Accounts

Synthesis of π-Conjugated Polymers by Organometallic Polycondensation

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Received December 22, 2009; E-mail: tyamamot@res.titech.ac.jp

Organometallic polycondensations give various π-conjugated polymers. For example, nickel complex-promoted dehalogenative polycondensation of dihaloaromatic compounds and dihalogenataed heterocyles, X–Ar–X (Ar = aromatic unit or heterocyclic unit), affords poly(arylene)s and poly(heterocycles), $(Ar)_n$, such as poly(*p*-phenylene), poly(thiophene-2,5-diyl), poly(3-alkylthiophene-2,5-diyl), and poly(pyridine-2,5-diyl). Pd-catalyzed polycondensation gives poly(aryleneethynylene) type polymers and alternating copolymers of Ar and Ar′. These polymers have well defined bonds between the monomeric units, and they are electrochemically active, electrically conductive, and light-emitting. Their well-characterized linear structure brings about unique packing of the polymer molecules in the solid and alignment of the polymer molecules on the surface of substrates. In this paper, we describe synthesis of π-conjugated polymers by organometallic polycondensations. Basic chemical and physical properties of the synthesized π-conjugated polymers, as well as ordered structures in the solid and applications for electronic and optical devices of the π-conjugated polymers, are also described.

π-Conjugated polymers with electronic and optical functionalities are the subject of many recent papers. They are usually prepared by (1) chemical and electrochemical oxidative polymerization of aromatic and heterocyclic compounds (n H–Ar–H → $(Ar)_n$; H–Ar–H = aromatic compound or heterocyclic compound) and (2) organometallic polycondensation using dihalo-organic compounds. We have been concerned with the organometallic polycondensation, and in this review we report (a) basic chemical reactions related to the organometallic polycondensation, (b) preparation of π-conjugated polymers using organometallic polycondensation, (c) basic chemical properties of the π-conjugated polymers, (d) structure of the π-conjugated polymers in solutions and solid, including self-assembling behavior of the π-conjugated polymers, and (e) functionalities of the π-conjugated polymers.

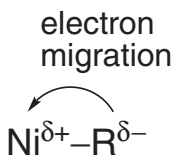
Reductive elimination (or reductive coupling) from diorganotransition metal complexes is one of the most important basic reactions in organometallic chemistry, and it is considered to be a crucial step in organometallic polycondensation. Diorganonickel(II) complexes $[NiR_2L_m]$ undergo reductive coupling (or reductive elimination) reactions to give R–R (eq 1).[1a–1x] 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 (PR_3)):

$$[NiR_2L_m] \rightarrow R\text{–}R \quad (1)$$

R = organic group such as Et. L = neutral ligand such as bpy.

This basic C–C coupling on Ni introduced the concept of reductive elimination to the field of organometallic chemistry and the first experimental support[1a] for the concept of back-donation to olefin[1y,1z] was given during the study. The coordination of molecules leading to the back-donation (e.g., electron-accepting olefin[1a] or aromatic compound[1k,1q]) to central Ni 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 believed to be polarized as $Ni^{\delta+}$–$R^{\delta-}$, whereas 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,



(2)

and this electron migration is thought to be enhanced by coordination of electron-withdrawing olefinic (e.g., CH_2=CHCN and CH_2=CHBr) and aromatic compounds (e.g., C_6H_5CN, C_6H_5Br, and C_6F_6).[1a,1k,1q,1r] Actually reductive elimination of Et–Et (butane) from $[NiEt_2(bpy)]$ is strongly enhanced by coordination of electron-accepting olefinic and aromatic compounds. An enhancement effect as large as 10^{10}–10^{13} has been calculated for reductive elimination based on experimental data,[1r] and the electron migration shown above has been associated with electronic transition from a σ_{Ni-C} orbital to a d* orbital of Ni[1a] which will bring about such an electron migration (Chart 1).

Published on the web April 29, 2010; doi:10.1246/bcsj.20090338

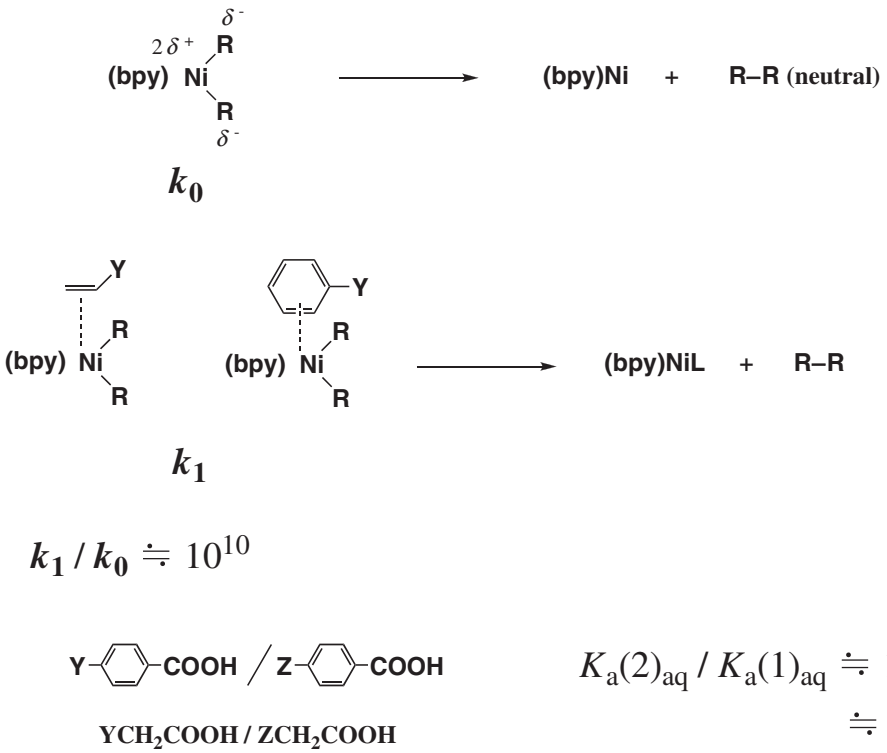


Chart 1. Reductive elimination involves electron migration from the R group (e.g., Et group) to Ni, and is enhanced by coordination of electron-accepting olefinic and aromatic compounds. This enhancement effect is similar to the enhancement effect of acid dissociation by introducing electron-accepting substituent(s) to organic acids (Hammett's effect). The enhancement effect for the reductive elimination is much larger than that observed for acid dissociation (dissociation constant = K_a) of organic acid; rate constant ratio, k_1/k_0, larger than 10^{10} is observed.[1r] Y and Z: electron-accepting and -donating substituents, respectively. In non-aqueous solutions, larger $K_a(2)/K_a(1)$ values are reported.

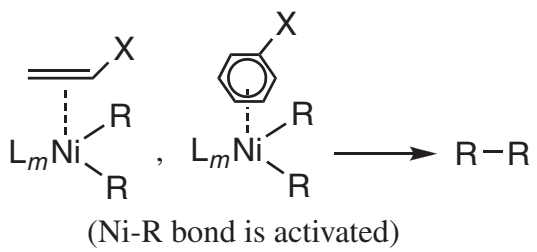


Chart 2. Activation of Ni–R bond by coordination of electron-accepting olefinic and aromatic compounds.

As described above, coordination of electron-accepting sp^2-compounds (or π-acid) to Ni strongly activate the Ni–R bond, which is assumed to be important in organometallic polycondensation using electron-accepting dihalo-organic compounds (Chart 2). This enhancement is similar to that of electron-withdrawing substituents in acid dissociation of benzoic acid (Hammett's effect), however, the enhancement effect on the reductive elimination is much larger than the Hammett effect on the acid dissociation as shown in Chart 1.

In an ^{1}H NMR spectrum of $[Ni(C_2H_5)_2(bpy)]$, the CH_2 signal appears at a higher magnetic field by 0.30 ppm than the CH_3 signal because the C_2H_5 group is attached at an electron-donating central Ni, which is essentially in a zero-valent state.[1a] The relative positions of the CH_2 and CH_3 signals become reversed when an electron-accepting olefin coordinates to $[Ni(C_2H_5)_2(bpy)]$. An ^{1}H NMR spectrum of $[Ni(C_2H_5)_2(CH_2{=}CHCN)(bpy)]$ shows the CH_2 signal at a lower magnetic field by 0.83 ppm than the CH_3 signal:[1u]

$$\delta(CH_2) < \delta(CH_3) \text{ by } 0.30 \text{ ppm for } [Ni(C_2H_5)_2(bpy)]$$
$$\delta(CH_2) > \delta(CH_3) \text{ by } 0.83 \text{ ppm for } [Ni(C_2H_5)_2(CH_2{=}CHCN)(bpy)] \quad (3)$$

From the ^{1}H NMR data, electronegativity χ of Ni in $[Ni(C_2H_5)_2(bpy)]$ and $[Ni(C_2H_5)_2(CH_2{=}CHCN)(bpy)]$ has been estimated using Narashimahan–Roger's equation:

$$\text{Electronegativity } \chi \text{ of Ni:}$$
$$2.58 \text{ of } [Ni(C_2H_5)_2(CH_2{=}CHCN)(bpy)] > 1.89 \text{ of } [Ni(C_2H_5)_2(bpy)] \quad (4)$$

Equation 4: increase in electronegativity χ of Ni by coordination with electron-accepting olefin (π-acid), evaluated from ^{1}H NMR data.[1u] The electronegativity (1.89) of Ni in $[Ni(C_2H_5)_2(bpy)]$ is comparable to Pauling's electronegativity of neutral Ni (1.8), whereas electronegativity (2.58) of Ni in $[Ni(C_2H_5)_2(CH_2{=}CHCN)(bpy)]$ is comparable to Pauling's electronegativity of carbon (2.5).

These data support the concept that the coordination of an electron accepting π-acid to $[NiR_2L_m]$ leads to the increase in the electronegativity of central Ni via electron back-donation from Ni to the π-acid.

Because the electron-withdrawing ability of the R group in $[NiR_2L_m]$ increases in the order of,

$$\text{Pr (propyl)} < \text{Et} < \text{Me} < \text{Ph} \quad (5)$$

reductive elimination of Ph–Ph from $[NiPh_2L_m]$ requires a higher degree of electron migration than that required for reductive elimination of the alkyl–alkyl compound from $[Ni(alkyl)_2L_m]$. Consequently stability of the Ni–R bond is thought to increase in this order. Actually thermal stability of $[Ni(alkyl)_2(bpy)]$ increases in the order of Pr (propyl) < Et < Me:[1a]

$$[NiPr_2(bpy)] < [NiEt_2(bpy)] < [NiMe_2(bpy)] \quad (6)$$

Higher stability of a Ni–CH_3 bond than a Ni–C_2H_5 bond is also suggested in the reaction of alkyl–nickel complexes such as $[Ni(alkyl)(acac)(PPh_3)]$ (alkyl = CH_3 and C_2H_5) with CO.[1s,1t] Insertion of CO to an Ni–Et bond of $[Ni(C_2H_5)(acac)(PPh_3)]$ to give an Ni–acyl complexes ($[Ni(COC_2H_5)(acac)(PPh_3)]$ in this case) is easier than that to an Ni–Me bond of $[Ni(CH_3)(acac)(PPh_3)]$.[1s] This is presumably due to lower stability of the Ni–Et bond than the Ni–Me bond.[1s,1t] Obtaining insertion products of CO to Ni–Ph complexes is difficult.

Although the Ni–Ph bond is thought to be more stable than a Ni–alkyl bond, a Ni–Ph bond in $[NiPh_2L_m]$ seems to be less stable and undergoes reductive elimination to give Ph–Ph easily.[1q,1v–1x] Attempts to isolate $[NiPh_2L_m]$ have not been successful, and they usually give the reductive elimination product Ph–Ph. Even when the Ph group has a moderately electron-accepting substituent such as a $NC(C_6H_4)$– group, it was not possible to isolate $[NiPh_2(bpy)]$ complexes.[1q] In the reaction of $NC(C_6H_4)Cl$-*p* with a mixture of $Ni(cod)_2$ (cod = 1,4-cyclooctadiene) and bpy, a reductive elimination of $NC(C_6H_4)_2CN$ seems to take place from $[Ni(C_6H_4CN\text{-}p)_2(bpy)]$, which is formed by oxidative addition of $NC(C_6H_4)Cl$-*p* to [Ni(cod)(bpy)] and disproportionation of an intermediate $[NiCl(C_6H_4CN\text{-}p)(bpy)]$.[1q]

When the Ph group is changed to a strongly electron-withdrawing groups such as C_6F_5, the $[NiPh_2L_m]$ complex (e.g., $[Ni(C_6F_5)_2(bpy)]$) 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:[1q] Two C_6F_5 groups in $[Ni(C_6F_5)_2(bpy)]$ are oriented almost perpendicularly which will bring about direct interaction between π-electrons at carbons attached to Ni. A similar electronic interaction between two phenyl groups seems to be present in postulated $[Ni(C_6H_5)_2(bpy)]$, and this seems to make reductive elimination of C_6H_5–C_6H_5 from $[Ni(C_6H_5)_2(bpy)]$ easy.

The presence of such π-electronic interaction between two aromatic groups (Chart 3) accounts for the ease of reductive elimination of Ph–Ph from $[NiPh_2L_m]$, which may be called π-electron-assisted reductive elimination. When the phenyl group attached to Ni has *o*-substituent(s), as in mesityl groups, $[Ni(Ar)_2L_m]$ (Ar = mesityl etc.) complexes can be isolated.[1v,1w] In this case, such π-electron interaction between two Ar groups seems to be weakened because of deviation of the phenyl rings[1v] from the mutually perpendicular orientation due to the presence of the *o*-substituent(s).

