1
Organometallic Polycondensation for Conjugated Polymers

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1.1
Basic Organometallic C–C Coupling

Diorganonickel(II) complexes NiR_2L_m undergo reductive coupling (or reductive elimination) reactions to give R–R (Eq. (1.1)) [1]. The controlling factors of this coupling reaction have long been studied by our research group and by others (L = neutral ligand such as 2,2'-bipyridyl (bpy) and tertiary phosphine):

$$L_mNi\underset{R}{\overset{R}{\diagdown}} \longrightarrow R-R \tag{1.1}$$

This basic C–C coupling on Ni introduced the concept of "reductive elimination" to the field of organometallic chemistry [1a–1p] and the first experimental support [1a] for the concept of "back-donation to an olefin [1q,1r]" was given during the study. The coordination of molecules leading to back-donation (e.g., electron-accepting olefin [1a] or aromatic compound [1k,1s]) to the central metal facilitates the reductive elimination of R–R, and the concepts of reductive elimination and back-donation are now widely accepted in chemistry.
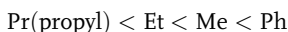
The Ni–R bond in NiR_2L_m is considered to be polarized as $Ni^{\delta+}-R^{\delta-}$, whereas the reductive elimination produces an electrically neutral R–R molecule. Consequently the reductive elimination is assumed to involve electron migration from the R group to Ni, and this electron migration is considered to be enhanced by coordination of an electron-withdrawing olefin (e.g., $CH_2=CHCN$ and $CH_2=CHBr$) and an aromatic compound (e.g., C_6H_5CN, C_6H_5Br, and C_6F_6) [1a,1k,1s,1t] (Figure 1.1). For $NiEt_2(bpy)$ (bpy = 2,2'-bipyridyl), the enhancement effect is as large as 10^{10}–10^{13} [1t].

This enhancement effect is similar to that of an electron-withdrawing group on the acid dissociation of substituted benzoic acid (Hammett's effect), however, the enhancement effect on the reductive elimination is much larger than the Hammett's
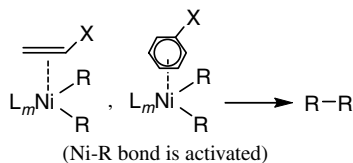
Figure 1.1 Activation of Ni–R bond by coordination of an electron-accepting olefin and aromatic compounds.

effect on the acid dissociation. Because the electron withdrawing ability of the R group increases in the order:

$$\text{Pr(propyl)} < \text{Et} < \text{Me} < \text{Ph}$$

The stability of the Ni–R bond is considered to increase in this order. Actually thermal stability of NiR$_2$(bpy) increases in the order:

$$\text{NiPr}_2(\text{bpy}) < \text{NiEt}_2(\text{bpy}) < \text{NiMe}_2(\text{bpy}),$$
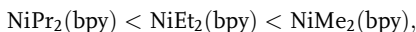
and insertion of CO into an Ni–Et bond is usually easier than into an Ni–Me bond [1u,1v]. However, the Ni–Ph bond in NiPh$_2$L$_m$ seems to be less stable and undergoes reductive elimination to give Ph–Ph. Attempts to isolate NiPh$_2$L$_m$ have not been successful, and they usually give the reductive elimination product Ph–Ph. When the Ph group has a strongly electron-withdrawing substituent(s) as in C$_6$F$_5$, the NiPh$_2$L$_m$ type complex (e.g., Ni(C$_6$F$_5$)$_2$(bpy)) can be isolated, and its molecular structure suggests the presence of electronic interaction between the two aromatic ligands through π-electrons in the two aromatic units [1s] (Figure 1.2):
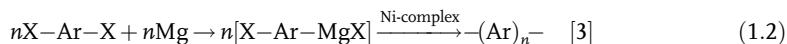
The presence of such an electronic interaction between the two aromatic groups accounts for the ease of reductive elimination of Ph–Ph from NiPh$_2$L$_m$. Because of (i) the enhancement effect of electron-accepting aromatic compounds on the reductive elimination and (ii) the ease of the reductive elimination from the NiPh$_2$L$_m$ type complex, organometallic dehalogenative polycondensation is considered to be especially suited to polymerization of dihaloaromatic monomers, X–Ar–X, which are considered to behave as typical electron-accepting ligands to Ni.

The basic coupling reaction (reductive elimination) is a key step in Ni-promoted organic syntheses (e.g., RMgX + R′X → R–R′; 2RX + Zn → R–R; 2RX + Ni(0)
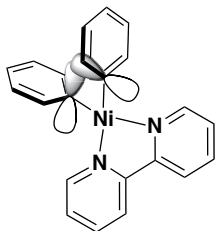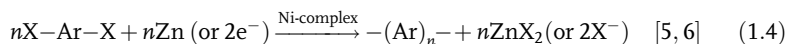

Figure 1.2 Electronic interaction between two aromatic groups through π-electrons in the aromatic ligands. For aromatic unit $= \text{C}_6\text{F}_5$, Ni(C$_6$F$_5$)$_2$(bpy) can be isolated [1s].

complex → R–R; X = halogen) [2]. We have developed further the utilization of this coupling reaction for the polycondensation of dihaloaromatic compounds:
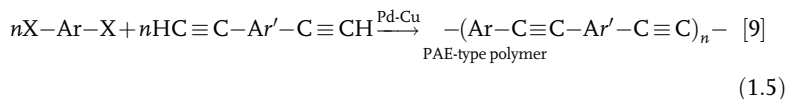
$$n\text{X}-\text{Ar}-\text{X} + n\text{Mg} \rightarrow n[\text{X}-\text{Ar}-\text{MgX}] \xrightarrow{\text{Ni-complex}} -(\text{Ar})_n- \quad [3] \tag{1.2}$$

$$n\text{X}-\text{Ar}-\text{X} + n\text{Ni(0)L}_m \rightarrow -(\text{Ar})_n- + n\text{NiX}_2\text{L}_m \quad [4] \tag{1.3}$$

In some cases, Ni(0)L_m formed *in situ* by chemical (e.g., by Zn) or electrochemical reduction of Ni(II)-compounds are also usable in this polycondensation, thus providing the following catalytic reactions (Eq. (1.4)) [5,6a–e]. It was reported that NaH and hydrazine hydrate could also be used as the reducing agents [6f,6g]

$$n\text{X}-\text{Ar}-\text{X} + n\text{Zn}\,(\text{or }2e^-) \xrightarrow{\text{Ni-complex}} -(\text{Ar})_n- + n\text{ZnX}_2\,(\text{or }2\text{X}^-) \quad [5,6] \tag{1.4}$$

Polyarylenes can be prepared by the organometallic polycondensation as well as by chemical and electrochemical oxidation of aromatic compounds, and books and reviews have been published concerning the preparation and properties of poly-arylenes [1t,7].
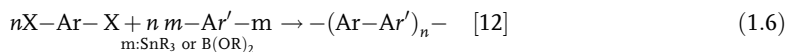
Organopalladium(II) complexes also undergo C–C coupling on Pd [8]. We applied C–C coupling to the following polycondensation [9a–e] which is based on Pd-promoted synthetic reactions of arylacetylenes [8b,8c,10a,b]. Acetylenic ligands of Cu complexes can migrate to Pd [8b,8c], and this migration reaction seems to occur in the C–C coupling reaction and the polycondensation to give PAE (poly (aryleneethynylene)) type polymers.

$$n\text{X}-\text{Ar}-\text{X} + n\text{HC}\equiv\text{C}-\text{Ar}'-\text{C}\equiv\text{CH} \xrightarrow{\text{Pd-Cu}} \underset{\text{PAE-type polymer}}{-(\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}'-\text{C}\equiv\text{C})_n-} \quad [9]$$
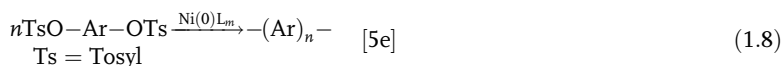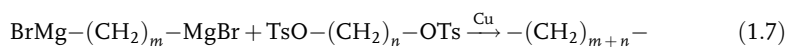
$$\tag{1.5}$$

Successful polycondensation usually requires highly effective basic coupling reactions. However, the polycondensations expressed by Eqs. (1.2)–(1.5) give polymers with high molecular weights even when the basic C–C coupling reaction is not so effective. One of the reasons for the successful polycondensation seems to be an energetic advantage of the polycondensation leading to poly(arylene)s which seem to be stabilized by forming the extended π-conjugation system along the polymer chain. In relation to this, it was reported that polymerization of propylene to give crystalline stereoregular poly(propylene) proceeded at a much faster velocity than that giving amorphous stereo-irregular poly(propylene), presumably due to the stabiliza-tion energy attained by forming the crystal in the stereoregular polymerization [10c].

