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Accounts

π-Conjugated Polymers Bearing Electronic and Optical Functionalities. Preparation by Organometallic Polycondensations, Properties, and Their Applications

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Various π-conjugated polymers have been obtained by using organometallic polycondensations mediated by organotransition metal complexes. For example, Ni(0) complex-promoted dehalogenation polycondensation of dihaloaromatic compounds X–Ar–X affords poly(arylene)s, -(Ar)-_n. Pd-catalyzed polycondensation gives poly(arylene–ethynylene)s, $\text{-(Ar–C≡C–Ar}'\text{–C≡C)-}_n$. These polymers are electrochemically active, electrically conductive, and light-emitting. Their well-characterized linear structure brings about unique packing of the polymer molecules in the solid. In this paper, we describe preparation by the organometallic polycondensations, basic properties, the ordered structure in the solid, and applications for electronic and optical devices of π-conjugated polymers.

Diorganonickel(II) complexes NiR_2L_m undergo reductive coupling (or reductive elimination) reactions to give R–R (Eq. 1).[1)] Controlling factors of this coupling reaction have long been studied by our research group and by others.

$$L_mNi\begin{matrix}R\\R\end{matrix} \longrightarrow R\text{–}R \qquad (1)$$

This basic C–C coupling on the metal introduced the concept of "reductive elimination" to the field or organometallic chemistry,[1a—1p)] and clear and quantitative support[1a)] for the concept of "back-donation to olefin[1q,1r)]" was given during the study. The coordination of molecules leading to the back-donation (e.g., electron-accepting olefin[1a)] or aromatic compound[1k)]) to the central metal facilitates the reductive elimination of R–R, and the concepts of reductive elimination and back-donation are now widely accepted in chemistry.

The basic coupling reactions have been utilized for Ni-promoted organic syntheses (e.g., RMgX+R′X→R–R′; 2RX+Zn→R–R; 2RX+Ni(0) complex→R–R; X = halogen).[2)] We have developed further the utilization of this coupling reaction for the polycondensation of dihaloaromatic compounds.

$$n\ \text{X-Ar-X} + n\ \text{Mg} \longrightarrow n\ [\text{X-Ar-MgX}] \xrightarrow{\text{Ni-complex}} \text{-(Ar)-}_n \qquad (2)^{3)}$$

$$n\ \text{X-Ar-X} + n\ \text{Ni(0)L}_m \longrightarrow \text{-(Ar)-}_n + n\ \text{NiX}_2\text{L}_m \qquad (3)^{4)}$$

In some cases, $Ni(0)L_m$ formed in situ by chemical (e.g., by Zn) or electrochemical reduction of Ni(II)-compounds are also usable in this polycondensation, thus providing following catalytic reactions (Eq. 4).[5,6a—6e)] It was recently reported that NaH was also usable as the reducing agents.[6f)]

$$n\ \text{X-Ar-X} + n\ \text{Zn(or 2e}^-) \xrightarrow{\text{Ni-complex}} \text{-(Ar)-}_n + n\ \text{ZnX}_2\ (\text{or 2X}^-) \qquad (4)^{5,6)}$$

Polyarylenes can be prepared by the organometallic polycondensation as well as by chemical and electrochemical oxidation of aromatic compounds, and books and reviews have been published concerning the preparation and properties of polyarylenes.[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)] These Ni- and Pd-promoted polycondensations were first reported by us.

$$n\ \text{X-Ar-X} + n\ \text{HC≡C-Ar}'\text{-C≡CH} \xrightarrow{\text{Pd-Cu}} \text{-(Ar-C≡C-Ar}'\text{-C≡C)-}_n \qquad (5)^{9)}$$

PAE-type polymer

Successful polycondensation usually requires highly effective basic coupling reactions. However, the polycondensations expressed by Eqs. 2, 3, 4, and 5 give polymers with high molecular weights even when the basic C–C coupling reaction is not so effective. One of the reasons for the successful polycondensation seems to be an energetistic advantage of the polycondensation leading to poly(arylene)s which seems 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]

After the publication of our papers reporting that the organometallic polycondensations can give the π-conjugated aromatic polymers effectively, various analogous polycondensations have been developed. For example, organostannanes and organoborons undergo similar Pd-catalyzed C–C coupling reactions.[11a—11d] Pd-promoted coupling reactions between ArX and olefin are also known.[11e,11f] They have also been applied to the polymerization,[12] e.g.,

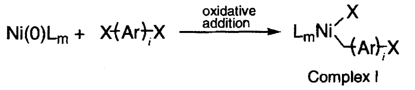
$$n\ \text{X-Ar-X} + n\ \text{m-Ar}'\text{-m} \longrightarrow \left(\text{Ar-Ar}'\right)_n \qquad \text{m}: \text{SnR}_3 \text{ or } \text{B(OR)}_2 \qquad (6)^{12)}$$

The polymerization expressed by Eq. 2 is applicable to dihaloalkanes (e.g., $X(CH_2)_nX$) by using Cu catalyst.[3g] Use of C–OY (Y = tosyl, etc.) compounds, instead of C–X compounds (OY = leaving group or pseudo-halogen), is also possible for the polycondensation,[3g,5e] which is considered to proceed through oxidative addition of C-OY to a transition metal studied here previously.[13a—13c]

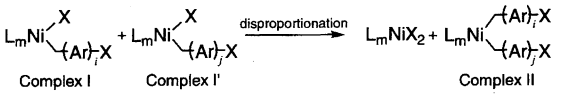
$$\text{BrMg}(\text{CH}_2)_m\text{MgBr} + \text{TsO}(\text{CH}_2)_n\text{OTs} \xrightarrow{\text{Cu}} (\text{CH}_2)_{m+n} \qquad (7)^{3g)}$$

$$n\ \text{TsO–Ar–OTs} \xrightarrow{\text{Ni(0)L}_m} (\text{Ar})_n \qquad \text{Ts = tosyl} \qquad (8)^{5e)}$$

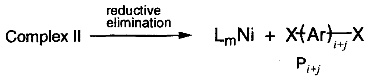
When the polymerization is carried out by using Ni(0)L_m (Eq. 3), the polymerization is considered to proceed through the following fundamental reactions:[2f,4c]



$$\text{Ni(0)L}_m + \text{X}(\text{Ar})_i\text{X} \xrightarrow[\text{addition}]{\text{oxidative}} \underset{\text{Complex I}}{\text{L}_m\text{Ni}\langle^{\text{X}}_{(\text{Ar})_i\text{X}}} \qquad (9)$$



$$\underset{\text{Complex I}}{\text{L}_m\text{Ni}\langle^{\text{X}}_{(\text{Ar})_i\text{X}}} + \underset{\text{Complex I}'}{\text{L}_m\text{Ni}\langle^{\text{X}}_{(\text{Ar})_j\text{X}}} \xrightarrow{\text{disproportionation}} \text{L}_m\text{NiX}_2 + \underset{\text{Complex II}}{\text{L}_m\text{Ni}\langle^{(\text{Ar})_i\text{X}}_{(\text{Ar})_j\text{X}}} \qquad (10)$$



$$\text{Complex II} \xrightarrow[\text{elimination}]{\text{reductive}} \text{L}_m\text{Ni} + \underset{P_{i+j}}{\text{X}(\text{Ar})_{i+j}\text{X}} \qquad (11)$$

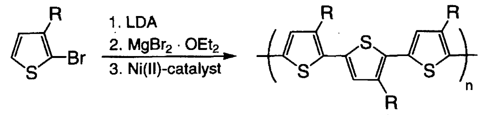
The oxidative addition of C–X[2e,13d—13f] and C–OY[13a—13c] to Ni(0)L_m (Eq. 9) is well known, and the disproportionation reaction[13g] is also known. When the Ni–C bond has high stability, the Complexes I[2e] and II[1k,1l] as well as a complex of a type Lm(X)Ni–Ar–Ni(X)Lm[1g] can be isolated. Thus, the basic concepts (reductive elimination, back-donation, oxdative addition) and the basic reactions in organometallic chemistry studied by us support the organometallic polycondensation.

Syntheses of π-Conjugated Polymers

By using the organometallic polycondensations expressed by Eqs. 2, 3, 4, and 5, various π-conjugated poly(arylene)s have been prepared. Figure 1 shows examples of the π-conjugated poly(arylene)s prepared by the organometallic polycondensation in our group. Many of the π-conjugated polymers shown in the figure were first prepared by the author's group and 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 university. 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.

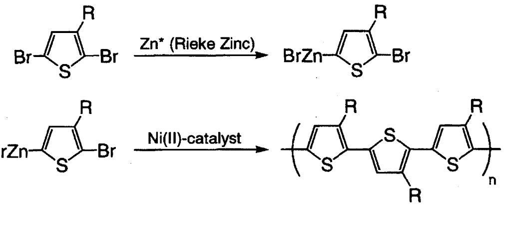
PTh was designed as the first well-characterized and stable π-conjugated conducting polymer composed of a five-membered ring.[15] It was first reported in 1982 that introduction of the alkyl group to PTh led to enhancement of solubility of PTh without losing the essential π-conjugation system of PTh.[14b,14c,16] Due to the increase in solubility, NMR analysis of microstructure of P3RTh became possible.[14c,15c,17] For example, the microstructure of P3RTh (R = CH_3) was discussed in term of head-to-tail and head-to-head joints (Chart 1).[14c,15c]

Recently it became possible to prepare P3RThs which possess a highly controlled regioregularity by modified organometallic polymerization methods. McCullough and his co-workers introduced Grignard reagent selectively to the 5-position of RTh ring and polymerized it with Ni-catalyst.[17a]



HT-P3RTh (12)

On the other hand, Rieke and his co-workers reported that regiocontrolled 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]

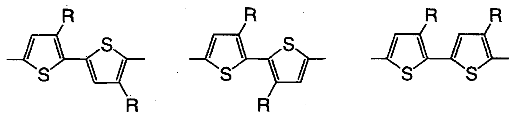


(13)

These regioregular P3RThs exhibit higher crystallinity and higher electrical conductivity values compared with those of regio-irregular P3RThs, as expected. They form a stacked structure, as discussed later. Syntheses of regioregular PAE-type polymers (e.g., PAE-6 in Fig. 1) are also possible.[9c,9g]

$$\text{X–Ar–C≡CH} \xrightarrow{\text{Pd-Cu}} \left(\text{Ar–C≡C}\right)_n \qquad (14)$$

For some of the π-conjugated polymers (e.g., RTh and

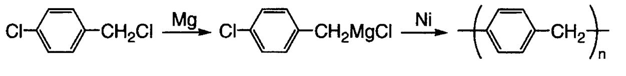


s-*trans* (head-to-tail) s-*trans* (head-to-head) s-*cis* (head-to-tail)

Chart 1. Microstructures of P3RTh.