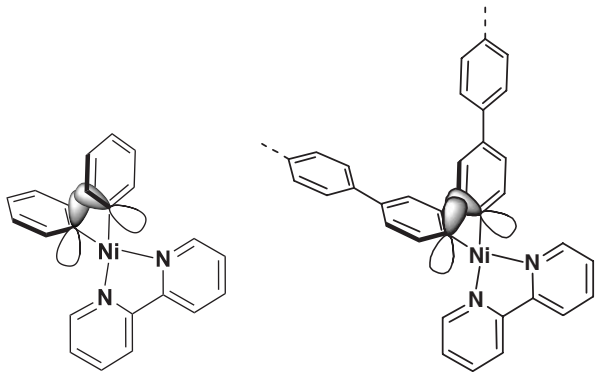


Chart 3. Left side: Postulated π-electronic interaction between two Ph groups through π-electrons in the Ph group. When Ph is fully fluorinated, $[Ni(C_6F_5)_2(bpy)]$ having a structure shown in the left side can be isolated.[1q] Right side: Similar π-electronic interaction between propagating $(C_6H_4)_m$ and $(C_6H_4)_n$ units on Ni. In the case of the coupling between $(C_6H_4)_m$ and $(C_6H_4)_n$ units, special electronic states (e.g., polaronic state) generated in the propagating oligophenylene may also contribute to the π-electron assisted coupling. Isolation of $[NiPh_2L_m]$ with non-substituted Ph has not been successful. However, introduction of an *o*-substituent to Ph causes twisting of the Ph groups and seems to make the π-electron interaction between the two Ph groups weak, and [Ni(*o*-substituted $Ph)_2L_m$] complex becomes isolable (cf. the text).

Because of (1) the enhancement effect of electron-accepting aromatic compounds on the reductive elimination and (2) ease of the reductive elimination from the $[NiPh_2L_m]$ complex, organometallic dehalogenative polycondensation is considered to be especially suited to polymerization of dihaloaromatic monomers, X–Ar–X, which is considered to behave as a typical electron-accepting ligand to Ni. In the supposed propagating Ni species with propagating oligo-aromatic units (right side of Chart 3), special electronic states (e.g., polaronic state) generated in the propagating oligophenylene unit may also contribute to the π-electron-assisted coupling. Recently the importance of reductive elimination in organometallic polycondensation was reported as described later.

The basic coupling reaction (reductive elimination) is a key step in Ni-promoted organic syntheses (e.g., $RMgX + R'X \rightarrow R–R'$; $2RX + Zn \rightarrow R–R$; $2RX + Ni^0$ complex $\rightarrow R–R$; X = halogen).[2] We have developed further the utilization of this coupling reaction for the polycondensation of dihaloaromatic compounds:

$$n\,\text{X-Ar-X} + n\,\text{Mg} \longrightarrow n\,[\text{X-Ar-MgX}] \xrightarrow{\text{Ni-complex}} \text{-(Ar)}_n\text{-} \quad (7)^3$$

$$n\,\text{X-Ar-X} + n\,\text{Ni}^0\text{L}_m \longrightarrow \text{-(Ar)}_n\text{-} + n\,\text{NiX}_2\text{L}_m \quad (8)^4$$

$$n\,\text{X-Ar-X} + n\,\text{Zn(or 2e}^-\text{)} \xrightarrow{\text{Ni-complex}} \text{-(Ar)}_n\text{-} + n\,\text{ZnX}_2\,\text{(or 2X}^-\text{)} \quad (9)^{5,6}$$

In reaction 9, $[Ni^0L_m]$ formed in situ by chemical (e.g., by Zn) or electrochemical reduction of Ni^{II}-compounds are used for polycondensation.[5,6a–6e] The Zn-based polycondensation has

recently been utilized to prepare proton-conductive poly(*p*-phenylene) polymers having $-SO_3H$ groups at the side chain.[6h,6j] It was reported that NaH and hydrazine hydrate were also usable as the reducing agents.[6f,6g] As described above, π-conjugated polyarylenes and polyheterocycles can be prepared by organometallic polycondensation as well as by chemical and electrochemical oxidation of aromatic compounds, and books, reviews, and papers have been published concerning the preparation and properties of π-conjugated polymers.[7]

Organopalladium(II) complexes also undergo C–C coupling on Pd.[8] We applied the C–C coupling to the following polycondensation[9a–9e] which is based on Pd-promoted synthetic reactions of arylacetylenes.[8b,8c,10a,10b] 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.

$$n\ \text{X-Ar-X} + n\ \text{HC}\equiv\text{C-Ar'-C}\equiv\text{CH} \xrightarrow{\text{Pd/Cu}} \text{-(Ar-C}\equiv\text{C-Ar'-C}\equiv\text{C-)}_n \quad (10)^9$$

PAE-type polymer

Successful polycondensation usually requires highly effective basic coupling reactions. However, the polycondensations expressed by eqs 7–10 can 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 π-conjugated polymers, 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 giving crystalline stereoregular poly(propylene) proceeded at a much faster velocity than that giving amorphous stereo-irregular poly(propylene), presumably due to the stabilization energy attained by forming the crystal in the stereoregular polymerization.[10c]

As described above, the basic C–C coupling reaction in the polycondensation is thought to proceed well especially when the dihalo compounds such as X–Ar–X comes (or coordinates) to the propagating species ([(polymer)$_a$–NiL$_m$–(polymer)$_b$]) to produce (polymer)$_a$–(polymer)$_b$ in the polycondensation. The concept that the propagation reaction proceeds selectively when the monomer comes to the propagating species also explains smooth polycondensation and obtaining high molecular weight polymer.[10d]

Because organometallic polycondensations can give π-conjugated aromatic polymers effectively, various analogous polycondensations have been developed. For example, organostannanes and organoborons undergo similar Pd-catalyzed C–C coupling reactions:[11a–11d]

$$n\ \text{X-Ar-X} + n\ \text{m-Ar'-m} \longrightarrow \text{-(Ar-Ar')}_n \quad (11)^{12}$$

m : SnR_3 or $B(OR)_2$

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 7 is applicable to dihaloalkanes (e.g., Br(CH$_2$)$_m$Br) 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 thought to proceed through oxidative addition of C–OY (e.g., CO–OPh, C–OTs; Ts = tosyl) to a transition metal studied previously.[1t,13a,13b]

$$\text{BrMg-(CH}_2\text{)}_m\text{-MgBr} + \text{TsO-(CH}_2\text{)}_m\text{-OTs} \xrightarrow{\text{Cu}} \text{-(CH}_2\text{)}_{mn} \quad (12)$$

$$n\ \text{YO-Ar-OY} \xrightarrow{\text{Ni}^0\text{L}_m} \text{-(Ar)}_n \quad (13)^{5e}$$

When the polymerization is carried out by using [Ni^{0}L$_m$] (eq 8), the polymerization is believed to proceed through the following fundamental reactions;[2f,4c]

$$\text{Ni}^0\text{L}_m + \text{X(Ar)}_i\text{X} \xrightarrow{\text{oxidative addition}} \text{L}_m\text{Ni}(\text{X})(\text{(Ar)}_i\text{X}) \quad (14)$$

Complex I

$$\text{L}_m\text{Ni}(\text{X})(\text{(Ar)}_i\text{X}) + \text{L}_m\text{Ni}(\text{X})(\text{(Ar)}_j\text{X})$$

Complex I Complex I'

$$\xrightarrow{\text{disproportionation}} \text{L}_m\text{NiX}_2 + \text{L}_m\text{Ni}(\text{(Ar)}_i\text{X})(\text{(Ar)}_j\text{X}) \quad (15)$$

Complex II

$$\text{Complex II} \xrightarrow{\text{reductive elimination}} \text{L}_m\text{Ni} + \text{X(Ar)}_{i+j}\text{X} \quad (16)$$

P_{i+j}

The oxidative addition of C–X[1m–1o,13c–13e] and C–OY[1t,13a,13b] to [Ni(0)L$_m$] (eq 14) is well known, and the disproportionation reaction[1s,13f] is also known. When the Ni–C bond has high stability, the Complexes I[2e] and II[1k,1l] as well as a complex of a type [L$_m$(X)Ni–Ar–Ni(X)L$_m$][1g] can be isolated.

Syntheses of π-Conjugated Polymers

By using the organometallic polycondensations expressed by eqs 7–10, various π-conjugated polymers have been prepared. Figure 1 shows examples of the π-conjugated polymers[3h,4b,12n,14–53] prepared by the organometallic polycondensation in our group.[3h,4b,12n,14–16,18–23,25–34,35a,36,38,40,41,43–45,49b,49c,51–53]

Some of the π-conjugated polymers shown in Figure 1 were patented as materials (e.g., poly(thiophene-2,5-diyl) (PTh)[14a] and poly(3-alkylthiophene-2,5-diyl) (P3RTh)[14b,14c]) under the name of our institute. PPP[3a,3b] and PFc[35a,39m] with high crystallinity and well-defined bonding between the monomer units were also first prepared by the polycondensation. Poly(quinoline-2,6-diyl)s with substituent(s) were reported by Professor Stille.[4o]

PTh was designed as well-characterized and stable π-conjugated conducting polymer composed of a five-membered ring,[15] and introduction of the alkyl group to PTh led to enhancement of solubility of PTh without losing the essential π-conjugation system of PTh.[14b,14c,16a] Due to the increase in solubility, NMR analysis of P3RTh and 3-substituted poly(thiophene)s such as HH-P3(C≡CR)Th became possible.[14b,14c,17,20l] For example, the microstructure of P3RTh