As described above, the basic C–C coupling reaction in the polycondensation is considered to proceed well, especially when the dihalo compounds, such as X–Ar–X, come (or coordinate) to the propagating species ((polymer)$_a$–NiL_m–(polymer)$_b$) to produce (polymer)$_a$–(polymer)$_b$ in the polycondensation. A concept that the prop-agation reaction proceeds selectively when the monomer comes to the propagating species also explains the smooth polycondensation and the high molecular weight polymer obtained by the polycondensation.
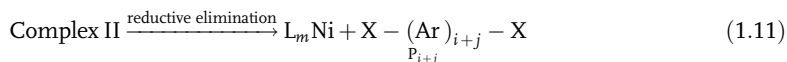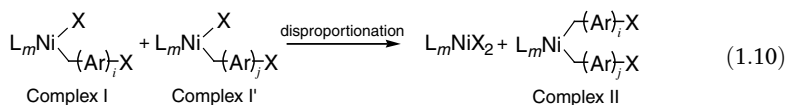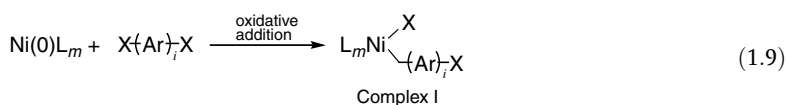
Because organometallic polycondensations can give the π-conjugated aromatic polymers effectively, various analogous polycondensations have been developed. For example, organostannanes and organoborons undergo similar Pd-catalyzed C–C coupling reactions [1t,7,11a–d]:

$$n\text{X}-\text{Ar}-\text{X} + n\,\underset{\text{m:SnR}_3\text{ or B(OR)}_2}{m-\text{Ar}'-m} \rightarrow -(\text{Ar}-\text{Ar}')_n- \quad [12] \tag{1.6}$$

Pd-promoted coupling reactions between ArX and olefin are also known [11e,11f]. They have also been applied to the polymerization [12]. The polymerization expressed by Eq. (1.2) is applicable to dihaloalkanes (e.g., $\text{X}-(\text{CH}_2)_n-\text{X}$) by using Cu catalyst [3g]. Use of C–OY (Y = tosyl, etc.) compounds, instead of C–X compounds (OY = leaving group or pseudo-halogen), is also possible for the polycondensation [3g,5e], which is considered to proceed through oxidative addition of C–OY to a transition metal as studied previously [13a–c].
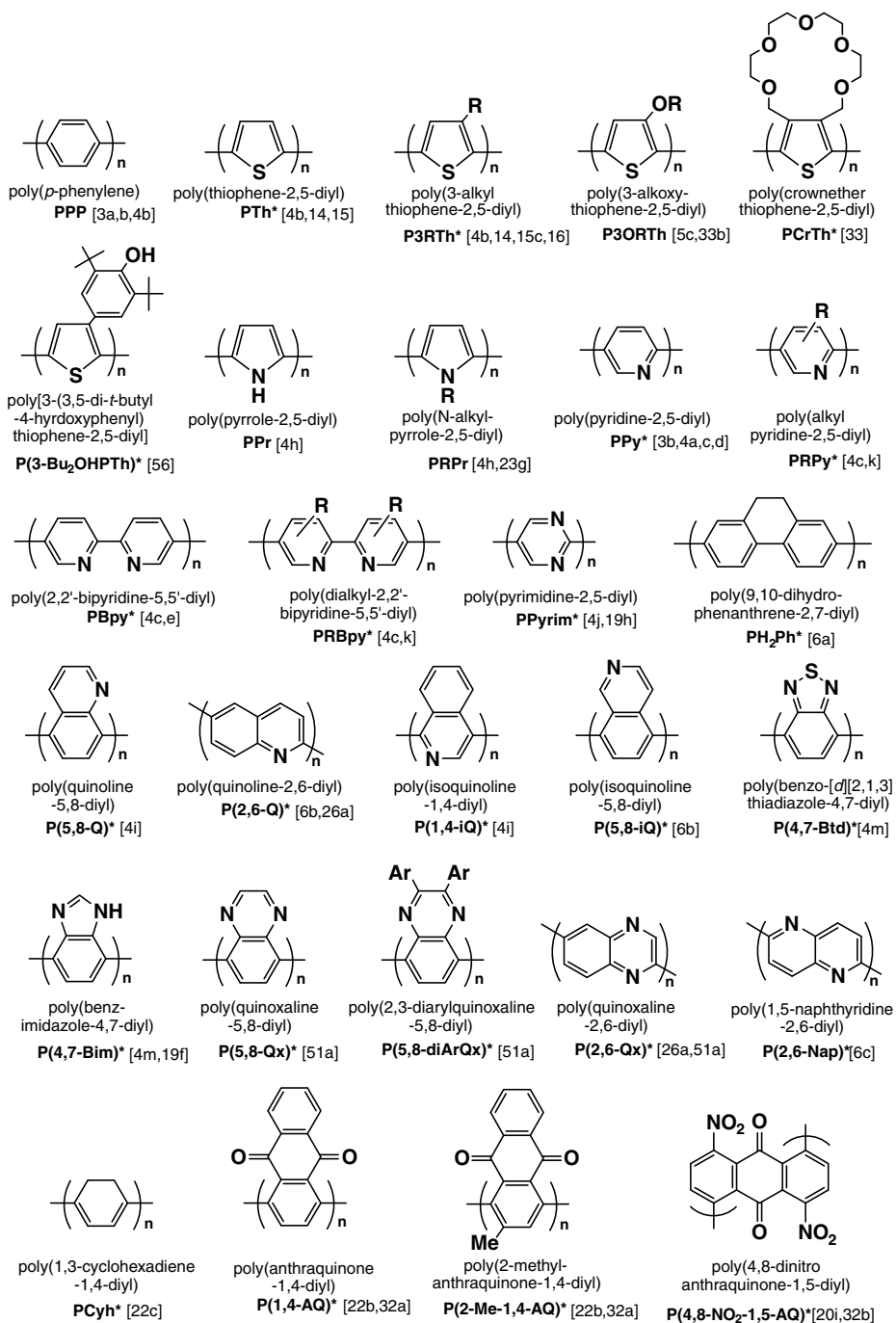
$$\text{BrMg}-(\text{CH}_2)_m-\text{MgBr} + \text{TsO}-(\text{CH}_2)_n-\text{OTs} \xrightarrow{\text{Cu}} -(\text{CH}_2)_{m+n}- \tag{1.7}$$

$$n\text{TsO}-\text{Ar}-\text{OTs} \xrightarrow{\text{Ni(0)L}_m} -(\text{Ar})_n- \quad [5e] \tag{1.8}$$
$$\text{Ts} = \text{Tosyl}$$

When the polymerization is carried out using Ni(0)L$_m$(Eq. (1.3)), the polymerization is considered to proceed through the following fundamental reactions [2f,4c];

$$ \tag{1.9}$$

$$ \tag{1.10}$$

$$\text{Complex II} \xrightarrow{\text{reductive elimination}} \text{L}_m\text{Ni} + \text{X} - \underset{\text{P}_{i+j}}{(\text{Ar})_{i+j}} - \text{X} \tag{1.11}$$

The oxidative addition of C–X [13d–f] and C–OY [13a–c] to Ni(0)L$_m$ (Eq. (1.9)) is well known, and the disproportionation reaction [1s,13g] is also known. When the Ni–C bond has high stability, the Complexes I [2e] and II [1k,l], as well as a complex of type L$_m$(X)Ni–Ar–Ni(X)L$_m$ [1g] can be isolated. Thus, the basic concepts (reductive elimination, back-donation, oxidative addition) and the basic reactions in organometallic chemistry studied by us support the organometallic polycondensation.

1.2
Syntheses of π-Conjugated Polymers

By using the organometallic polycondensations expressed by Eqs. (1.2)–(1.6), various π-conjugated poly(arylene)s have been prepared. Figure 1.3 shows examples of the

poly(*p*-phenylene)
PPP [3a,b,4b]

poly(thiophene-2,5-diyl)
PTh* [4b,14,15]

poly(3-alkyl
thiophene-2,5-diyl)
P3RTh* [4b,14,15c,16]

poly(3-alkoxy-
thiophene-2,5-diyl)
P3ORTh [5c,33b]

poly(crownether
thiophene-2,5-diyl)
PCrTh* [33]

poly[3-(3,5-di-*t*-butyl
-4-hyrdoxyphenyl)
thiophene-2,5-diyl]
P(3-Bu₂OHPTh)* [56]

poly(pyrrole-2,5-diyl)
PPr [4h]

poly(N-alkyl-
pyrrole-2,5-diyl)
PRPr [4h,23g]

poly(pyridine-2,5-diyl)
PPy* [3b,4a,c,d]

poly(alkyl
pyridine-2,5-diyl)
PRPy* [4c,k]

poly(2,2'-bipyridine-5,5'-diyl)
PBpy* [4c,e]

poly(dialkyl-2,2'-
bipyridine-5,5'-diyl)
PRBpy* [4c,k]

poly(pyrimidine-2,5-diyl)
PPyrim* [4j,19h]

poly(9,10-dihydro-
phenanthrene-2,7-diyl)
PH₂Ph* [6a]

poly(quinoline
-5,8-diyl)
P(5,8-Q)* [4i]

poly(quinoline-2,6-diyl)
P(2,6-Q)* [6b,26a]

poly(isoquinoline
-1,4-diyl)
P(1,4-iQ)* [4i]

poly(isoquinoline
-5,8-diyl)
P(5,8-iQ)* [6b]

poly(benzo-[*d*][2,1,3]
thiadiazole-4,7-diyl)
P(4,7-Btd)* [4m]

poly(benz-
imidazole-4,7-diyl)
P(4,7-Bim)* [4m,19f]

poly(quinoxaline
-5,8-diyl)
P(5,8-Qx)* [51a]

poly(2,3-diarylquinoxaline
-5,8-diyl)
P(5,8-diArQx)* [51a]

poly(quinoxaline
-2,6-diyl)
P(2,6-Qx)* [26a,51a]

poly(1,5-naphthyridine
-2,6-diyl)
P(2,6-Nap)* [6c]

poly(1,3-cyclohexadiene
-1,4-diyl)
PCyh* [22c]

poly(anthraquinone
-1,4-diyl)
P(1,4-AQ)* [22b,32a]

poly(2-methyl-
anthraquinone-1,4-diyl)
P(2-Me-1,4-AQ)* [22b,32a]

poly(4,8-dinitro
anthraquinone-1,5-diyl)
P(4,8-NO₂-1,5-AQ)* [20i,32b]

