	[52]
P95	Methanol	435	476	13	[53]
P96	Methanol	457	497	9.0	[53]
P97	Methanol	495	642	0.20	[53]
P98	Water[b]	419	465	8.0	[54]
P99	Water[b]	425	466	33	[54]
P100	Water	~419	~465	8.0	[55]
P101	Water	421	460	2.0	[56]
P102	Water	446	547	1.0	[57]
P103	Water	419	503	—	[58]
P104	Water	484	478	3.6	[57]
P105	Water	506	—	—	[57]
P106	Water	455	532	18.7	[57]
P107	Water	549	634	0.34	[57]
P108	Water	425	460	53	[59]
P109	Water	325	445	—	[60]
P110	Water	444	518	3.0	[61]
P113	Water	378	444	—	[62]
P114	Water	394	436	4.7	[63]
P115	Water	429	478	7.1	[63]
P116	Water	455	496	1.1	[63]
P117	Water	426	508	0.8	[63]
P118	Water	520	630	0.06	[63]
P119	Water	403	436	—	[64]
P120	Water	418	431	—	[64]
P121	Water	415	431	—	[64]
P122	Water	364	428	—	[65]
P123	Water	389	425	22	[66]
P124	Water	339	450	1.1	[67]
P125	Water	390	405	0.23	[68]
P126	Water	339	450	0.9	[67]

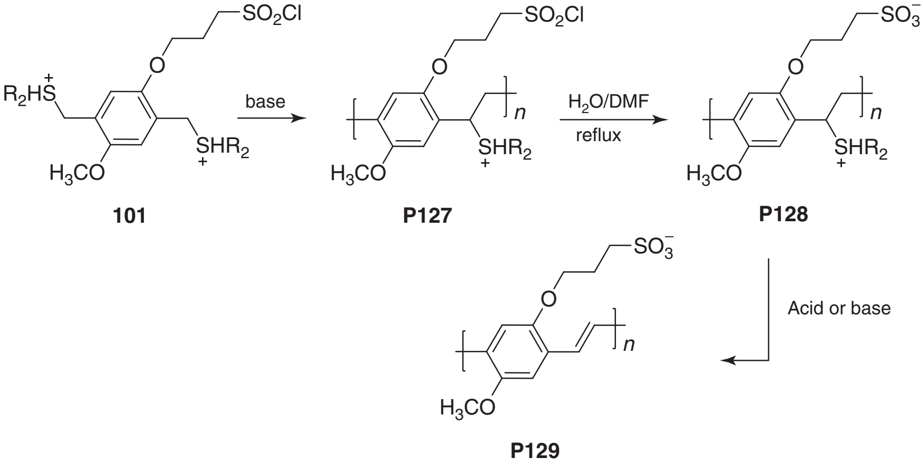
[a] λ_{abs} and λ_{em} are the maximum absorption and emission wavelengths, respectively; Φ_F is the fluorescence quantum yield.
[b] At pH = 7.