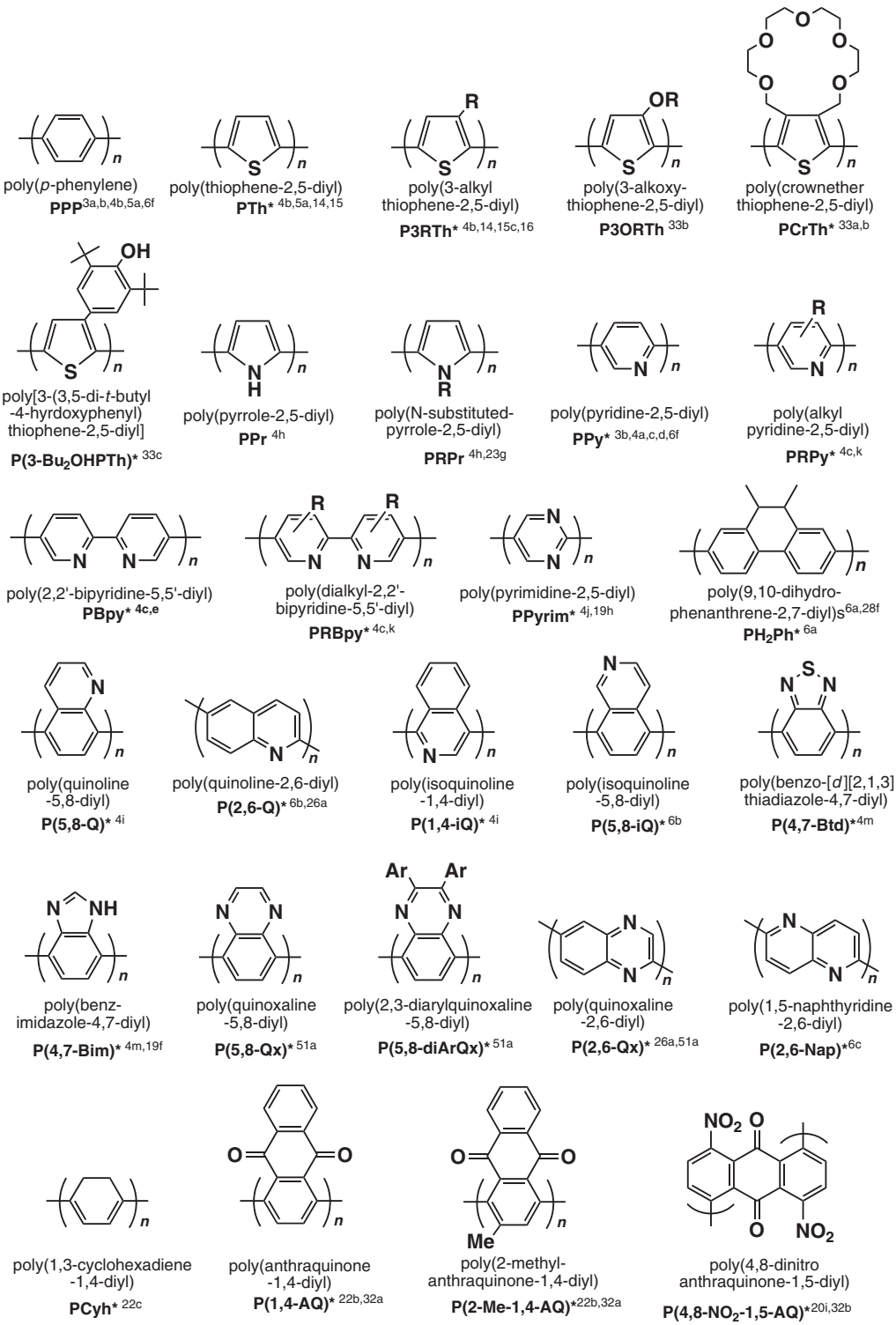
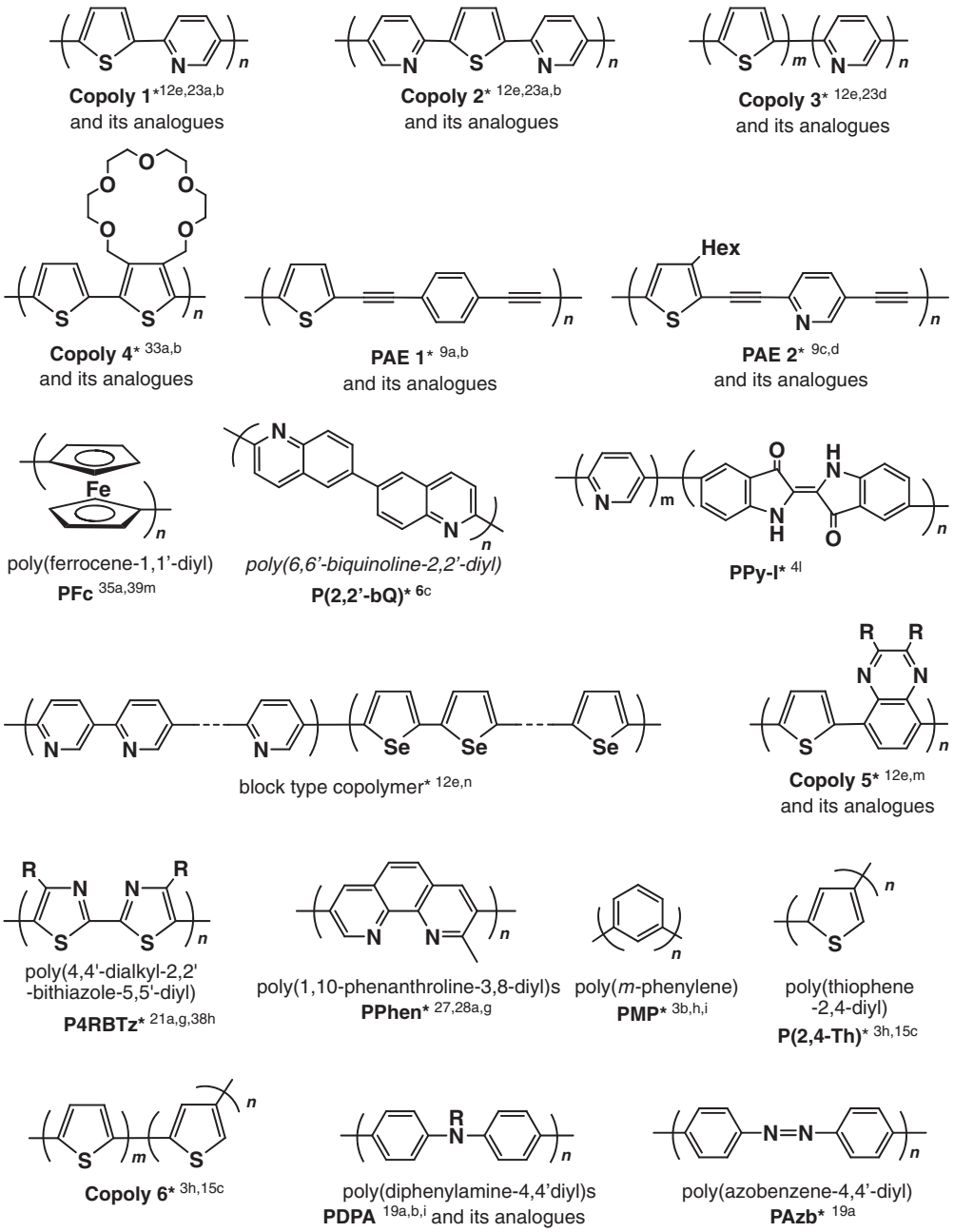


Figure 1. *Continued on next page.*

($R = CH_3$ etc.) was discussed in term of head-to-tail and head-to-head joints (Chart 4).[14c,15c,17a–17f]

It has become possible to prepare head-to-tail type HT-P3RThs, which possess a highly controlled regioregularity, by organometallic polymerization methods.[17a–17f] McCullough and his co-workers introduced Grignard reagent selectively to the 5-position of RTh ring and polymerized it with Ni-catalyst.[17a] On the other hand, Rieke and his co-workers reported that region-controlled organozinc reagent was obtained with highly activated zinc (Rieke zinc) and that the organozinc reagent afforded regioregular P3RTh, in which the head-to-tail joint predominated as high as 98.5%.[17b] These regioregular HT-P3RThs exhibit higher crystallinity in solid and higher electrical conductivity compared with those of



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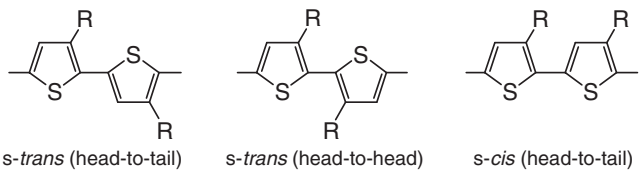


Chart 4. Microstructures of P3RTh.

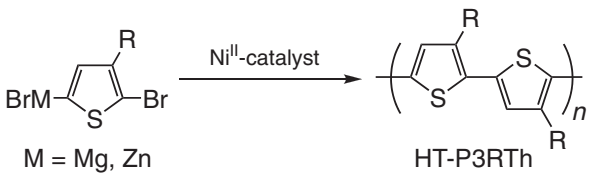


Chart 5. Preparation of regio-regular head-to-tail HT-P3RTh via selective metalation (magnesium[17a] and zinc[17b]).

regio-random rand-P3RThs. HT-P3RTh forms a π-stacked structure, as discussed later. Preparation of regio-regular HT-type polythiophene with substituents such as *p*-alkylphenyl groups[17g,17h] at the 3-position by oxidative polymerization has also been reported.[17g–17i] As shown in Chart 5, selective metalation of 3-alkyl-2,5-dibromothiophene is considered to be important for obtaining HT-P3RTh. However, stabilization of formed HT-P3RTh by forming a well packed structure in solid[21c,21d] is also considered to contribute to formation of regio-regular HT-

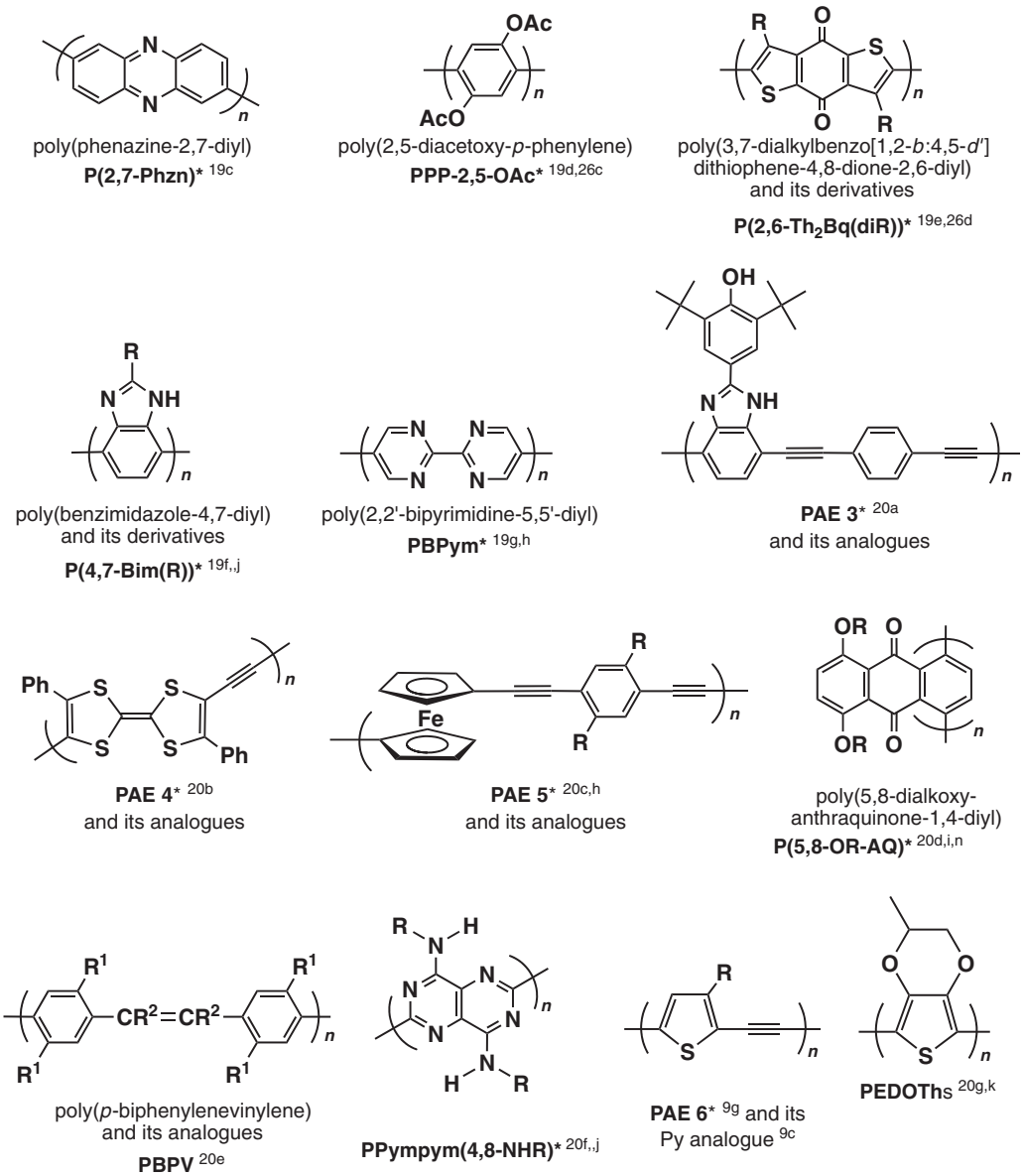
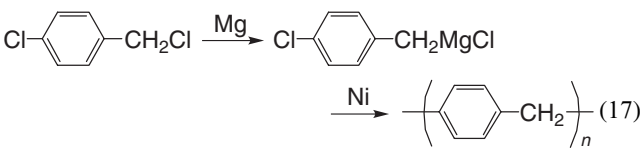


Figure 1. *Continued on next page.*

P3RTh. Recently new developments have been made on Ni-promoted polycondensation using Grignard reagent intermediates for the preparation of substituted polythiophenes and poly(*p*-phenylenes),[17j–17p] and discussion of the mechanism of the polymerization has been made. The importance of reductive elimination in the polymerization has been pointed out.[17o]

Head-to-head polythiophene with acetylenic –C≡CR side chains shows a strong tendency to form a π-stacked solid structure[20l–20n] as discussed later. Syntheses of regioregular PAE polymers (e.g., PAE-6 in Figure 1) are also possible.[9c,9g] For some of the π-conjugated polymers (e.g., PTh and P3RTh) depicted in Figure 1, other preparative methods (e.g., oxidative polymerization)[7a–7g,17g] have also been developed. Use of 4-chlorobenzyl chloride in polycondensation using Mg also seems to give a regio-controlled polymer due to a large difference in the reactivity between the two C–Cl bonds.



The polymer gives rise to sharp X-ray diffraction peaks, supporting its crystalline structure.[3b,4n] The polycondensation proceeds well even by addition of the transition metal complex prior to the formation of the Grignard reagent (eq 7).[3b] In this case, Mg may serve as a reducing reagent for the catalyst, similar to Zn in eq 9. For the catalyst 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. However, other transition metal (e.g., Pd and Fe) compounds sometimes exhibit the catalytic activity.[3b]