Figure 1.3 π-Conjugated polymers prepared by organometallic processes in our group. Polymers marked with an asterix were reported for the first time from the author's group.
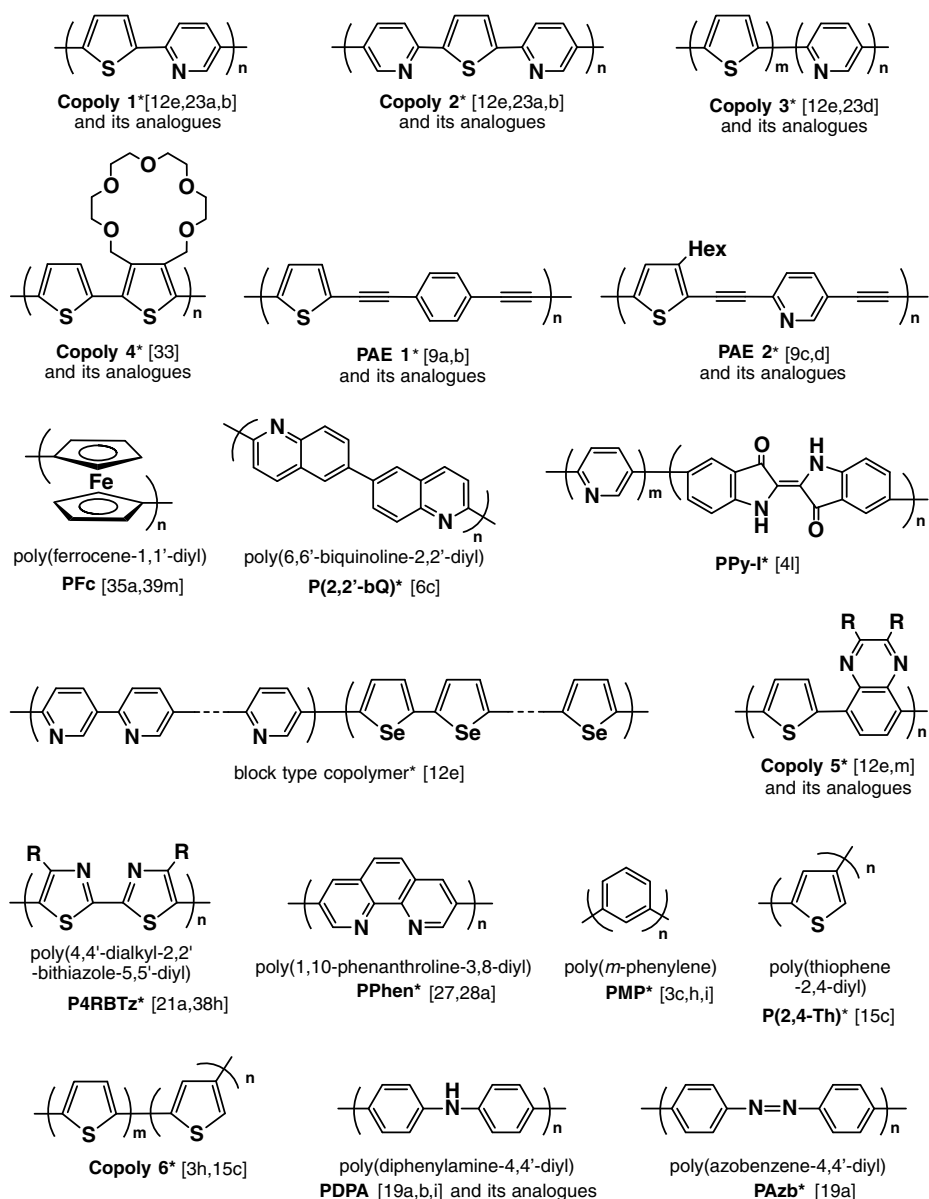
Copoly 1*[12e,23a,b]
and its analogues

Copoly 2* [12e,23a,b]
and its analogues

Copoly 3* [12e,23d]
and its analogues

Copoly 4* [33]
and its analogues

PAE 1* [9a,b]
and its analogues

PAE 2* [9c,d]
and its analogues

poly(ferrocene-1,1'-diyl)
PFc [35a,39m]

poly(6,6'-biquinoline-2,2'-diyl)
P(2,2'-bQ)* [6c]

PPy-I* [4l]

block type copolymer* [12e]

Copoly 5* [12e,m]
and its analogues

poly(4,4'-dialkyl-2,2'
-bithiazole-5,5'-diyl)
P4RBTz* [21a,38h]

poly(1,10-phenanthroline-3,8-diyl)
PPhen* [27,28a]

poly(*m*-phenylene)
PMP* [3c,h,i]

poly(thiophene
-2,4-diyl)
P(2,4-Th)* [15c]

Copoly 6* [3h,15c]

poly(diphenylamine-4,4'-diyl)
PDPA [19a,b,i] and its analogues

poly(azobenzene-4,4'-diyl)
PAzb* [19a]

Figure 1.3 (*Continued*)

π-conjugated poly(arylene)s prepared by the organometallic polycondensation in our group. The polymers shown in Figure 1.3 are based on our previous review paper [3o], and examples of recently reported polymers will be shown later.

Some of the π-conjugated polymers shown in Figure 1.3 were patented as materials (e.g., poly(thiophene-2,5-diyl) PTh [14a] and poly(3-alkylthiophene-2,5-diyl)

poly(phenazine-2,7-diyl)
P(2,7-Phzn)* [19c]

poly(2,5-diacetoxy-*p*-phenylene)
PPP-2,5-OAc* [19d,26c]

poly(3,7-dialkylbenzo[1,2-*b*:4,5-*d'*]
dithiophene-4,8-dione-2,6-diyl)
and its derivatives

P(2,6-Th₂Bq(diR))* [19e,26d]

poly(benzimidazole-4,7-diyl)
and its derivatives
P(4,7-Bim(R))* [19f,i]

poly(2,2'-bipyrimidine-5,5'-diyl)
PBPym* [19g,h]

PAE 3* [20a]
and its analogues

PAE 4* [20b]
and its analogues

PAE 5* [20c,h]
and its analogues

poly(5,8-dialkoxy-
anthraquinone-1,4-diyl)
P(5,8-OR-AQ)* [20d,i]

poly(*p*-biphenylenevinylene)
and its analogues
PBPV [20e]

PPympym(4,8-NHR)* [20f,j]

PAE 6* [9g] and its
Py analogue [9c]

PEDOTh [20g]
and alkyl
derivative [20k]

Figure 1.3   (*Continued*)

P3RTh [14b,c]) under the name of our institute. PPP [3a,b] and PFc [35a,39m] with high crystallinity and well-defined bonding between the monomer units were also first prepared by the polycondensation.

PTh was designed as the first well-characterized and stable π-conjugated conducting polymer composed of a five-membered ring [15]. It was reported in 1982 that introduction of the alkyl group to PTh led to enhancement of solubility without losing the essential π-conjugation system [14b,c,16a]. Due to the increase in solubility, NMR analysis of the microstructure of P3RTh became possible [14c,15c,17]. For example,
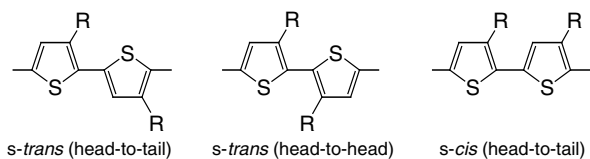
Figure 1.4 Microstructures of P3RTh.

the microstructure of P3RTh (R = CH$_3$) was discussed in term of head-to-tail and head-to-head joints (Figure 1.4) [14c,15c,17].

It has become possible to prepare head-to-tail type HT-P3RThs, which possess a highly controlled regioregularity, by organometallic polymerization methods [17a–f]. McCullough and his coworkers introduced Grignard reagent selectively to the 5-position of the RTh ring and polymerized it with Ni-catalyst [17a].

$$(1.12)$$
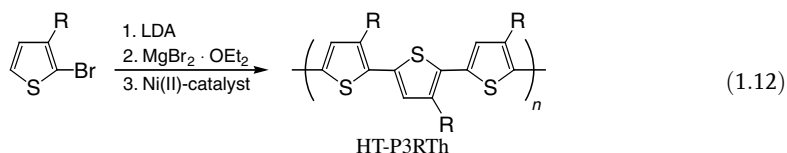
On the other hand, Rieke and his coworkers reported that regio-controlled organozinc reagent was obtained with highly activated zinc (Rieke zinc) and that the organozinc reagent afforded regioregular P3RTh, in which the amount of head-to-tail product was as high as 98.5% [17b].

$$(1.13)$$
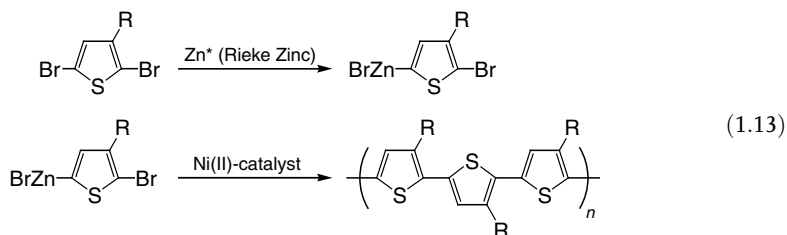
These regioregular HT-P3RThs exhibit higher crystallinity and higher electrical conductivity than the regio-irregular P3RThs, and form a π-stacked structure, as discussed later. Preparation of regio-regular HT-type polythiophene, with a *p*-alkylphenyl group at the 3-position, by oxidative polymerization has also been reported [17g]. Head-to-head type polythiophene with acetylenic –C≡CR side chains shows a strong tendency to form a π-stacked solid structure [17h–k], as discussed later. Syntheses of regioregular PAE-type polymers (e.g., PAE-6 in Figure 1.3) are also possible [9c,g].

$$X-Ar-C \equiv CH \xrightarrow{Pd-Cu} -(Ar-C\equiv C)_n-$$

$$(1.14)$$
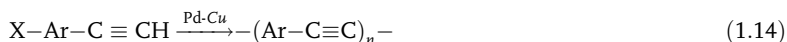
For some of the π-conjugated polymers (e.g., RTh and P3RTh) depicted in Figure 1.3, other preparative methods (e.g., oxdative polymerization) [7a–g,17g] have also been developed.