P3RTh) depicted in Fig. 1, other preparative methods (e.g., oxdative polymerizatron)[7)] have also been developed later.

Use of 4-chlorobenzyl chloride in the polycondensation using Mg (Eq. 15) also seems to give a regiocontrolled polymer due to a large difference in the reactivity between the two C–Cl bonds.



(15)

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. 2);[3b)] in this case, Mg may serve as a reducing reagent for the catalyst, similar to Zn in Eq. 4. For the catalyst of the polycondensations, Ni-compounds are usually most effective, however, other transition metal (e.g., Pd and Fe) compounds sometimes exhibit the catalytic activity.[3b)]

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

PPy : $M_w = 4300$,[4c)] 6300[18a)]
PBpy : 3200
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

For PPy, its recent preparation[18a)] in a larger (50 g) scale gave the polymer with a higher molecular weight ($M_w = 6300$) than the previously reported[4c)] preparation in a 1 g scale, which afforded the polymer with M_w of 4300. Data from elemental analyses agreed with the structure of the polymers. Worked-up PPy prepared by $Ni(0)L_m$ (Eq. 3) contained Ni only in 13 ppm[18a)] and contained negligible halogen. The polymers prepared by $Ni(0)L_m$ usually possess an H-terminated end group,[4c)] which is considered to be formed from Ni-terminated aryl groups[1g,2e)] during the work-up including treatment with HCl.

All of the poly(arylene)s shown in Fig. 1, except for PPr[4h)] and PCyh, are stable in air, which is in contrast to the highly air sensitive polyacetylene. For example, PTh and P3RTh which have been stored for 19 and 17 years,[14—16)] respectively, in an open atmosphere underwent virtually no change, although after 18 years certain IR changes suggesting occurrence of p-doping by oxygen in air were observed with PTh. PPr receives chemical redox reactions,[4h)] and PCyh is air-sensitive (vide infra). Many of the π-conjugated polymers shown in Fig. 1 are soluble in solvents, however, PPP, PTh, and PCyh are insoluble. Syntheses of the most of the polymers shown in Fig. 1 were reported in papers cited in our review articles:[3d—3f,18b)] however, the following polymers (last 15 polymers) have recently been prepared and reported in the following papers.[19,20)] PDPA,[19a,19b)] PAzb,[19a)] P(2,7-Phzn),[19c)] PPP-2,5-OAc,[19d)] P(2,6-Th_2Bq(diR)),[19e)] P(4,7-Bim(R)),[19f)] PBpym,[19g)] PAE-3,[20a)] PAE-4,[20b)] PAE-5,[20c)] PAE-6,[9g,9h)] P(5,8-OR-1,4-AQ),[20d)] PBPV,[20e)] PPympym(4,8-NHR),[20f)] and PEDOTh.[20g)]

Optical Properties

UV-vis. Due to the expansion of the π-conjugation system, π–π* absorption bands of the poly(arylene)s show red shifts from the bands of their corresponding monomeric compounds. The degree of the red shift reflects steric hindrance around the bond connecting the monomeric units. Thus PTh, P3RTh ($R = CH_3$), and P4RBTz ($R = CH_3$) which all inherently have minor steric hindrances in their intramonomer bonds accordingly show large red shifts:[3d,3f,18b,21a)]

Degree of red shift (Chart 2):
Thiophene-PTh : ca. 21000 cm^{-1}
3-Methylthiophene-P3RTh ($R = CH_3$) : 19700 cm^{-1}
4-Methylthiazole-P4RBTz ($R = CH_3$) : 21600 cm^{-1}

On the other hand benzene (255 nm)–PPP (375 nm)[22a)] and pyridine (248 nm)-PPy (373 nm)[4c)] couples give somewhat smaller red shifts of about 13000 cm^{-1}, partly due to a larger π-conjugation system of the basic unit and to the steric repulsion caused by the *o*-CH group. For an anthraquinone–P(1,4-AQ) couple, the red shift becomes much smaller (3500 cm^{-1})[22b)] owing to analogous reasons.

In the case of copolymers composed of electron-donating arylene and electron-withdrawing arylene units (see below), the copolymers are considered to have an intramolecular charge transfer structure. Copoly 1 gives rise to an absorption band at wavelengths longer than the λ_{max} of the corresponding homopolymers PPy and PTh.[12e,23a—23d)]

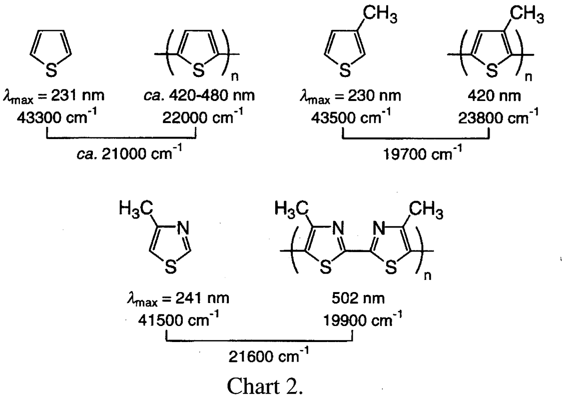


Chart 2.

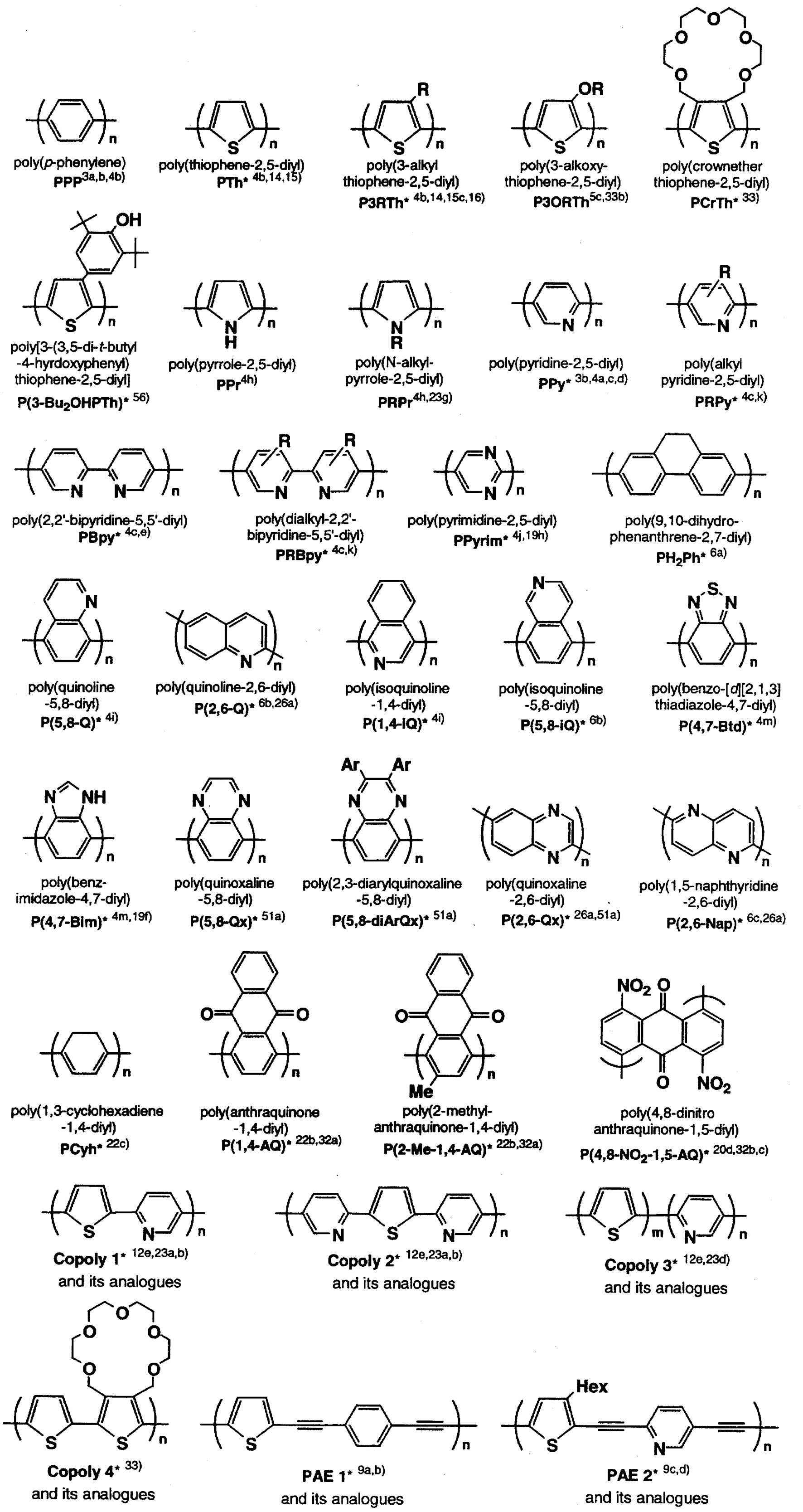
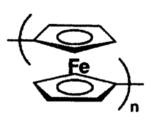
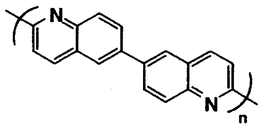


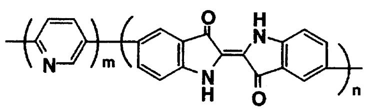
Fig. 1. π-Conjugated polymers prepared by the organometallic processes in our group. Polymers with * mark were first prepared in the author's group.