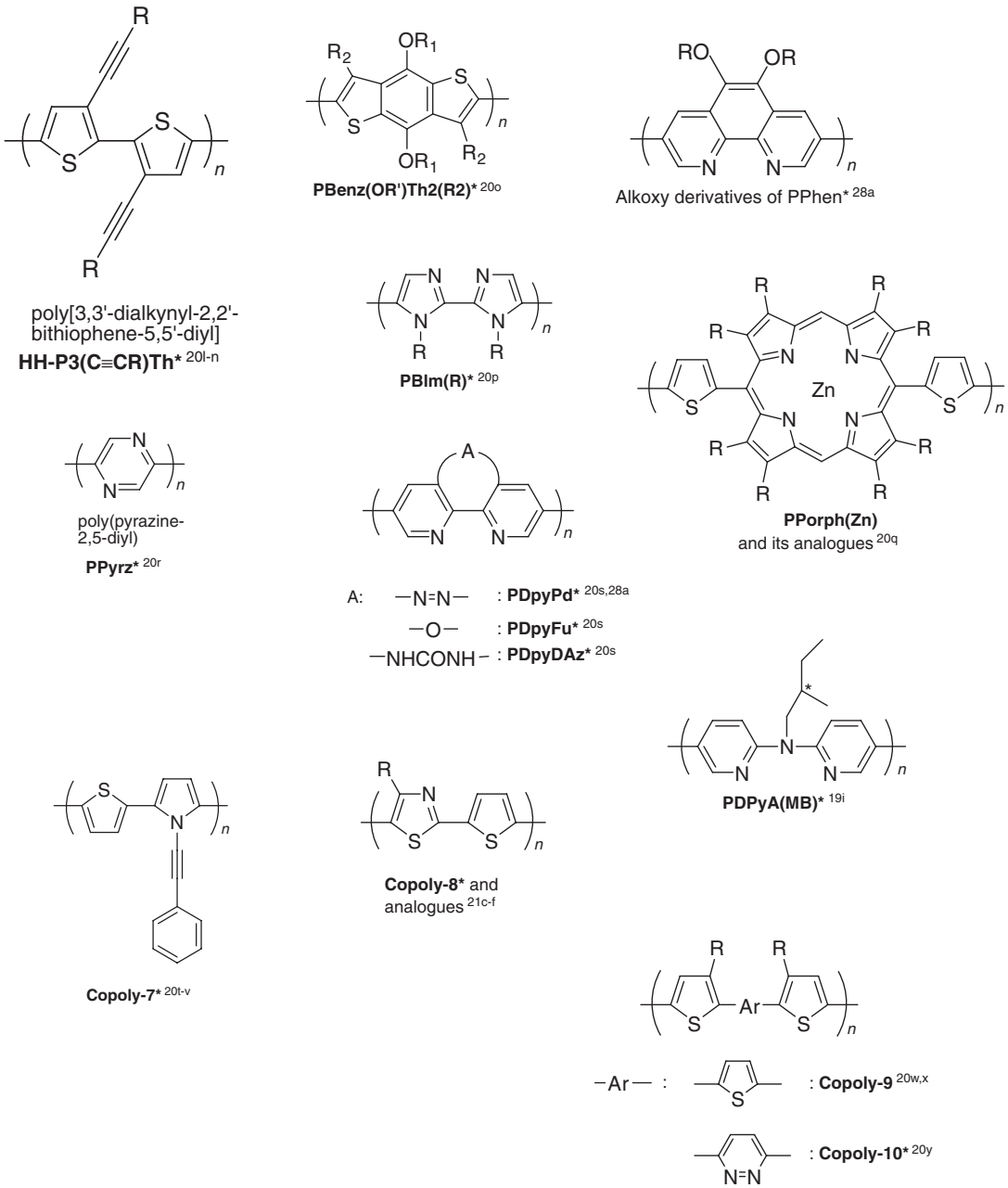


Figure 1. *Continued on next page.*

The molecular weight of the π-conjugated poly(arylene)s and poly(heterocycle)s prepared by organometallic polycondensation seems to depend on solubility and crystallinity of the polymers. The polymerization is believed to proceed even in slurries of oligomeric or polymeric propagating species deposited from the solvent.[4b,4c] 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 alkyl chain) give higher molecular weight polymer. For example poly(arylene)s prepared using $[Ni^0L_m]$ and the Grignard reagent have the following molecular weights (M_n = number average molecular weight; M_w = weight average molecular weight): PPy: $M_w = 4300$,[4c] 6300[18a] (both by light scattering method) with $[\eta]$ of 2.29 dL g^{-1} in formic acid. GPC (gel permeation chromatography) in $(CF_3)_2CHOH$ showed essentially a unimodal GPC trace with a peak molecular weight of about 40000;[18a] PBpy: 3200;[4c] PRPy: 12000–27000 (R = CH_3), 36000 (R = 2-hexyl); PRBpy: 21000 (R = 2-hexyl); P3RTh: 190000 (R = hexyl); P(2-Me-1,4-AQ): 190000; Copoly 3: ca. 5×10^4–5×10^6; PH_2Ph(9,10-OR) (R = $SiMe_2$(n-$C_{18}H_{37}$): $M_n = 9100$-6×10^5 (by gel permeation chromatography) depending on the amount of Ni(0) complex added;[28f] PPP: $M_n = 5200$;[3h] Soluble polyphenylene (p-phenylene:m-phenylene = 2:8, **Copoly-13**): 5400;[3h] PTh: $M_n = 5500$.[3h] For PPy, its preparation[18] in a larger (50 g) scale gave the polymer with a higher molecular weight (M_w (weight average molecular weight) = 6300 determined by light scattering) than the preparation in a 1 g scale,[4c] which afforded the

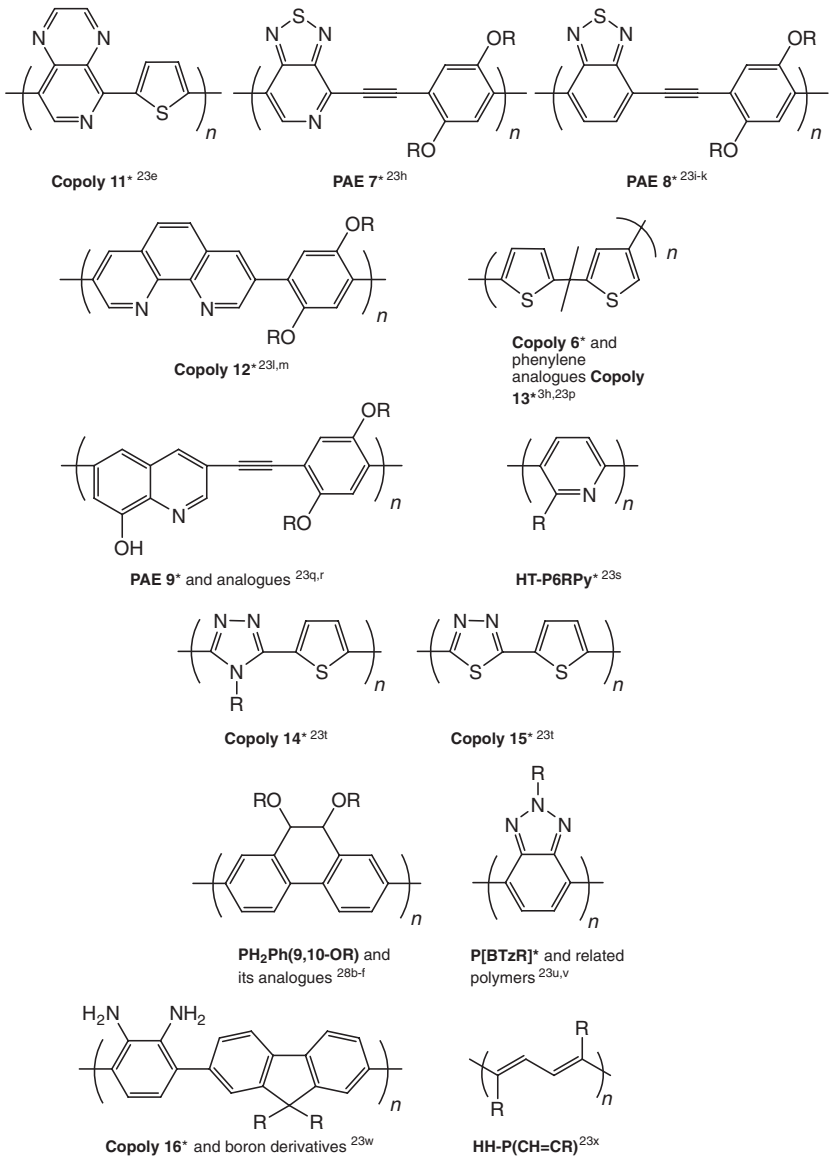


Figure 1. π-Conjugated polymers prepared by the organometallic processes in our group. Polymers with * were for the first time reported from our group.

polymer with M_w of 4300. PPy with $M_w = 6300$ showed intrinsic viscosity $[\eta]$ 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 8) contained 13 ppm Ni[18a] and contained 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 thought to be formed from Ni-terminated aryl groups[1g,2e] during the work-up including treatment with acids such as HCl;

$$\cdots\text{polymer–NiL}_m + \text{H}^+ \rightarrow \cdots\text{polymer–H} \quad (18)$$

However, quenching conditions of the polymerization system may sometimes affect the molecular weight of the polymer. A [(polymer)$_i$–NiL$_m$–(polymer)$_j$] intermediate (cf. Complex II in eq 15) can undergo both the acidolysis shown in eqs 18 and 19 and reductive elimination reaction shown in eq 20:[1q,8g]

$$[(\text{polymer})_i\text{–NiL}_m\text{–(polymer)}_j] + \text{H}^+$$
$$\rightarrow (\text{polymer})_i\text{–H} + (\text{polymer})_j\text{–H (acidolysis)} \quad (19)$$
$$\rightarrow (\text{polymer})_i\text{–(polymer)}_j \text{ (reductive elimination)} \quad (20)$$

Changes of the GPC pattern of the obtained polymer on the kind of proton source added during work-up have been reported.[1q,54] [Pd(C$_6$F$_5$)$_2$L$_m$] also underdoes the acidolysis and reductive elimination in the reaction with protic acids.[8g] Poly(9,9-dialkylfluorene)s synthesized by organometallic polycondensation have M_n of an order of 10^5.[50j]

Ni^{0}L$_m$ complexes serve as condensing agents in the dehalogenative polycondensation shown in eq 8, and the amount of the [Ni^{0}L$_m$] complex influences the molecular weight of the polymer. Addition of an excess amount of the [Ni^{0}L$_m$] complex usually gives polymers with a higher molecular weight.

All of the polymers shown in Figure 1, except for PPr,[4h] PCyh,[22c] and HH-P(CH=CR),[23x] are stable in air. For example,

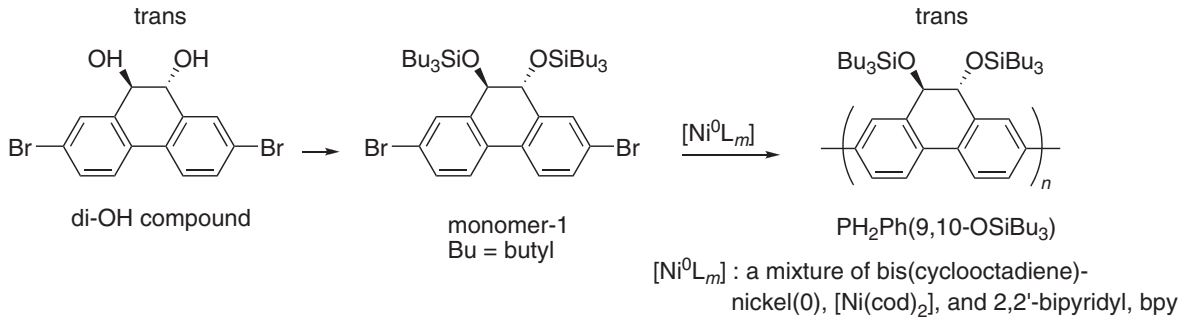
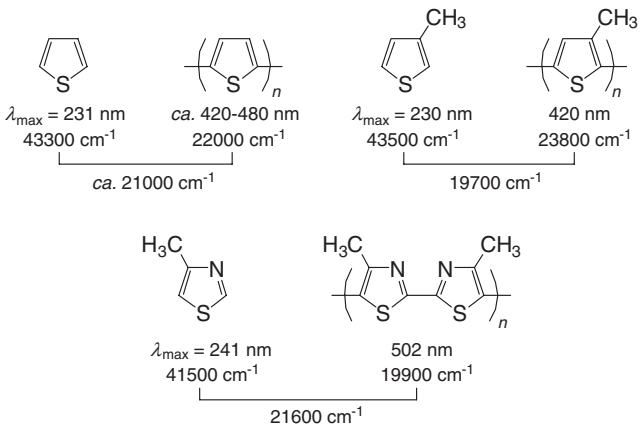
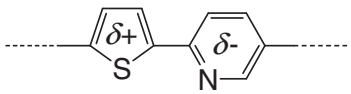


Chart 6. Preparation of poly(9,10-disubstituted-9,10-dihydrophenanthrene-2,7-diyl). An example for the preparation of (*R*,*R*)-$PH_2Ph(9,10\text{-}OSiBu_3)$.



Thiophene with -C≡CR at the 3-position (260 nm) –
HH-P3(C≡CR)Th (R = decyl; 520 nm): 19200 cm^{-1}

Chart 7. Shift of π–π^* transition energy by forming polymer system.



Copoly 1

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

Chart 8.

PTh and P3RTh which can be stored many years[4b,14–16] in an open atmosphere underwent virtually no change. Vacuum-deposited PTh film showed some electrical conductivity under air.[22a] Many of the π-conjugated polymers shown in Figure 1 are soluble in solvents. However, PPP, PTh, and PCyh were insoluble.