Use of 4-chlorobenzyl chloride in the polycondensation using Mg (Eq. (1.15)) also seems to give a regio-controlled polymer due to a large difference in the reactivity between the two C–Cl bonds.

$$Cl-\langle C_6H_4\rangle-CH_2Cl \xrightarrow{Mg} Cl-\langle C_6H_4\rangle-CH_2MgCl \xrightarrow{Ni} -\left(\langle C_6H_4\rangle-CH_2\right)_n$$

$$(1.15)$$
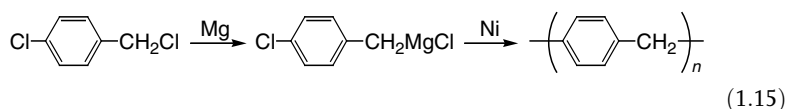
The polymer gives rise to sharp X-ray diffraction peaks, supporting its crystalline structure [3b,4n]. The polycondensation proceeds well, even on addition of the transition metal complex prior to the formation of the Grignard reagent (Eq. (1.2)) [3b]; in this case, Mg may serve as a reducing reagent for the catalyst, similar to Zn in Eq. (1.4). For catalysis of the polycondensation with Mg, Ni-compounds are usually most effective, and conditions and catalysts have been examined for synthesis of PPP, PTh, and related copolymers [3h]. However, other transition metal (e.g., Pd and Fe) compounds sometimes exhibit catalytic activity [3b].

The molecular weight of the π-conjugated poly(arylene)s prepared by the organometallic polycondensation seems to depend on the solubility and crystallinity of the polymers. The polymerization is considered to proceed even in slurrys of oligomeric or polymeric propagating species deposited from the solvent [4b,c]. There seems to be a trend that crystalline polymers have a lower molecular weight whereas less crystalline and/or soluble propagating species (especially those with an alkyl chain) give a higher molecular weight polymer. For example the poly(arylene)s prepared by using $Ni(0)L_m$ have the following molecular weights:

PPy: $M_w = 4300$ [4c], 6300 [18a] with [η] of 2.29 dL g^{-1}
PBpy: 3200 [4c]
PRPy: 120 00–27 000 (R = CH$_3$), 36 000 (R = 2-hexyl)
PRBpy: 21 000 (R = 2-hexyl)
P3RTh: 190 000 (R = hexyl)
P(2-Me-1,4-AQ): 190 000
Copoly 3: about 5×10^4–5×10^6.

For PPy, its preparation [18a] on a larger (50 g) scale gave the polymer with a higher molecular weight ($M_w = 6300$, determined by light scattering method) than the preparation on a 1 g scale [4c], which afforded a polymer with $M_w = 4300$. PPy with $M_w = 6300$ showed an intrinsic viscosity [η] of as large as 2.29 dL g^{-1} [18a]. Data from elemental analyses agreed with the structure of the polymers. Worked-up PPy prepared by $Ni(0)L_m$ (Eq. (1.3)) contained 13 ppm Ni [18a] and negligible halogen. Sometimes Ni was not detected in ICP analysis of polymers prepared using the Ni(0) complex. The polymers prepared by $Ni(0)L_m$ often possess an H-terminated end group [4c,26c]. which is considered to be formed from Ni-terminated aryl groups [1g,2e] during the work-up, including treatment with acids such as HCl;

$$\text{----polymer-Ni}L_m + H^+ \rightarrow \text{---polymer-H}$$
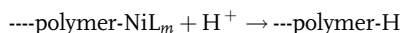
All of the poly(arylene)s shown in Figures 1.3 and 1.5, except for PPr [4h] and PCyh [22c], are stable in air. For example, PTh and P3RTh which can be stored long years [14–16] in an open atmosphere underwent virtually no change. Vacuum-deposited PTh film showed some electrical conductivity under air [22a]. PPr receives chemical redox reactions [4h] and PCyh is air-sensitive (*vide infra*). Many of the π-conjugated polymers shown in Figure 1.3 are soluble. However, PPP, PTh, and PCyh are insoluble.

poly[3,3'-dialkynyl-2,2'-bithiophene-5,5'-diyl]
HH-P3(C≡CR)Th* [20 l-n]

PBenz(OR')Th2(R2)*[20o]

Alkoxyderivativesof PPhen*[28a]

poly(pyrazine-2,5-diyl)
PPyrz* [20r]

PBIm(R)* [20p]

A: —N=N—   : **PDpyPd*** [20s,28a]
     —O—   : **PDpyFu*** [20 s]
     —NHCONH—: **PDpyDAz*** [20 s]

PPorph(Zn)
and itsanalogues[20q]

PDPyA(MB)*[19i]]

Copoly-7*[20 t-v]

Copoly-8* and analogues[21c-f]

−Ar— :   : **Copoly-9**[20 w,x]]

   : **Copoly-10***[20 y]
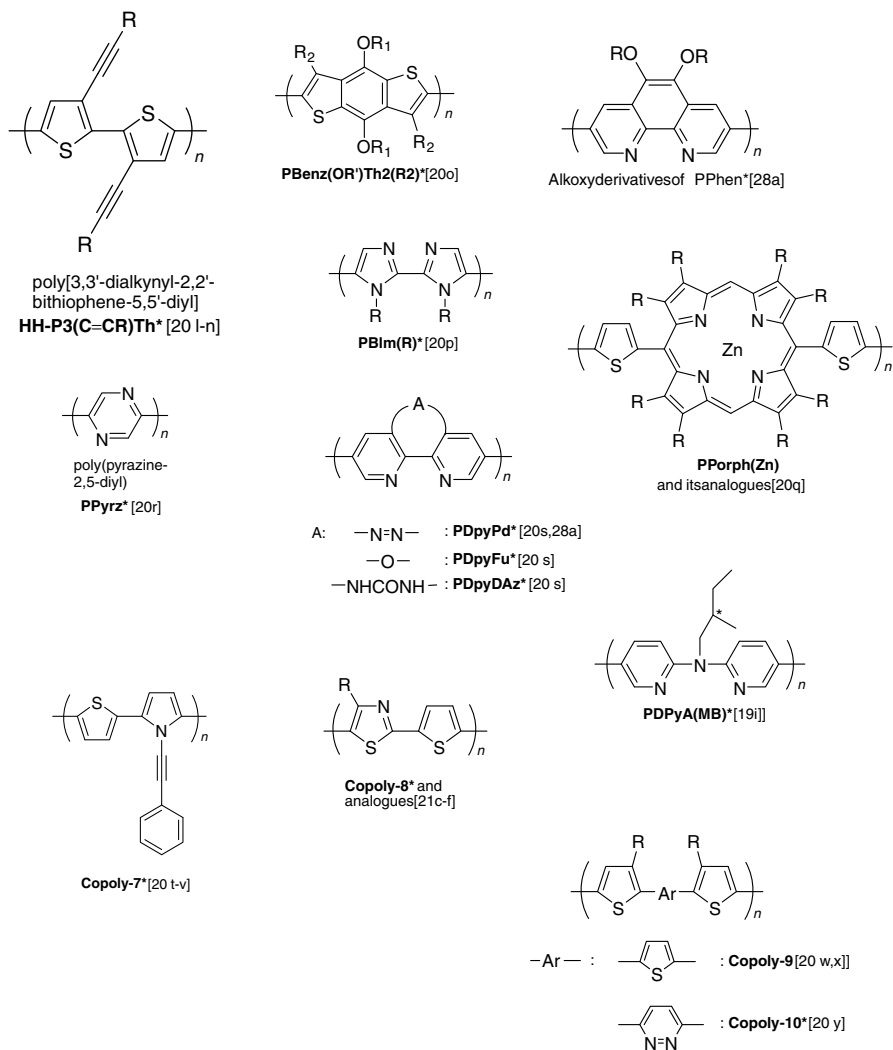
Figure 1.5 Examples of recently prepared π-conjugated polymers.

Copoly 7* [23 e]

PAE 7* [23 h]

PAE 8* [23 i-k]

Copoly 8* [23 l,m]

Copoly 6* and phenylene analogues [23 n,q]

PAE 9* and analogues [23 r,s]

HT-P6RPy* [23 t]

Copoly 9* [23 u]

Copoly 10* [23 u]

PH$_2$Ph(9,10-OR)* and its analogues [23 b-f]

P[BTzR] and related polymers [23 v,w]

Copoly 11* and boron derivatives [23 x]

HH-P(CH=CR) [23 y]
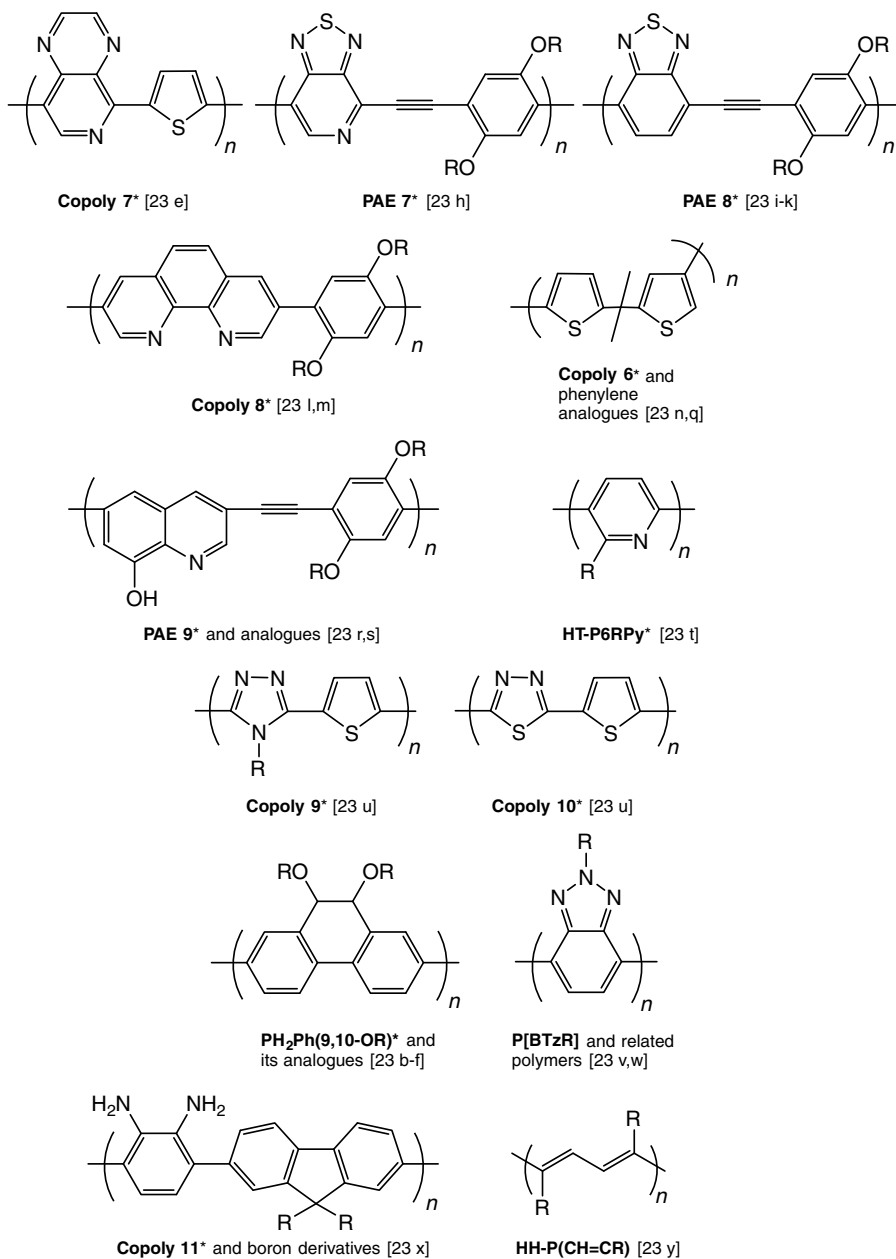
Figure 1.5 (*Continued*)