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

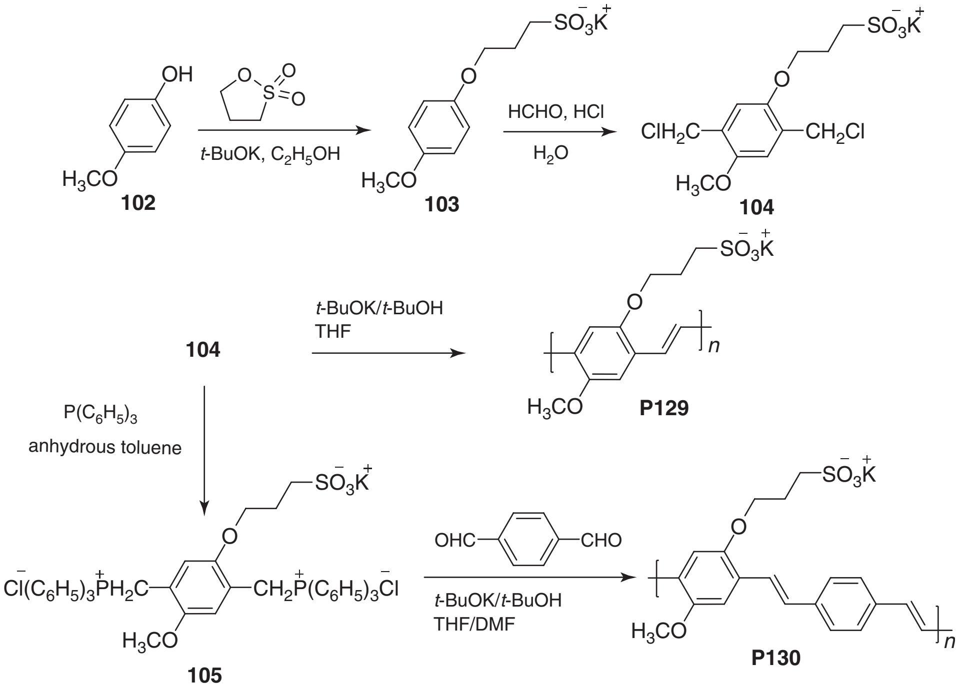


Scheme 1.50 Synthesis of a sulfonated poly(phenylene vinylene) (**P129**).

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-propane sultone 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 PPh_3. 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 NEt_3/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.



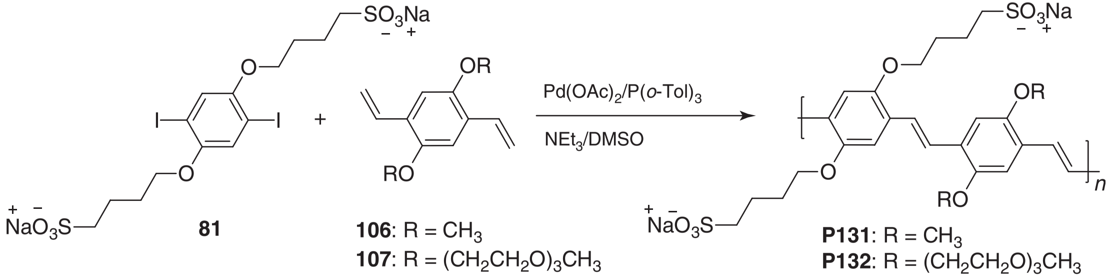
Scheme 1.51 Synthesis of sulfonated poly(phenylene vinylene)s (**P129**) and (**P130**).

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 PPh_3 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 same group also synthesized a cationic poly(phenylene vinylene) **P144** via the Gilch reaction (Scheme 1.56) [76]. The key monomer **120** was synthesized in four steps as shown in Scheme 1.56. The neutral polymer (**P143**) was obtained after polymerization of **120** in the presence of *t*-BuOK in THF. Quaternization of **P143** with bromoethane yielded **P144**.