Poly(9,10-disubstituted-9,10-dihydrophenanthrene-2,7-diyl)s[28b–28f] such as $PH_2Ph(9,10\text{-}OSiBu_3)$ were light emitting. When a chiral monomer was employed, obtained polymer showed strong circular dichroism (Chart 6).[28d]

UV–Vis Absorption

Because of the expansion of the π-conjugated system, π–π^* absorption peaks of the poly(arylene)s and poly(heterocycle)s show red shifts from the peaks of the 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), P4RBTz (R = CH_3), and HH-P3(C≡CR)Th which all inherently have minor steric hindrances in their intramonomer bonds accordingly show large red shifts:[3d,3f,3o,18b,20n] Degree of red shift: Thiophene–PTh: ca. 21000 cm^{-1}, 3-Methylthiophene–P3RTh (R = CH_3): 19700 cm^{-1}, 4-Methylthiazole–P4RBTz (R = CH_3): 21600 cm^{-1}, HH-P3(C≡CR)Th (R = decyl): 19200 cm^{-1} (Chart 7). 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 13000 cm^{-1}, partly due to the 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 cm^{-1}) because of the presence of the considerably large π-conjugation system even in the monomeric unit.[22b]

In the case of copolymers composed of electron-donating heterocycle units such as thiophene and electron-withdrawing heterocycles such as pyridine and quinoxaline units, the copolymers are considered to have an intramolecular charge-transfer (CT) structure. Copoly 1 gives rise to an absorption band at wavelengths longer than the λ_{max} of the corresponding homopolymers PPy and PTh (Chart 8).[12e,20y,23a–23d] Preparation of similar CT copolymers, which also give λ_{max} at a longer wavelength, have been reported.[21b,24,55a] CT π-conjugated polymers and oligomers seem to have a larger cross section of two-photon absorption, σ_{2PE}, than non-CT polymers and oligomers.[55e]

For poly(naphthylene) polymers, a difference in the degree of the red shift has been noted between poly(naphthalene-2,6-diyl) and poly(naphthalene-1,4-diyl) polymers:[3o,6b,6c,25,26a] e.g., 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 because of twisting of the main chain caused by steric repulsion.[6f,7a,26b,26c] Because PPympym(4,8-NHR) has no *o*-CH group, there seems to be no effective steric repulsion between the repeating units. Consequently PPympym(4,8-NHR) shows the π–π^* absorption band at a longer wavelength than that of P(2,6-Q):[20f,20j] λ_{max}: PPympym(4,8-NHOct) (Oct = octyl), 452 nm > P(2,6-Q), 403 nm (both for film). In the case of PCyh, its color (black) indicates the formation of an effective π-conjugation system

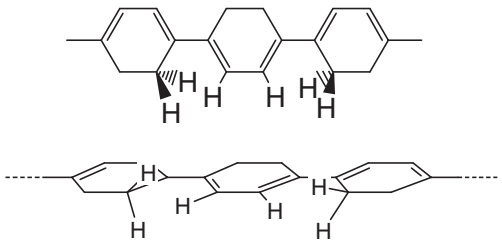
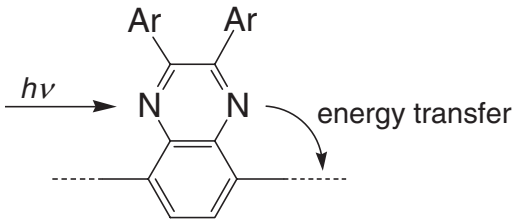
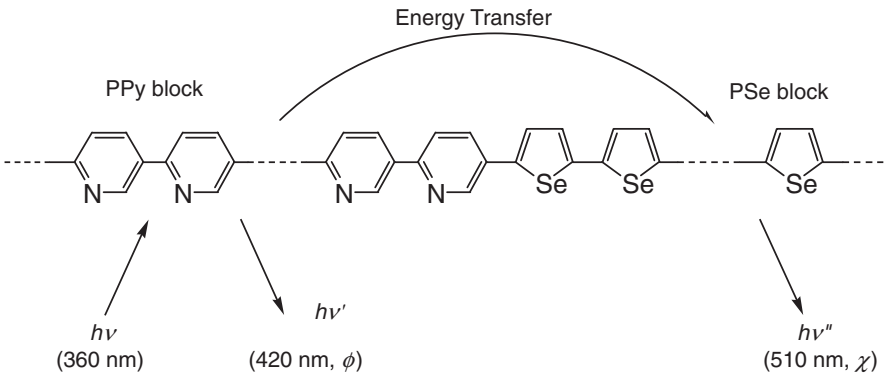


Chart 9. Postulated arrangement of the recurring units of PCyh along the main chain.



Life time of emission: 0.3-1.0 ns

Chart 11. Energy transfer in P(5,8-diArQx) (Ar = *p*-tolyl) (perpendicular type).[12n]



Time scale of energy transfer: ca. 5 ps

Chart 10. Energy transfer from excited PPy block to PSe block (parallel type).[12n]

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,22f] which may be due to the presence of the coplanar expanded π-conjugation system without the aromatic stabilization (Chart 9).

Photoluminescence

Most of the polymers shown in Figure 1 exhibit photoluminescence with an emission peak appearing at the onset of π–π^* absorption. Linear rod-like polymers such as PPy,[4c] PPhen,[28a] and PAE-2[9d] often show excimer emission in films and solutions with high concentrations. Among PAE-1 polymers, those containing an anthracene unit show especially strong fluorescence.[9a] Poly(9,9-disubstituted fluorene-2,7-diyl)s[50i,50j] and PH_2Ph(9,10-OR)s,[28b–28f] which essentially have a PPP main chain framework, are strongly light emitting and give a high quantum yields. They and related copolymers are expected to be useful materials for light emitting polymer diode.

In several cases, energy transfer from a photoactivated π-conjugated unit (e.g., PPy unit) to an energy-accepting π-conjugated unit is observed during fluorescence.[12e,12n,29a] For example, a block structure of a Py–Se copolymer shown in Figure 1 and Chart 10 is confirmed by its UV–visible spectrum and solubility, and it 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 takes place (Chart 11).[12n,29b,29c] 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,29e]

Third-Order Nonlinear Optical Properties, Photoresponse, and Circular Dichroism

An interesting finding with Copolys 1–3,[12e,23b] Copoly-5,[12d,12e,12m] PAE-2,[9c,9d] HT-P3RTh,[55b] and HH-P3(C≡CR)Th[20n] is that they give large $\chi(3)$ (third-order nonlinear optical susceptibility) of $3–5 \times 10^{-11}$ esu, which is essentially attributed to a small band gap of the polymers. However, contribution of a special electronic state(s) formed in π-stacked molecular assembly to the large $\chi(3)$ is suggested.

π-Conjugated polymers are thought to possess energy band structure similar to that of inorganic semiconductors such as TiO_2.[43a] 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 dissosiation of excitons.[31] Moving behavior of photogenerated carrier along the HT-P3RTh has been examined by ESR.[55c] Chiral (*R*,*R*)-PH_2Ph(9,10-$OSiBu_3$) shows strong circular dichroism (CD) when it forms a colloidal solution and film (for film the CD effect = ca. $5° \mu m^{-1}$ of thickness of the film).[28e] Similar enhancement of the CD effect by forming a colloidal solution and film is observed with π-conjugated polynaphthalene with axial chirality.[55d] Chiroptical properties of π-conjugated polymers with optically active groups are the subject of recent interest,[56] and similar enhancement of the CD effect by molecular assembly has been observed.

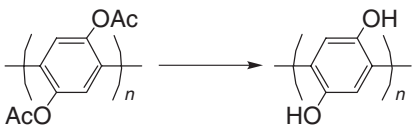
Redox Behavior

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,4d]) 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, with coupled oxidation (n-dedoping) peak of the reduced PPy, E_{pa}, at -1.90 V vs. Ag^+/Ag. The n-doping and n-dedoping of π-conjugated poly(arylene)s and poly(heterocycle)s are usually accompanied by a color change, and effort has been made for application of this electrochromism to devices. In the case of PPy, its original yellow color turns reddish purple after n-doping.

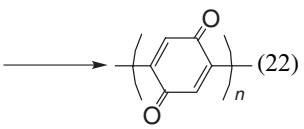
PPy (neutral: yellow) $\rightarrow$ PPy (reduced: reddish purple) (21)

The electrochemical reaction and color change are reversible.

When P(2-Me-1,4-AQ) is reduced, the polymer is believed to contain an original neutral 2-Me-1,4-AQ unit, one-electron reduced anion radical unit, and 2-electron reduced 2-methyl-1,4-dihydroxyanthracence unit. CV (cyclic voltammetry) data of P(2-Me-1,4-AQ) has been discussed based on a mixed reduced state and electronic communication between the three units in reduced P(2-Me-1,4-AQ).[22b,32a] P(4,8-NO_2-1,5-AQ)[32b] and poly(*p*-benzoquinone)[19d,26c,32d] prepared from PPP-2,5-OAc[19d,26c] show very low reduction potential, ($E^0{}_1 = -0.74$ and -0.5 vs. Ag^+/Ag, respectively), because of the attachment of electron-withdrawing NO_2 and direct bonding of the *p*-benzoquinone unit in the π-conjugation system, respectively.



PPP-2,5-OAc



(22)

PPBQ

The ease of the electrochemical reduction and oxidation 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 *EA* of the corresponding monomeric compound H–Ar–H for a wide range of poly(*p*-phenylene), poly(naphthalene-1,4-diyl), and poly(naphthalene-2,6-diyl) polymers.[19c,19d,25,26]

$$E_{red} \text{ of } (Ar)_n = a_{red} + \rho_{red} \times EA \text{ of H–Ar–H} \quad (23)$$

$$E_{ox} \text{ of } (Ar)_n = a_{ox} + \rho_{ox} \times IP \text{ of H–Ar–H} \quad (24)$$

EA = electron affinity. *IP* = ionization potential.

ρ_{red} of 0.75–0.8 has been obtained. A similar linear correlation is observed between oxidation (or p-doping) potential E_{ox} of PPP, PTh, and PPr (Figure 1) and ionization potential *IP* of the corresponding monomeric compounds with ρ_{ox} of ca. 1.4,[25b] although such a correlation is not observed between E_{ox} of bulk metal in water and *IP* of atomic metal due to a strong effect of solvation.[25a] The CT copolymers (e.g., Copolys 1–3) show great differences in p-doping and p-dedoping potential, which is ascribed to an EC mechanism.[12e,23a–23e] Due to an electron-withdrawing effect of the –C≡C– unit, the PAE polymers are susceptible to electrochemical reduction.[9c,9d]

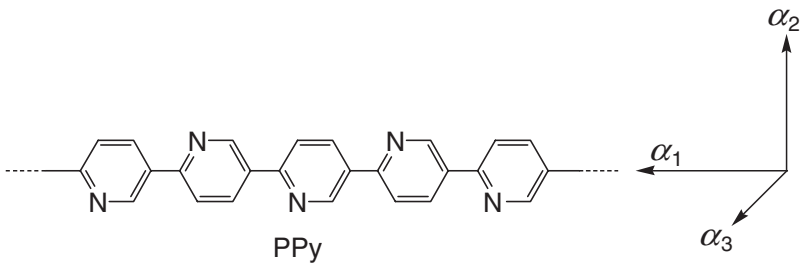
The π-conjugated polymers undergo chemical redox reactions (e.g., oxidation (or p-doping) by I_2 and $FeCl_3$[4b,7h–7j,14–16,17a,17b,23f,23g] and reduction (or n-doping) by Na[4a,4c,7h–7j,26a,51a]). The electrochemically and chemically oxidized or reduced polymers shows electrical conductivity in the 10^{-3} to 10^3 S cm^{-1} range, presumably due to formed cationic (positive) or anionic (negative) carriers along the π-conjugated system. For some cases, 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 acceptors like TCNQ also gives electrically conducting materials.[35a,39m] Electric conduction in π-conjugated polymers has been explained in terms of "polaron," "bipolaron," "soliton," and "band model,"[7,34] and the UPS spectrum of K-doped PBpy showed a peak assigned to the polaron state.[34a] Iodine-doped crystalline PTh has an I_n^- (*n*: presumably 5) counter ion,[4b] and shows electrical conductivity (σ) of 30 S cm^{-1}. Derivatives of PTh (especially PEDOTh[35b,35c] (Figure 1)) and its derivatives and PPr[35d] are now used as conducting materials (e.g., as capacitor electrodes[35d]) industrially. Electron exchange between Fe^{II} and Fe^{III} species in oxidized PFc, which is related to the electrical conductivity, takes place on the Mössbauer time scale (10^{-6} s).[35a]

Linear Structure, Alignment on the Surface of Substrates, and Packing Structure

Because the organometallic polycondensations attain π-conjugated poly(arylene) and poly(heterocycle) systems with a well-defined bonding between the recurring arylene and heterocyclic units, the polymers are considered to assume interesting structures such as rigid linear and helical structures. Furthermore, they often take a molecularly assembled structure. The rigid linear structure has been confirmed for several π-conjugated poly(arylene)s and poly(hetrocycle)s without substituents (without side chains), 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 ($\rho_v = 0.2$–0.33).[4a,4c,6a] For example PPy gives a theoretically limiting ρ_v of 0.33 when irradiated with Ar laser light, indicating that it takes an ideally linear structure with a very large anisotropy of polarizability (Chart 12).[4a,4c]

2) PPP, PTh, and PBpy molecules in their vacuum evaporated thin films on carbon and metal substrates are aligned perpendicularly to the surface of substrates.[3d,4b,4c,22a,36] The alignment has been analyzed by a clear electron diffraction pattern, and similar (or somewhat tilted) perpendicular alignment of oligomers of PPP and PTh has been followed by many papers.[7g,37]

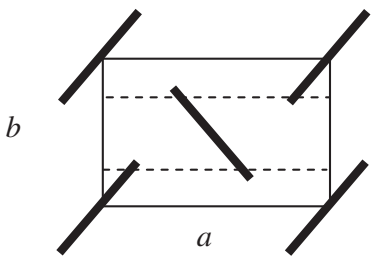


PPy

$\rho_v = 0.33$

$\alpha_1 >> \alpha_2, \alpha_3$

Chart 12. Linear structure of PPy in a solution. ρ_v = degree of depolarization. PPhen also shows a large ρ_v of 0.15.[28a]



	a/Å	*b*/Å
PE	7.4	4.9
PPP	7.8	5.5
PTh	7.8	5.5

Chart 13. Herringbone packing of polyethylene (PE), PPP, and PTh.