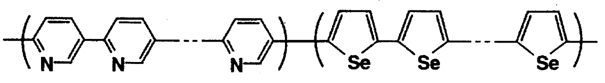
poly(ferrocene-1,1'-diyl)
PFc 35a,39m)



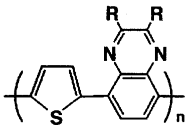
poly(6,6'-biquinoline-2,2'-diyl)
P(2,2'-bQ)* 6c)



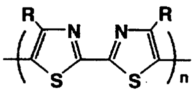
PPy-I* 4l)



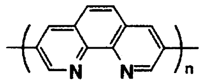
block type copolymer* 12e)



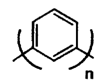
Copoly 5* 12d,e)
and its analogues



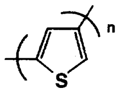
poly(4,4'-dialkyl-2,2'
-bithiazole-5,5'-diyl)
P4RBTz* 21a,38h)



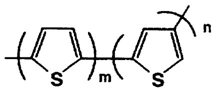
poly(1,10-phenanthroline-3,8-diyl)
PPhen* 28)



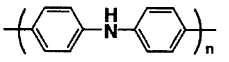
poly(*m*-phenylene)
PMP* 3b)



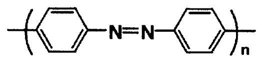
poly(thiophene
-2,4-diyl)
P(2,4-Th)* 15c)



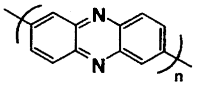
Copoly 6* 15c)



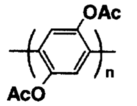
poly(diphenylamine-4,4'-diyl)
PDPA 19a,b)



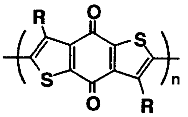
poly(azobenzene-4,4'-diyl)
PAzb* 19a)



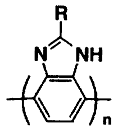
poly(phenazine-2,7-diyl)
P(2,7-Phzn)* 19c)



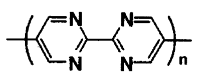
poly(2,5-diacetoxy-*p*-phenylene)
PPP-2,5-OAc* 19d,26c)



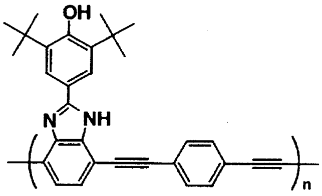
poly(3,7-dialkylbenzo[1,2-*b*:4,5-*d'*]
dithiophene-4,8-dione-2,6-diyl)
and its derivatives
P(2,6-Th$_2$Bq(diR))* 19e,26c)



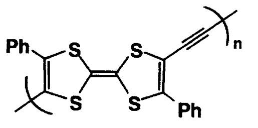
poly(benzimidazole-4,7-di
yl) and its derivatives
P(4,7-Bim(R))* 19f)



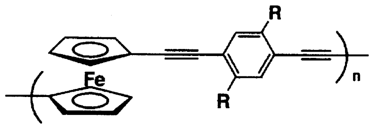
poly(2,2'-bipyrimidine-5,5'-diyl)
PBPym* 19g,h)



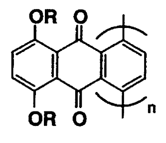
PAE 3* 20a)
and its analogues



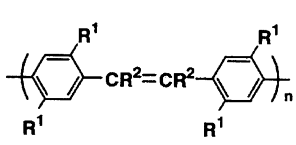
PAE 4* 20b)
and its analogues



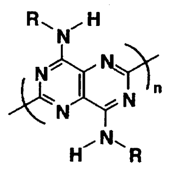
PAE 5* 20c)
and its analogues



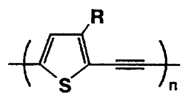
poly(5,8-dialkoxy-
anthraquinone-1,4-diyl)
P(5,8-OR-1,4-AQ)* 20d)



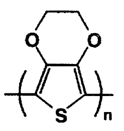
poly(*p*-biphenylenevinylene)
and its analogues
PBPV 20e)



PPympym(4,8-NHR)* 20f)

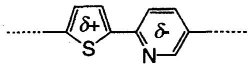


PAE 6* 9g)
and its Py analogues 9c)



PEDOTh 20g)

Fig. 1.



Copoly1

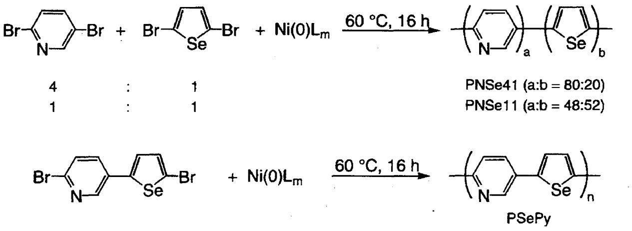
Copoly1 : $\lambda_{\max} = 490$ nm (PThPy)
PPy : $\lambda_{\max} = 370$ nm

and Copoly 5 (R = Ph) : $\lambda_{\max} = 603$ nm
Homopolymer : P (5, 8-diArQx) : $\lambda_{\max} = 444$ nm
: PTh : $\lambda_{\max} = 420 - 480$ nm

More recently, preparation of similar CT type copolymers, which also give $\lambda_{\max}$ at a longer wavelength, have been reported by several research groups.[24]

Selenophene has electron-donating properties similar to those of thiophene. The following copolymerization affords block-type copolymers (Scheme 1).

As shown in Fig. 2, the block-type copolymers give rise to absorption bands assigned to the PPy block, the PSe block, and the CT unit formed between the two blocks. On the other hand, the alternating copolymer PSePy gives only the CT absorption band.[12e]



Scheme 1.

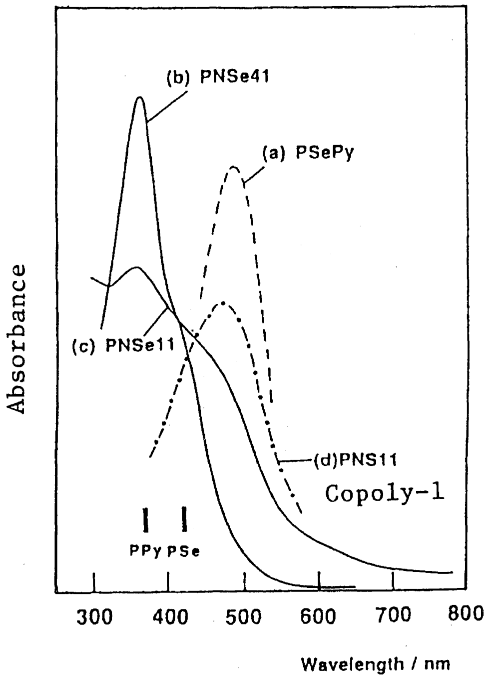


Fig. 2. UV-visible spectra of copolymers: (a) PSePy; (b) PNSe41; (c) PNSe11; (d) PNS11 (1 : 1 random copolymer of pyridine and thiophene).[12e] $\lambda_{\max}$ positions of PPy and PSe are also shown. The peak at about 500 nm is due to the CT unit (cf. the text). Solvent: HCOOH for PPy, PNSe, PSePy, and PNS; $CHCl_3$ for PSe.

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

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

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

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

In the case of PCyh, its color (black) indicates the formation of an effective π-conjugation system along the polymer chain, presumably due to the coplanarity of the polymer chain in the following *s-trans* conformation (Chart 3).[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.

Photoluminescence. Most of the polymers shown in Fig. 1 exhibit photoluminescence with an emission peak appearing at the onset of π–π^* absorption. Linear rod-like polymers such as PPy,[4c] PPhen (Fig. 3)[28] and PAE-2[9d] often show excimer-like emission in films and solutions with high concentrations. Among PAE-1-type polymers, those containing an anthracene unit shows especially strong fluorescence (Table 1).[9a]

In several cases, especially those concerned with PPy,[12e,29a] energy transfer from a photoactivated π-conjugated unit to an energy-accepting π-conjugated unit has been observed during fluorescence (Scheme 2). The block structure of the above copolymer (Py–Se copolymer; Scheme 1) is confirmed by its UV-visible spectrum (Fig. 2) and solubility, and it undergoes such energy transfer. Transfer of photoenergy accepted by the monomeric unit of P(5,8-di-ArQx) to the main chain π-conjugated system also take place (Chart 4).[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] Recently, many examples of similar energy transfers have been reported.[29d,29e]

Other Optical Properties. An interesting finding with

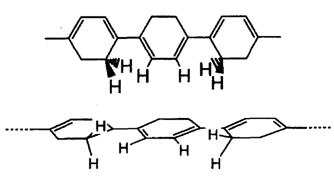


Chart 3.