Examples of π-conjugated polymers prepared recently in our group are shown in Figure 1.5. Poly(9,10-disubstituted-9,10-dihydrophenanthrene-2,7-diyl)s (Scheme 1.1) such as $PH_2Ph(9,10\text{-}OSiBu_3)$ were light emitting and showed strong circular dichroism [28b–e].
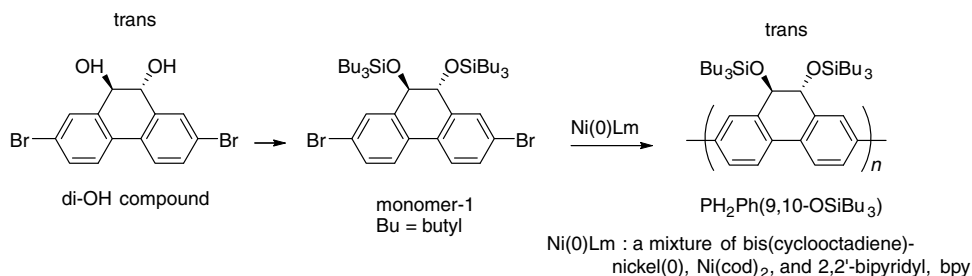
Scheme 1.1 Preparation of poly(9,10-disubstituted-9,10-dihydrophenanthrene-2,7-diyl).

1.3
Optical Properties

1.3.1
UV–Vis Data

Because of the expansion of the π-conjugation system, π–π* absorption bands of the poly(arylene)s show red shifts from the bands of their corresponding monomeric compounds. The degree of the red shift reflects steric hindrance around the bond connecting the monomeric units. Thus PTh, P3RTh (R = CH_3), and P4RBTz (R = CH_3), which all inherently have minor steric hindrances in their intramonomer bonds, show large red shifts (Figure 1.6) [3d,3f,3o,18b]:

> Degree of red shift:
> Thiophene-PTh: about $21\,000\,\text{cm}^{-1}$
> 3-Methylthiophene-P3RTh (R = CH_3): $19\,700\,\text{cm}^{-1}$
> 4-Methylthiazole-P4RBTz (R = CH_3): $21\,600\,\text{cm}^{-1}$.

On the other hand benzene (255 nm)–PPP (375 nm) [22a] and pyridine (248 nm)–PPy (373 nm) [4c] couples give somewhat smaller red shifts of about $13\,000\,\text{cm}^{-1}$, partly due to a larger π-conjugation system of the basic unit and to the steric repulsion caused by the *o*-CH group. For an anthraquinone–P(1,4-AQ) couple, the red shift becomes much smaller ($3500\,\text{cm}^{-1}$) [22b] for analogous reasons.

In the case of copolymers composed of electron-donating arylene and electron-withdrawing arylene units (see below), the copolymers are considered to have an intramolecular charge transfer structure. Copoly 1 gives rise to an absorption band at

λ_{max} = 231 nm   *ca.* 420-480 nm λ_{max} = 230 nm   420 nm
43300 cm^{-1} 22000 cm^{-1} 43500 cm^{-1} 23800 cm^{-1}

ca. 21000 cm^{-1} 19700 cm^{-1}

λ_{max} = 241 nm   502 nm
41500 cm^{-1} 19900 cm^{-1}

21600 cm^{-1}
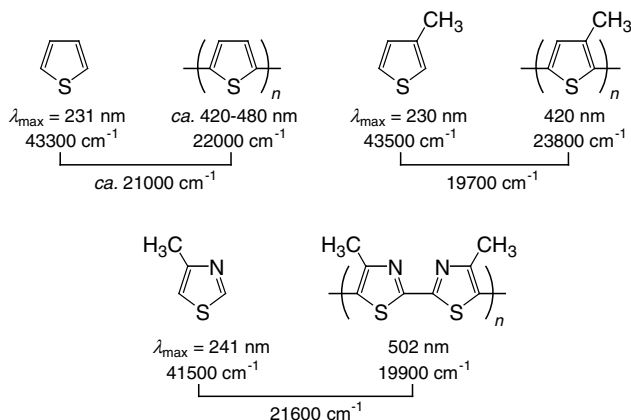
Figure 1.6 Shift of π–π* transition energy by forming a polymer system.

wavelengths longer than the λ_{max} of the corresponding homopolymers PPy and PTh [12e,20y,21,23a–d].

Copoly 1   : λ_{max}=490 nm (PThPy)
PPy   : λ_{max}=370 nm

Copoly 1

and **Copoly 5** (R=Ph)   : λ_{max}=603 nm
Homopolymer : P(5,8-diArQx)   : λ_{max}=444 nm
: PTh   : λ_{max}=420-480 nm
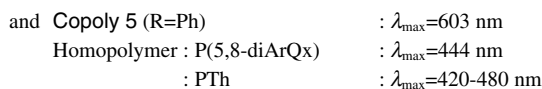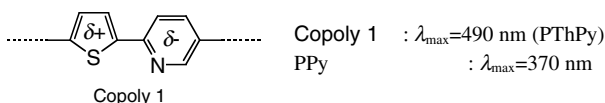
    Preparation of similar CT type copolymers, which also give λ_{max} at a longer wavelength, have been reported [21b,24].

    Selenophene has electron-donating properties similar to those of thiophene, and the following copolymerization affords block-type copolymers (Scheme 1.2).

    4   :   1   PNSe41 (a:b = 80:20)
    1   :   1   PNSe11 (a:b = 48:52)
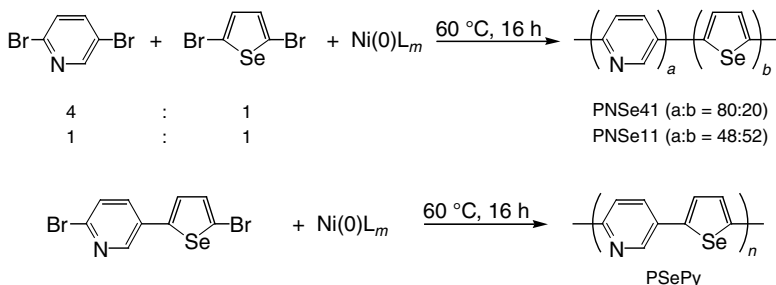
Scheme 1.2 Synthesis of block copolymer and alternating copolymer.

    The block-type copolymers give rise to absorption bands assigned to the PPy block, the PSe block, and the CT unit formed between the two blocks. On the other hand, the

alternating copolymer PSePy gives only the CT absorption band [12e]. Transfer of photo-energy in the block copolymer of pyridine and selenophene takes place very rapidly [29f].

For poly(naphthylene)-type polymers, a difference in the degree of the red shift has been noted between poly(naphthalene-2,6-diyl)-type and poly(naphthalene-1,4-diyl)-type polymers [3o,6b,6c,25,26a]:

Quinoline-P(2, 6-Q) : red shift = about $7500 \, cm^{-1}$
Quinoline-P(5, 8-Q) : red shift = $2500 \, cm^{-1}$

It was reported that o-substitution of PPP caused a shift of the π–π^* absorption band to a shorter wavelength [6f,7a,26b,c]. PPympym(4,8-NHR) has no o-CH group, which gives the steric repulsion and may cause some twisting out of the main chain, and shows the π–π^* absorption band at a longer wavelength than that of P(2,6-Q) [20f,j]:

$$\lambda_{max} : PPympym\,(4, 8\text{-NHOct})$$
$$Oct = octyl \qquad > \qquad P(2, 6\text{-}Q)$$
$$452 \, nm \qquad\qquad 403 \, nm \,(both \, for \, film)$$

In the case of PCyh, its color (black) indicates the formation of an effective π-conjugation system along the polymer chain, presumably due to the coplanarity of the polymer chain in the following *s-cis* conformation [22c]. In this conformation, the $=C-H$ hydrogen of the diene unit can get between the $-CH_2$ hydrogens to form the coplanar chain. PCyh is highly reactive to oxygen in air [22c], similar to polyacetylene [22e,f], which may be due to the presence of the coplanar expanded π–conjugation system without the aromatic stabilization.
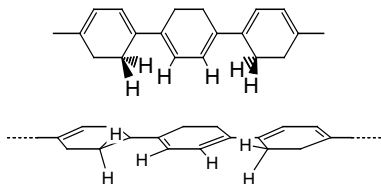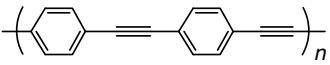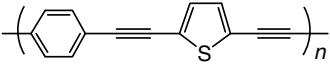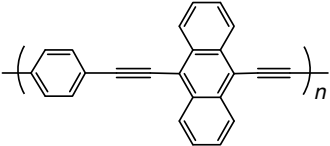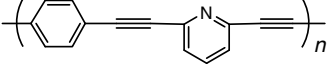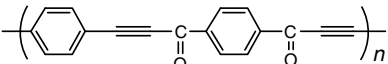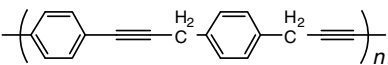

1.3.2
Photoluminescence

Most of the polymers shown in Figures 1.3 and 1.5 exhibit photoluminescence with an emission peak appearing at the onset of π–π^* absorption. Linear rod-like polymers such as PPy [4c], PPhen [28] and PAE-2 [9d] often show excimer-like emission in films and solutions with high concentrations. Among PAE-1-type polymers, those containing an anthracene unit show especially strong fluorescence (Table 1.1) [9a].