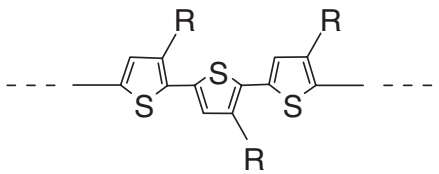
3) Many of the linear π-conjugated polymers exhibit excimer-like emissions in films and high concentrated solutions, which can be attributed to a strong interaction between the linear rod-like molecules.[4c,4g,9c,9d,28]

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, PPhen, and similar linear polymers give excellent polarizing films when included in stretched polymer (e.g., poly(vinyl alcohol)) films.[4c,12e,28]

Such a linear π-conjugated polymer without side chain often assumes herringbone packing in solid, similar to polyethylene, and lateral dimensions of polyethylene (PE), PPP, and PTh are as follows.[3d,20n] Polyacetylene also assumes a herringbone packing (Chart 13). PPP and PTh have somewhat larger lateral dimensions (or cross section) than PE. However, the difference is not large.

Recently, polythiophenes with long side chains (e.g., alkyl side chains) and regio-regular structures along the polythiophene main chain (e.g., HT-P3RTh described above) have been attracting strong interest. The synthesis of HT-P3RTh (Chart 14),[7f,17a,17b] initiated active studies of the molecular assembly of π-conjugated polymers, and it is now recognized that molecularly assembled π-conjugated polymers show superior electronic[7f,57] and optical[55b,58] functionalities.[59] For example, HT-P3RTh shows higher electrical conductivity than regio-random poly(3-alkylthiophene-2,5-diyl), rand-P3RTh.[7f] A packing model of HT-P3RTh is shown in Chart 15. HT-P3RTh can form a well-packed structure with pseudo-hexagonal packing of side chains (or side chain crystallization). On the other hand, the regular repeating of the R side chains is disturbed in rand-P3RTh, and side chain crystallization is impossible. Consequently self-assembly of rand-P3RTh is retarded.[38g]



HT-P3RTh

Chart 14.

Packed Structure in Solid

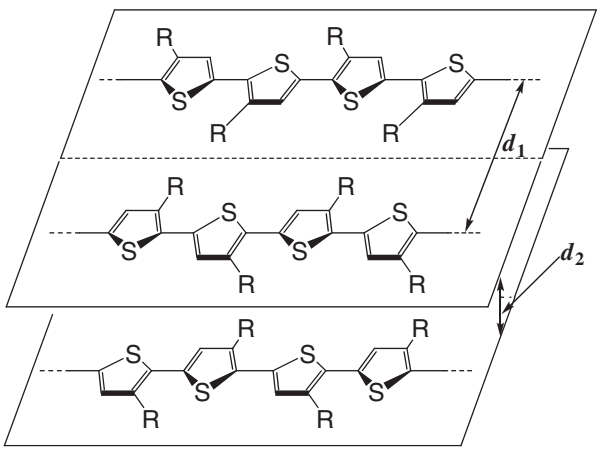


Chart 15. A packing model of HT-P3RTh.

Spin-coated HT-P3TTh film shows a Verdet (Faraday rotation) constant ($/10^4\,°/\mathrm{Tm}$) as high as about 6 at 532 nm, whereas rand-P3RTh film has only a small Verdet constant.[58] HT-P3RTh, particularly HT-poly(3-hexylthiophene-2,5-diyl), HT-P3HexTh, is now widely studied for electronic and optical applications (e.g., for applications to organic transistors and solar cells). The superior electronic and optical functionalities of HT-P3RTh are associated with molecular assembly of HT-P3RTh, which is understood in term of a face-to-face π-stacking of the polymer.

Various other types of thiophene-based polymers consisting of regularly repeating units also show a tendency to self-assemble. For example, Th(R)–(π)–Th(R) polythiophenes

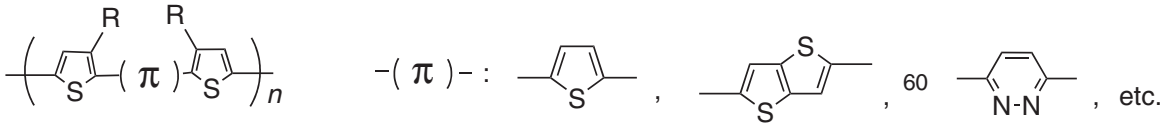


Chart 16. π-Conjugated polymers with Th(R)–(π)–Th(R) repeating units.

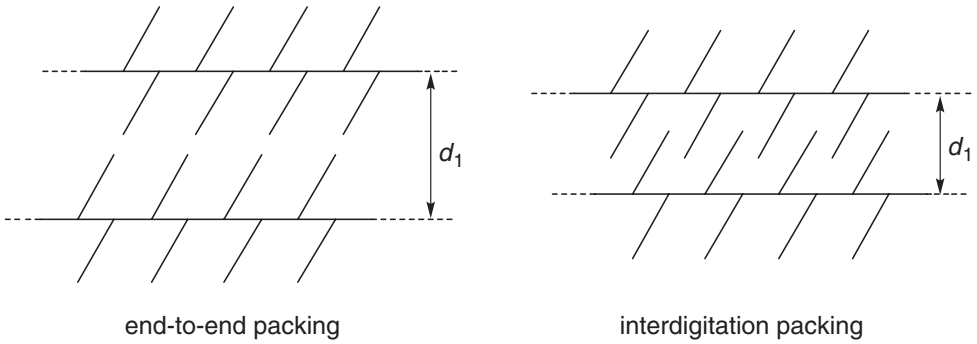


Chart 17. Packing modes of π-conjugated poly(arylene) with long side chains. One layer is depicted, and layers are considered to form the stacked structure, with the pseudo-crystallized side R chains.

shown below and HH-P3(–C≡C–R)Th[20l–20n] form self-assembled structures in colloidal solutions and in the solid phase.

It has been reported that π-conjugated polymers with Th(R)–(π)–Th(R) repeating units (Chart 16) also produced π-stacked molecular assemblies,[20w,60] and McCulloch and co-workers synthesized such polythiophenes with fused thiophene units as the central –(π)– unit. The resulting polymer showed a large hole mobility of about 1 $cm^2 V^{-1} s^{-1}$,[60] which is comparable to that of amorphous silicon.

Various (π) units, including (a) ethene-1,2-diyl,[20x,61] (b) pyridine-2,5-diyl,[62] (c) pyridazine-2,5-diyl,[20y,63] (d) thieno[3,4-*b*]pyrazine,[64,65] (e) azulene,[66] (f) 2,2′-bithiophene,[67,68] (g) *p*-phenylene,[20x,69–71] (h) two thiophene units and benzothiadiazole,[72,73] (i) selenophene-2,5-diyl,[74] and (j) dithino[3,2-*b*:2′,3′-*d*]pyrrole[75] have been used to construct Th(R)–(π)–Th(R) polymers. The Th(R)–(π)–Th(R) polymers often form π-stacked molecular assemblies,[20x,76,77] and their applicability to polymer transistors[60,75,76,78] and solar cells[79a] has actively been tested.

Some of Th(R)–(π)–Th(R) polymers are thought to have a coplanar structure, and the coplanar polymers in particular show a strong tendency to self-assemble to form a face-to-face packed structure similar to that shown in Chart 15. Self-assembly of the polymer is considered to be crucial for superior electronic and optical functionalities.

Among the reported –(π)– units, pyridine-2,5-diyl, pyrazine-2,5-diyl, thieno[3,4-*b*]pyrazine, and benzothiadiazole with electron-withdrawing –C=N– imine nitrogen are electron-accepting –(π)– units.[4c,4i,6b,6c,19h] Because the 3-alkylthiophene unit, Th(R), is electron-donating, some of the Th(R)–(π)–Th(R) polymer molecules are considered to have an intramolecular charge transferred (CT) electronic structure along the polymer main chain, with negatively charged $–(\pi)–^{\delta-}$ units and positively charged $Th(R)^{\delta+}$ units. In this case, an intermolecular attractive electronic force (a kind of Madelung force) between the negatively charged $–(\pi)–^{\delta-}$ units and positively charged $Th(R)^{\delta+}$ units is believed to occur between face-to-face π-stacked Th(R)–(π)–Th(R) polymer molecules. Such an electronic interaction is thought to promote the molecular assembly.

In the case of HT-P3RTh, the repeating height of the Th unit (3.8 Å) and diameter of the R side chain (ca. 4.2 Å) make it difficult to form interdigitation packing, and the polymer molecules are thought to be packed in an end-to-end mode, as shown in Chart 15 and Chart 17.

The number density along the polymer main chain is believed to determine the packing mode (end-to-end or interdigitation packing mode). Plots of d_1 (Charts 15 and 17) vs. number of carbons in the R side 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),[3o,38g] the polymer does not have the interdigitation packing mode and is thought to take the end-to-end packing mode. On the other hand, the number density of the R group in the Th(R)–(π)–Th(R) polymers is smaller than in HT-P3RTh and some of the polymers are believed to be packed in the interdigitation mode. Some poly(thiophene-2,5-diyl)s with –C≡C–R side chains also can be packed in the intergigitation mode, as discussed below.

The π-conjugated linear polymers take the packing mode not only in the solid (film) but also in colloidal solutions, whose light scattering analyses sometimes reveal assembling of 10^3 polymer molecules.[38g] Revealing the driving force for the π-stacking of π-conjugated polymers is expected to give basic information for controlling force of similar π-stacking observed with various molecules including graphite and DNA. In many cases, the π-stacking usually brings about a shift of UV–vis absorption peak to a longer wavelength.[20w,20x,38g]

In cast films of HT-P3RTh and other regular π-conjugated polymers, they are often arranged with the R side chains oriented toward the surface of substrate, as shown in Chart 18.[3o,17a,20x,23i–23k,77,80]

Linear alkyl chains seem to have a strong and inherent tendency to be arranged on substrates with the orientation toward the surface of substrates.[23i–23k,81] Even p-doped HT-

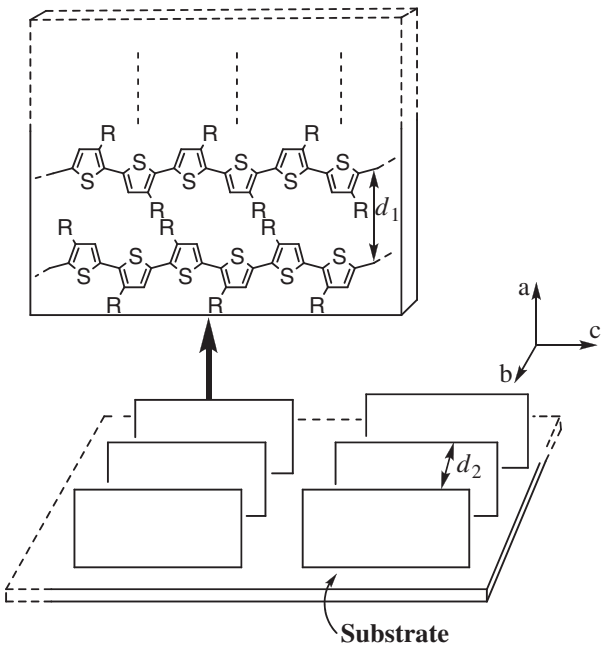


Chart 18. Alignment of HT-P3HexTh molecules on the surface of substrate (e.g., Pt).

P3RTh molecules are arranged in the manner shown in Chart 18.[80] P-doped π-conjugated polymers often have the dopant (e.g., BF_4^- and tosyl$^-$) at the end of the side chain (direction of d_1 in Charts 15 and 18; e.g., end of the R chain in HT-P3RTh[80] and outside of the $-OCH_2CH_2O-$ group in PEDOTh[81]), rather than between the π-stacked π-conjugated molecular sheets (direction of d_2 in Charts 15 and 18). For example, p-doping of HT-P3RTh brings about shortening of d_2 and elongation of d_1.

Drying a mixture solution of HT-P3R^{1}Th and HT-P3R^{2}Th give microcrystals of HT-P3R^{1}Th and HT-P3R^{2}Th separately,[82] in accordance with the strong tendency of HT-P3RTh to self-assemble, which is assisted by side-chain crystallization. Preparation of HT-P3RTh in the organometallic polycondensation is considered to be essentially based on selective metalation of X–Th(R)–X as shown in Chart 5. However, steric requirements to form a stable molecular assembly assisted by side-chain crystallization may be another driving force to control the regio-regularity of π-conjugated polymers,[21c] similar to the steric requirement observed in DNA. The regio-regularity of HT-P3RTh usually increases with increase in molecular weight of the polymer, which suggests that the π-stacking force becomes stronger with increase in the molecular weight;[83] e.g., for P3HexThs (R = hexyl) (Table 1). Increase in intermolecular π-stacking force of HT-P3RTh by increasing the molecular weight of HT-P3RTh has been suggested,[38g,83] and effects of ultrasonic oscillating on the molecular assembly has recently been reported.[79b]

Because HH-P3(C≡C–R)Th is a coplanar polymer, it also shows a strong tendency to self-assemble. For polythiophenes with –C≡C–R side chains, the following various polymers have been prepared (Chart 19).[20l–20n] Because no significant steric repulsion occurs between the main polythiophene chain and the –C≡C–R side chain, the polymers, except for P(Th–Ph), are thought to have a coplanar linear structure.