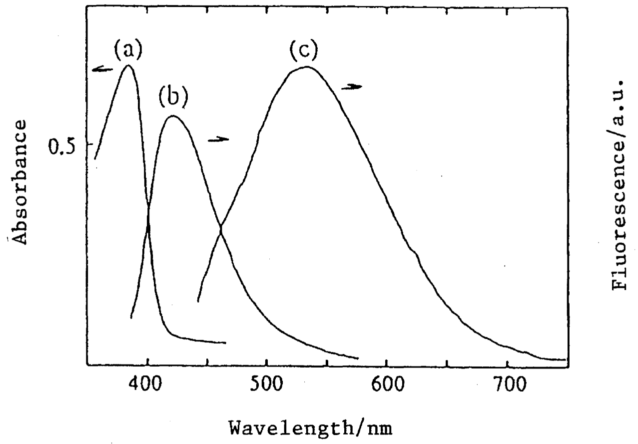
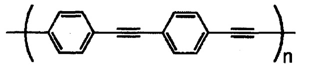
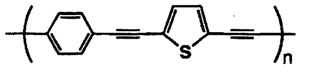
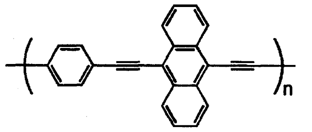
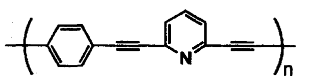
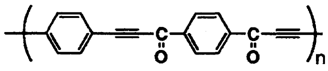
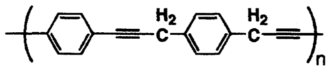
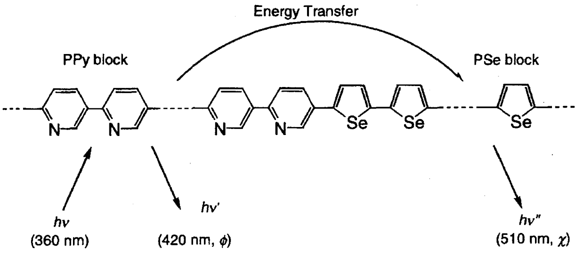


Fig. 3. UV-visible spectra of PPhen in formic acid (a), fluorescence of PPhen in formic acid (b), and fluorescence of PPhen film on a quartz glass plate.

Table 1. Visible Features of Poly(arylene ethynylene)s[9a)]

Polymer	Color	Fluorescence
	Yellow	Bluish purple
	Yellow	Bluish purple
	Red	Green
	Light yellow	Purple
	White	None
	Yellow	Purple



Scheme 2. Energy transfer from excited PPy block to PSe block.

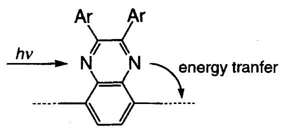


Chart 4.

Copolys 1—3,[12e,23b)] Copoly-5,[12d,12e)] and PAE-2[9c,9d,30)] is that they give large $\chi(3)$ (third-order non-linear optical susceptibility) values of 3—5×10^{-11} esu. Figure 4 shows the UV-vis spectrum and $\chi(3)$ profile of the CT-type copolymers.

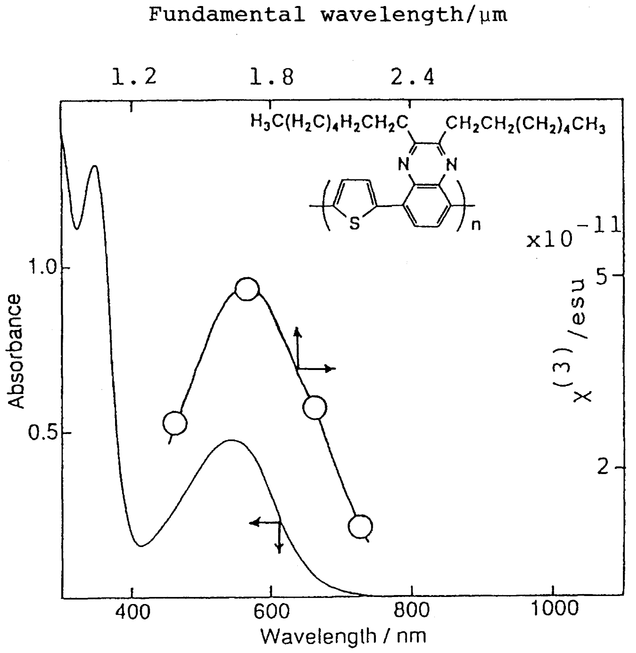
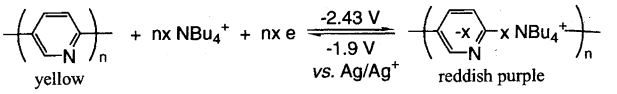


Fig. 4. UV-visible spectrum of an analogue of Copoly 5 in CF_3COOH and THG measured $\chi^{(3)}$ data with its film.

π-Conjugated polymers are considered to possess energy band structure similar to that of inorganic semiconductor (vide infra); photogeneration of carriers is therefore expected to be possible in most kinds of π-conjugated polymers. Indeed, P(5,8-diArQx) (Ar = *p*-tolyl) gives rise to a photocurrent, and it was proposed that photocarriers are generated by the dissosiation of excitons.[31)]

Redox Behavior and Electrical Conductivity

Figure 5 shows a cyclic voltammogram of poly(pyridine-2,5-diyl) PPy film on a Pt electrode.[4c,4d)] As shown in Fig. 5, reduction (n-doping) of PPy attains a peak cathodic potential E_{pc} of −2.43 V vs. Ag/Ag$^+$; changing the scanning direction leads to oxidation (n-undoping) of the reduced PPy, giving rise to a peak anodic potential E_{pa} of −1.90 V. The n-doping and n-undoping are accompanied by a color change, as shown in Fig. 5 and Eq. 16; the doping level x in Eq. 16 is about 0.3.



(16)

Figure 6 depicts CVs of P(2-Me-1,4-AQ) and its corresponding low molecular weight quinone; the CV of P(2-Me-1,4-AQ) is discussed based on a mixed oxidized state (Eq. 17).[22b,32a)]

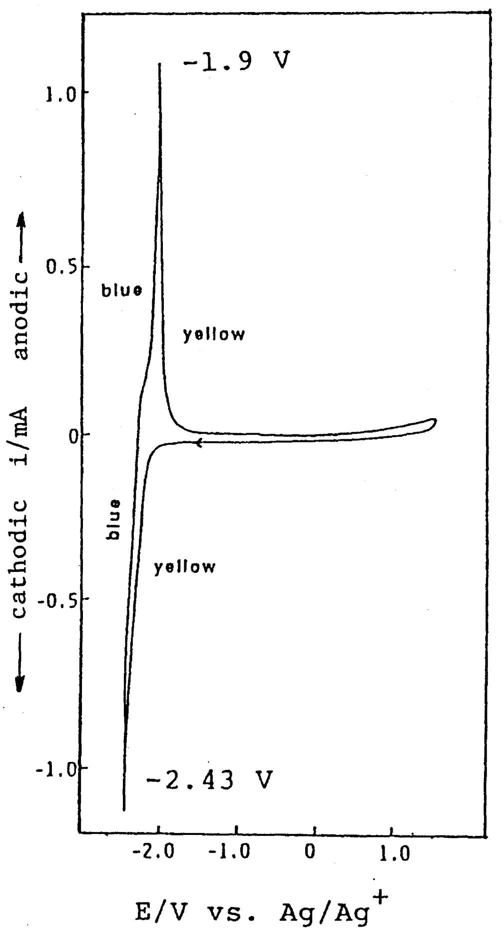
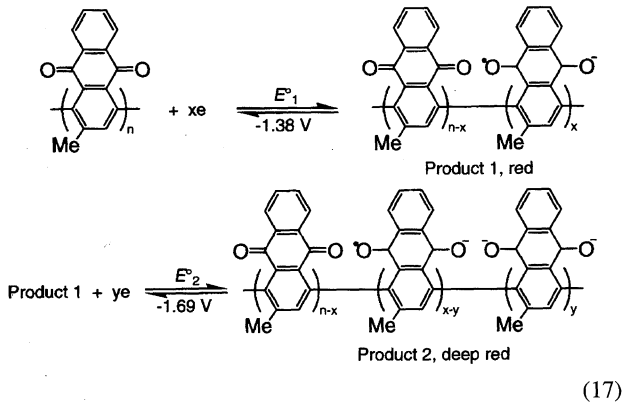


Fig. 5. Cyclic voltammogram of PPy film laid on a Pt electrode in an acetonitrile solution containing 0.1 M [N (n-C_4H_9)$_4$][BF_4] (1 M = 1 mol dm^{-3}). At room temperature under N_2 and at scan rate of 60 mV s^{-1}.



(17)

On the other hand, P(4,8-NO_2-1,5-AQ) bearing a strongly electron-withdrawing NO_2 group shows an extremely low reduction potential ($E_1^0 = -0.74$ vs. Ag/Ag$^+$), as depicted (Fig. 7).[32b]

Poly(p-benzoquinone) PPBQ prepared from PPP-2,5-OAc 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.[19d,26c,32d]

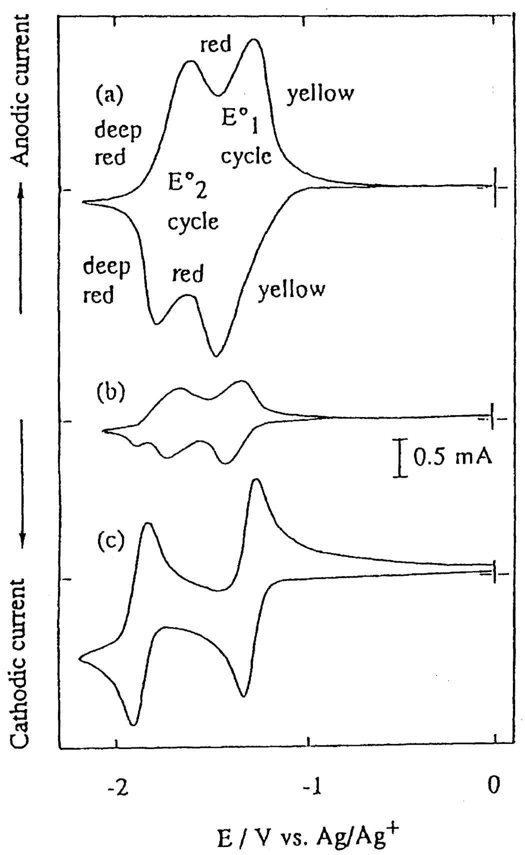


Fig. 6. Cyclic voltammograms of P(2-Me-1,4-AQ) laid on a Pt electrode in an acetonitrile solution of 0.1 M [N(n-C_4H_9)$_4$][ClO_4] at scanning rate of (a) 20 mV s^{-1} and (b) 10 mV s^{-1}, respectively, and (c) that of 2×10^{-3} M 2-methyl-9,10-anthraquinone in an acetonitrile solution of 0.1 M [N(n-C_4H_9)$_4$][ClO_4] at scanning rate of 100 mV s^{-1}.

