**polymer**

Feature Article

# Synthesis of π-conjugated polymers bearing electronic and optical functionalities by organometallic polycondensations and their chemical properties

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## Abstract

A wide variety of π-conjugated polymers have been synthesized by using organometallic polycondensations. For instance, Ni(0) complex-promoted dehalogenative polycondensation of dihaloaromatic compounds, X—Ar—X, affords poly(arylene)s, —(Ar)$_n$—. Pd-catalyzed polycondensation gives alternating copolymers, —(Ar—Ar′)$_n$—, and poly(arylene-ethynylene)s, —(Ar—C≡C—Ar′—C≡C)$_n$—. These polymers show distinguishing optical and electrochemical properties and functionalities. Their well-characterized linear structures lead to molecular assembly and packing of the polymer molecules in solutions and in the solid state. In this article, we describe the synthesis of π-conjugated polymers by the organometallic polycondensations, chemical properties of the synthesized polymers, and applications of the polymers for electronic and optical devices.
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*Keywords:* π-Conjugated polymer; Organometallic polycondensation; Electronic and optical devices

## 1. Introduction

π-Conjugated polymers have received much attention because of their attractive electronic and optical properties. In 1977, Heeger, MacDiarmid, and Shirakawa reported that conductivity of polyacetylene increased remarkably by doping with iodine. Up to now, a wide variety of π-conjugated polymers have been synthesized, and their physical and chemical properties have been investigated by many researchers [1–10]. Many of the polymers are electrochemically active, electrically conductive, and light emitting [1–12]. Polyacetylenes are usually prepared by addition polymerization of acetylenes. However, many of the other π-conjugated polymers such as polypyrroles and polythiophenes are polymerized by oxidative polymerization and organometallic polycondensation [1,2,4–15]. Oxidative polycondensation is suited for monomers with a low oxidation potential (e.g., pyrrole and anilines) whereas the organometallic polycondensation can give π-conjugated polymers composed of electron-accepting monomeric units and π-conjugated polymers with well-defined bonds between the monomeric units. We have been concerned with the organometallic polycondensation, and in this paper we report preparation of π-conjugated polymers via the organometallic polycondensation, chemical properties of the obtained π-conjugated polymers, and functionalities of the π-conjugated polymers. This review focuses on π-conjugated polymers synthesized in our group.
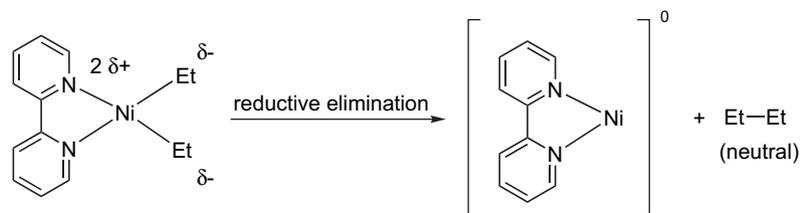
## 2. C—C bond formation on Ni and Pd

### 2.1. Ni

#### 2.1.1. Basic organometallic reactions of Ni

Reductive elimination of R—R from diorganonickel(II) complexes NiR$_2$L$_m$ (Eq. (1)) [16–31] is known as one of the

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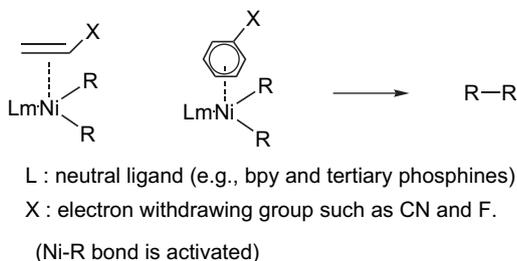*E-mail address:* tyamamot@res.titech.ac.jp (T. Yamamoto).

Scheme 1. NiEt$_2$(bpy) and elimination of neutral Et-Et (butane).

important basic organometallic reactions related to organometallic C–C coupling reactions. The original Ni complex is an Ni(II) complex, whereas the Ni(II) complex is formally reduced to an Ni(0) complex after the elimination of R–R. Consequently the reaction is called a "reductive elimination" reaction. Controlling factors of this reductive elimination reaction (or the C–C coupling reaction on Ni) have long been studied by our research group and by other research groups.



L: neutral ligand such as 2,2'-bipyridyl (bpy)
R: organic group (e.g., alkyl or aryl)
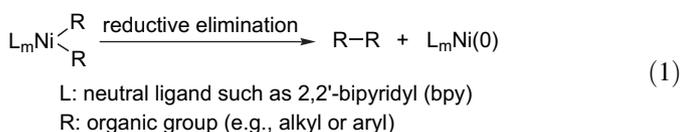
The Ni–R bond is considered to be polarized as $Ni^{\delta+}$–$R^{\delta-}$ because of the difference in the electronegativity between Ni and C. From the negatively charged $R^{\delta-}$ group, the electrically neutral R–R is produced in the reductive elimination reaction as shown in Scheme 1.

This suggests that the reductive elimination is enhanced by coordination of an electron-accepting ligand to Ni. Actually, coordination of molecules leading to the back-donation [16b,32,33] (e.g., back-donation from Ni to electron-accepting olefin [16,21,32,33] or aromatic compound [26]) to Ni strongly enhances the reductive elimination of R–R.



L : neutral ligand (e.g., bpy and tertiary phosphines)

X : electron withdrawing group such as CN and F.

(Ni-R bond is activated)

The enhancement effect of the coordination of electron-accepting olefin and aromatic compound is as large as $10^{10}$–$10^{13}$ [26c,d]. This effect is larger than the effect of an electron-withdrawing group on the dissociation constant of carboxylic acid in aqueous media. This situation is shown in Fig. 1.

The concept of the "reductive elimination" is accepted in organometallic chemistry and synthetic chemistry. Because dihalo-olefins and dihaloaromatic compounds are strong electron acceptors, they are considered to accelerate the reductive elimination reaction. Consequently the dihalogenated olefinic and aromatic monomers are suited for the Ni complex-promoted polycondensation, which proceeds through the reductive



$k_1 / k_0 \approx 10^{10}$

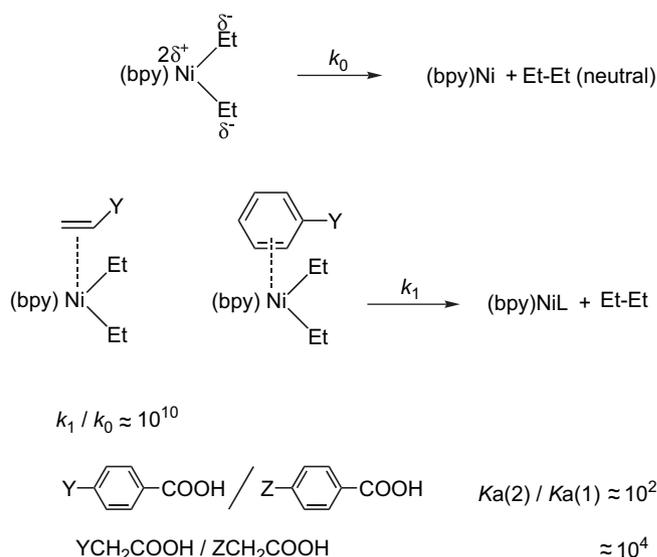$K_a(2) / K_a(1) \approx 10^2$

$\approx 10^4$

Fig. 1. Effects of electron-accepting olefin and aromatic compounds on the reductive elimination and effects of electron-withdrawing group on the dissociation of carboxylic acids in aqueous media. In non-aqueous solvents such as acetonitrile, the $K_a(2)/K_a(1)$ value can become $10^{12}$ [26d].

elimination from a diorganonickel(II) intermediate. Recently, it was reported that the reductive elimination reaction of diarylnickel complexes, NiAr$_2$(bpy) (bpy = 2,2'-bipyridyl), with electron-accepting aryl (Ar) groups such as pentafluorobenzene ring and pyrazoyl ring was induced by Lewis acid and protic acids (Eq. (2)) [26b–e,27].
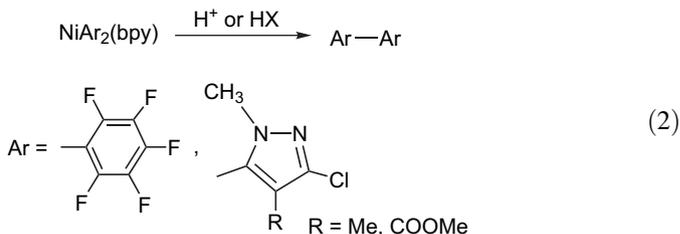


These basic reductive elimination reactions on Ni give basis for organometallic C–C couplings, and have been utilized for organic syntheses (e.g., $RMgX + R'X \rightarrow R–R'$ (Ni-catalyzed); $2RX + Zn \rightarrow R–R$ (Ni-catalyzed); $2RX + Ni(0)$ complex $\rightarrow R–R$; X = halogen) [34–39]. Because the Ni-based C–C coupling reaction is promoted by coordination of the electron-accepting olefinic and aromatic compounds, the Ni-based organic synthesis proceeds well with olefinic and aromatic halides.
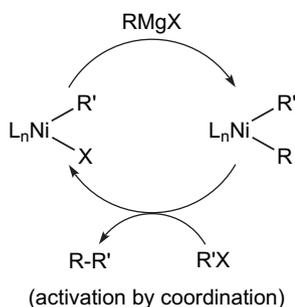
Scheme 2. Coupling reaction between RMgX and R′X and the reaction mechanism involving the formation of a diorganonickel(II) complex.
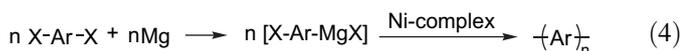
For example, there is no restriction about the R group in RMgX for the coupling between RMgX and R′X. However, for the organic halides R′X, the Ni-catalyzed reaction proceeds only with olefinic halides and aromatic halides. These results suggest that enhancement of the reductive elimination on the intermediate diorganonickel(II) Ni(R)(R′)$L_n$ complex by coordination of the electron-accepting olefinic halide or aromatic halide is crucial for the Ni-catalyzed C−C coupling [26b,c] (Scheme 2).
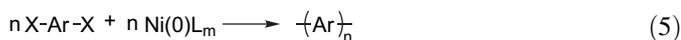
$$RMgX + R'X \xrightarrow{Ni} R\text{-}R' + MgX_2 \qquad (3)$$
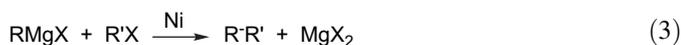
Recently, it has been reported that the Ni-catalyzed C−C coupling between RMgX and R′X can proceed even with aliphatic R′X when dienes such as 1,5-cyclooctadiene are present in the reaction system [35a]. Dienes are considered to activate the $L_n$Ni(R)(R′) intermediate [26b,c], because they have a good coordinating ability to Ni and are considered to lead to the back-donation from Ni to them.

### 2.1.2. Ni-promoted synthesis of π-conjugated polymers

We have utilized this coupling reaction for the polycondensation of dihaloaromatic compounds since 1976 [40−46].

$$n\, X\text{-}Ar\text{-}X + nMg \longrightarrow n\,[X\text{-}Ar\text{-}MgX] \xrightarrow{Ni\text{-complex}} +(Ar)_n \qquad (4)$$

Refs. [40−46]

$$n\, X\text{-}Ar\text{-}X + n\, Ni(0)L_m \longrightarrow +(Ar)_n \qquad (5)$$

Refs. [47−60]

In some cases, Ni(0)$L_m$ complexes 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. (6)) [61−70]. It was reported that NaH and hydrazine hydrate were also usable as the reducing agents of the Ni(II) compound [71,72].
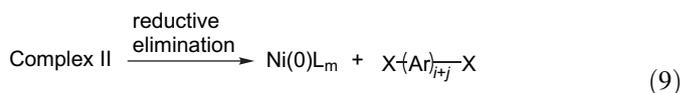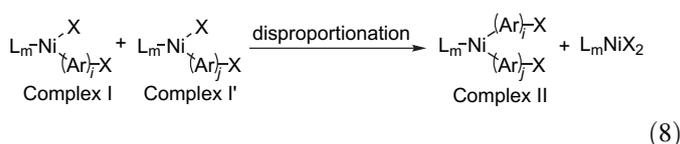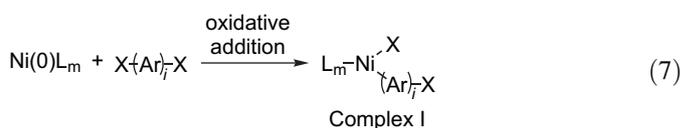
$$n\, X\text{-}Ar\text{-}X + nZn\ (\text{or } 2e^-) \xrightarrow{Ni\text{-complex}} +(Ar)_n + n\, ZnX_2\ (\text{or } 2X^-) \qquad (6)$$
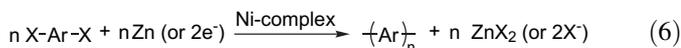
Refs. [61−72]

Poly(arylene)s can be prepared by the organometallic polycondensation as well as by chemical and electrochemical oxidations of aromatic compounds as reported in review articles and books [73−79].