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

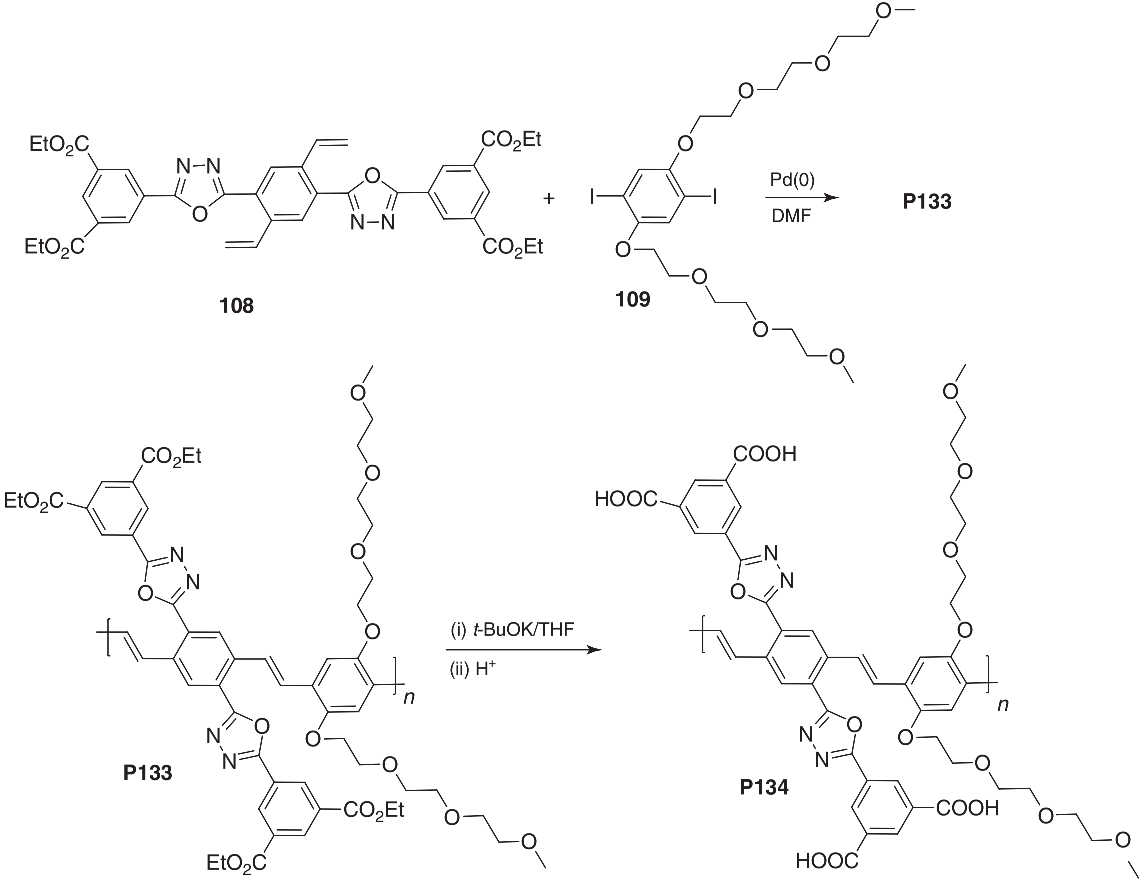


81

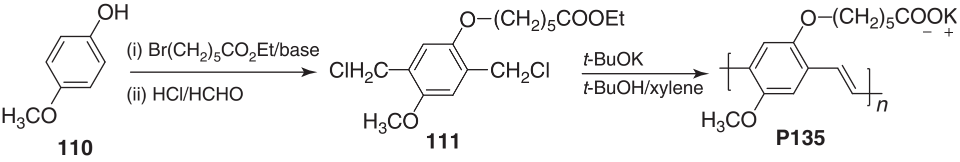
106: R = CH_3
107: R = $(CH_2CH_2O)_3CH_3$

P131: R = CH_3
P132: R = $(CH_2CH_2O)_3CH_3$

Scheme 1.52 Synthesis of sulfonated poly(phenylene vinylene)s (**P131**) and (**P132**).



Scheme 1.53 Synthesis of a carboxylated poly(phenylene vinylene) (**P134**).



Scheme 1.54 Synthesis of a carboxylated poly(phenylene vinylene) (**P135**).

those for the Gilch and Wittig reactions. As shown in Scheme 1.57, polymerization between **33** and 1,4-divinylbenzene catalyzed by $Pd(OAc)_2/P(o\text{-}Tol)_3$ in tri-*n*-butylamine/DMF, followed by quaternization yielded **P145** [77].