In several cases, especially those concerned with PPy [12e,29a] energy transfer from a photoactivated π-conjugated unit to an energy-accepting π-conjugated unit

**Table 1.1** Visible features of poly(aryleneethynylene) [9a].

Polymer	Color	Fluorescence
	Yellow	Bluish purple
	Yellow	Bluish purple
	Red	Green
	Light yellow	Purple
	White	None
	Yellow	Purple
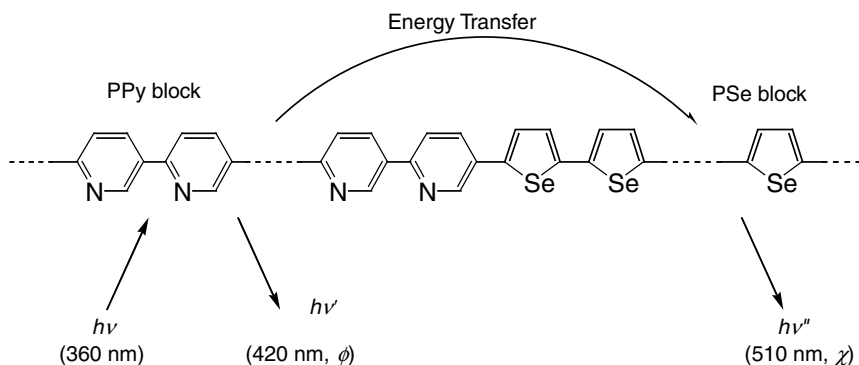
Scheme 1.3 Energy transfer from excited PPy block to PSe block.

has been observed during fluorescence (Scheme 1.3). The block structure of the above copolymer (Py-Se copolymer; Scheme 1.2) is confirmed by its UV–visible spectrum and solubility, and the copolymer undergoes such energy transfer.

Transfer of photoenergy accepted by the monomeric unit of P(5,8-diArQx) to the main chain π-conjugated system also take place [29b,c,f].
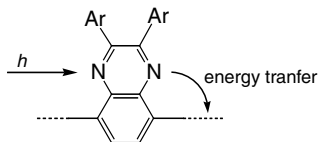
When PBpy forms a Ru complex (*vide infra*), the photoenergy accepted by the PBpy main chain is transferred into the Ru complex, and the photoemission occurs from the Ru complex [29a]. Similar energy transfers have been reported [29d,e].

1.3.3
Other Optical Properties

An interesting finding with Copolys 1–3 [12e,23b], Copoly-5 [12d,e,m], PAE-2 [9c, d,39], HT-P3RTh, and HH-P3(C≡CR)Th [20n] is that they give large χ(3) (third-order non-linear optical susceptibility) values of 3–5×10^{-11} esu.

π-Conjugated polymers are considered to possess energy band structures similar to that of inorganic semiconductors such as TiO_2 (*vide infra*). Photogeneration of carriers is therefore expected to be possible in most kinds of π-conjugated polymers. Indeed, P(5,8-diArQx) (Ar = *p*-tolyl) gives rise to a photocurrent, and it was proposed that photocarriers are generated by the dissociation of excitons [31]. Chiral (*R,R*)-$PH_2Ph(9,10\text{-}OSiBu_3)$ shows strong circular dichroism (CD) when it forms a colloidal solution and film (for film the CD effect is about 5°/μm thickness of the film [28e]).

1.4
Redox Behavior and Electrical Conductivity

π-Conjugated polymers are generally electrochemically active, and their cyclic voltammograms (e.g., that of poly(pyridine-2,5-diyl) PPy film on a Pt electrode [4c,d]) show p-doping (or oxidation) and n-doping (or reduction) peaks when the polymers are composed of electron-excessive units (e.g., pyrrole and thiophene) and electron-deficient units (e.g., pyridine and quinoxaline), respectively. Electrochemical reduction (n-doping) of PPy attains a peak cathodic potential E_{pc} of -2.43 V *vs.* Ag^+/Ag. Changing the scanning direction leads to oxidation (n-undoping) of the reduced PPy, giving rise to a peak anodic potential E_{pa} of -1.90 V. The n-doping and n-undoping are accompanied by a color change, as shown in Eq. (1.16); the doping level x in Eq. (1.16) is about 0.3.


$$\tag{1.16}$$
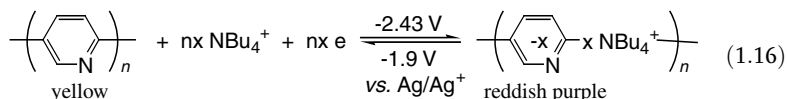
Cyclic voltammographic (CV) data of P(2-Me-1,4-AQ) and its corresponding low molecular weight quinine have been recorded; the CV of P(2-Me-1,4-AQ) has been discussed based on a mixed oxidized state (Eq. (1.17)) [22b,32a].

$$\text{(1.17)}$$

Product 1, red

Product 2, deep red
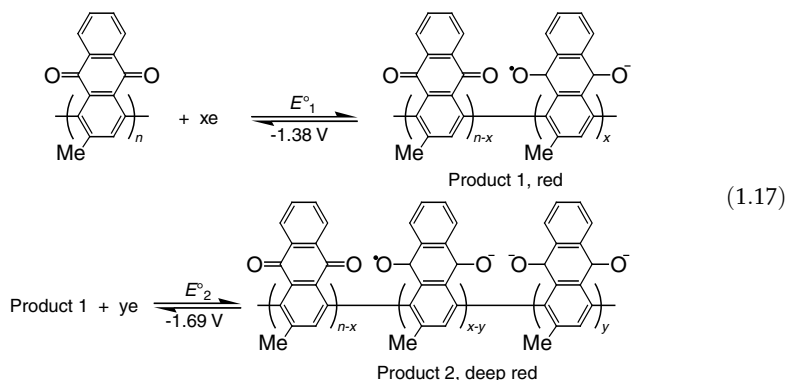
On the other hand, P(4,8-NO$_2$-1,5-AQ), bearing a strongly electron-withdrawing NO$_2$ group, shows an extremely low reduction potential ($E_1^0 = -0.74$ *vs.* Ag/Ag$^+$) [32b].

Poly(*p*-benzoquinone) PPBQ prepared from PPP-2,5-OAc undergoes electrochemical reduction (or n-doping) at a lower reduction potential (–0.5 V *vs.* Ag/Ag$^+$) due to the direct bonding of the *p*-benzoquinone unit in the π-conjugation system [19d,26c,32d].

$$\text{(1.18)}$$

PPP-2,5-OAc   PPBQ
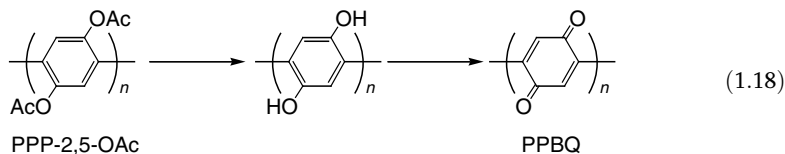
To our knowledge, this reduction potential is the lowest among those so far reported for π-conjugated poly(arylene)s.

Interestingly, P(4,8-NO2-1,5-AQ) gives rise to some electrical conductivity ($\sigma = 1.4 \times 10^{-6}$ S cm^{-1} at room temperature) even in the non-doped state [32b,c]. Some π-conjugated polymeric compounds (e.g., PBpy-transition metal complex [4c] and poly(arylene)-*N*-oxides) show similar electrical conductivity even in the non-doped state. The electrical conducting properties are considered to originate from generation of carrier by MLCT or from participation of resonance structures.

The ease of the electrochemical reduction of π-conjugated polymers simply reflects the electron-accepting ability of the monomeric repeating units [25]. A linear correlation holds between the reduction potential, E_{red}, of the polymer and the electron affinity E_a of the corresponding monomeric compound HArH for a wide range of poly(*p*-phenylene), poly(naphthalene-1,4-diyl), and poly(naphtalene-2,6-diyl) type polymers [19c,d,25,26].

$$E_{red} \text{ of } -(Ar)_n- = a + \varrho \times E_a \text{ of } X-Ar-X \qquad (1.19)$$

ϱ values of 0.75–0.8 have been obtained. A similar linear correlation is observed between the oxidation (or p-doping) potential E_{ox} of PPP, PTh, and PPr (*cf.* Figure 1.3) and the ionization potential IP of the corresponding monomeric compounds, although such a correlation is not observed between the E_{ox} of bulk metal in water and the IP of atomic metal due to a strong salvation effect [25]. A linear correlation between E_{red} of various poly(anthraquinone)s and the calculated E_a of the corresponding monomeric compounds has also been observed with a ϱ value of about 0.8 [20d].