### 2.1.3. Mechanistic aspects for Ni(0)-promoted polycondensation

The Ni(0)-promoted dehalogenative polycondensation is considered to proceed as shown in Eqs. (7)−(9) [39,49].

$$Ni(0)L_m + X(Ar)_i X \xrightarrow[\text{addition}]{\text{oxidative}} L_m\text{-}Ni \begin{smallmatrix} X \\ (Ar)_i\text{-}X \end{smallmatrix} \qquad (7)$$
Complex I

$$L_m\text{-}Ni\begin{smallmatrix} X \\ (Ar)_i\text{-}X \end{smallmatrix} + L_m\text{-}Ni\begin{smallmatrix} X \\ (Ar)_j\text{-}X \end{smallmatrix} \xrightarrow{\text{disproportionation}} L_m\text{-}Ni\begin{smallmatrix} (Ar)_i\text{-}X \\ (Ar)_j\text{-}X \end{smallmatrix} + L_mNiX_2 \qquad (8)$$
Complex I   Complex I′   Complex II

$$\text{Complex II} \xrightarrow[\text{elimination}]{\text{reductive}} Ni(0)L_m + X(Ar)_{i+j} X \qquad (9)$$

Ar = arylene (e.g., *p*-phenylene)
X(Ar)$_i$X : propagating oligomeric species

The C−C coupling reaction contains three fundamental reaction steps; namely, oxidative addition of C−X to Ni(0)$L_m$ (Eq. (7)) [38,80−85], the disproportionation reaction (Eq. (8)) [86], and reductive elimination of Ar−Ar (or X(Ar)$_{i+j}$X) from the diorganonickel(II) complex (Eq. (9)). When the Ni−C bond has high stability, the complexes I [38] and II [26,27] as well as a complex of a type $L_m$(X)Ni−Ar−Ni(X)$L_m$ [22] 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 Ni-promoted polycondensation.

### 2.2. Pd

Pd complexes are also known as useful catalysts for various C−C coupling reactions. Reductive elimination of R−R from diorganopalladium(II) complexes, Pd$R_2L_m$, is also known [87−89].

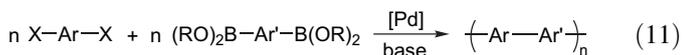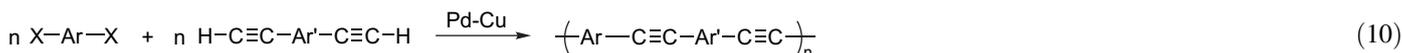$$L_mPd\begin{smallmatrix} R \\ R \end{smallmatrix} \longrightarrow R\text{—}R + L_mPd(0)$$
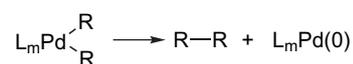
### 2.2.1. Pd-promoted synthesis of poly(arylene-ethynylene) and other π-conjugated polymers
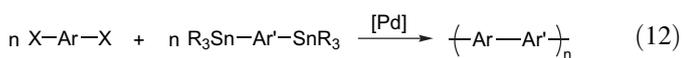
Various Pd-catalyzed C−C coupling reactions have been developed, and they have been utilized for organic synthesis.

We [90–97] and other groups [98–111] applied the C−C coupling to polycondensations.
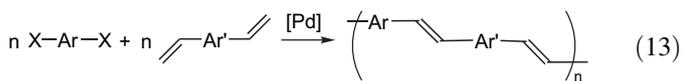
Several Pd-catalyzed C−C coupling reactions have been applied to the π-conjugated polymer synthesis, e.g., Refs. [112,113]

$$n \; X–Ar–X \; + \; n \; H–C{\equiv}C–Ar'–C{\equiv}C–H \; \xrightarrow{\text{Pd-Cu}} \; {\left(\!\!\left.Ar–C{\equiv}C–Ar'–C{\equiv}C\right)\!\!\right._n} \tag{10}$$

$$n \; X–Ar–X \; + \; n \; (RO)_2B–Ar'–B(OR)_2 \; \xrightarrow[\text{base}]{\text{[Pd]}} \; {\left(\!\!\left.Ar–Ar'\right)\!\!\right._n} \tag{11}$$

Refs. [114,115] (basic reaction)

$$n \; X–Ar–X \; + \; n \; R_3Sn–Ar'–SnR_3 \; \xrightarrow{\text{[Pd]}} \; {\left(\!\!\left.Ar–Ar'\right)\!\!\right._n} \tag{12}$$

Refs. [116,117] (basic reaction)

$$n \; X–Ar–X + n \; {\diagup}{–}Ar'{\diagup} \; \xrightarrow{\text{[Pd]}} \; {\left(\!\!\left.Ar{=\!\!\!=}Ar'{=\!\!\!=}\right)\!\!\right._n} \tag{13}$$

Refs. [118,119] (basic reaction)

From the reaction of the dihalogenated monomer with the diethynyl compound (cf. Eq. (10)), poly(arylene-ethynylene)s (PAEs) can be synthesized [90,91,105,106]. From the study of the alkynyl ligand transfer from Cu−acetylide complexes to Pd [88a], it is clear that Cu(I) compounds play an important role in the C−C coupling reactions. Because organometallic polycondensations are very useful for the synthesis of π-conjugated polymers, various methods utilizing other Pd-catalyzed C−C coupling reactions have been developed. For example, reactions shown in Eqs. (11) and (12) promote the alternating copolymers containing −Ar− and −Ar′− units, and poly(arylene-vinylene)s (PAV) can be obtained by the reaction shown in Eq. (13) [99–101]. By the development of these cross-coupling utilized polymerizations, alternating copolymers have been prepared easily, and variation of the π-conjugated polymers has been dramatically increased.

C−OY bonds (OY = leaving group or pseudohalogen; Y = tosyl, etc.) are also workable similar to the C−X bonds, therefore, YO−Ar−OY can be used for the polycondensation [46,65]. New synthetic methods for π-conjugated poly(arylene)s using bis(pinacolato)diborane [110,111] and distannane as a condensation reagent have been reported.

These Ni- and Pd-promoted polycondensations were reported by our group for the first time (e.g., the polymerization expressed by Eq. (3) in 1976−1977 [40,42] and by Eq. (10) [90,91]) in 1981−1984.

## 3. Synthesis and chemical properties of π-conjugated polymers

### 3.1. Synthesis

Various π-conjugated polymers have been synthesized by using the organometallic polycondensations expressed by Eqs. (4)−(6) and (10)−(13). Fig. 2 displays the examples of the π-conjugated poly(arylene)s prepared by the organometallic polycondensation methods in our group.

PTh was designed as the first well-characterized and stable π-conjugated conducting polymer composed of a five-membered ring [120−126]. Recently, $^{13}C$-labeled PThs have been prepared [48c]:
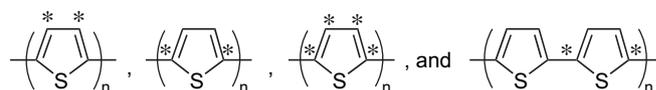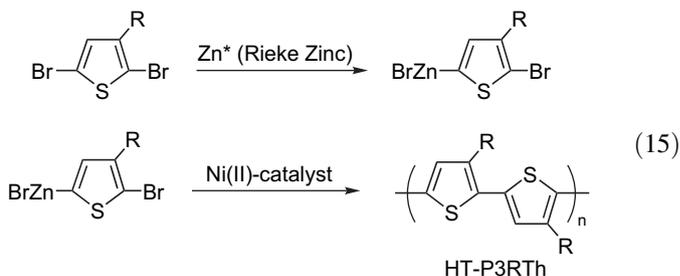
Alkyl group-substitution of PTh increased the solubility of PTh without losing the essential π-conjugation system of PTh [127,129], therefore, NMR analysis of microstructure of P3RTh became possible [123,192−196]. For example, the microstructure of P3RTh was discussed in terms of head-to-tail and head-to-head joints (Chart 1) [123,180,192−196].

In recent years, high-regioregular P3RThs have been prepared by modified organometallic polycondensations. McCullough et al. introduced Grignard reagent selectively to the 5-position of RTh ring and polymerized it with Ni-catalyst (Eq. (14)) [192,193].

$$\tag{14}$$
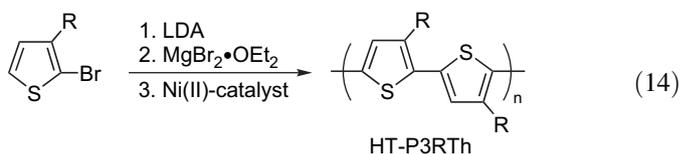
Rieke et al. reported highly regioregular HT-P3RTh which was prepared using regiocontrolled organozinc reagent. The produced polymer contains the head-to-tail joint as high as 98.5% (Eq. (15)) [196].

$$\tag{15}$$

Polymerization of isolated 2-halo-5-organometallic-3-alkylthiophene gives HT-P3RTh with higher regularity [180,192,193].

poly(thiophene-2,5-diyl)
**PTh*** [48,120-126]

poly(3-alkyl
thiophene-2,5-diyl)
**P3RTh*** [48,123,127-130]

poly(3-alkoxy-
thiophene-2,5-diyl)
**P3ORTh** [131,132]

poly(thiophene-2,4-diyl)
**P(2,4-Th)*** [123,125,126]

poly(ethylenedioxy-
thiophene-2,5-diyl)
**PEDOTh** [133,134]

poly[3-(3,5-di-*t*-butyl
-4-hyrdoxyphenyl)
thiophene-2,5-diyl]
**P(3-Bu₂OHPTh)*** [135]

poly(crownether
thiophene-2,5-diyl)
**PCrTh*** [131,132]

HH-poly(3-alkynyl-
thiophene-2,5-diyl)
**HH-P3(C≡CR)Th*** [136-138]

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)]*** [139a]

**PBenz(OR')Th₂(R)*** [139b]

poly(*p*-phenylene)
**PPP** [40,41,48a,48b,126]

poly(*m*-phenylene) **PCyh*** [140]
**PMP*** [41,126]

poly(2,5-diacetoxy-*p*-phenylene)
**PPP-2,5-OAc*** [142,143]

R = H, alkyl
poly(pyrrole-2,5-diyl)s
**PPr** [54,144]

poly(N-alkyl-
pyrrole-2,5-diyl)
**PRPr** [54,145]

poly(pyridine-2,5-diyl)
**PPy*** [47,49,50,146-148]

poly(alkyl
pyridine-2,5-diyl)
**PRPy*** [49,57,147,148]

poly(pyrimidine-2,5-diyl)
**PPyrim*** [56,149a]

poly(2,2'-bipyridine-5,5'-diyl)
**PBpy*** [49,51,149]

poly(dialkyl-2,2'-
bipyridine-5,5'-diyl)
**PRBpy*** [49,57]

poly(quinoline-2,6-diyl)
**P(2,6-Q)*** [67,150]

poly(quinoxaline-2,6-diyl)
**P(2,6-Qx)*** [150,151]

poly(1,5-naphthyridine
-2,6-diyl)
**P(2,6-Nap)*** [68]

poly(quinoline
-5,8-diyl)
**P(5,8-Q)*** [55]

poly(isoquinoline
-1,4-diyl)
**P(1,4-iQ)*** [55]

poly(isoquinoline
-5,8-diyl)
**P(5,8-iQ)*** [67]

poly(quinoxaline
-5,8-diyl)
**P(5,8-Qx)*** [151]

poly(2,3-diaryl
quinoxaline
-5,8-diyl)
**P(5,8-diArQx)*** [151]

poly(phenazine-2,7-diyl)
**P(2,7-Phzn)*** [152]

poly(6,6'-biquinoline-2,2'-diyl)
**P(2,2'-bQ)*** [68]
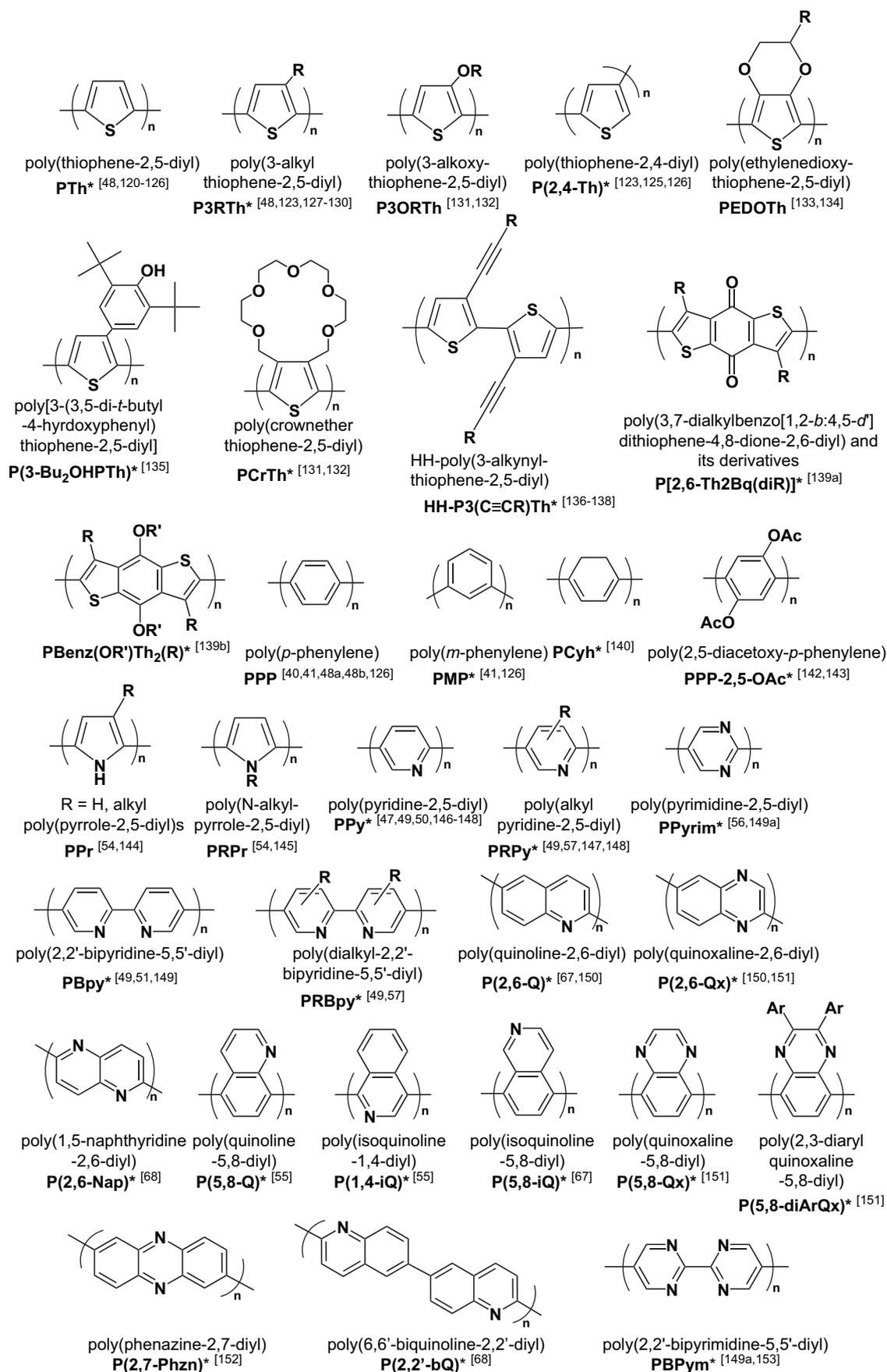
poly(2,2'-bipyrimidine-5,5'-diyl)
**PBPym*** [149a,153]