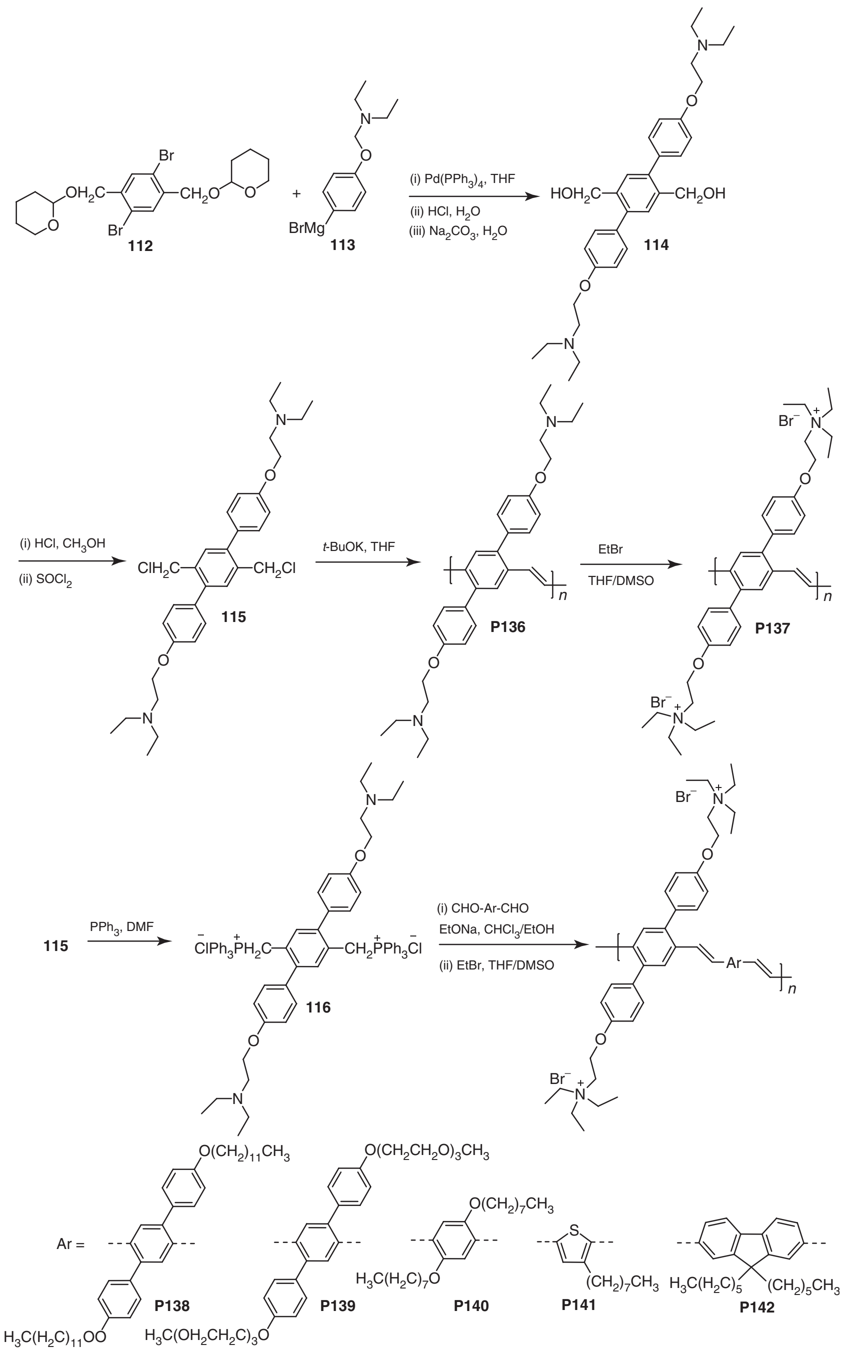
1.4.2
Poly(fluorene vinylene)s

1.4.2.1 Cationic Poly(fluorene vinylene)s

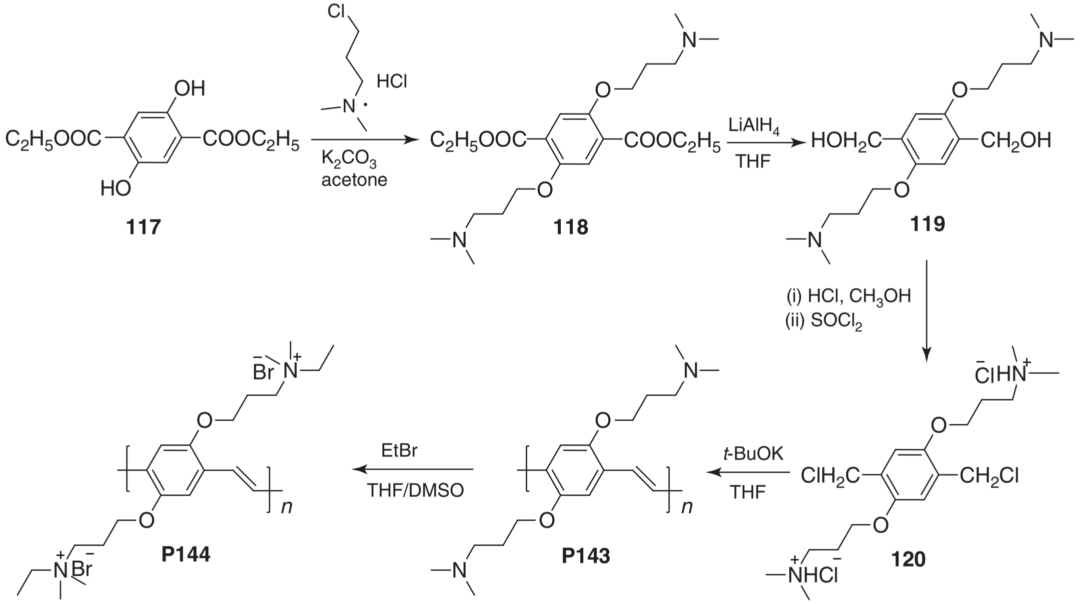
Poly(fluorene vinylene)-based CPEs are commonly synthesized by the Heck coupling and the Wittig–Horner reactions. Mikroyannidis and Barberis [78] first designed and synthesized cationic poly(fluorene vinylene) and poly(phenylene vinylene-*alt*-fluorenevinylene) derivatives. Divinylfluorene monomer (**122**, Scheme 1.58) was prepared via the Stille coupling reaction between **121** and tributylvinyltin catalyzed by $PdCl_2(PPh_3)_2$ in toluene. The neutral polymer **P146** was obtained by the Heck coupling between monomers **121** and **122** catalyzed by $Pd(OAc)_2/P(o\text{-}Tol)_3$ 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 $DMF/H_2O/Et_3N$ using $Pd(OAc)_2/P(o\text{-}tolyl)_3$ as the catalyst afforded **P150**. Similarly, **P151** was synthesized via polymerization between **126** and 1,4-dibromobenzene [80].

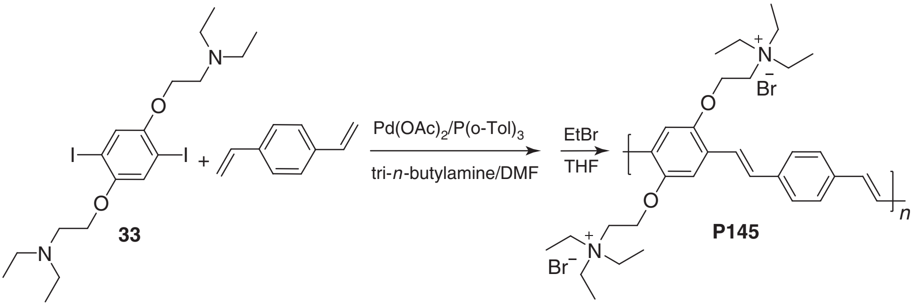
Wang's group [81] synthesized a cationic poly(fluorene vinylene) via the Wittig–Horner reaction (Scheme 1.60). **36** was reacted with morpholine-4-carbaldehyde in the presence of *n*-BuLi to afford 9,9-bis(6-bromohexyl)-fluorene-2,7-dicarbaldehyde (**127**) that was then reacted with (1,3-dioxolan-2-yl-methyl)-triphenyl phosphonium 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-diacryl aldehyde (**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 NMe_3 treatment yielded **P153**. Similarly, **P151** was synthesized from **127**