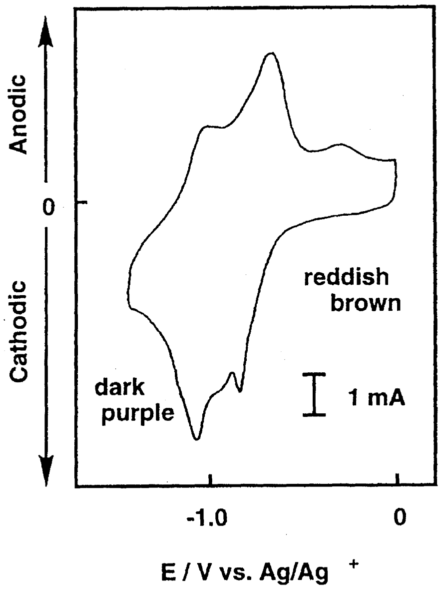
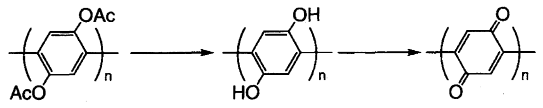


Fig. 7. Cyclic voltammogram of a film of P(4,8-NO_2-1,5-AQ) laid on a Pt electrode in an acetonitrile solution of [NEt_4][BF_4] (0.10 M) at a scanning rate of 50 mV s^{-1}.



PPP-2,5-OAc PPBQ

(18)

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

More interestingly, P(4,8-NO_2-1,5-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.[32b,32c] Recently, we have found that several π-conjugated polymeric compounds (e.g., PBpy–transition metal complex and poly(arylene)-*N*-oxides) show similar electrical conductivity even at the non-doped state (vide infra). The electrical conducting properties are considered to originate from generation of carrier by MLCT or from participation of resonance structures. For P(4,8-NO_2-1,5-AQ), one possible mechanism for the carrier generation is illustrated in Fig. 8.[32c]

The ease of the electrochemical reduction of π-conjugated polymers simply reflects the electron-accepting ability of the monomeric repeating units.[25] As depicted in Fig. 9, linear correlationships holds between the reduction potential E_red of the polymer and the electron affinity EA of the corresponding monomeric compound HArH for a wide range of poly(*p*-phenylene), poly(naphthalene-1,4-diyl), and poly(naphthalene-2,6-diyl) type polymers.[19c,19d,25,26c]

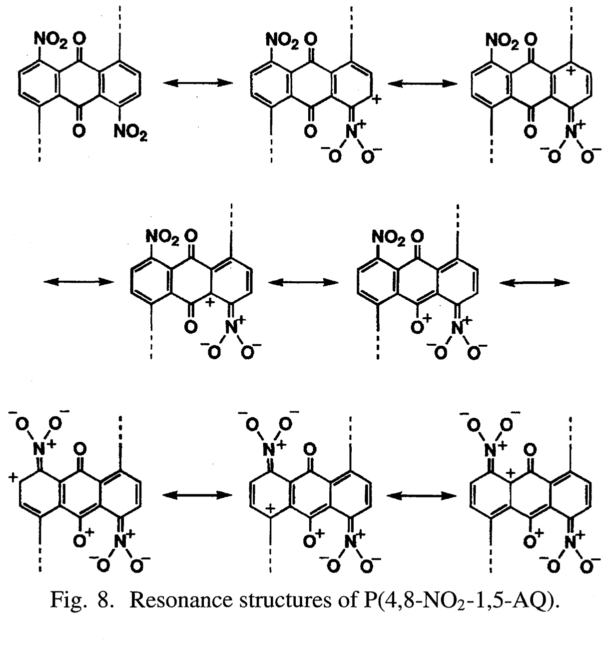
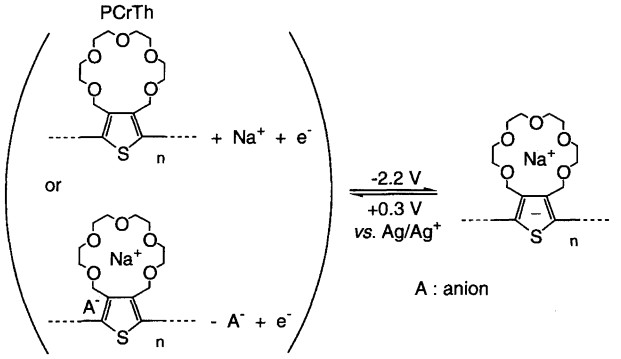


Fig. 8. Resonance structures of P(4,8-NO_2-1,5-AQ).

$$E_\mathrm{red} \text{ of } \left(\mathrm{Ar}\right)_n = a + \rho \times E_\mathrm{a} \text{ of X–Ar–X} \qquad (19)$$

ρ values of 0.75—0.8 have been obtained. A similar linear correlationship is observed between oxidation (or p-doping) potential E_ox of PPP, PTh, and PPr (cf. Fig. 1) and ionization potential IP of the corresponding monomeric compounds, 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.[25] A linear correlation between E_red of various poly(anthraquinone)s and calculated EA of the corresponding monomeric compounds has also been observed with a ρ value of about 0.8.[20d]

PCrTh readily undergoes n-doping in contrast to the other PTh analogues. The n-doped state is stabilized (even under air to some extent) due to a strong interaction of cations with ethereal oxygen, and n-undoping takes place at a potential considerably different from that of n-doping (Eq. 20).[33]



(20)

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

The π-conjugated polymers can also be chemically induced to undergo redox reactions (e.g., oxidation (or p-doping) by I_2 and $FeCl_3$[4b,14—17a,17b,23f,23g] and reduction (or n-doping) by Na[4a,4c,4i,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. Spectroscopic and XRD data suppot 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 chair. Oxidation of PFc with donor acceptors like TCNQ also gives electrically conducting materials.[35a,39m]

Table 2. Redox Potential of π-Conjugated Polymers

	PTh	PPP	PPy	PPyrim	P(2-Me-1,4-AQ)	P(4,8-NO_2-1,5-AQ)	PPBQ
				← Incresse in ease of oxidation			
E_p/V	0.49	1.18	No	No	No	No	No
E_n/V		−2.6	−2.1	−1.7	−1.3	−0.74	−0.50
				Incresse in ease of reduction →			

E_p: oxidation (p-doping) potential versus Ag/Ag$^+$. E_n: reduction (n-doping) potential versus Ag/Ag$^+$.

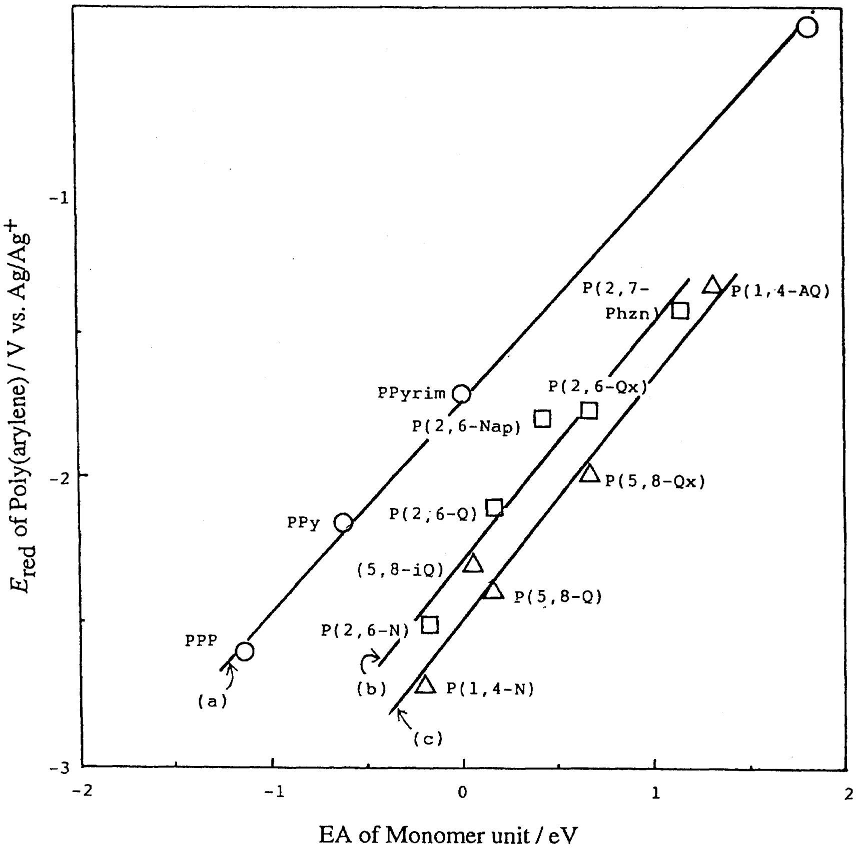
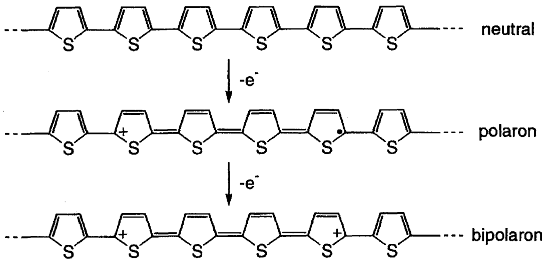


Fig. 9. Relationship between $E_{\rm red}$ of $\left(\mathrm{Ar}\right)_n$ and $E_{\rm a}$ of H–Ar–H. (a) for poly (p-phenylene) type polymers (○). (b) for poly (naphthalene-2,6-diyl) type polymers (□). (c) for poly (naphthalene-1,4-diyl) type polymers (△).