Fig. 2. π-Conjugated polymers and related polymers prepared by the organometallic processes in our group. Polymers with an * mark were for the first time reported from the authors' group [40,41,47−51,54−57,59,66−68,90−97,120−138,139a,139b,142−191].
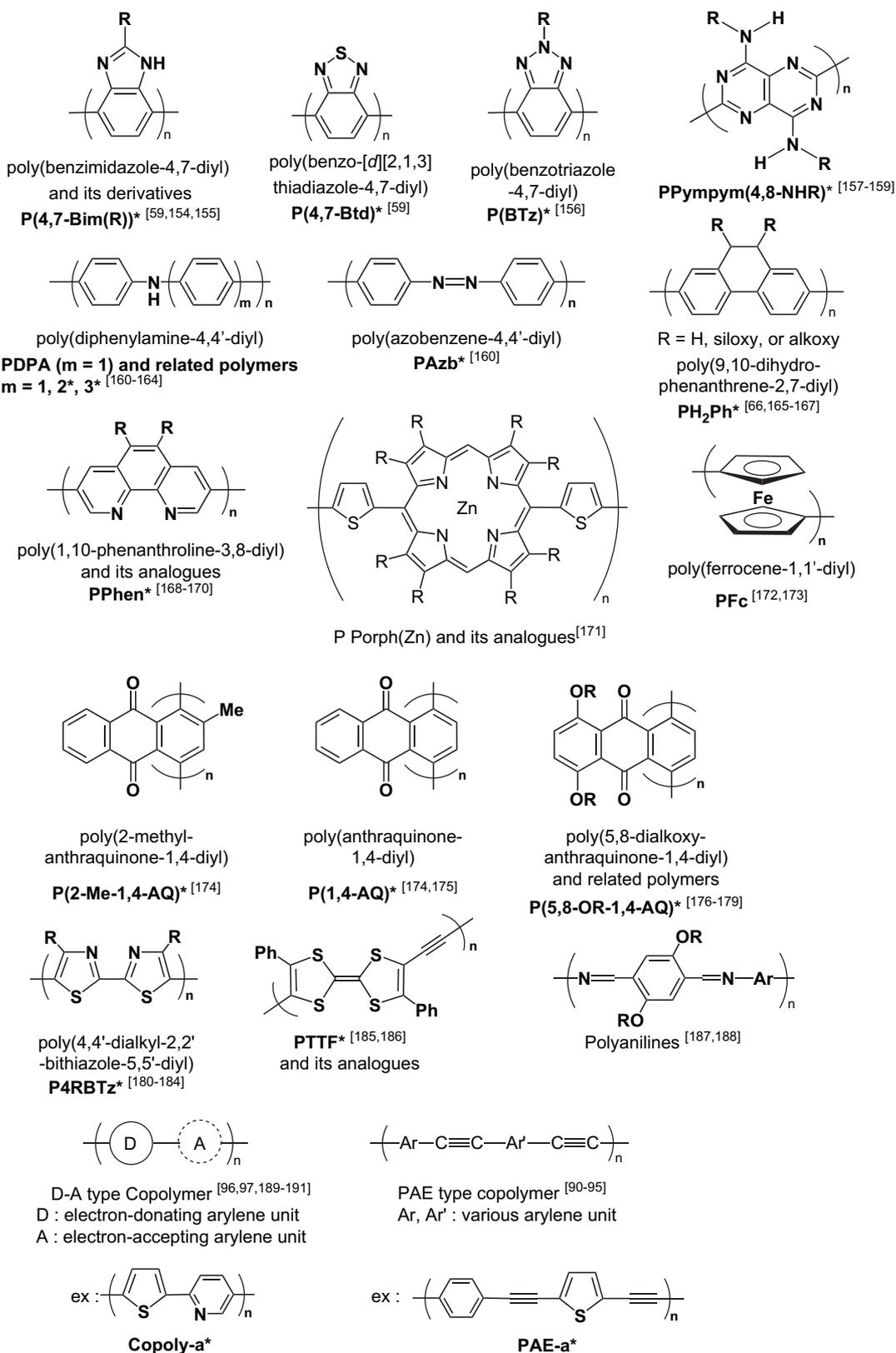
poly(benzimidazole-4,7-diyl)
and its derivatives
**P(4,7-Bim(R))*** [59,154,155]

poly(benzo-[d][2,1,3]
thiadiazole-4,7-diyl)
**P(4,7-Btd)*** [59]

poly(benzotriazole
-4,7-diyl)
**P(BTz)*** [156]

**PPympym(4,8-NHR)*** [157-159]

poly(diphenylamine-4,4'-diyl)
**PDPA (m = 1) and related polymers
m = 1, 2*, 3*** [160-164]

poly(azobenzene-4,4'-diyl)
**PAzb*** [160]

R = H, siloxy, or alkoxy
poly(9,10-dihydro-
phenanthrene-2,7-diyl)
**PH₂Ph*** [66,165-167]

poly(1,10-phenanthroline-3,8-diyl)
and its analogues
**PPhen*** [168-170]

P Porph(Zn) and its analogues[171]

poly(ferrocene-1,1'-diyl)
**PFc** [172,173]

poly(2-methyl-
anthraquinone-1,4-diyl)
**P(2-Me-1,4-AQ)*** [174]

poly(anthraquinone-
1,4-diyl)
**P(1,4-AQ)*** [174,175]

poly(5,8-dialkoxy-
anthraquinone-1,4-diyl)
and related polymers
**P(5,8-OR-1,4-AQ)*** [176-179]

poly(4,4'-dialkyl-2,2'
-bithiazole-5,5'-diyl)
**P4RBTz*** [180-184]

**PTTF*** [185,186]
and its analogues

Polyanilines [187,188]

D-A type Copolymer [96,97,189-191]
D : electron-donating arylene unit
A : electron-accepting arylene unit

PAE type copolymer [90-95]
Ar, Ar' : various arylene unit

ex : **Copoly-a***

ex : **PAE-a***

Fig. 2. (*continued*).

These regioregular HT-P3RThs form a stacked structure (*vide infra*), therefore, it is expected that they exhibit higher crystallinity and higher electrical conductivity than regio-irregular P3RThs. For example, electrical conductivities of HT-P3DodTh (Dod = dodececyl), HT-P3OctTh (Oct = octyl), and HT-P3HexTh are 1000 S cm⁻¹, 200 S cm⁻¹, and

s-*trans* (head-to-tail)    s-*trans* (head-to-head)    s-*cis* (head-to-tail)
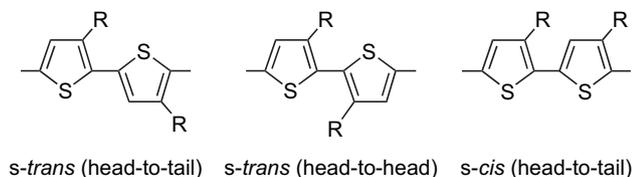
Chart 1. Microstructures of P3RTh.

150 S cm$^{-1}$ [193], respectively. In contrast, those of the corresponding regiorandom polymers are 20 S cm$^{-1}$, 1 S cm$^{-1}$, and 1 S cm$^{-1}$ [193], respectively.
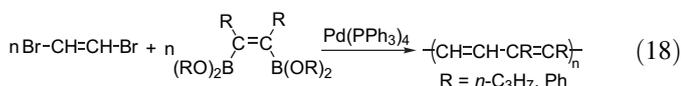
Regioregular PAE type polymers have also been synthesized [92,95].

$$ \text{X–Ar–C}\equiv\text{CH} \xrightarrow{\text{Pd-Cu}} \text{+Ar–C}\equiv\text{C+}_n \qquad (16) $$
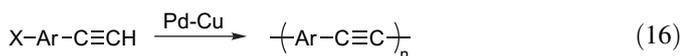
For some of the π-conjugated polymers (e.g., PTh and P3RTh) depicted in Fig. 2, other preparative methods (e.g., oxidative polymerization) [1,2,5–15,73–79] have also been developed later.

Polyacetylenes can also be prepared by the organometallic polycondensations. Dehalogenative polycondensation of 1,2-dihalogenated ethylenes with the Ni(0) complex afforded a black polymer (Eq. (17)). The IR spectrum of the polymer showed characteristic peaks at 3010 cm$^{-1}$ ($\nu$(C–H)) and 1010 cm$^{-1}$ ($\delta$(C–H)), whose positions agreed with those of *trans*-polyacetylene [48b,197].

$$ \text{n X-CH=CH-X} \xrightarrow[\text{L}]{\text{Ni(cod)}_2} \text{+CH=CH+}_n \qquad (17) $$
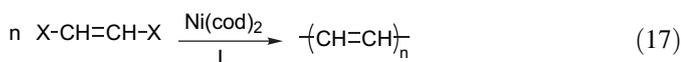
Pd-catalyzed cross-coupling gave substituted polyacetylenes (Eq. (18)) [197].

$$ \text{nBr–CH=CH-Br} + \text{n} \underset{(RO)_2B \quad B(OR)_2}{\overset{R \quad R}{C=C}} \xrightarrow{\text{Pd(PPh}_3)_4} \text{+CH=CH-CR=CR+}_n \qquad (18) $$
$$ R = n\text{-C}_3\text{H}_7, \text{ Ph} $$

Poly(aniline)s are usually prepared by oxidative polymerization of anilines, however, the following organometallic C–N coupling reaction also gives polyanilines [187,188], e.g.,

$$ \text{n NCl} = \overset{R}{\underset{R}{\bigcirc}} = \text{NCl} + \text{n XMg-Ar'-MgX} \longrightarrow \left( \text{N} = \overset{R}{\underset{R}{\bigcirc}} = \text{N-Ar'} \right)_n \qquad (19) $$
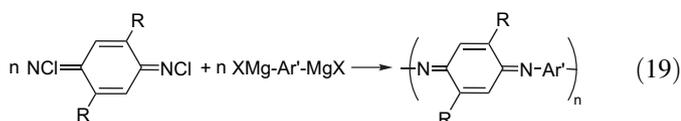
## 3.2. Molecular weight and stability in air

The molecular weight of the π-conjugated poly(arylene)s prepared by the organometallic polycondensations seems to depend on solubility and crystallinity of the polymers. The polymerization is considered to proceed even in slurries of oligomeric or polymeric propagating species deposited from the solvent [41a,48a,49]. There is a trend that crystalline polymers

have a lower molecular weight whereas less crystalline polymers (especially those with alkyl chain) give a higher molecular weight. For example the poly(arylene)s prepared by using the Ni(0)L$_m$ complex or a Pd/distannane system have the following molecular weights:

PPy: $M_w = 4300$ [49], 6300 with [$\eta$] of 2.29 dL g$^{-1}$ [146]
HH-P3(C≡CR)Th: 7900
PRPy: 12,000–27,000 (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
Random copolymer of thiophene and pyridine: *ca.* $5 \times 10^4$–$5 \times 10^6$

For some polymers, their densities ($\rho$s) have been measured:

PPy (HT-type): $\rho = 1.23$ g cm$^{-3}$. HH-P3(C≡CR)Th (R = *n*-C$_{10}$H$_{21}$): $\rho = 1.15$ g cm$^{-3}$. HT-P2RPy (R = *n*-C$_{12}$H$_{25}$): $\rho = 1.02$ g cm$^{-3}$. PPP: $\rho = 1.39$ g cm$^{-3}$. PMP: $\rho = 1.24$ g cm$^{-3}$. P(2,4-Th): $\rho = 1.59$ g cm$^{-3}$.

PPP is insoluble, however, it can be dissolved in organic solvents by nitration [41d,126]. Modification of conducting polymers with nitroso groups has also been carried out to improve their solubility [198,199]. The molecular weight of the nitrated polymer indicates that the original PPP prepared according to Eq. (4) has a degree of polymerization of about 60 [41d]. Copolymers of *p*-phenylene and *m*-phenylene are soluble and show similar molecular weights [126]. Data of elemental analyses of the polymers agreed with the structure of the polymers. For example, PPy prepared by Ni(0)L$_m$ (Eq. (5)) contained Ni only in 13 ppm [146] and negligible halogen. Ni was not detected in the copolymer of *p*-phenylene and *m*-phenylene after treatment with chelating reagents [126]. The polymers prepared by Ni(0)L$_m$ often possess an H-terminated end group [49], which is considered to be formed from polymer-NiL$_m$ terminal groups [22,38] during the work-up including treatment with HCl.