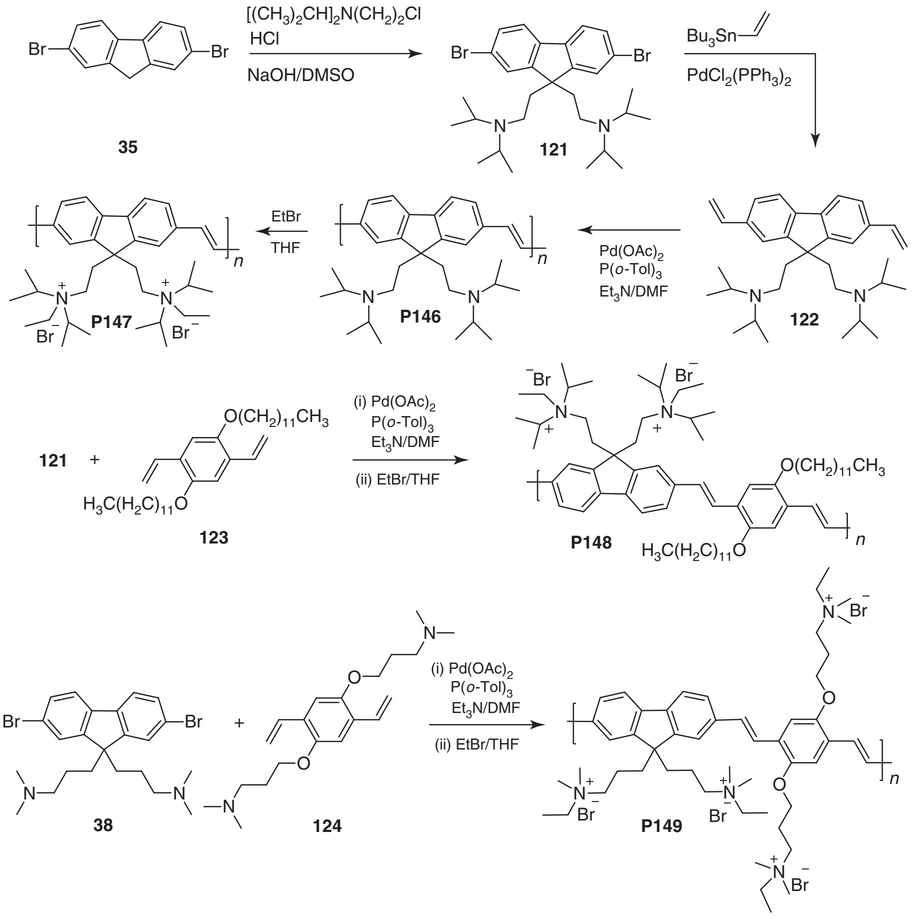
Scheme 1.55 Synthesis of cationic poly(phenylene vinylene)s (**P137**–**P142**).