Table 1.[83]

	M_n	TH-content/%
P3HexTh(Fe) prepared by oxidative polymerization using $FeCl_3$		
Fraction-1	10000	75
Fraction-2	21000	81
Fraction-3	34000	85
P3HexTh(Zn/Ni) prepared by organometallic polycondensation using Zn		
Fraction-1	9000	91
Fraction-2	25000	97
Fraction-3	33000	98

The $-CH_2-CH_2-R'$ side group in HT-P3RTh seems to have some steric repulsion with the polythiophene main chain, and the UV–vis shift to a longer wavelength as a result of forming the π-stacked structure may arise from two factors: (1) π–π electronic interactions between the polythiophene main chains and (2) higher coplanarity of the polythiophene main chain in the π-stacked molecular assembly than in a single HT-P3RTh molecule. Formation of the π-stacked molecular assembly may force the polythiophene main chain to form in a coplanar fashion, even if the original HT-P3RTh main chain is somewhat twisted by the steric repulsion between the polythiophene main chain and the $-CH_2-CH_2-R'$ group.

In contrast, there seems to be no steric repulsion between the –C≡C–R side group and the polythiophene main chain even in the single polymer molecule, as judged from CPK molecular models and calculations.[20n] In addition, the regio-regularity of HH-P3(C≡C–R)Th polymers is controlled to 100% by the synthetic route, e.g., palladium-catalyzed dehalogenative polycondensation of HH-Br–Th(C≡C–R)$_2$–Br (Chart 20). Consequently, analysis of the HH-P3(C≡C–R)Th polymers is expected to provide fundamental information about the effects of π-stacking of polythiophenes with long side chains on their electronic states and about π-stacking forces between π-conjugated polymers. HH-PTh$_3$, TT-PTh$_3$, HH-PTh$_4$, and TT-PTh$_4$ have molecular structures similar to those of the Th(R)–(π)–Th(R) polymers, with the –(π)– units between the two Th(C≡C–R) units.

Comparison of UV–vis spectra of HH-P3(C≡C–Dec)Th in a 1,2-dichlorobenzene solution and in a cast film (Figure 2) reveals a large shift of the UV–vis peak and suggests formation of the π-stacked structure in the solid. The UV–vis shift is larger when the polymer has a higher molecular weight, as shown in Figure 2. A longer polymer molecular chain is believed to provide a larger number of interacting sites between the HH-P3(C≡C–R)Th polymer molecules, which increases the interactive forces between the polymer molecules. As described, the UV–vis shift of the HH-P3(C≡C–R)Th polymer as a result of forming the cast film is considered to originate from electronic interactions between the polymer molecules, not from higher coplanarization of the polythiophene main chains in the solid, because even the original single HH-P3(C≡C–R)Th molecule is thought to have a coplanar structure. As described above, longer region-regular π-conjugated polythiophenes (HT-P3RTh and HH-P3(C≡C–R)Th)

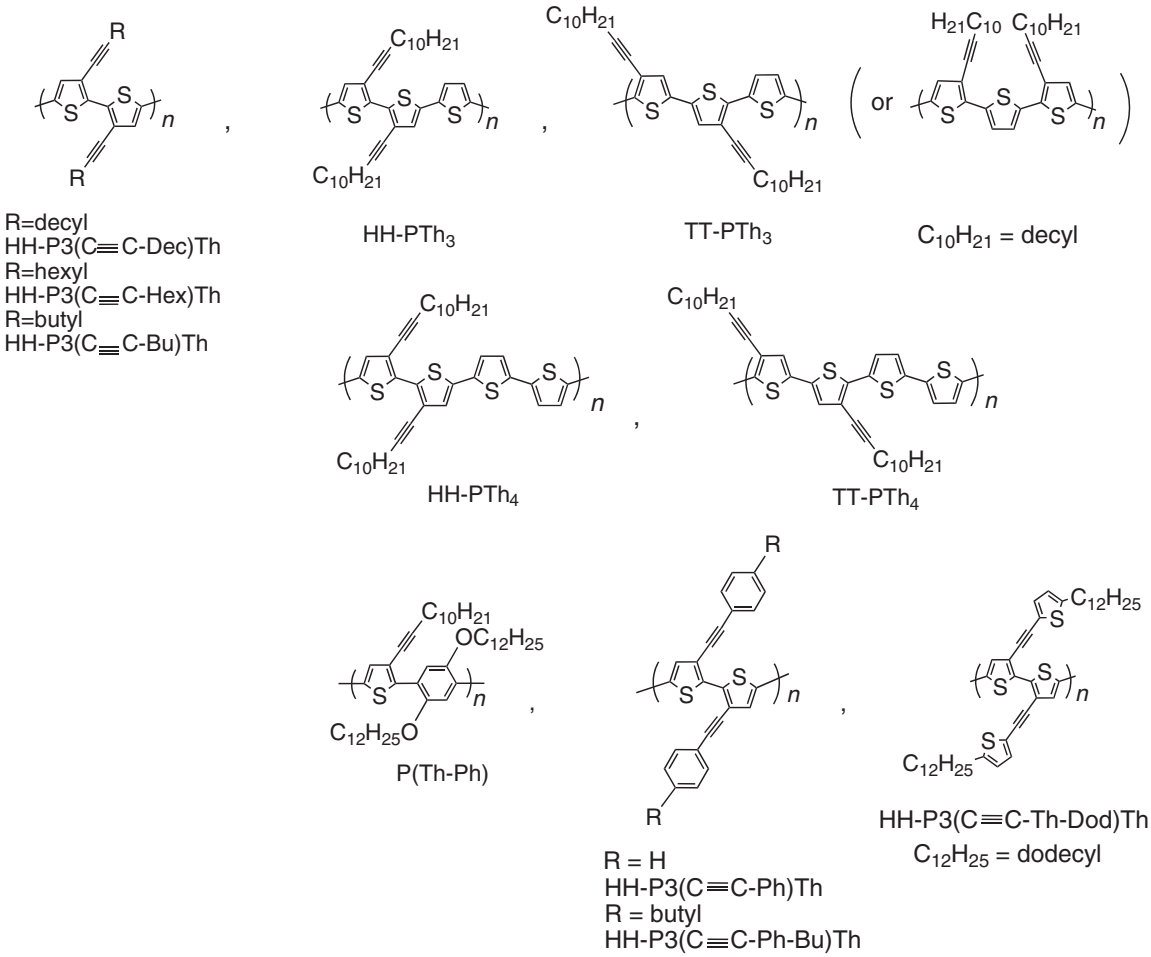


Chart 19. New polythiophenes with –C≡C–R side chains.[20n]

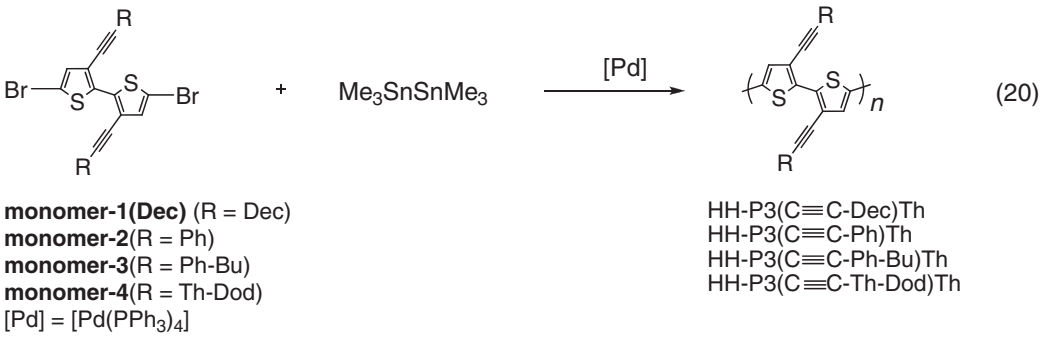


Chart 20. Synthetic route of HH-P3(C≡C–R)Th.

are believed to have a stronger π-stacking intermolecular interaction.[20n,38g,79b,83]

The XRD patterns of HH-P3(C≡C–alkyl)Ths in the solid state are interpreted by assuming the following π-stacked structure, similar to the case of HT-P3RTh (Chart 21). It is reasonable that the d_1 distance estimated from X-ray diffraction patterns of the polymers becomes longer when the –C≡C–alkyl side chain is longer. The increase in the d_1 distance per increase in the number of carbon atoms in the –C≡C–alkyl side chain, $\Delta(d_1)/\Delta$(number of carbon atoms in the alkyl group) = about 2.0 Å/C, is longer than the repeating length of the $–CH_2–$ group (1.25 Å/CH_2). These data exclude an interdigitation packing mode and support the end-to-end packing mode shown in Chart 17, similar to the case of HT-P3RTh shown in Chart 15.

The well-packed –C≡C–alkyl side chains (Chart 21b) assist the π-stacking of HH-P3(C≡C–alkyl)Th. HT-3RTh molecules are usually aligned only in the edge-on mode shown in Chart 18 on the surface of substrates. However, because of strong π-stacking of HH-P3(C≡C–alkyl)Th, HH-P3(C≡C–alkyl)Th can align in two ways on the surface of substrates. When the polymer is cast from a solution, the polymer molecules are aligned in an edge-on fashion shown in the upper part of Chart 22, similar to the case of HT-P3RTh shown in Chart 18. On the other hand, when the cast film or a polymer

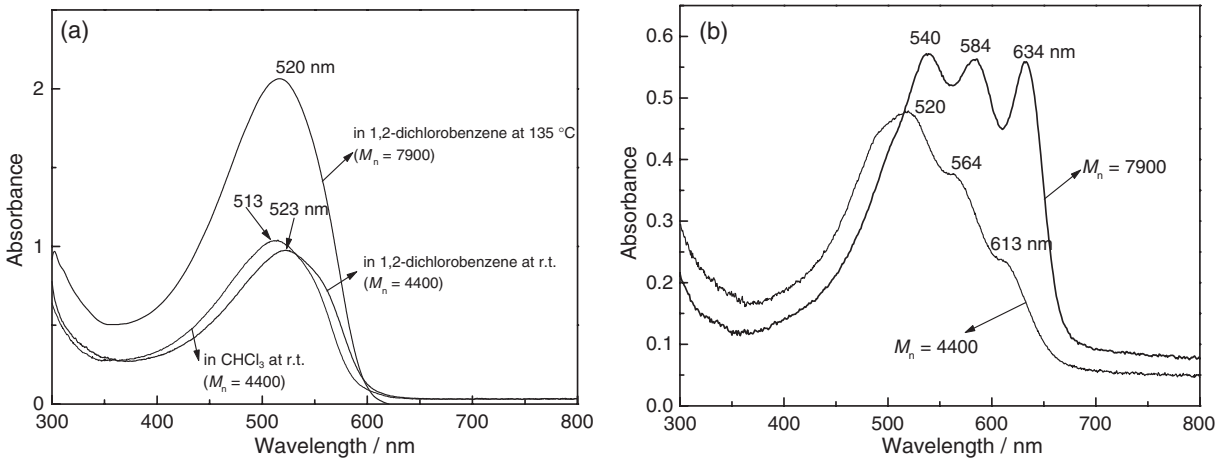


Figure 2. UV–vis spectra of HH-P3(C≡C–Dec)Th in (a) 1,2-dichlorobenzene and chloroform and (b) cast film.[20n] Data for the polymers with number-average molecular weight, M_n, of 7900 (original polymer) and 4400 (chloroform-soluble part) are shown.

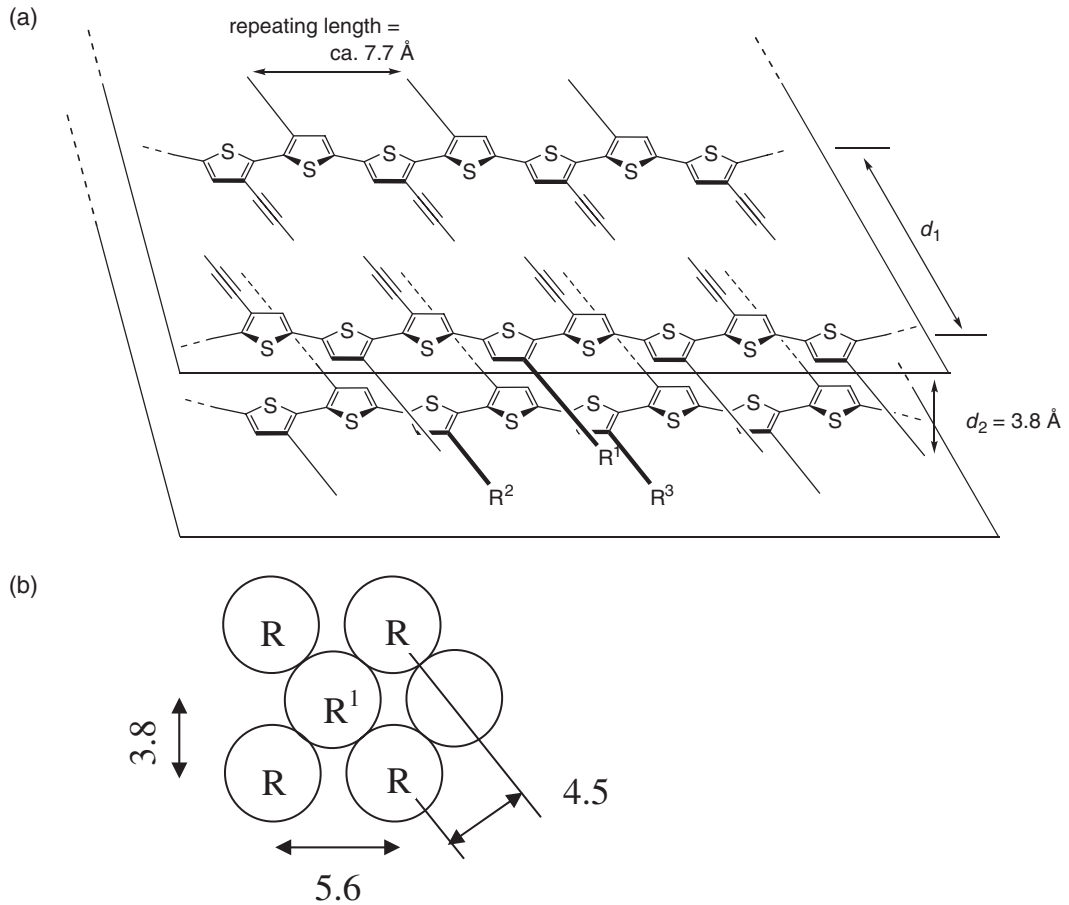


Chart 21. (a) Packing model of HH-P3(C≡C–alkyl)Th and side view of the packed –C≡C–alkyl side chains. (b) Side view of the packed –C≡C–alkyl side chains, seen from the direction of the –C≡C–alkyl side chain.

powder is rubbed with a spatula on a substrate, the polymer molecules are aligned in a side-on fashion shown in the lower part of Chart 22,[20m,20n] similar to graphite and mica.