All the poly(arylene)s shown in Fig. 2, except for PPr [54] and PCyh [140], are stable in air, which is in contrast to the highly air-sensitive polyacetylene [141,200,201]. For example, PTh and P3RTh which have been stored for over 25 years [120–129] in an open atmosphere underwent virtually no change. PPr receives chemical redox reactions [54] and PCyh is air-sensitive. Many of the π-conjugated polymers shown in Fig. 2 are soluble in solvents, however, PPP, PTh, and PCyh are insoluble.

## 3.3. Chemical and physical properties

### 3.3.1. UV–vis

Poly(arylene)s show the π–π* absorption bands at longer wavelengths than those of their corresponding monomeric compounds. The degree of the red shift reflects steric hindrance around the bond connecting the monomeric units. π-Conjugated polymers consisting of five-membered heteroaromatic

units, such as PTh, P3RTh (R = CH₃), and P4RBTz (R = CH₃), have less steric hindrances, therefore, their $\lambda_{max}$ values show a large red shift of about 20,000 cm$^{-1}$ from those of the corresponding monomeric compounds as shown in Chart 2.

On the other hand, benzene (255 nm)−PPP (375 nm) [202,203] and pyridine (248 nm)−PPy (373 nm) [49] couples give somewhat smaller red shifts of about 13,000 cm$^{-1}$, partly due to a larger π-conjugation system of the basic unit and due to the steric repulsion caused by the *o*-CH group.

A conceivable N···HC interaction may assist coplanarization of the main chain to afford an effectively π-conjugated system (Chart 3). For example, P(BTz)s [156] give the lowest energy π−π* peak at a longer wavelength than polymers having an analogous main chain. An intramolecular N···HC interaction seems to make the main chain planar.

*3.3.1.1. UV−vis of CT-type copolymers.* Copolymers consisting of alternating electron-donating and electron-withdrawing units are considered to have an intramolecular charge transferred (CT) electronic structure [97,189−191].

Recently, (ABA)$_n$ type π-conjugated copolymers, −[Th(R)−Ar−Th(R)]−, have been prepared (Chart 4).

The absorption peaks of these copolymers located at about 400 nm for Ar = 1,4-phenylene and thiophene-2,5-diyl [204], 429−432 nm for Ar = pyridine-2,5-diyl, and 439−449 nm for Ar = pyridazine-3,6-diyl [205]. These data indicate that the UV−vis peak shifts to a longer wavelength according to an increase in the electron-accepting ability of the Ar group, and seem to reflect the CT electronic structure in the polymer.

Poly(arylene-ethynylene)s (PAEs) consisting of electron-accepting units such as benzothiadiazole, 1,3,4-thiadiazole, 4-alkyl-1,2,4-triazole, and 3,4-dinitrothiophene, and electron-donating units such as 2,5-dialkoxy-*p*-phenylene [143,206−208] and *N*-alkylpyrrolylene have a strong tendency to form a molecular assembly due to the intermolecular CT interaction. The CT-type copolymers often form a well-stacked and highly ordered solid structure (*vide infra*).
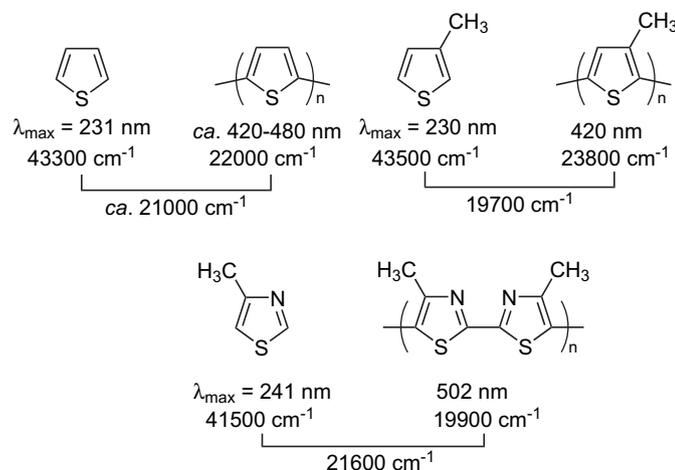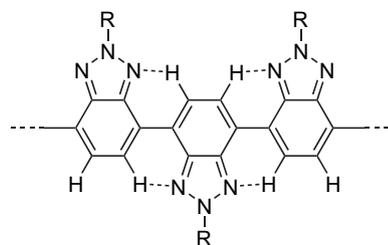


Chart 3. Intramolecular N−CH interaction of P(BTz)s, e.g., P[BTz(C12-CBz)] [156].

*3.3.2. Photoluminescence*

Most of the polymers shown in Fig. 2 exhibit photoluminescence with an emission peak near the onset of the π−π* absorption band. Linear rod-like polymers such as PPy [49], PPhen [170a] and PAE type polymers [93] often show an excimer-like emission in films and solutions with high concentrations. Among PAE polymers, those containing an anthracene unit show strong fluorescence [90].

Energy transfer from a photoactivated π-conjugated unit to an energy-accepting π-conjugated unit has been observed using photoluminescence techniques. We have reported two types of energy transfer [209]: type I, perpendicular-type energy transfer in π-conjugated quinoxaline polymer, and type II, parallel-type energy transfer in block-type π-conjugated copolymer (Chart 5).

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 [210]. Recently, many examples of similar energy transfers have been reported.

Poly(fluorene-2,7-diyl) is known as a strong luminescent polymer [211−214]. 9,10-Dihydrophenanthrene (H₂Ph) has an ethylene-type bridge instead of the methylene-type bridge in the fluorene structure, and the H₂Ph unit-based polymers also show light emission with high quantum yield [165].

*3.3.3. Other optical properties*

Poly(5,8-dihexadecyloxyanthraquinone-1,4-diyl), P(5,8-OC₁₆H₃₃-1,4-AQ) [178,179], and HH-P3(C≡CR)Th (R = decyl) [138b] showed piezochromism at high pressures (5−11 GPa), similar to HT-P3RTh [215]. The UV−vis absorption peak of a pressed powder of P(5,8-OC₁₆H₃₃-1,4-AQ) at 520 nm at 0.55 GPa shifts to 550 nm, 585 nm, and 600 nm at 3.3 GPa, 6.9 GPa, and 11 GPa, respectively. A pressed powder of HH-P3(C≡CR)Th (R = decyl) gives rise to a longest wavelength UV−vis peak at 606 nm, 625 nm, 661 nm, 664 nm, and 672 nm at weakly added pressure, 1.17 GPa, 2.57 GPa, 5.20 GPa, and 7.25 GPa, respectively.
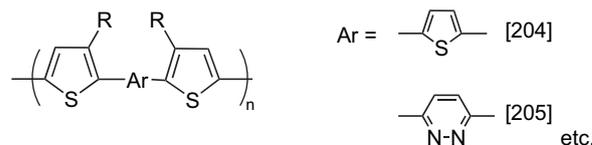


$\lambda_{max}$ = 231 nm
43300 cm$^{-1}$

*ca.* 420-480 nm
22000 cm$^{-1}$

$\lambda_{max}$ = 230 nm
43500 cm$^{-1}$

420 nm
23800 cm$^{-1}$

*ca.* 21000 cm$^{-1}$

19700 cm$^{-1}$

$\lambda_{max}$ = 241 nm
41500 cm$^{-1}$

502 nm
19900 cm$^{-1}$

21600 cm$^{-1}$

Chart 2. Shift of π−π* transition.



Ar = [204]

[205]

etc.

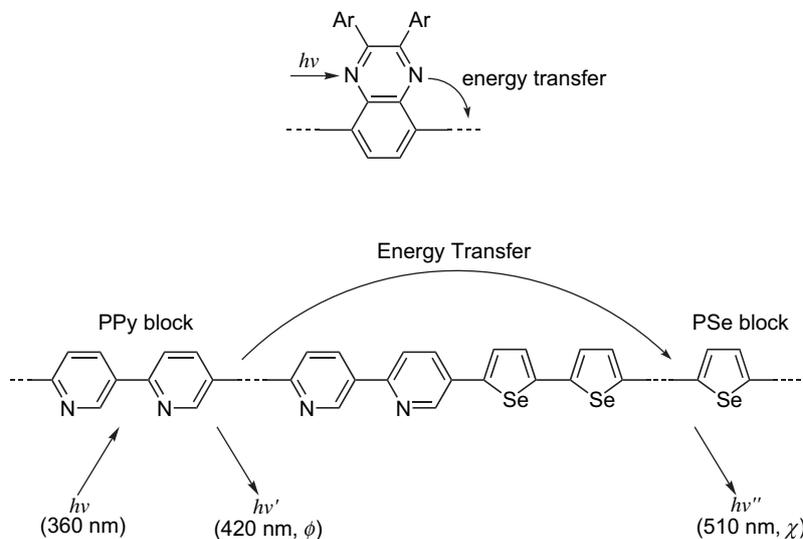Chart 4. Th(R)−Ar−Th(R) type π-conjugated polymers [204,205].

Chart 5. Two types of intramolecular energy transfer.

### 3.3.4. Redox behavior and electrical conductivity

The polymers shown in Fig. 2 are electrochemically active. For example, poly(pyridine-2,5-diyl) PPy film on a Pt electrode shows a reduction (n-doping) peak cathodic potential $E_{pc}$ of $-2.43$ V (vs. $Ag^+$/Ag), and an oxidation (n-undoping) peak anodic potential $E_{pa}$ of $-1.90$ V [49,50]. The n-doping and n-undoping are accompanied by a color change, and the doping level $x$ is about 0.3.



$$\text{(20)}$$
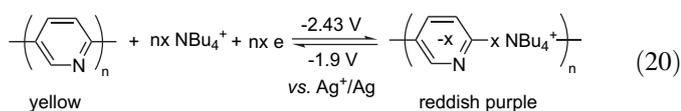
9,10-Anthraquinone (AQ) is a typical redox-active compound, and π-conjugated polymers containing AQ derivatives have been synthesized. The redox behavior of P(2-Me-1,4-AQ) has been discussed based on a mixed oxidized state formed from neutral anthraquinone, anion radical of anthraquinone, and dianion of 9,10-dihydroxyanthracene [174]. P(4,8-NO₂-1,5-AQ) bearing a strongly electron-withdrawing NO₂ group shows an extremely low reduction potential ($E_1^0 = -0.74$ vs. $Ag^+$/Ag) [179]. 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 at the non-doped state [179]. Poly(p-benzoquinone) also receives the 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 [143]. To our knowledge, this reduction potential is the lowest among those reported for π-conjugated poly(arylene)s.

The ease of the electrochemical reduction of π-conjugated polymers simply reflects the electron-accepting ability of the monomeric repeating units [26d,216]. For a wide range of the polymers such as poly(p-phenylene), poly(naphthalene-1,4-diyl), poly(naphthalene-2,6-diyl), and poly(anthraquinone) type polymers, linear relationships between the reduction potential $E_{red}$ of the polymer and the electron affinity EA of the

corresponding monomeric compound HArH (Eq. (21)) are observed, and $\rho$ values of 0.75–0.8 have been obtained [26d,216].

$$E_{red} \text{ of } \left(Ar\right)_n = a + \rho \times EA \text{ of HArH} \tag{21}$$

A similar linear correlationship is observed between oxidation (or p-doping) potential $E_{ox}$ of PPP, PTh, and PPr (cf. Fig. 2) and ionization potential (IP) of the corresponding monomeric compounds [26d] and a slope of about 1.5 is obtained when $E_{ox}$ values are plotted vs. IPs of the monomeric compounds.

PCrTh readily undergoes n-doping. 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. (22)) [132]. Poly(1,10-phenanthroline)s PPhens [170] and their Ru(II) complexes [217] also showed high stability as an n-type conducting material. PPhens have a strong affinity toward Li, and give an irreversible electrochemical n-doping peak in the presence of $Li^+$ [170a].

π-Conjugated polymers containing crown ethereal subunits are the subject of recent interest [218,219].

The π-conjugated polymers undergo chemical redox reactions (e.g., oxidation (or p-doping) by $I_2$ and $FeCl_3$ and reduction (or n-doping) by Na). The chemically and electrochemically oxidized or reduced polymers show electrical conductivity in the range of $10^{-3}$–$10^3$ S cm$^{-1}$, due to the formed cationic (positive) or anionic (negative) carriers 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 [48a,145], in the chemical p-doping. $I_5^-$ and $FeCl_4^-$ form an ionic pair with the cationic center generated in the polymer chain. Oxidation of PFc with donor acceptors such as TCNQ also gives electrically conducting materials [172].