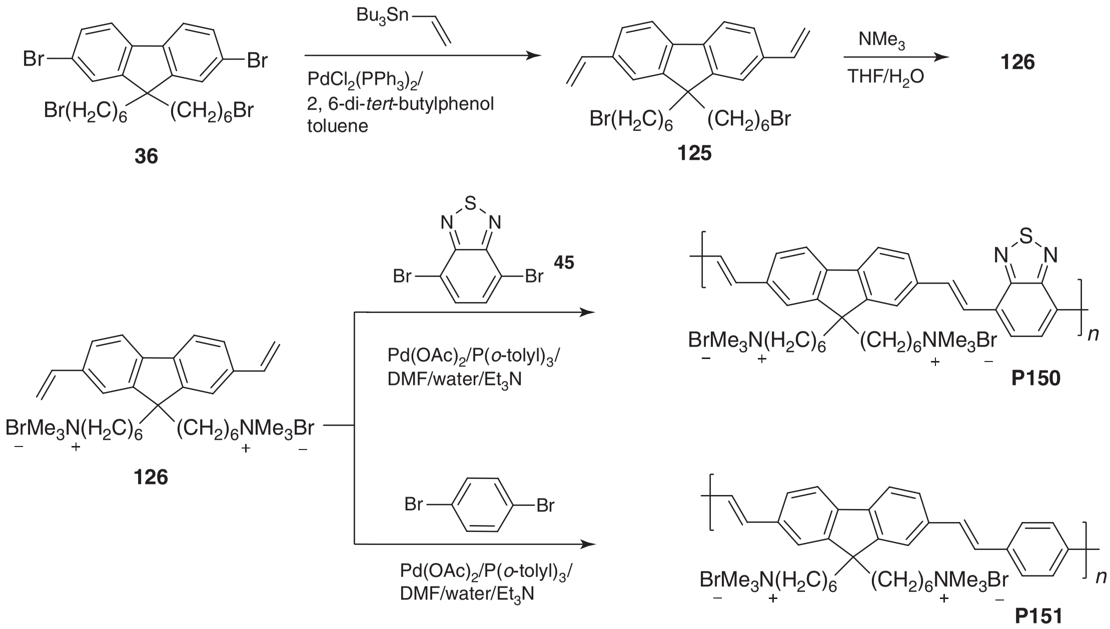
Scheme 1.56 Synthesis of a cationic poly(phenylene vinylene) (**P144**).



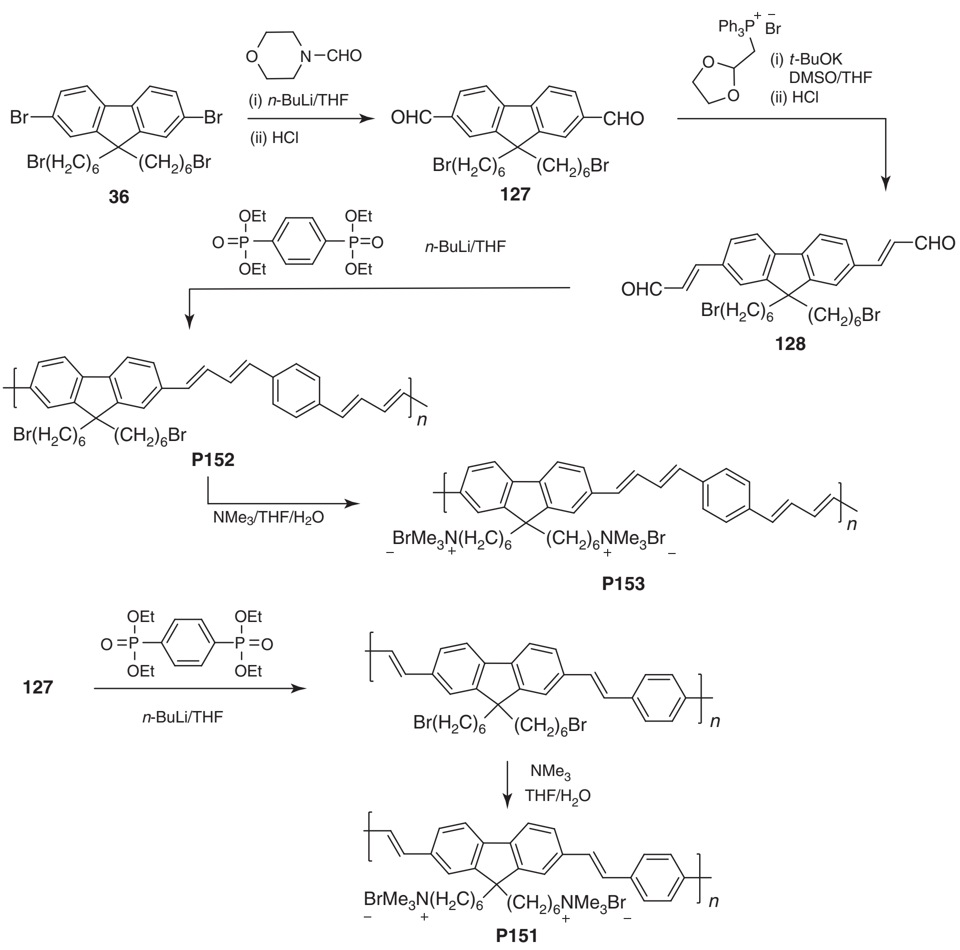
Scheme 1.57 Synthesis of a cationic poly(phenylene vinylene) (**P145**).