The plane (or sheet) structure formed by HH-P3(C≡C–alkyl)Th molecules by end-to-end packing of the polymer molecules is thought to be highly stable, similar to the structures of graphite and mica. In contrast, the plane (or sheet) formed by HT-P3RTh molecules does not seem to have such a high stability, and the formation of a side-on alignment of HT-3RTh on the surface of a substrate is not easy. As described above, π-stacking is considered to be important to realize better electronic and optical functionalities of π-conjugated polymers, and HH-P3(C≡C–alkyl)Th gives fundamental information about the π-stacking.

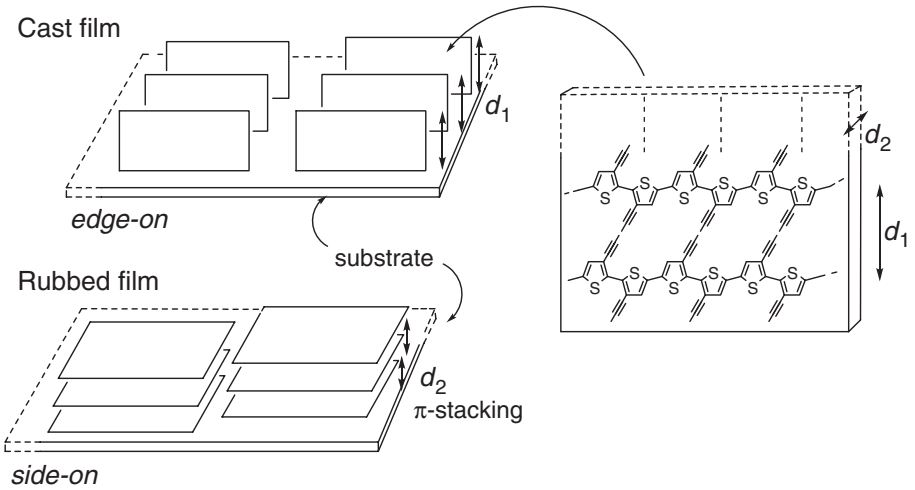


Chart 22. Two types of alignment of HH-P3(–C≡C–alkyl)Th on the surface of substrates.

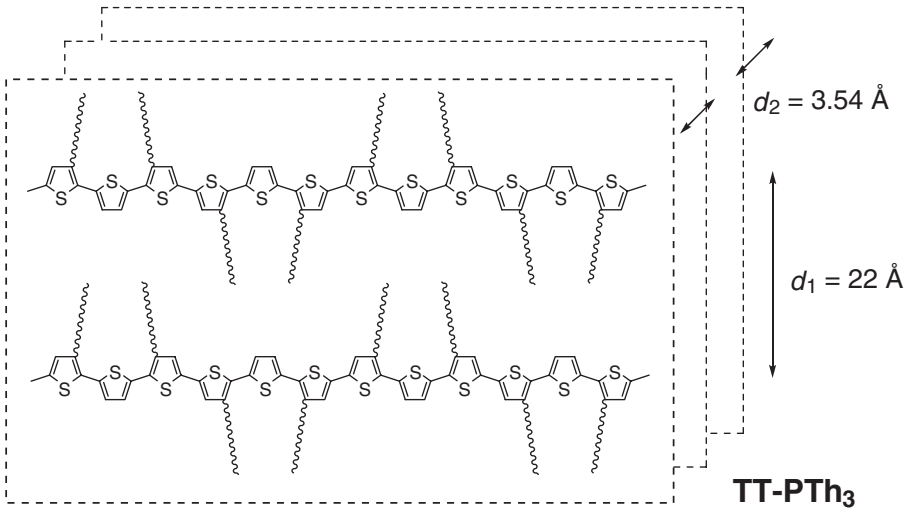


Chart 23. Interdigitation packing model of TT-PTh_3.[20n]

Number density of long side chains in TT-PTh_3 (Chart 19) is comparable to that of Th(R)–(π)–Th(R) polymers with –(π)– = Th, and the XRD pattern of TT-PTh_3[20n] agrees with the interdigitation packing which was proposed above for Th(R)–(π)–Th(R) polymers (Chart 23).

Chemical Reactivity and Catalysis

Metal Complexes and Modification of Nitrogen. N-Containing poly(heterocycle)s, especially those with chelating units such as bpy, 2,2′-bipyrimidyl, and 1,10-phenanthroline units (e.g., PBpy, PBPym, PPhen, and Copoly 12), form metal complexes.[4c,4e,4f,19g,19h,23l,23m,28a,28g,39] Examples of metal complexes are shown in Figure 3.

PBpy forms metal complexes, and various π-conjugated chelating polymers and their metal complexes have been synthesized. Their electrical and optical properties have been investigated. Other types of transition-metal complexes have also been synthesized using PPP and its analogs.[39h–39k] Ferrocene polymers have also been reported.[20c,35a,39k–39m] 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 behaviors. 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.[40]

Because π-conjugated polymers can be regarded as organic semiconductors, numerous investigations have been made to derive functions similar to those of inorganic semiconductors (e.g., TiO_2) from π-conjugated polymers. For example, photo-induced enhancement of electrical conductivity is observed for P(5,8-diArQx) (Ar = *p*-tolyl) (vide supra).[31] PPP and PPy prepared by the organometallic polycondensation have been utilized for photocatalysts by Professor S. Yanagida.[42] PBpy also serves as a photocatalyst for hydrogen evolution from aqueous media,[43a] and its catalytic efficiency is superior to those of the other π-conjugated poly(arylene)s such as PPP and

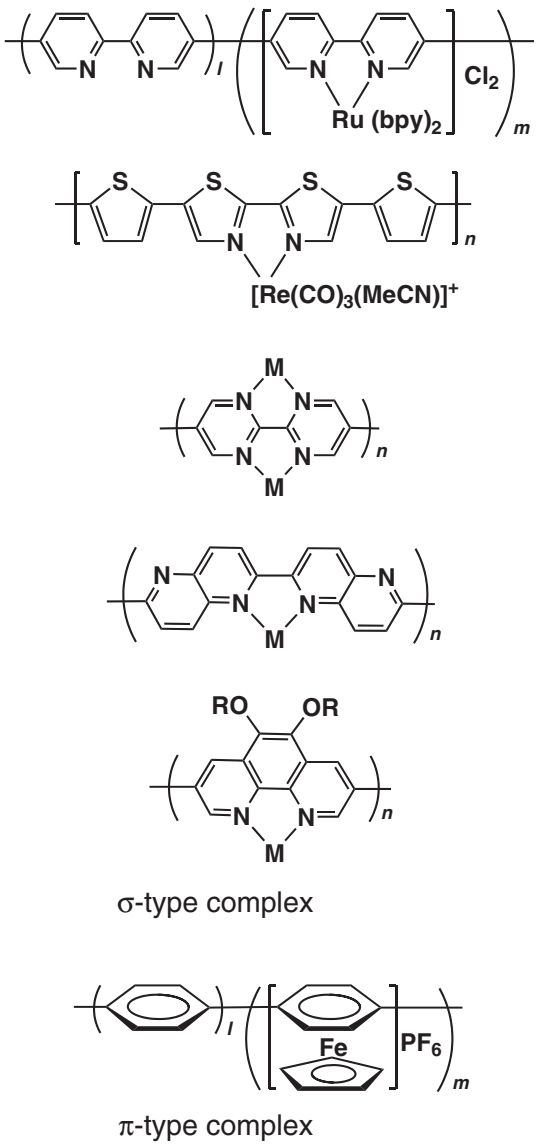


Figure 3. Examples of metal complexes of π-conjugated polymer ligands.

PPy.[42] The higher catalytic activity is attributed to the chelating ability and high hydrophilicity of PBpy. Electronic structures of PPP, PPy, and PBpy have been discussed using photoelectron spectroscopy and by comparing with that of TiO_2.[22a,34,43a] UPS (ultraviolet photoelectron spectroscopy) of K-doped PBpy indicates formation of a new electronic state which is assigned to a bipolaronic state.[34a]

The metal complexes of the π-conjugated polymers sometimes show active and stable catalytic effects (e.g., for metal-catalyzed oxidative carbonylation[43b–43e] of methanol; $2CH_3OH + CO + 1/2O_2 \rightarrow CH_3OCO_2CH_3 + H_2O$) which cannot be attained with low-molecular-weight metal complexes and metal complexes of non π-conjugated polymers.[43b–43e,84]

Electronic and Optical Devices. As described above, π-conjugated polymers change color when electrochemically oxidized or reduced (eq 21). This phenomenon is called electrochromism and much effort has been made to derive practical benefits from it. Poly(vinyl alcohol) having oligomeric PTh pendant groups serves as an excellent polymer electrolyte which shows electrochromism;[44a,44b] poly(vinyl alcohol) serves as an excellent matrix polymer for polymer electrolytes.[44c,44d]

The electrochemical redox behavior of π-conjugated polymers has been applied to batteries by many research groups.[46,47] The polymer batteries were reported by two groups in 1981.[46a,46b] PTh serves as a positive electrode material for Li and Zn batteries.[46d–46f] Li/LiI/PTh-I_2 solid electrolyte cell was also fabricated, and, the cell gave a high utilization of iodine.[46f,46g] For a "storehouse of charge" not only π-conjugated polymers but also graphite can be used. Dr. K. Sanechika, who carried out his doctorate work in our group and learned the concepts of the polymer battery, participated in development of a graphite-based Li battery, which is now widely used as a lithium ion cell.[48] PDPA (poly(diphenylamine-4,4′-diyl), cf. Figure 1) and its analogs have been tested as a sensor for lead batteries.[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 (nicotinamide adenine dinucleotide) and serve as an active material of a battery operating in acidic media.[49c]

Utilization of π-conjugated polymers as a material for an electroluminescence device (EL device or light emitting diode, LED)[50] is the subject of recent strong interest, and many papers have been published about polymer-based organic LED. In the polymer-based organic LED, PTh, P(5,8-diArQx), and P4RBTz emits light at wavelengths essentially agreeing with the wavelength of PL.[21g,22a,45b,51] PTh[51b] and its derivatives such as PEDOTh serve as excellent materials for the hole-transporting layer (HTL) in EL devices. Many papers have been published on utilization of poly(9,9-dialkylfluorene-2,7-diyl)s and their related polymers in EL devices,[50f–50j] and the polymers are usually prepared by organometallic polycondensation. An Au/PTh/Al electric junction behaves as a rectifying diode.[22a]

As described above, thin layer transition (TLT) based on π-conjugated polymers or organic molecules is a target device for π-conjugated polymers. TFT behavior of PTh, HT-P3RTh, Copoly-8, and related π-conjugated polymers prepared by organometallic polycondensation have been examined.[21d,22a,23t,57,60,85] Because the copolymers, Copoly 1–3,[12e,23b] PAE-2 and its analogs,[9c,9d,30] HT-P3RTh,[55b] and HH-P3(C≡CR)Th[20n] show large $\chi^{(3)}$ values, preparation of nonlinear optical devices using the materials is expected. A waveguide using PAE-2 has been prepared.[30b]

Conclusion

Organometallic polycondensations based on organometallic chemistry have contributed to the preparation of π-conjugated polymers (e.g., PTh and PRTh). π-Conjugated polymers prepared by organometallic polycondensation have a well-characterized structure, and π-conjugated polymers with high regio-regularity form π-stacked molecular assembly, which is important for superior electronic and optical properties of the polymers. π-Conjugated polymers synthesized by organometallic polycondensation have contributed to understanding of basic chemical and physical properties of the π-conjugated polymers as well as structure 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.

The author is grateful to emeritus professors the late S. Kambara, the late S. Ikeda, and A. Yamamoto of our institute for their guidance in chemistry, discussion, and collaboration. Especially he thanks emeritus professor the late S. Kambara for encouraging him for a long period and emeritus professor A. Yamamoto for organometallic research. Thanks are also due to professors K. Osakada, T.-A. Koizumi, and H. Fukumoto and professor Maruyama (now at Yokohama Rubber Co., Ltd.) of our institute, professor T. Kanbara of University of Tsukuba, professor I. Yamaguchi of Shimane University, and all other co-workers.

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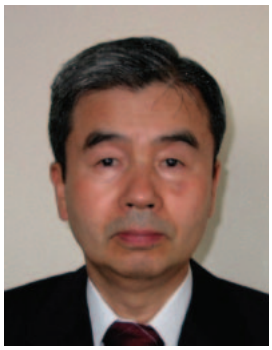

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