The electric conduction in π-conjugated polymers has been explained in terms of "polaron", "bipolaron", "soliton", and

PCrTh



(22)
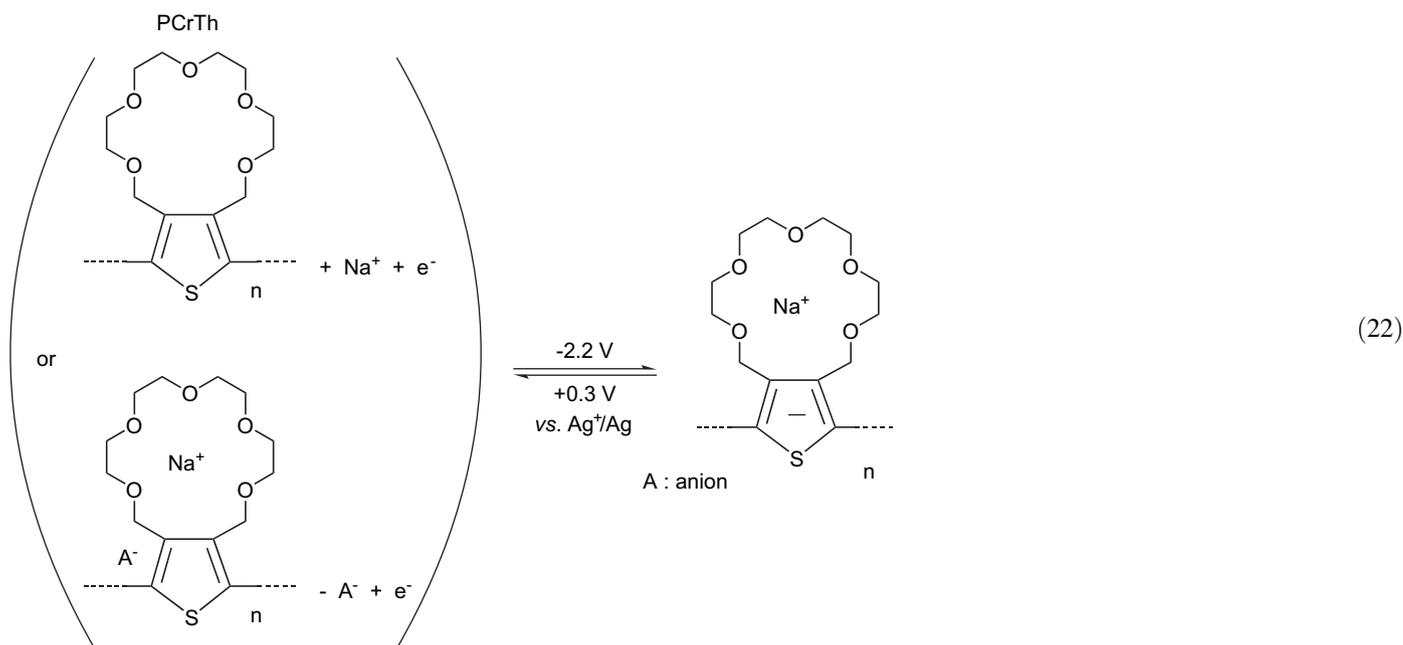
"band model" [73–79]. The UPS spectrum of K-doped PBpy and PPhen showed a peak assigned to the polaron state [149b,c,170b].

The iodine-doped PTh has a high crystallinity with an $I_n^-$ ($n$: presumably 5) counter ion [48], and it gives the electrical conductivity ($\sigma$) of 30 S cm$^{-1}$. Derivatives of PTh [220,221] and PPr [222] are now used as conducting materials (e.g., as electrodes of capacitors and hole-transporting layer in organic electroluminescence devices).

PTh having a sulfonic pendant [221,223] receives the so-called "self-doping" in the presence of O$_2$.

Use of sulfonic acids also leads to p-doping of PThs. For instance, P3HexTh is p-doped by sulfonic acids in the presence of O$_2$ [224,225]. The following reaction is suggested in the case of regioregular (head-to-tail content of 98.5%) P3HexTh, molecular assembly takes place prior to the p-doping.



(23)
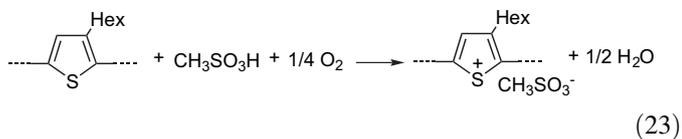
### 3.4. Linear structure and alignment on the surface of substrates

$\pi$-Conjugated poly(arylene)s synthesized using organo-metallic polycondensations attain a well-defined bonding between the repeating arylene units. Therefore, the polymers are considered to assume interesting structures such as rigidly linear and helical structures. 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, HT-P3RTh and P(2,6-Q) yields a very large degree of depolarization ($\rho_v = 0.2-0.33$) [47,49,67,146,180]. For example, PPy gives a theoretically limiting $\rho_v$ value of 0.33 when irradiated with Ar laser, indicating that it takes an ideally linear structure with a very large anisotropy of polarizability (Chart 6) [47,49].



PPy
$\rho_v = 0.33$
$\alpha_1 \gg \alpha_2, \alpha_3$
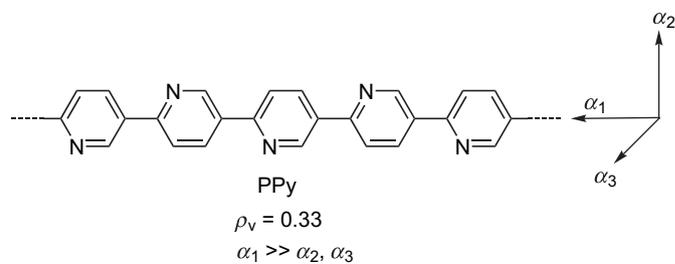
Chart 6. Ideally linear structure of PPy.

(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 substrates as shown in Fig. 3 [43,48a,49,202,203,226,227].

The alignment has been analyzed by clear electron diffraction patterns. Thiophene-based oligomers are also arranged perpendicularly or somewhat tilted to the surface of substrates [79b,228–233]. The ease of the perpendicular alignment of PPP increases in the following order by changing the substrate: Au, Ag < Al < C.

The order is considered to reflect the magnitude of the interface energy between the PPP and the substrate [203], which originates from a known metal–π-aromatic interaction for the Group 11 metals (Au and Ag) [234]. The order agrees with the order of heat of wetting between benzene and the substrate [203].
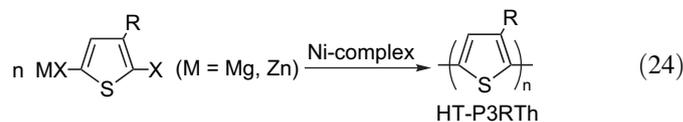
(3) Many π-conjugated poly(arylene)s exhibit excimer-like emissions in films and high concentrated solutions, which can be attributed to a strong interaction between the linear rod-like molecules [49,53,92,93,168,170a].
(4) PBpy molecules can be aligned in parallel with the surface of a glass substrate due to coordination of the 2,2′-bipyridyl unit with Si–O–H hydrogens on the surface of the substrate (right part of Fig. 3) [43,49].
(5) PPy, PBpy, and similar linear polymers give excellent polarizing films when included in stretched polymer (e.g., poly(vinyl alcohol)) films [49,97].

An Al|vd-PTh|Au diode (vd-PTh = vacuum-deposited poly(thiophene-2,5-diyl)) shows rectification of electric current and vd-PTh serves as an active layer of a field-effect transistor [202,203]. It is now recognized that molecular morphology of π-conjugated polymers on substrates is an important factor for electric behavior of electric devices (e.g., field-effect transistor) as discussed in Section 4.3.

## 3.5. Stacking in the solid state and colloid

### 3.5.1. Polymer with long alkyl or alkoxy side chains

As described above, McCullough's group and Rieke's group succeeded in the preparation of regioregular head-to-tail poly(3-alkylthiophene-2,5-diyl) [192–194,196]:

$$n \; MX\text{–}\underset{S}{\overset{R}{\text{Th}}}\text{–}X \; (M = Mg, Zn) \xrightarrow{\text{Ni-complex}} \left(\!\!\left(\underset{S}{\overset{R}{\text{Th}}}\right)\!\!\right)_n \qquad (24)$$

HT-P3RTh

Regioregulated polymers, such as head-to-tail HT-P3RTh, head-to-head P4RBTz, and HH-P3(C≡CR)Th (cf. Fig. 2), with long R chains show attractive electronic and optical properties. These regioregular five-membered ring heteroaromatic π-conjugated polymers containing long alkyl side chains form a π-stacked structure assisted by the side chain aggregation in the solid state and in colloidal solutions [180,204,205,235–245].

The long alkyl side-chain containing π-conjugated polymers, such as HT-P3RTh [180,192–194,196,235,236], P4RBTz [180–184], P(2,6-Th$_2$Bq(diR)) [139a,c], PAE type polymers [206–208], P(5,8-OR-1,4-AQ) [178,179], poly(biphenylene-vinylene) [238], copolymer of thiazole and thiophene [237,239,240] give a sharp X-ray diffraction (XRD) peak at a low angle region ($2\theta = 2$–$8°$ for Cu Kα). The peak is assigned to a distance $d_1$ between core main chains separated by the long side chains, and the peak corresponding to a face-to-face stacking distance $d_2$ of the polymer planes is observed at around $2\theta$ of $23°$ in the solid state.

Unique alignment of a cast film of HT-P3HexTh, dialkoxy-$p$-phenylene polymers, polymers with the Th(R)–Ar–Th(R) type repeating unit (cf. Chart 4 and Fig. 2), and HH–P3(C≡CR)Th on the substrates has been observed [136,137,193,204b,206,235,236,239–245]. The XRD pattern of a cast film of HT-P3HexTh on a Pt plate does not exhibit the peak due to the face-to-face distance $d_2$ of the polymer planes. However, the XRD pattern of this film clearly exhibits a peak due to the face-to-face distance $d_2$ after the film is
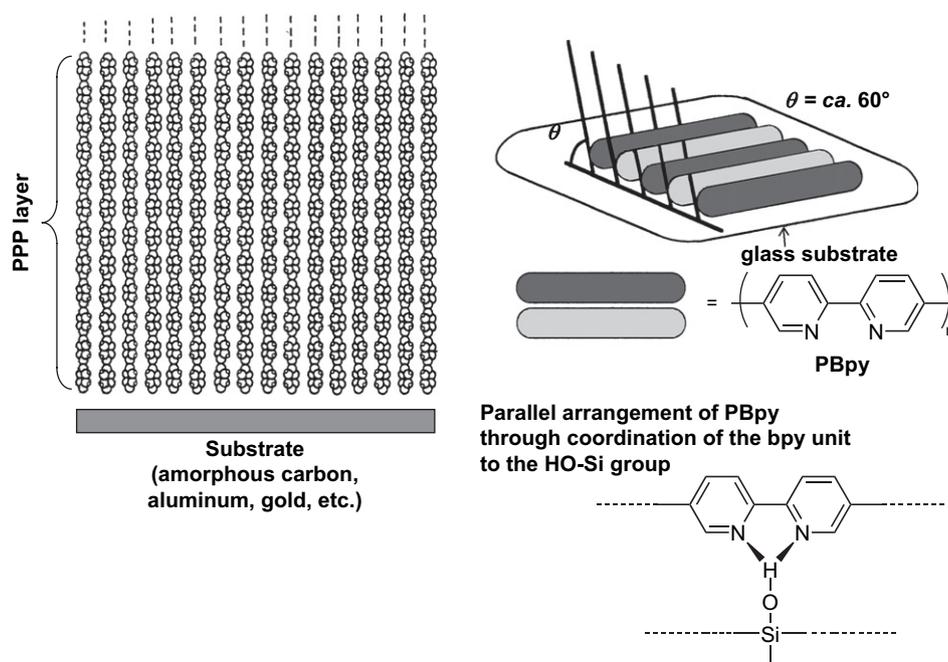


Fig. 3. Perpendicular alignment of PPP on substrates (left) and parallel alignment of PBpy on the surface of a glass substrate (right).

peeled from the Pt plate and crushed. These results indicate that the HT-P3HexTh molecules are well aligned with the hexyl group oriented toward the surface of the Pt plate. The perpendicular alignment on the surfaces of the substrates leads to a high carrier mobility.

Electrochemically deposited p-doped HT-P3HexTh molecules are also aligned with the hexyl groups oriented toward the surface of the Pt plate in the electrochemically deposited film of p-doped HT-P3HexTh [26d,242,243a]. The vacuum-deposited *n*-alkane molecules, such as triacontane and nonacosane, are also aligned perpendicularly on the surface of substrates [206,245], and this finding agrees with the trend that the side alkyl groups of the π-conjugated polymers are oriented toward the surface of the substrates. Electrochemical p-doping and chemical p-doping (dopant $= BF_4^-$ for both types of doping) of HT-P3HexTh [26d] and a copolymer of isothianaphthene with *p*-dialkoxybenzene [244] lead to an increase in the distance $d_1$ between the π-conjugated main chains (cf. Chart 7). By contrary, the face-to-face stacking distance becomes shorter after the p-doping. The $BF_4^-$ dopant seems to be located near the end of the alkyl side chain to increase $d_1$ [26d] and the p-doping is considered to increase the face-to-face stacking intermolecular attractive force. π-Stacking distance of PEDOTh is also shortened after p-doping [243c].

The number density along the polymer main chain seems to determine the packing mode (the end-to-end or interdigitation packing modes shown in Chart 7). Plots of the $d_1$ value *vs.* number of carbons in the R group of the above described polymers give a straight line. When the slope is larger than the height of the $CH_2$ group (1.25 Å/C), the polymer does not have the interdigitation packing mode and is considered to take the end-to-end packing mode. When the number density of the R group in polymers is smaller as in P(2,6-Th$_2$Bq(diR)) [139a] and copolymer of bithiophene and bithiazole [240], the polymers afford a linear line with a slope smaller than 1.25 Å/C. This smaller slope corresponds to the interdigitation packing mode.