The concept of electric conduction in π-conjugated polymers has been used to be explained in terms of "polaron", "bipolaron", "soliton", and "band model" (Scheme 3).[7,34] The UPS spectrum of K-doped PBpy showed a peak assigned to the polaron state.[34a] The iodine-doping of crystalline PTh prepared by the organometallic method gives another crystalline material with an I_n^- (n: presumably 5) counter ion;[15d] the iodine-doped crystalline PTh gives the electrical conductivity (σ) of 30 S cm^{-1} whereas the introduction of thiophene-2,4-diyl unit (Copoly 6) causes a large decrease in the σ value. Derivatives of PTh[35b,35c] and PPr[35d] are now used as conducting materials (e.g., as electrodes of capacitor[35d]) industrially. In partially oxidized PFc, exchange of electrons between Fe(II) and Fe(III) species, which is related to the electrical conductivity, takes place on the Mösbauer time scale (10^{-6} s).[35a]



Scheme 3. Schematic model of polaron and bipolaron.

Due to the stabilization of the n-doped state of PCrTh (Eq. 20), Na-doped (n-doped) PCrTh exhibits stability under air as indicated by small changes in conductivity and by the IR spectrum of the Na-doped PCrTh under air. The n-doped PPy and PCrTh have electrical conductivities of 1.1×10^{-1} and 2×10^{-4} S cm^{-1}, respectively.

Linear Structure and Alignment on the Surface of Substrates

Since the organometallic polycondensations attain a π-conjugated poly(arylene) system with a well-defined bonding between the recurring arylene units, the polymers are considered to assume interesting structures such as rigid linear and helical structures. Furthermore, they often take an assembled structure. The rigid linear structure has been confirmed for several poly(arylene)s, based on the following observations.

1) The light-scattering analysis of PPy, PBpy, and P(2,6-Q) yields a very large degree of depolarization ($\rho_{\rm v}$ = 0.2—0.33).[4a,4c,26a] For example PPy gives a theoretically limiting $\rho_{\rm v}$ value 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 5).[4a,4c]

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 (Fig. 11).[3d,4b,4c,22a,36] The alignment has

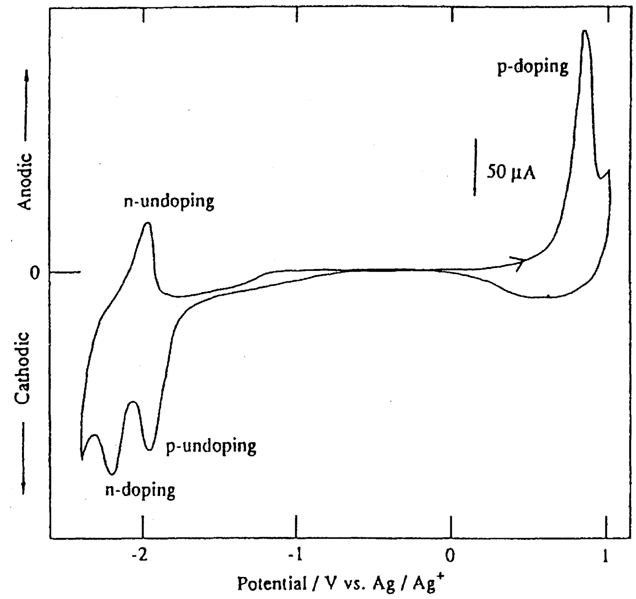


Fig. 10. Cyclic voltammogram of Copoly 3 (m : n = 3 : 1) laid on an ITO electrode. In an acetonitrile solution [N(n-C_4H_9)$_4$][BF_4] (0.10 M). At 10 mV s^{-1} at room temperature.

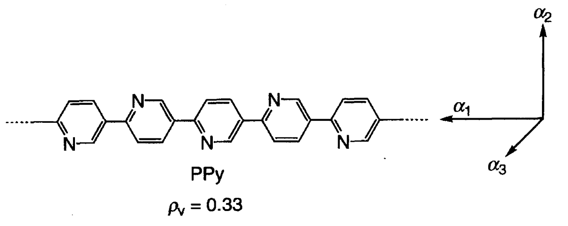


Chart 5.

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

$$\text{Au,Ag} < \text{Al} < \text{C}.$$

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

3) Many of the π-conjugated poly(arylene)s exhibit excimer-like emissions in films and high concentrated solutions (Fig. 3), 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 the 2,2′-bipyridyl unit with Si–O–H hydrogens on the surface of the substrate.[3d,4c)]

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

Control of the alignment of the poly(arylene) molecule may be crucial for the preparation of effective electronic and optical devices.[22a)]

Stacking in the Solid and Colloid

Regioregular head-to-tail (HT)–P3RTh (Eqs. 12 and 13)[17,38)] and head-to-head (HH)–P4RBTz[21)] with long R chains form stacked structures (Fig. 12) both in the solid and in colloidal solutions.[17,38)] HT-P3RTh,[38)] HH-P4RBTz,[38)] P(2,6-Th_2Bq(diR)),[19e,26c)] P(4,7-Bim(R)),[19f)] P(5,8-OR-1,4-AQ),[20d)] PBPV,[20e)] (cf. Fig. 1) with long side chains all give a sharp diffraction peak at a low angle region (2θ = 2—8° for

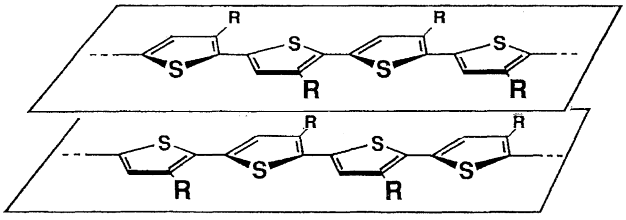


Fig. 12. Schematic illustration of intermolecular stacking of P3RTh.

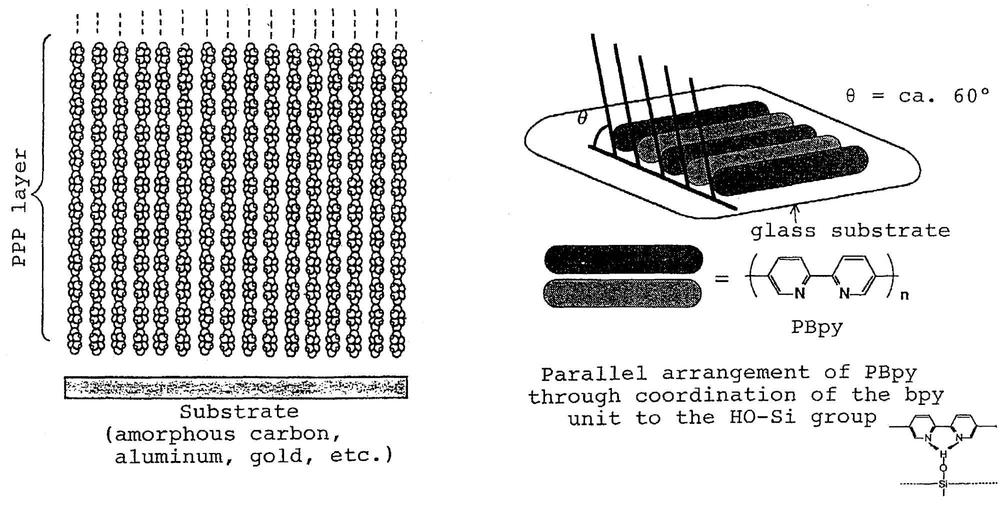


Fig. 11. Perpendicular orientation of PPP on substrate.

Cu *Kα*), which is assigned to a distance between core main chains separated by the long side chain (Scheme 4).

The number density along the polymer main chain seems to determine the packing mode (the end-to-end or interdigitation packing). Plots of the *d* value vs. number of carbons in the R group of the above described polymers give straight lines as shown in Fig. 13. When the slope is larger than the height of the CH_2 group (1.25 Å/C),[38h] the polymer does not have the interdigitation packing mode and is considered to take the end-to-end packing mode. On the other hand, the number density of the R group in P(2,6-Th_2Bq(diR)) is smaller than that in other polymers, and P(2,6-Th_2Bq(diR)) affords a linear line with a slope of about 1.2 Å/C, which corresponds to the interdigitation packing mode.

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.[38h] Revealing of the driving force for the π-stacking of π-conjugated polymers is expected to give basic information for controlling the force of similar π-stacking observed with various molecules including graphite and DNA.

Chemical Reactivity and Catalysis

Metal Complexes and Modification of Nitrogen. The N-containing poly(arylene)s, especially those with the chelating units like a bpy or 2, 2′-bipyridmidine unit (PBpy and PBpym), form metal complexes (Fig. 14).[4c,4e,4f,19g,29a] Since the first preparation of PBpy and its metal complexes,[4e,4f] various π-conjugated chelating polymers and their metal complexes have been synthesized and their electric and optical properties have been investigated.[4c,12i,21,28,39a,39g] Other types of transition metal complexes have also been synthesized using PPP and its analogues,[39h,39k] or ferrocene units.[20c,35a,39k,39m]