PCrTh readily undergoes n-doping, in contrast to the other PTh analogues. The n-doped state is stabilized (even under air to some extent) due to a strong interaction of cations with ethereal oxygen, and n-undoping takes place at a potential considerably different from that of n-doping (Eq. (1.20)) [33].


$$(1.20)$$
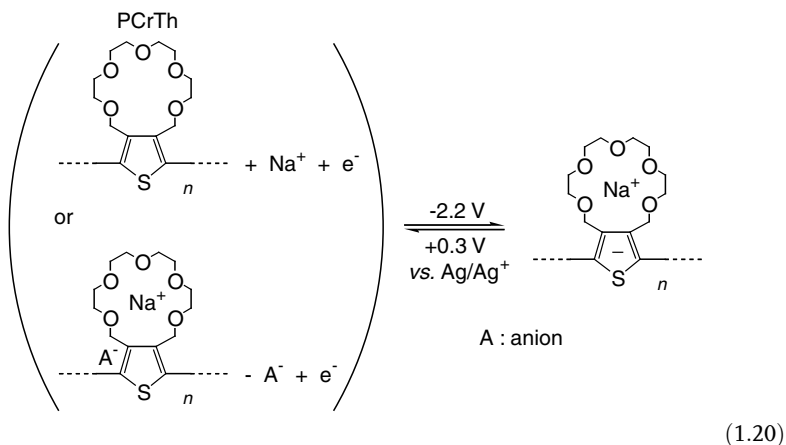
The CT-type copolymers (e.g., Copolys 1–3) show great differences in p-doping and p-undoping potential due to an EC mechanism [12e,23a–e]. Due to an electron-withdrawing effect of the $-C\equiv C-$ unit, the PAE type polymers are susceptible to electrochemical reduction [9c,d].

The π-conjugated polymers can also be chemically induced to undergo redox reactions (e.g., oxidation (or p-doping) by I_2 and $FeCl_3$ [4b,7h–j,14,16,17a,b,23f,g] and reduction (or n-doping) by Na [4a,c,I,7h–j,26a,51a]). The electrochemically and chemically oxidized or reduced polymers show electrical conductivity in the range 10^{-3} to 10^3 S cm^{-1} range, presumably due to cationic (positive) or anionic (negative) carriers formed along the π-conjugated system. Spectroscopic and XRD data support that I_2 and $FeCl_3$ are converted into I_5^- and $FeCl_4^-$ counter anions, respectively [4b,23g], in the chemical p-doping to form an ionic pair with the cationic center

generated in the polymer chain. Oxidation of PFc with donor acceptors like TCNQ also gives electrically conducting materials [35a,39m].

The concept of electric conduction in π-conjugated polymers has been used to explain the "polaron", "bipolaron", "soliton", and "band model" (e.g., *cf.* Scheme 1.4) [7, 34]. The UPS spectrum of K-doped PBpy showed a peak assigned to the polaron state [34a].
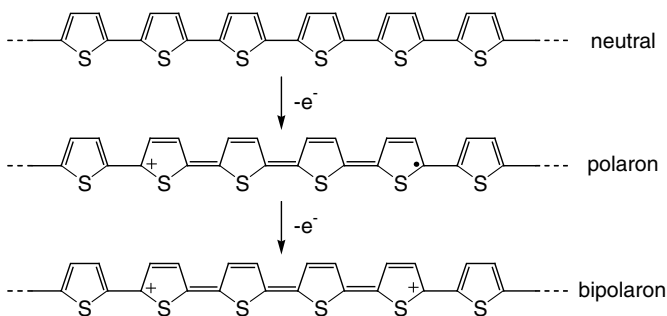
Scheme 1.4 Schematic model of polaron and bipolaron.

The iodine-doping of crystalline PTh prepared by the organometallic method gives another crystalline material with an I_n^- (*n*: presumably 5) counter ion [15d]; the iodine-doped crystalline PTh has electrical conductivity (σ) 30 S cm^{-1} whereas the introduction of thiophene-2,4-diyl unit (Copoly 6) causes a large decrease in the σ value. Derivatives of PTh [7,35b,c] and PPr [35d] are now used as conducting materials (e.g., as electrodes of a capacitor [35d])) industrially. In partially oxidized PFc, exchange of electrons between Fe(II) and Fe(III) species, which is related to the electrical conductivity, takes place on the Mössbauer time scale (10^{-6}s) [35a].

Due to the stabilization of the n-doped state of PCrTh (Eq. (1.20)), Na-doped (n-doped) PCrTh exhibits stability under air, as indicated by small changes in conductivity and by the IR spectrum of the Na-doped PCrTh under air. The n-doped PPy and PCrTh have electrical conductivities of 1.1×10^{-1} and 2×10^{-4} S cm^{-1}, respectively.

1.5
Linear Structure and Alignment on the Surface of Substrates

Because organometallic polycondensations give a π-conjugated poly(arylene) system with a well-defined bonding between the recurring arylene units, the polymers are considered to assume interesting structures such as rigid linear and helical structures. Furthermore, they often take an assembled structure. The rigid linear

structure has been confirmed for several poly(arylene)s, based on the following observations.

1) The light-scattering analysis of PPy, PBpy and P(2,6-Q) yields a very large degree of depolarization ($\varrho_v = 0.2$–0.33) [4a,c,26a]. For example PPy gives a theoretically limiting ϱ_v value of 0.33 when irradiated with Ar laser light, indicating that it adopts an ideally linear structure with a very large anisotropy of polarizability [4a,c].

PPy
$\rho_v = 0.33$
$\alpha_1 >> \alpha_2, \alpha_3$
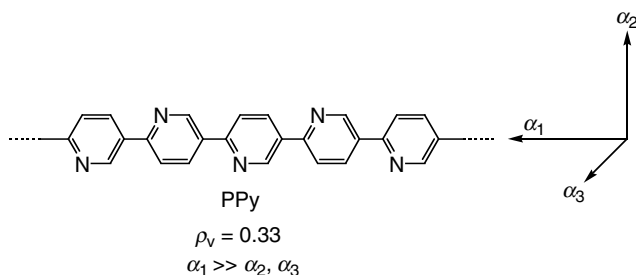
2) Vacuum evaporation of PPP, PTh and PBpy on carbon and metal substrates gives thin films in which the poly(arylene) molecules are aligned perpendicularly to the surface of the substrates (Figure 1.7) [3d,4b,c,22a,36].

   The alignment has been analyzed by a clear electron diffraction pattern. The report of the perpendicular alignment of PPP and PTh [36b] has been followed by many papers [7g,37] which report that oligomers (e.g., the hexamer) of thiophene are also arranged perpendicularly or somewhat tilted to the surface of the substrates. The ease of the perpendicular alignment of PPP increases in the following order on changing the substrate:

   $$Au, Ag < Al < C.$$

   The order is considered to reflect the magnitude of the interface energy between PPP and the substrate [22a,36c], which originates from a known metal–π–aromatic interaction for the Group 11 metals (Au and Ag).

3) Many of the π-conjugated poly(arylene)s exhibit excimer-like emissions in films and highly concentrated solutions, which can be attributed to a strong interaction between the linear rod-like molecules [4c,g,9c,d,28].

4) PBpy molecules can be aligned in parallel with the surface of a glass substrate due to coordination of 2,2′-bipyridyl with Si–O–H hydrogens on the surface of the substrate [3d,4c].

5) PPy, PBpy, and similar linear polymers give excellent polarizing films when included in stretched polymer (e.g., poly(vinyl alcohol)) films [4c,12e].

Control of the alignment of the poly(arylene) molecule may be crucial for the preparation of effective electronic and optical devices.
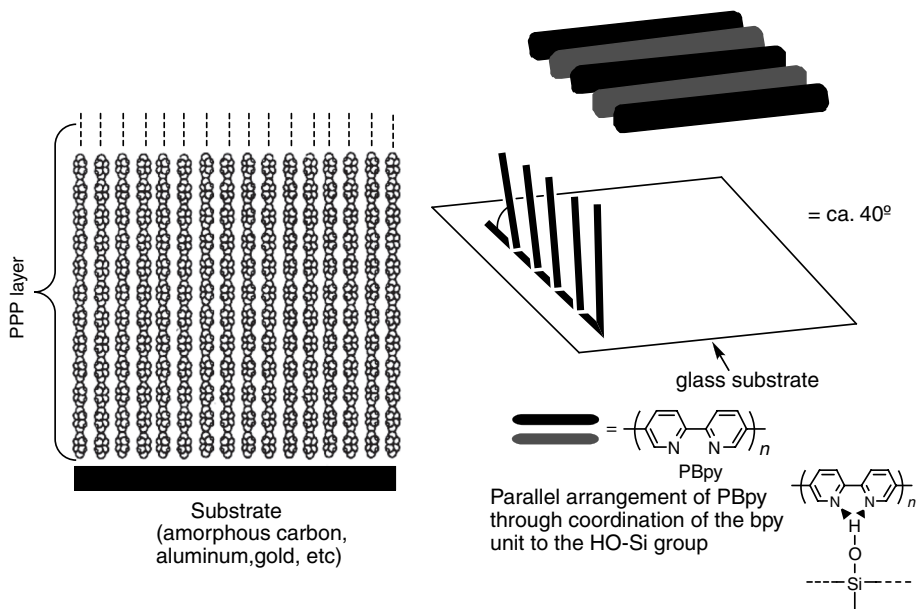
Figure 1.7 Perpendicular orientation of PPP on substrate and parallel arrangement of PBpy on a glass substrate.

1.6
Stacking in the Solid and Colloid

Regioregular head-to-tail HT-P3RTh (Eqs. (1.12) and (1.13)) [17, 38], head-to-head HH-P4RBTz [21], PAE-type polymers with CT structures (e.g., [23h–k]), and Copoly 10 [23u] with long R form stacked structures both in the solid and in colloidal solutions [17, 38]. They show sharp XRD (X-ray diffraction) peaks in a low angle region. HH-P4RBTz [38], P(2,6-Th$_2$Bq(diR)) [19e,26c], P(4,7-Bim(R)) [19f], P(5,8-OR-1,4-AQ) [29d], PBPV [20e], and HH-P3(C≡CR)Th (*cf.* Figures 1.3 and 1.5) with long side chains also give a sharp diffraction peak in a low angle region ($2\theta = 2$–$8°$ for CuK$_\alpha$). The XRD peak in the low angle region is assigned to a distance between the core main chains separated by the long side chain (Figure 1.8).