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**).

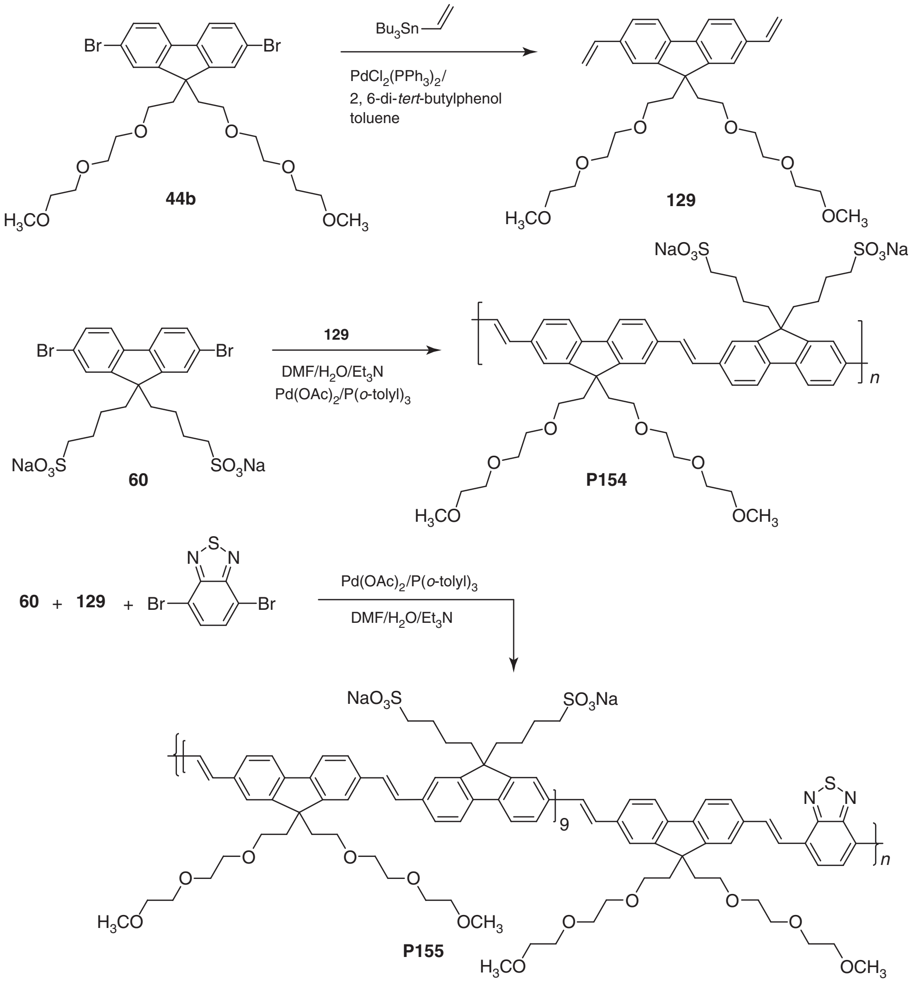


Scheme 1.60 Synthesis of cationic poly(fluorene vinylene) derivatives (**P151** and **P153**).

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-(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



Scheme 1.61 Synthesis of sulfonated poly(fluorene vinylene)s (**P154**) and (**P155**).

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.

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

Table 1.3 Physical properties of poly(arylene vinylene)-based CPEs.[a]

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

[a] λ_{abs} and λ_{em} are the maximum absorption and emission wavelengths, respectively; Φ_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.

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