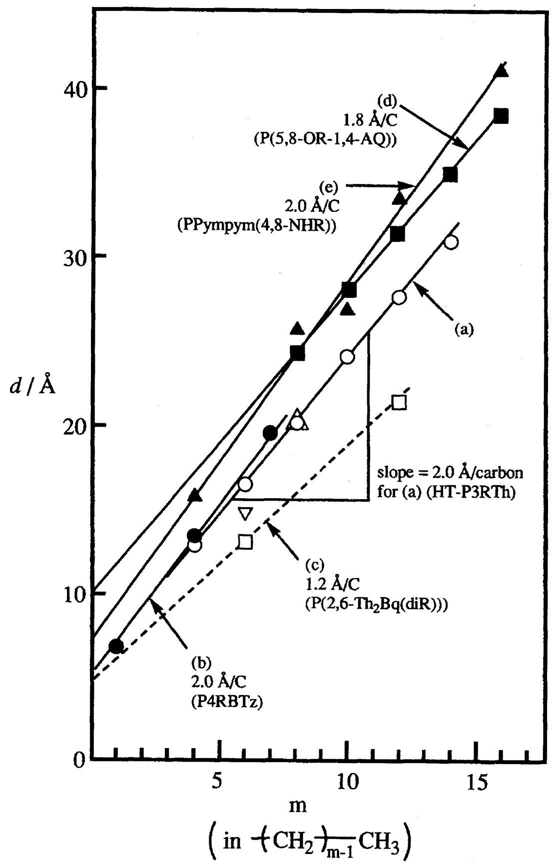
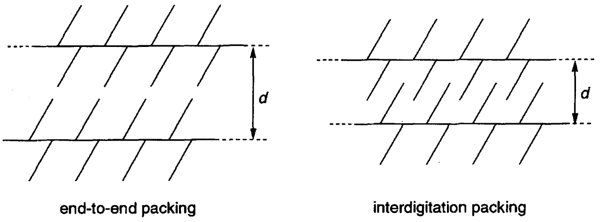
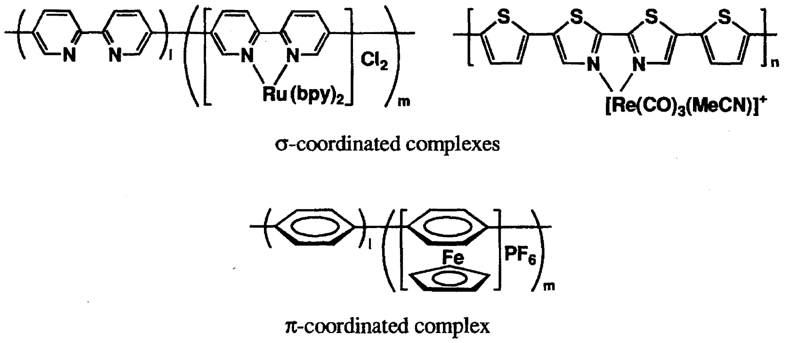


Fig. 13. Plots of the *d* value vs. number of carbon in the R chain. (a) HT-P3RTh.[38h] (b) P4RBTz.[38h] (c) P(2,6-Th_2Bq (diR)).[19e] (d) P(5,8-OR-1,4-AQ)).[20d] (e) PPympym(4,8-NHR).[20f] △ at $m = 9$: PBPV (R^1 = octyl, R^2 = H).[20e] ▽ at $m = 6$: P(4,7-Bim (R)) (R = hexyl).[19f]



Scheme 4. Packing modes of π-conjugated poly(arylene) with long side chains. One layer is depited, and layers are considered to form the stacked structure shown in Fig. 12.

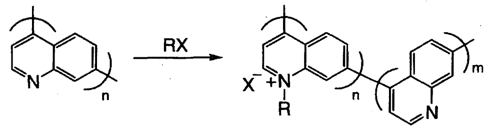
In the case of N-containing poly(arylene)s, chemical modification of imine nitrogen is also possible. For instance, quaternization with RX (Eq. 21),[40] *N*-oxidation with H_2O_2 (Eq. 22),[41] and *N*-ylidation with tetracyanoethylene oxide[41b] have been carried out for these polymers.



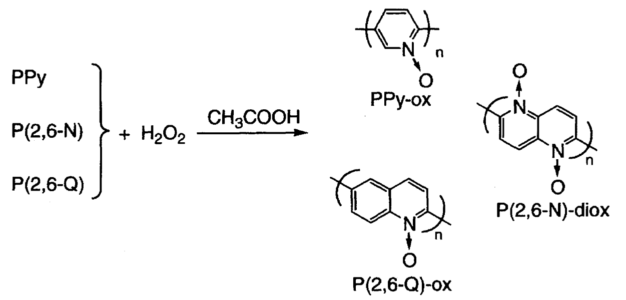
σ-coordinated complexes

π-coordinated complex

Fig. 14. Polymer complexes using π-conjugated polymers as ligands.[3f,4c,39a,39k]

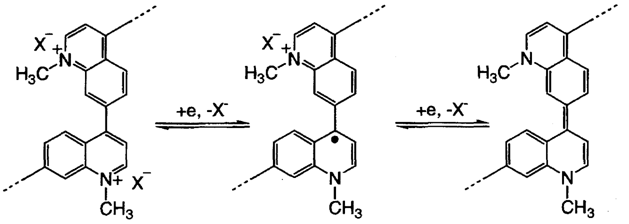


(21)



(22)

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 (Eq. 23) (vide infra).[40)]



(23)

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

From the viewpoint that 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, photoinduced enhancement of electrical conductivity is observed for P(5,8-diArQx) (Ar = *p*-tolyl)[31)] (vide supra). PPP and PPy prepared by the organometallic polycondensation have been utilized for photcatalysts by other researchers.[42)] On the other hand, PBpy serves as a highly efficient photocatalyst for hydrogen evolution from aqueous media.[43a)] This catalytic efficiency is superior to those of the other π-conjugated poly(arylene)s such as PPP and PPy,[42)] and this is attributed to the chelating ability and high hydrophilicity of PBpy. Electronic structures of PPP, PPy, and PBpy are compared with that of TiO_2 in Fig. 15.[22a,34,43a)]

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

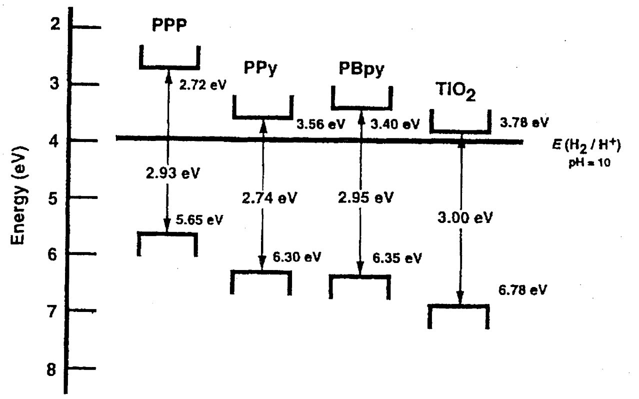


Fig. 15. Electronic structures of PPP, PPy, PBpy, and TiO_2.

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

Redox Functions. All π-conjugated poly(arylene)s change their colors when electrochemically oxidized or reduced (cf. Eqs. 16 and 17). This phenomenon is called "electrochromism" and much effort has been made to derive practical benefits from it. Poly(vinyl alcohol) having a PTh pendant group serves as an excellent polymer electrolyte which shows electrochromism;[44a,44b)] poly(vinyl alcohol) serves as an excellent matrix polymer for polymer electrolytes.[44c,44d)] Figure 16 shows an example of a change of UV-visible spectrum on electrochemical n-doping of P(5, 8-diArQx) (Ar = C_6H_5).[45a)]

The electrochemical redox behavior of π-conjugated polymers has been applied to batteries by many research groups.[46,47)] The polymer batteries were first reported inde-

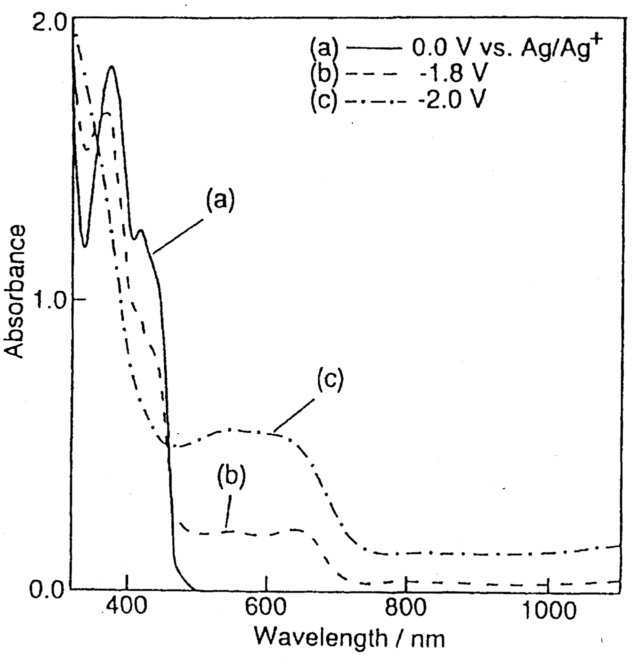


Fig. 16. Changes in absorption spectrum of a film of P(5,8-diArQx) (Ar = C_6H_5) on an ITO-glass electrode during electrochemical n-doping in an acetonitrile solution of $[NEt_4][ClO_4]$ (0.1 M).

pendently by two groups including the author's group 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, due to the excellent electrical conductivity of PTh-I_2, the cell gave a high utilization of iodine.[46f,46g] For a "storehouse of charge" not only the 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 developed a graphite-based Li battery, which is now widely used as a lithium ion cell.[48] PDPA and its analogues serve as a sensor of lead battery.[19b,49a] The N-containing polymers like PPy can transport H^+ in electrochemical processes,[49b] and protonated polymers exhibits electrochemical activity similar to that of NAD and serves as an active material of an battery operating in acidic media.[49c]

Electronic and Optical Devices. Recently the utility of π-conjugated polymers as a material for an electroluminescence device (EL device or light emitting diode, LED) has been demonstrated.[50] PTh, P(5,8-diArQx), and P4RBTz serve as materials for the EL device.[22a,38c,45b,51] PTh works as an excellent material for the hole-transporting layer (HTL) in the EL device.[51b]

The following LEDs have been prepared by using P(5,8-diArQx) (Ar = C_6H_5):[51a]

ITO/P(5,8-diArQx)/MgAg (Type I)
ITO/vd-PTh/P(5,8-diArQx)/MgAg (Type II)
(vd: vacuum deposited)
ITO/P(5,8-diArQx) and TPD/MgAg (Type III)

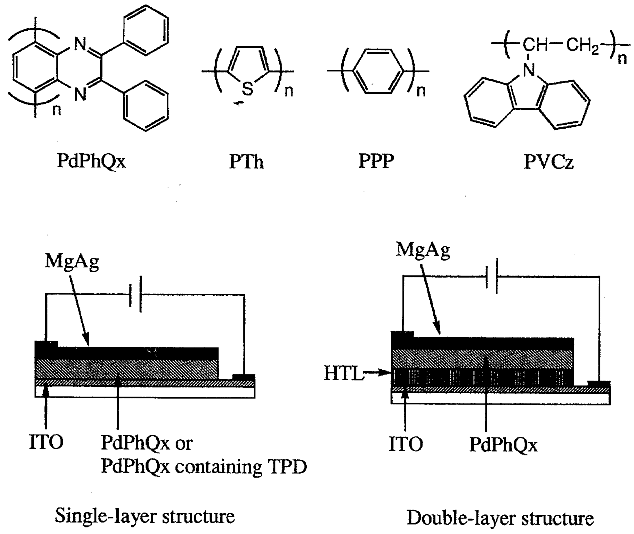


Fig. 17. Molecular structures of polymers and schematic diagrams of the LEDs: (a) single-layer structure and (b) double-layer structure. PdPhQx = P (5,8-diArQx) (Ar = C_6H_5).