The π-conjugated linear polymers assume the packed structure not only in the solid state (film) but also in colloidal solutions. Light-scattering analysis of the colloidal solution sometimes reveals assembling of $10^3$ polymer molecules [180]. Revealing the driving force for the π-stacking of π-conjugated polymers is expected to give basic information for the controlling force of similar π-stacking observed with various molecules including graphite and DNA.
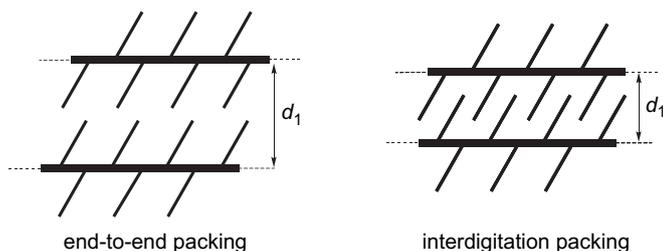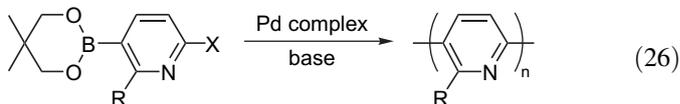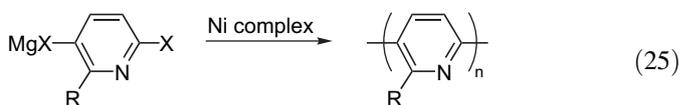


Chart 7. Two types of packing. The π-conjugated main chains are separated with a distance $d_1$. A sheet is shown, and the sheets are considered to form a face-to-face stacked structure with a distance $d_2$ (3.3−3.8 Å). For $d_2$, see the examples shown in Figs. 8 and 9.

HT-P6RPys have been prepared by organometallic polycondensation methods as shown in Eqs. (25) and (26) [147,148].



The XRD analysis of HT-P6RPys having various R groups indicates that the polymers form a loosely stacked assembly in the solid state as shown in Fig. 4.

The well-ordered π-stacked structures are disadvantageous for electroluminescence because they often provide energy decay routes through excimer-like adduct(s). However, it is advantageous for higher electrical conductivity, larger mobility of carrier [235,236,241], and large third-order optical non-linear susceptibility [137,246] due to the formation of expanded electronic state(s).

For several polymers, a characteristic packing mode, named ''doubly running packing structure'' has been observed in the solid state. For example, an alternating copolymer of thiophene and 4-alkylthiazole is considered to form a doubly running stacked structure as shown in Fig. 5 [237,239].

Copolymers of thiophene and *N*-arylethynyl substituted pyrrole also assume a doubly running packing structure as depicted in Fig. 6 [247−249].

A CT structure between the electron-donating unit and electron-accepting unit is considered to assist the formation of the doubly running packing structure.

### 3.5.2. Stacking in alkynyl-substituted polymer

π-Conjugated polymers with acetylenic side groups have also been prepared [136−138,250,251]. Molecular structures of HH−P3(C≡C−R)Th and its starting monomeric compound reveal the absence of steric repulsion between the −C≡CR side chain and the polythiophene main chain. Consequently HH−P3(C≡CR)Th is expected to assume a coplanar structure and easily forms a stacked assembly. XRD patterns of HH−P3(C≡CDec)Th (Dec = decyl) under various conditions are shown in Fig. 7. An original powder of HH−P3(C≡CDec)Th gives $d_1$, $d_2$, and $d_3$ peaks at 24.3 Å, 3.8 Å, and 4.5 Å, respectively. However, the XRD pattern obtained at a reflection mode varies depending on the preparative conditions of the sample. Fig. 8 shows the packing model for HH−P3(C≡CDec)Th. The distance $d_1$ is considered to correspond to the distance between the polythiophene main chains separated by the −C≡CR side chains, $d_2$ is assignable to the stacking distance, and $d_3$ corresponds to a side-to-side distance between the packed alkyl chains.
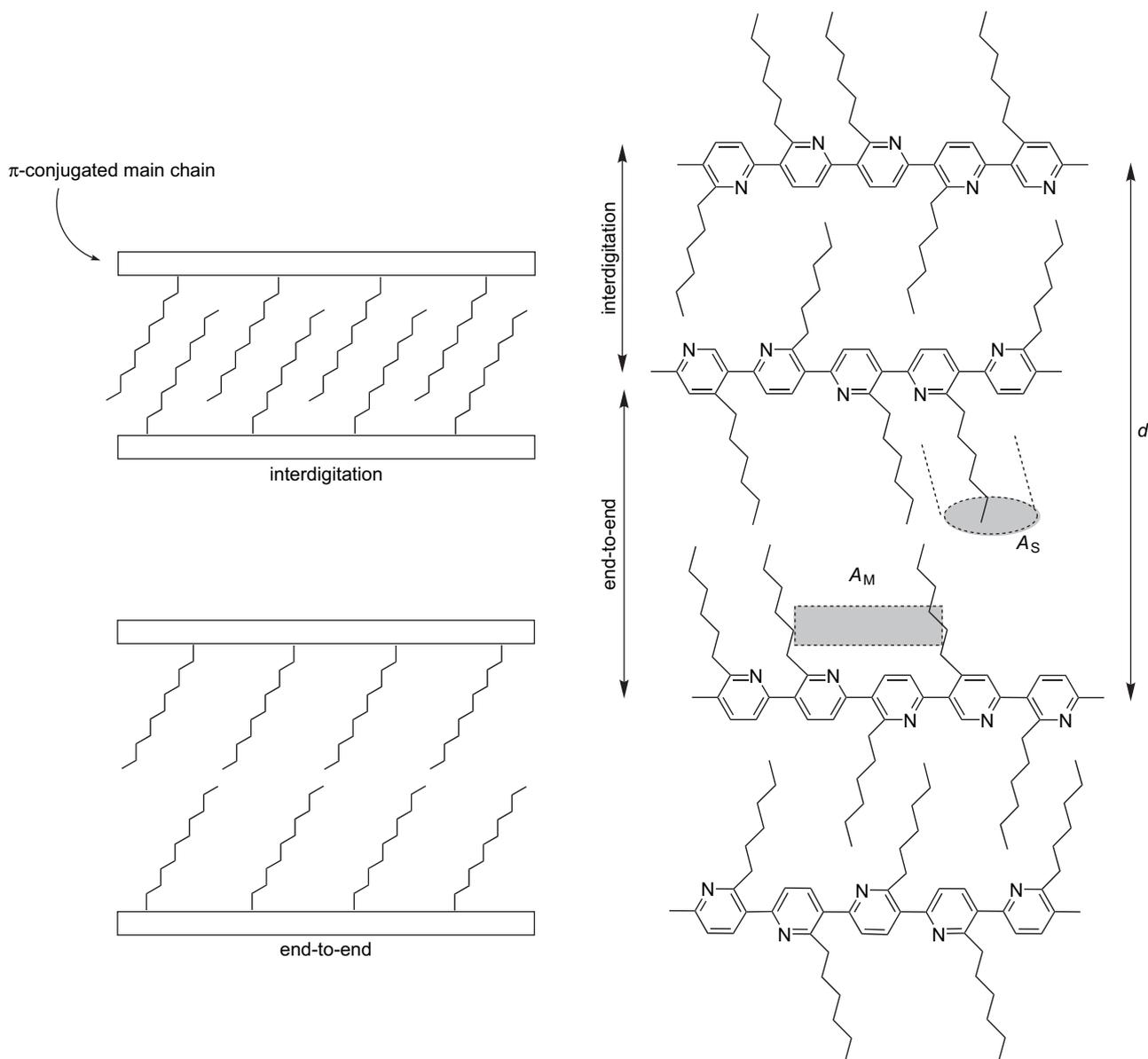
Fig. 4. Packing model of HT-P6RPy. Only one sheet is shown, and sheets are considered to form a loosely stacked assembly.

On the other hand, the XRD pattern (middle in Fig. 7) of the cast film of HH−P3(C≡CR)Th on a Pt plate exhibits only $d_1$ and $d_1/3$ peaks, suggesting the formation of an ordered structure of HH−P3(C≡CR)Th on the surface of substrates (*edge-on* alignment depicted in Fig. 9). When the polymer film is formed on an amorphous silicon plate by rubbing the powder or film of HH−P3(C≡CR)Th on the Si plate under added pressure of about 30 Mpa (bottom in Fig. 7), the $d_2$ peak becomes a main peak and the $d_1$ peak is weakened. These facts strongly suggest that the polymer molecules are aligned in the direction of stacking on the surface of the substrate (*face-on* alignment displayed in Fig. 9).

### 3.5.3. Chiral polymer

The following π-conjugated polymer with chiral repeating units has been prepared. The 9,10-disubstituted-9,10-dihydro-phenanthrene unit in the substituted PH$_2$Ph (cf. Fig. 2) have

a $C_2$ symmetry chirality. Polymerization of an optically resolved monomer, $(R,R)$-H$_2$Ph(9,10-OSiBu$_3$)Br$_2$, gives an optically active π-conjugated polymer [166,167].



(27)
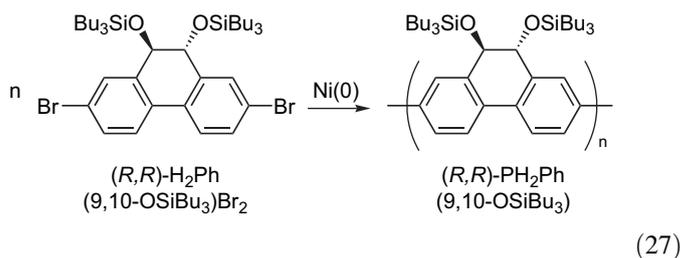
The polymer forms a molecular assembly and its film shows a strong circular dichromism of 6°/μm. The packing structure of the $C_2$ symmetry chiral polymer was analyzed based on its XRD data [167]. Two $(R,R)$-PH$_2$Ph(9,10-OSiBu$_3$)
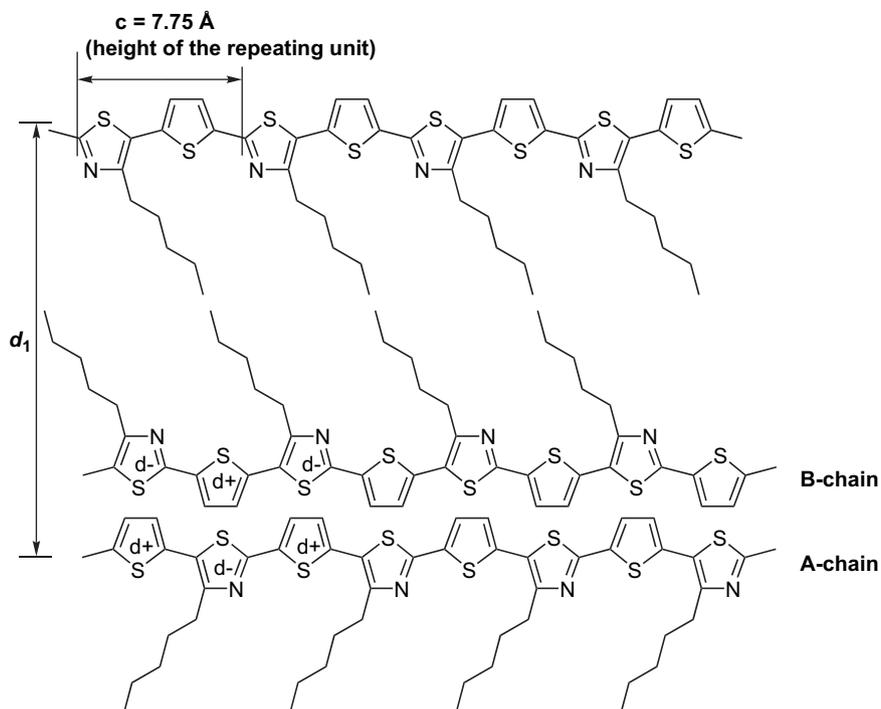
Fig. 5. Packing model of a copolymer of 4-alkylthiazole and thiophene, PTz(R)Th, in the solid state. One sheet is shown. Below this sheet, another sheet comes.

molecules form a face-to-face aligned pair and the pairs assume *pgg* type herringbone packing. The large circular dichroism is considered to originate from excitonic electronic structure(s) formed in the paired $(R,R)$-PH$_2$Ph(9,10-OSiBu$_3$) molecules. π-Conjugated polymers with chirality are the subject of recent interest [252−257].

## 3.6. Chemical reactivity and catalysis

### 3.6.1. Acid−base response

*N*-Containing heteroaromatic polymers often act as a proton acceptor (e.g., poly(pyridine)s, poly(quinoxaline)s, poly(pyrimidine)s, poly(bisimidazole)s, PBim [258], etc.)

or as a proton donor (e.g., poly(benzimidazole)s, P(4,7-Bim(R))s).