The number density along the polymer main chain seems to determine the packing mode (the end-to-end or interdigitation packing). Plots of the *d* value *versus* number of carbons in the R group of the above described polymers give straight lines. When the slope is larger than the height of the CH$_2$ group (1.25 Å/C) [38h], the polymer does not have the interdigitation packing mode and is considered to take the end-to-end packing mode. On the other hand, the number density of the R group in P(2,6-Th$_2$Bq(diR)) is smaller than that in other polymers, and P(2,6-Th$_2$Bq(diR)) affords a linear line with a slope of about 1.2 Å/C, which corresponds to the interdigitation packing mode.
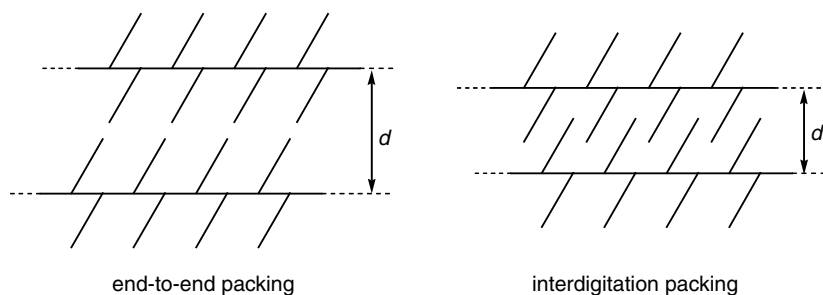
Figure 1.8 Packing modes of π-conjugated poly(arylene) with long side chains. One layer is depicted, and layers are considered to form the stacked structure.

The π-conjugated linear polymers adopt the packing mode, not only in the solid (film) but also in colloidal solutions, whose light scattering analyses sometimes reveal assembly of 10^3 polymer molecules [38h]. Revealing the driving force for the π-stacking of π-conjugated polymers is expected to give basic information on the controlling force for similar π-stacking observed with various molecules including graphite and DNA.

1.7
Chemical Reactivity and Catalysis

1.7.1
Metal Complexes and Modification of Nitrogen

The N-containing poly(arylene)s, especially those with chelating units like a bpy or 2,2′-bipyridmidine unit (PBpy and PBpym), form metal complexes (Figure 1.9) [4c,e, f,19g,29a].

PBpy forms metal complexes [4e,f], and various π-conjugated chelating polymers and their metal complexes have been synthesized and their electric and optical properties investigated [4c,12i,21,28,39a–g]. Other types of transition metal complexes have also been synthesized using PPP and its analogues [39h–k]. Ferrocene polymers have also been reported [20c,35,39k–m].

In the case of N-containing poly(arylene)s, chemical modification of imine nitrogen is also possible. For instance, quaternization with RX [40], N-oxidation with H_2O_2 [41], and N-ylidation with tetracyanoethylene oxide [41b] have been carried out for these polymers.

These polymer complexes and N-modified polymers show interesting electrochemical behavior. For example, a cyclic voltammogram of a film of a Ru-PBpy complex indicates an electron-exchange between Ru species, presumably *via* the π-conjugated system [4c], and RX (CH_3I, $(CH_3O)_2SO_2$, etc.) adducts of poly(quinoline)s show viologen-like redox behavior including electrochromism (Eq. (1.21)) [40].

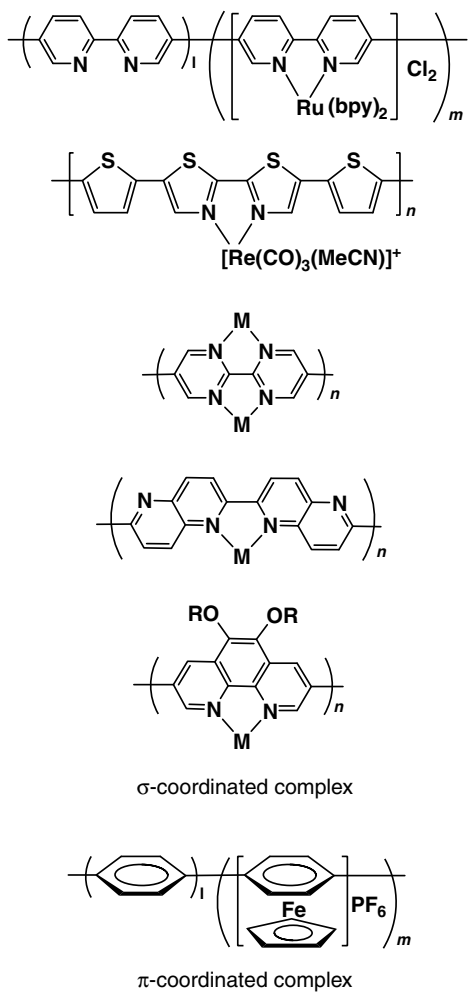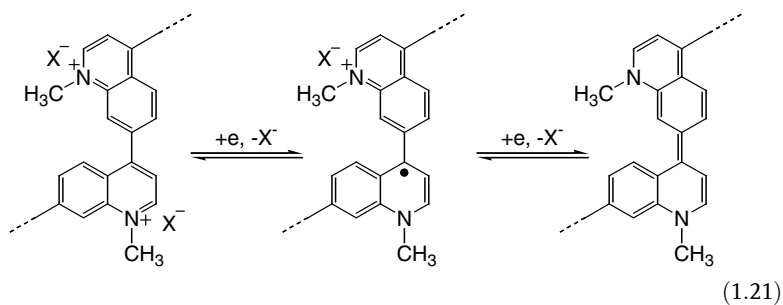**Figure 1.9** Polymer complexes using π-conjugated polymers as ligands.

$$(1.21)$$

As described above, these *N*-modified polymers and the nitrated polymers give rise to some electrical conductivity even in the non-doped state.

From the viewpoint that π-conjugated polymers can be regarded as organic semiconductors, numerous attempts have been made to derive functions similar to those of inorganic semiconductors (e.g., TiO_2) from π-conjugated polymers. For example, photoinduced enhancement of electrical conductivity is observed for P(5,8-diArQx) (Ar = *p*-tolyl) [31] (*vide supra*). PPP and PPy prepared by organometallic polycondensation have been utilized as photocatalysts by Yanagida [42]. On the other hand, PBpy serves as a highly efficient photocatalyst for hydrogen evolution from aqueous media [43a]. This catalytic efficiency is superior to those of the other π-conjugated poly(arylene)s such as PPP and PPy [42], and this is attributed to the chelating ability and high hydrophilicity of PBpy. Electronic structures of PPP, PPy, and PBpy are compared with that of TiO_2 [22a,34,43a].

The metal complexes of the π-conjugated polymers sometimes show a highly active and stable catalytic effect (e.g., for oxidation reactions) which cannot be attained with low-molecular-weight metal complexes and metal complexes of non π-conjugated polymers [43b–d].

1.8
Electronic and Optical Devices (ECD, Battery, EL, Diode, Transistor, Nonlinear Optical Device, etc.)

1.8.1
Redox Functions

All π-conjugated poly(arylene)s change color when electrochemically oxidized or reduced (*cf.* Eqs. (1.16) and (1.17)). This phenomenon is called "electrochromism" and much effort has been made to derive practical benefits from it. Poly(vinyl alcohol) having a PTh pendant group serves as an excellent polymer electrolyte which shows electrochromism [44a,b]; poly(vinyl alcohol) serves as an excellent matrix polymer for polymer electrolytes [44c,d]. Changes in UV–visible spectra on electrochemical doping of π-conjugated polymers (e.g., n-doping of P(5,8-diArQx), Ar = C_6H_5) [45a]) have been reported.

The electrochemical redox behavior of π-conjugated polymers has been applied to batteries by many research groups [46f, 47]. Polymer batteries were reported by two groups in 1981 [46a,b]. PTh serves as a positive electrode material for Li and Zn batteries [46d–f]. The Li/LiI/PTh-I_2 solid electrolyte cell was also fabricated, and gave a high utilization of iodine [46f,g]. For a "storehouse of charge" not only π-conjugated polymers but also graphite can be used. Sanechika, who carried out his doctorate work in our group and learned the concepts of the polymer battery participated in the development of a graphite-based Li battery, which is now widely used as a lithium ion cell [48]. PDPA and its analogues have been tested as sensors for a lead battery [19b, 49a]. The N-containing polymers like PPy can transport H^+ in electrochemical

processes [49b], and protonated polymers exhibit electrochemical activity similar to that of NAD and serve as an active material for a battery operating in an acidic medium [49c].

1.8.2
Electronic and Optical Devices

Recently, the utility of π-conjugated polymers as the material for an electroluminescence (EL) device or light emitting diode (LED) has been demonstrated [50]. PTh, P(5,8-diArQx), and P4RBTz serve as materials for the EL device [22a, 38c, 45b, 51]. PTh works as an excellent material for the hole-transporting layer (HTL) in the EL device [51b]. Many papers have been published on the utilization of poly(9,9-dialkylfluorene- 2,7-diyl)s and their related polymers in EL devices [50f–j], and the polymers are usually prepared by organometallic polycondensation. An Au/PTh/Al electric junction behaves as a rectifying diode [22a].

Thin layer transition (TLT) based on π-conjugated polymers or organic molecules is another target device of the π-conjugated polymers. The TFT behavior of PTh [22a, 52], Copoly-8, and Copoly-11 prepared by organometallic polycondensation has been examined [21d, 22a, 23u, 52].

Because the copolymers, Copoly 1–3 [12d, 23], PAE-2 and its analogues [9c,d, 30], and HH-P3(C≡CR)Th [20n] show large $\chi^{(3)}$ values, preparation of nonlinear optical devices using the materials is expected. A wave-guide using PAE-2 has been prepared [30b].

1.9
Conclusions

Organometallic polycondensation, based on organometallic chemistry, has contributed much to the preparation of π-conjugated polymers such as PTh and PRTh. The π-conjugated polymers prepared by organometallic polycondensation have a well-characterized structure. They have contributed to our understanding of basic chemical and physical properties as well as to elucidation of the structure of π-conjugated polymers. In addition, they are useful materials for electric and optical devices and are expected to be invaluable in their future application.

Koizumi, and H. Fukumoto and Dr. Maruyama (now at Yokohama Rubber Co. Ltd.) of our Institute, Professor T. Kanbara of the University of Tsukuba, Professor I. Yamaguchi of Shimane University, and all other coworkers.

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