PBim
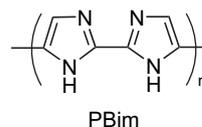
Protonation and deprotonation of these polymers lead to changes in optical properties of the polymer [154,155,258−261].
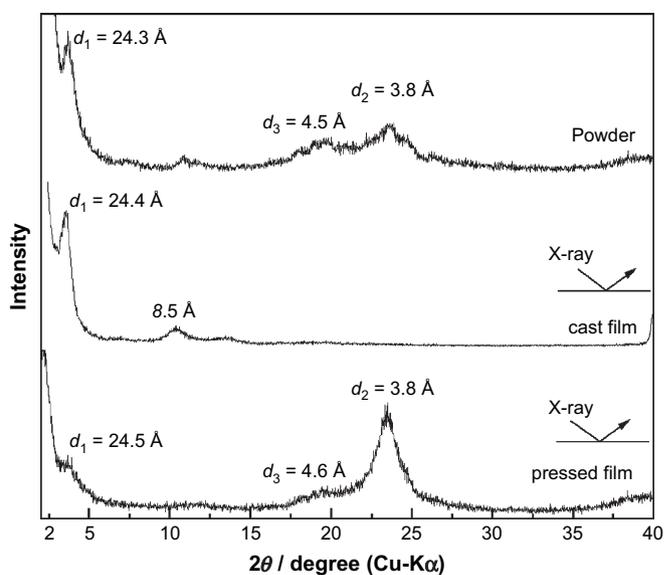


Fig. 7. XRD patterns of HH-P3(C≡CDec)Th (R = decyl) obtained at a reflection mode [136,137]. Top: powder; middle: cast film on a Pt plate; bottom: film on an amorphous Si plate, prepared by rubbing a polymer powder sample.
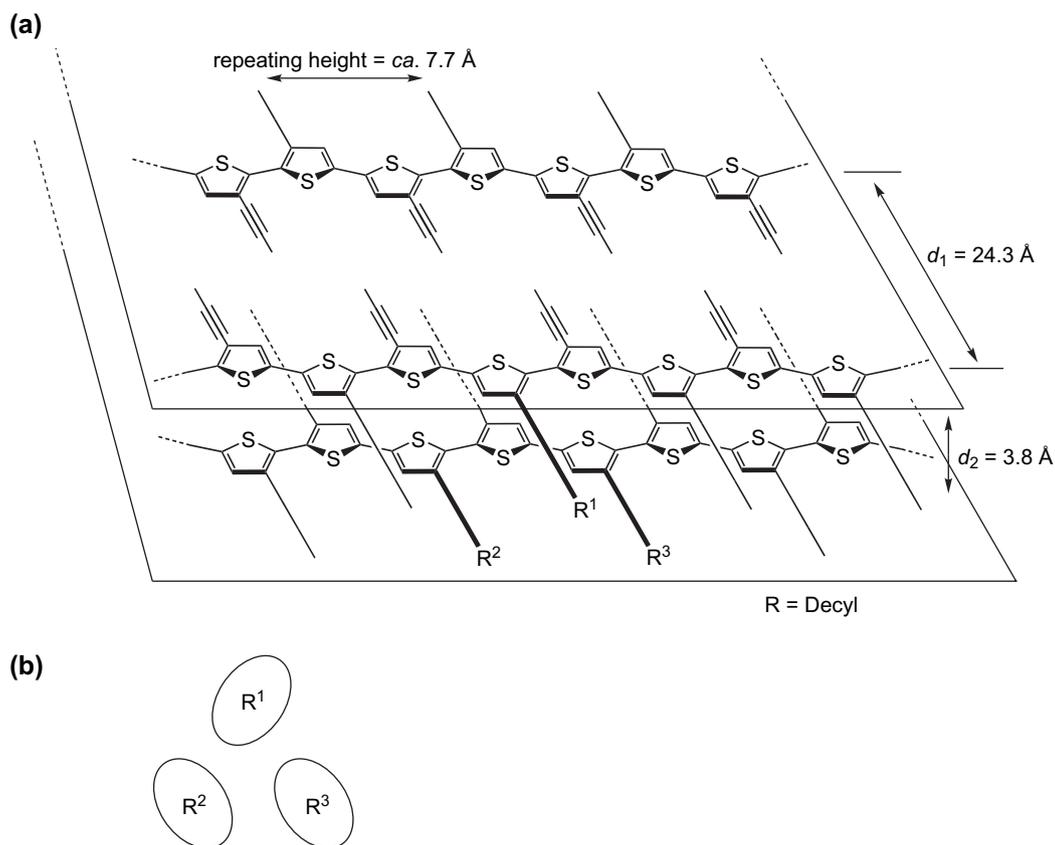


Fig. 6. Model for the doubly running main chains of a copolymer of thiophene and pyrrole.

**(a)**



repeating height = *ca.* 7.7 Å

$d_1$ = 24.3 Å

$d_2$ = 3.8 Å

$R^2$   $R^1$   $R^3$

R = Decyl

**(b)**



$R^1$

$R^2$   $R^3$

Fig. 8. (a) Packing model for HH-P3(C≡CDec)Th. (b) Side view of $R^1$, $R^2$, and $R^3$ chains. The $R^1$–$R^3$ chains are considered to be packed in a pseudohexagonal mode, similar to the case of HT-P3RTh.

For example, 1,10-phenanthroline or pyridine unit-containing π-conjugated polymers respond well to $H^+$ with a large red shift about 40–60 nm of the absorption peak in UV–vis spectra [260].

P[4,7-Bim(hep)] and a copolymer of benzimidazole receive a large bathochromic shift of the UV–vis peak on deprotonation. The $\lambda_{max}$ of the polymer is shifted to a longer wavelength



cast film

edge-on

substrate

pressed film

side-on (or face-on)

$d_1$

$d_2$
π-stacking

$d_2$

$d_1$

$\theta$

$\theta$ = ca. 45°

end-to-end packing
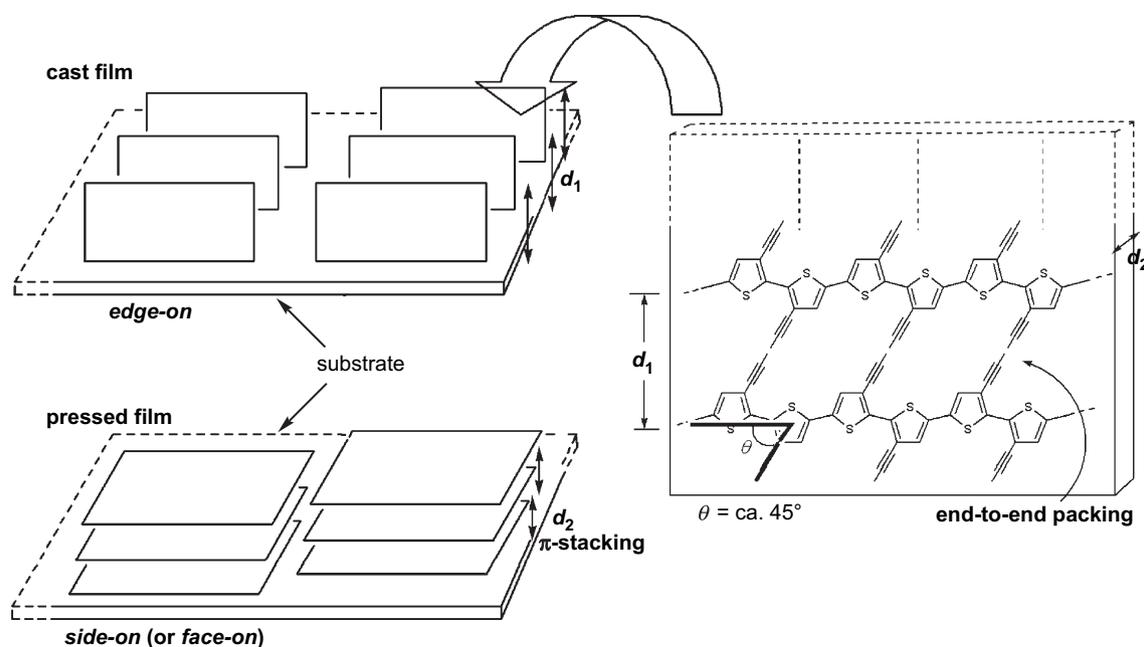
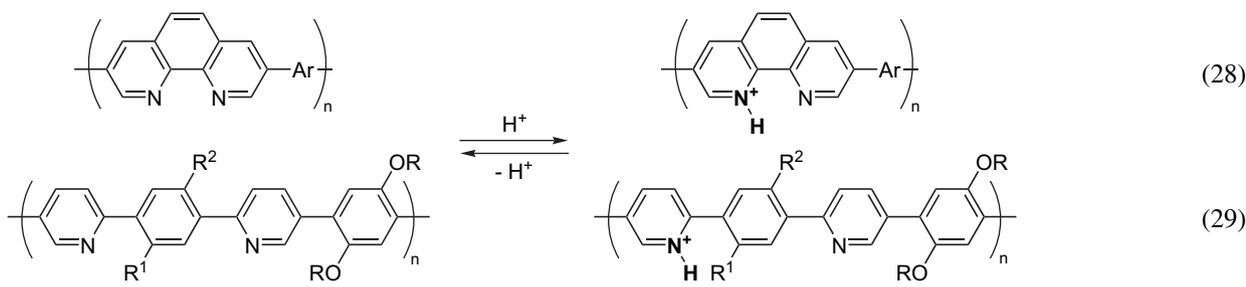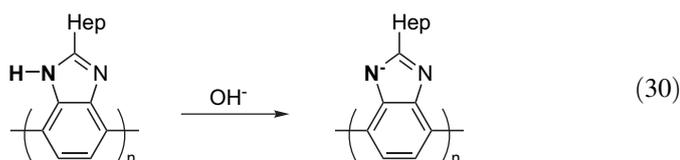Fig. 9. Two types of alignment of HH-P3(C≡CR)Th molecules on substrate. Top: *edge-on* alignment. Bottom: *side-on* (or *face-on*) alignment.

$$\text{(structure)} \quad \underset{-\,H^+}{\overset{H^+}{\rightleftharpoons}} \quad \text{(structure)} \qquad (28)$$

$$\text{(structure)} \qquad (29)$$

by 45 nm, and its quantum efficiency of PL increased by deprotonation [155,259,261].

$$\text{(structure)} \quad \xrightarrow{\;OH^-\;} \quad \text{(structure)} \qquad (30)$$

### 3.6.2. Metal complexes and modification of nitrogen

π-Conjugated polymers constituted of chelating ligands such as 2,2′-bipyridyl (bpy) and 2,2′-bipyrimidine (bpym) form metal complexes [49,51,52,149,258]. Recently, various π-conjugated chelating polymers and their metal complexes have been prepared [183,260,262–273]. The obtained polymer complexes and *N*-modified polymers (e.g., *N*-quaternized polymers [274] and *N*-oxide polymers [275,276]) show interesting opto- and electrochemical behaviors.

A soluble 1,10-phenanthroline (phen)-containing polymer exhibits a strong blue PL with a maximum at $\lambda_{EM} = 434$ nm, and the emitted color is tuned through the metal complexation as shown in Fig. 10 [260,277].

### 3.6.3. Catalytic reactions

Because the π-conjugated polymers are regarded as organic semiconductors, numerous investigations have been made to derive functions similar to those of inorganic semiconductors (e.g., $TiO_2$) from the π-conjugated polymers. For example, photoinduced enhancement of electrical conductivity is observed for P(5,8-diArQx) (Ar = *p*-tolyl) [278]. PPP and PPy prepared by the organometallic polycondensation have been utilized for photocatalysts [279,280]. PBpy serves as a highly efficient photocatalyst for $H_2$ evolution from aqueous media [149a,281], and this is attributed to the chelating ability and high hydrophilicity of PBpy (Chart 8).

Ni-coordinated PBpy catalyzes the electrochemical reduction of $CO_2$ to CO [49].
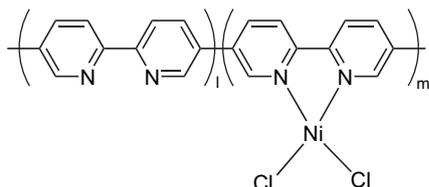


Cu(I) complex of PBpy and PPy serves as excellent catalysts for oxycarbonylation of methanol [282–284]:

$$2\,CH_3OH + 2\,CO + 1/2\,O_2 \xrightarrow{\;PBpy\text{-}Cu(I)\;} CH_3COOCOCH_3 + H_2O \qquad (31)$$
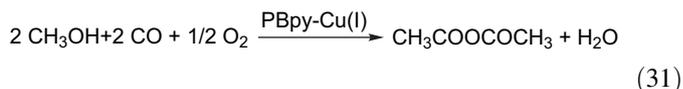
P6MePy, P6HexPy, P6MeBpy, and P6HexBpy serve as a photocatalyst for oxidation of benzene and toluene to give phenol and benzaldehyde, respectively. PPPs and PThs show catalytic activity for photodegradation of agrochemicals [285,286].

## 4. Electronic and optical devices (ECD, battery, EL, diode, transistor, non-linear optical devices, etc.)

Applications of π-conjugated polymers and related polymers in electronic and optical devices are actively investigated [1–15,287–293]. For example, polyfluorenes [287–293], polythiophenes [294–297], poly(phenylenevinylene)s [298–300], and bipolar polymers [301–303] have also been synthesized by other research groups and their applications to electronic and optical devices have been carried out. Non-linear optical properties of polymer materials are also attracting interest [304–309]. In the following sections, we describe results of our researches obtained with the π-conjugated polymers synthesized by us.

### 4.1. Redox functions and battery

Most of the π-conjugated poly(arylene)s (e.g., P(5,8-diArQx) [151,310]) exhibit electrochromism. Poly(vinyl alcohol) having an oligo-thiophene pendant serves as an excellent polymer electrolyte which shows electrochromism [311,312]. Poly(vinyl alcohol) serves as an excellent matrix polymer for polymer electrolytes [313,314].

The electrochemical redox behavior of π-conjugated polymers has been applied to batteries by many research groups [315–327]. The polymer batteries were first reported independently by us [315] and by MacDiarmid's group [316] in 1981. PTh serves as a positive electrode material for Li and Zn cells [320,321]. Li/LiI/PTh–$I_2$ solid electrolyte cell was also fabricated and, due to the excellent electrical conductivity of PTh–$I_2$, the cell gave a high utilization of iodine [320,321].

Metal-free batteries using PTh, polyacetylene, and PPP as cathode and anode have been prepared because these polymers are susceptible to both p- and n-doping. For a ''storehouse of
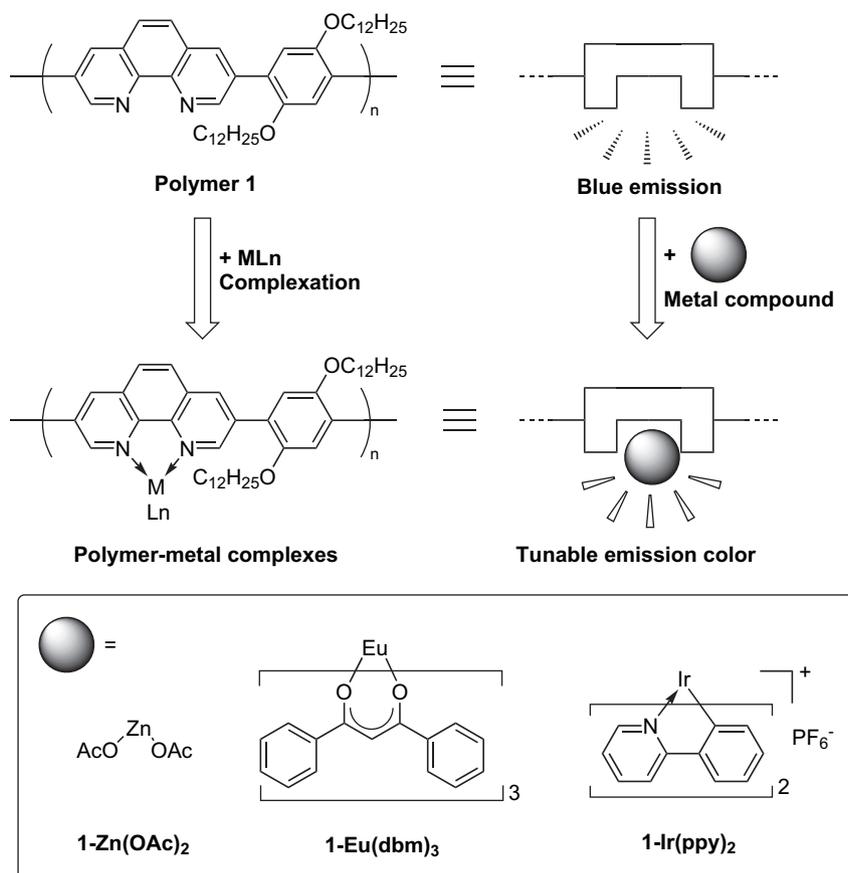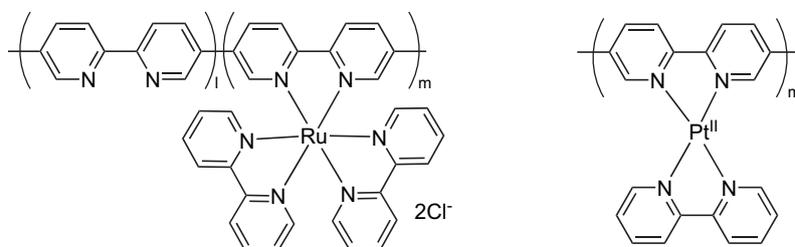
Fig. 10. Metal complexation and tuning the PL color.

charge'', not only the π-conjugated polymers but also graphite can be used [328]. PDPA (cf. Fig. 2) and its analogues serve as a sensor of lead battery [161,162,329].

The *N*-containing polymers like PPy can transport $H^+$ in electrochemical processes [330], and protonated polymers exhibit electrochemical activity similar to that of NAD and serve as an active material of a battery operating in acidic media [331]. Similar batteries based on protonated *N*-containing polyheterocycles are industrialized.



$$(32)$$
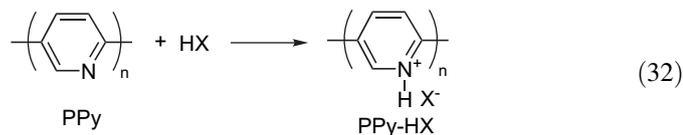
Active material for $H^+$ transport [330] and $H^+$-battery [331]

### 4.2. Diode and EL (LED)

The utility of π-conjugated polymers as a material for an electroluminescence device (EL device or light emitting diode, LED) has been demonstrated [332–336]. Recently, many papers have been published on application of π-conjugated polymers to LED [211–214,337–340]. We have also been investigating EL of the π-conjugated polymers [131,151, 183,203].

### 4.3. Transistor

Thin layer transistor (TLT) is another target device of the π-conjugated polymers [217,235,236,341–355], and PTh prepared by the organometallic polycondensation also works as an active layer for TLT [203,356].



Chart 8. Structures of PBpy–Ru and PBpy–Pt complexes for photoevolution of $H_2$ from aqueous media.

PTh and its derivatives are the most studied polymers for the transistor application. The first TLT with PTh showed a carrier mobility of $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ [342,343]. HT-P3RThs show larger carrier mobilities than those of the corresponding regiorandom P3RThs because HT-P3RThs adapt a preferred orientation in their thin films as mentioned above [235,236]. Especially, HT-P3HexTh has a high carrier mobility of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$, which is in the same level of that of amorphous silicon FET (field-effect transistor).

The molecular morphology of the π-conjugated polymers on the gate substrate layer is considered to be an important factor for a better carrier mobility. As discussed in Section 3.5, regio-controlled π-conjugated polymers such as HT-P3HexTh form an aligned well-organized structure on the surface of various substrates and the carrier seems to move more rapidly in the well-organized polymer material than in amorphous polymer material. Many efforts have been carried out to have a better-organized polymer material on substrates by choosing preparation conditions (e.g., solvent for casting) to prepare the polymer film. In addition to the HT-P3HexTh, various Th(R)—Ar—Th(R) type π-conjugated polymers (cf. Chart 4) self-assemble [204a,205,349,355a], and one of them gives a high mobility of 0.72 cm$^2$ V$^{-1}$ s$^{-1}$ [349a]. The CT-type π-conjugated copolymers serve as a good active material for FETs. The copolymer of thiophene and 4-alkylthiazoles [239], copolymers of thiophene and thiadiazole [354,357], and bithiophene and pyrazine [358] have been prepared,



$$(33)$$
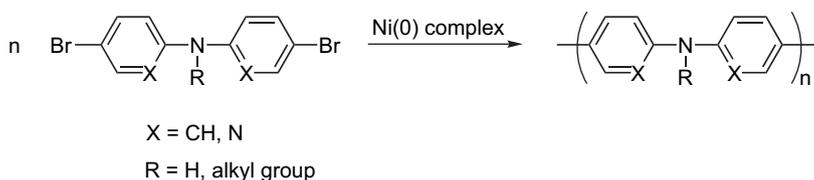
and they give a mobility of $2.5–5.4 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. [Ru(bpy)$_2$] complexes of poly(2-nonyl-1,10-phenanthroline-3,8-diyl) and poly(1,10-phenanthroline-3,8-diyl) also act as an n-channel in FETs even under air [217]. They showed electron mobility of $5.5 \times 10^{-3}$ and $1.9 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively.

### 4.4. Non-linear optics

Non-linear optical (NLO) materials have attracted attention, because of their potential usability for optical switching, frequency modulation, waveguiding, and eventually practical all-optical computing [359,360]. Polydiacetylene (PDA) and its derivatives show large $\chi^{(3)}$ (third-order non-linear optical susceptibility) among π-conjugated polymers. PTh derivatives and thiophene-containing copolymers also have large $\chi^{(3)}$ of about $3–5 \times 10^{-11}$ esu [138a,360–363].

For poly(3-hexylthiophene)s with various head-to-tail coupling ratios ($r$s), an increase in $r$ leads to an increase in the $\chi^{(3)}$ as shown in Table 1. HH-P3(C≡CR)Th gave a larger $\chi^{(3)}$ than HT-P3RTh [138a].

Table 1
Densities of spin-coated films, absorption peak energies ($E_g$), maximum absorption coefficients ($\alpha_{max}$), peak energies ($\hbar\omega'_1$) in third-order non-linear susceptibility ($|\chi^{(3)}|$) spectra, and maximum values of $|\chi^{(3)}|$ (max$|\chi^{(3)}|$) with the various head-to-tail coupling ratios $r$

| $R$ | Density (g cm$^{-3}$) | $E_g$ (=$\hbar\omega_1$) (eV) | $\alpha_{max}$ (cm$^{-1}$) | $\hbar\omega'_1$ (eV) | max$|\chi^{(3)}|$ (esu) |
|---|---|---|---|---|---|
| 0 | 1.07 | 3.22 | $6.46 \times 10^4$ | 3.01 | $1.81 \times 10^{-12}$ |
| 0.30 | 1.07 | 3.04 | $8.27 \times 10^4$ | 2.89 | $2.71 \times 10^{-12}$ |
| 0.80 | 1.09 | 2.53 | $10.5 \times 10^4$ | 2.45 | $9.08 \times 10^{-12}$ |
| 0.985 | 1.14 | 2.43 | $13.8 \times 10^4$ | 2.44 | $27.2 \times 10^{-12}$ |

## 5. Recently synthesized polymers

### 5.1. Polyaniline analogues

We have also been interested in the chemistry of polyaniline PAn and its analogues [160–164,364–372]. Redox behavior of PAn [364–366,369] and dynamic H exchange of PAn on NMR time scale [367,368] have been reported. PAn and its analogues seem to be useful materials for removing static electricity, and electrochemical devices using PAn have been investigated by many researchers. Poly(di-phenylamine-4,4'-diyl) (P(DPA)) and poly(di(2-pyridyl-amine-4,4'-diyl) (P(DpyA)) are analogues of PAn, and they can be prepared by organometallic polycondensations [164].

Buchwald et al. reported other Pd-catalyzed organometallic preparation of polyanilines [373,374].

### 5.2. Poly(benzoazole)s

Poly(benzoazole)s such as P(4,7-Bim(R)), P(4,7-Btd), and P(BTz) have been prepared as shown in Fig. 2. Recently, we prepared the following new π-conjugated benzoazole polymers [375,376].
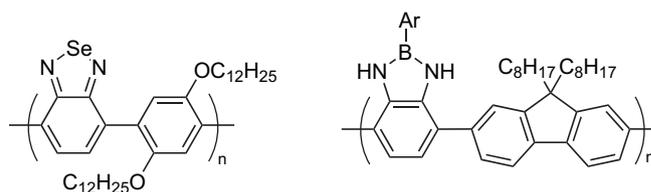


### 5.3. Meta-linked polymers

Poly(*m*-phenylene) (PMP) [41a,e,126] assumes a helical structure in the solid state [41e,377]. Copolymers of *p*-

phenylene and *m*-phenylene are soluble in organic solvents [126,378,379] when the fraction of the *m*-phenylene unit is about 80%.

*p*-Phenylene/*m*-phenylene (PP/MP) and 2,5-pyridyl/3,5-pyridyl (PPy/MPy) copolymers show strong blue luminescence. PL data of P(PP-*ran*-MP)s, P(PPy-*ran*-MPy)s, and P(PP-*alt*-MP)s indicate that the combination of [PMPy/P(PP-*ran*-MP-5/5)] gives the strongest blue luminescent bilayer film [380].

Random copolymer of 2,5-thienylene and 2,4-thienylene has also been synthesized by the Ni-catalyzed polycondensation [125,126].
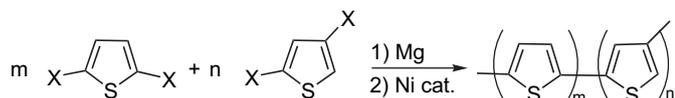


1,3,5-Triazine (Trz) is a typical electron-accepting heteroaromatic unit, and Trz-based polymers have been prepared [381–384]. A copolymer of the Trz unit and thiophene shows an n-type time-of-flight electron drift mobility of $2.0 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$ [384], which is larger than that of the widely used Alq$_3$.

### 5.4. Cross-conjugated polymers

Recently, cross-conjugated system-containing polymers have been reported. In the polymers, the π-conjugation system may be broken because they involve the consecutive two single bond units as shown in Chart 9.
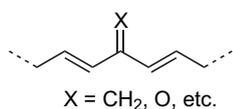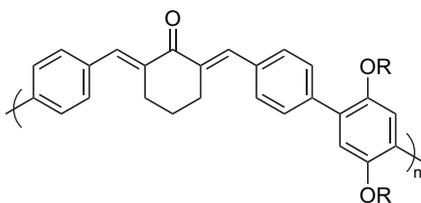


X = CH$_2$, O, etc.

Chart 9. An example of the cross-conjugated unit.

However, the optical properties of such polymers indicate that they often have a moderately expanded π-conjugated system. The following polymer shows $\lambda_{max}$ at 392 nm in chloroform, which indicates that the polymer has an expanded π-conjugated system [385].



Benzophenone- and di(2-pyridyl)ketone-containing copolymers have also been synthesized [386].
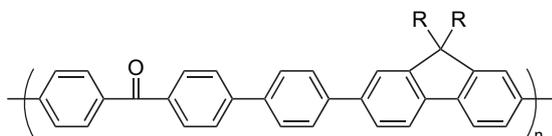


They show photoluminescence with long delay lifetime ($\tau$) of an order of 0.1–1 s, both in a CHCl$_3$ solution at room temperature and in a glassy frozen state. These long $\tau$ values are indicative of phosphorescent emission from the polymers.

## 6. Conclusions

Organometallic polycondensations based on basic organometallic chemistry have contributed much to the preparation of π-conjugated polymers and represented the first preparations of this kind (e.g., PTh, PRTh, PPy, and PBpy). The π-conjugated polymers prepared by the organometallic polycondensations have a well-characterized structure. They have contributed to the understanding of basic chemical and physical properties as well as structural elucidation of the π-conjugated polymers. In addition, they are useful materials for electric and optical devices, and are expected to be invaluable in their future application.

## Acknowledgements

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