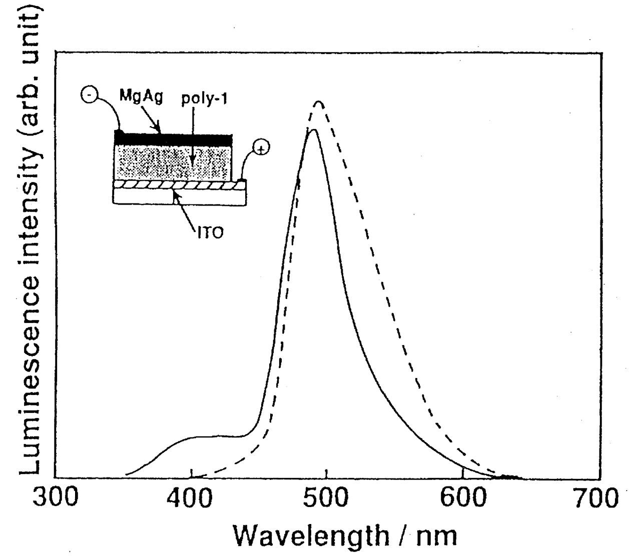


Fig. 18. Photoluminescence spectrum of spin-cast film of P (5,8-diArQx) (Ar = C_6H_5) (broken) and electroluminescence spectrum of ITO/P(5,8-diArQx) (Ar = C_6H_5)/MgAg LED at 11 V (solid).

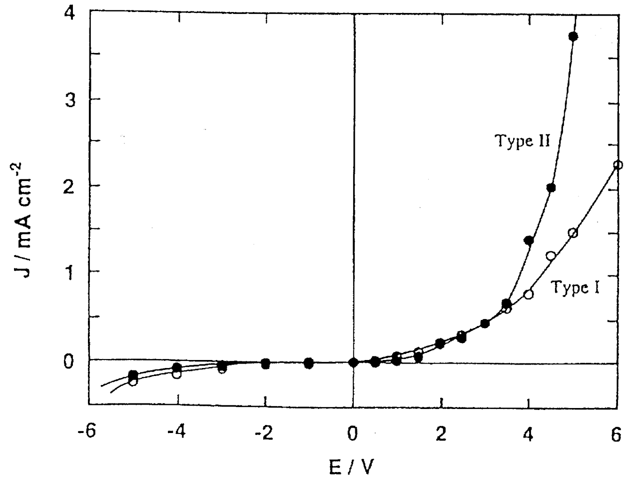


Fig. 19. Current density–voltage (*J–V*) characteristics of the diodes: (○) ITO/PdPhQx/MgAg (Type I) and (●) ITO/vd-PTh/PdPhQx/MgAg (Type II). PdPhQx = P(5,8-diArQx) (Ar = C_6H_5).

Figure 17 shows structures of LEDs with and without HTL, and Fig. 18 displays agreement of the photoluminescence and electroluminescence (Type I) spectra of P(5,8-diArQx). As shown in Fig. 19, an LED with HTL allows higher electric current flow and gives a larger emission intensity[45b,51a] as usually observed with LEDs. Tuning of the EL light by an additive (e.g., an aromatic amine, TPD)[51a] is possible. In PCrTh and Copoly 4, the peak position of EL is shifted to a longer wavelength by insertion of the thiophene-2,5-diyl unit between the bulky thiophene-2,5-diyl unit with the crown ether substituent.[33] An Au/PTh/Al electric junction behaves as a rectifying diode.[22a]

Thin layer transistor (TLT) based on π-conjugated polymers or organic molecules is another target device of the π-conjugated polymers[52,53] and PTh prepared by the organometallic polycondensation also works as an active layer for TLT.[22a,53]

Since the copolymers, Copoly 1—3,[12d,12e,23] and PAE-2 and its analogues[9c,9d,30] have large $\chi^{(3)}$ values, preparation of nonlinear optical devices using the materials is expected. Recently, a wave-guide using PAE-2 has been prepared.[30b]

Other Polymers

In addition to the π-conjugated poly(arylene)s prepared by the organometallic processes, we have been concerned with the chemistry of polyaniline PAn and its analogues.[19a,19b,54,55] Redox behaviour of PAn[54a,54c,54f] and dynamic H exchange of PAn on NMR time scale[54d,54e] have been reported. Polymerization of PAn and PPr on polymer latexes gives polymer latexes covered with the conductive polymer.[55] PAn and its analogues seem to be useful materials for removing static electricity and electrochemical devices, as investigated by many researchers. π-Conjugated polymers with hindered phenoxy groups in the side chain (e.g., P(3-Bu_2OHTh)[56]) and PAE-3[20a]) have also been prepared.[9g,20a,56]

Conclusions

Organometallic polycondensations based on basic organometallic chemistry carried out here have contributed much to the preparation of π-conjugated polymers and represented the first preparations of this kind (e.g., PTh and P3RTh). The π-conjugated polymers prepared by the organometallic polycondensations have a well-characterized structure. They have contributed to understanding of basic chemical and physical properties 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.

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References

1) a) T. Yamamoto, A, Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 and 3360 (1971); b) T. Kohara, T. Yamamoto, and A. Yamamoto, *J. Organomet. Chem.*, **192**, 265 (1980); c) K. Tatsumi, A. Nakamura, S. Komiya, T. Yamamoto, and A. Yamamoto, *J. Am. Chem. Soc.*, **106**, 8181 (1984); d) S. Komiya, Y. Abe, A. Yamamoto, and T. Yamamoto, *Organometallics*, **2**, 1466 (1983); e) B. Åkermark and A. Ljungqvist, *J. Organomet. Chem.*, **149**, 97 (1978); f) B. Åkermark, H. Johnasen, B. Roos, and U. Wahlgren, *J. Am. Chem. Soc.*, **101**, 5876 (1979); g) Y.-J. Kim, R. Sato, T. Maruyama, K. Osakada, and T. Yamamoto, *J. Chem. Soc., Dalton Trans.*, **1994**, 943; h) M. Uchino, K. Asagi, A. Yamamoto, and S. Ikeda, *J. Organomet. Chem.*, **84**, 93 (1975); i) T. Yamamoto and A. Yamamoto, *J. Organomet. Chem.*, **57**, 127 (1973); j) P. Binger and M. Doyle, *J. Organomet. Chem.*, **162**, 195 (1978); k) T. Yamamoto and M. Abla, *J. Organomet. Chem.*, **535**, 209 (1997); l) Y. Murakami and T. Yamamoto, *Inorg. Chem.*, **36**, 5682 (1997); m) J. K. Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York (1978); n) J. P. Collmann, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organometallic Chemistry," University Science, Mill Valley, Carfornia (1987), pp. 322 and 326; o) A. Yamamoto, "Organotransition Metal Chemistry," John Wiley, New York (1986); p) R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," John Wiley, New York (1988); q) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951); r) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, **1953**, 2939.

2) a) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, K. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Jpn.*, **49**, 1958 (1976), and references therein; b) A. S. Kende, L. S. Lieberskind, and D. Braitsch, *Tetrahedron Lett.*, **1977**, 3375; c) M. Zembayashi, K. Tamao, J. Yoshida, and M. Kumada, *Tetrahedron Lett.*, **1977**, 4089; d) M. F. Semmelhack and L. S. Ryono, *J. Am. Chem. Soc.*, **97**, 3873 (1975); e) Z.-H. Zhou and T. Yamamoto, *J. Organomet. Chem.*, **414**, 119 (1991); f) T. Yamamoto, S. Wakabayashi, and K. Osakada, *J. Organomet. Chem.*, **428**, 223 (1992).

3) a) T. Yamamoto and A. Yamamoto, *Chem. Lett.*, **1977**, 353; b) T. Yamamoto, Y. Hayashi, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2091 (1978); c) T. Yamamoto and A. Yamamoto, *Polym. Prepr. Jpn.*, **25**, G2B07 (1976); d) T. Yamamoto, *Prog. Polym. Sci.*, **17**, 1153 (1992); e) T. Yamamoto, *J. Synth. Org. Chem. Jpn.*, **53**, 999 (1995); f) T. Yamamoto and H. Hayashida, *React. Functional Polym.*, **37**, 1 (1998); g) T. Yamamoto, T. Taguchi, K. Sanechika, Y. Hayashi, and A. Yamamoto, *Macromolecules*, **16**, 1555 (1983).

4) a) T. Yamamoto, T. Ito, and K. Kubota, *Chem. Lett.*, **1988**, 153; b) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992); c) T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.*, **116**, 4832 (1994); d) T. Yamamoto, T. Ito, K. Sanechika, and M. Hishinuma, *Synth. Met.*, **25**, 103 (1988); e) T. Yamamoto, Z.-H. Zhou, T. Maruyama, Y. Yoneda, and T. Kanbara, *Chem. Lett.*, **1990**, 223; f) T. Yamamoto, Y. Yoneda, and T. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1992**, 1652; g) T. Yamamoto, T. Maruyama, T. Ikeda, and M. Sisido, *J. Chem. Soc., Chem. Commun.*, **1990**, 1306; h) T. Yamamoto, Z.-H. Zhou, I. Ando, and M. Kikuchi, *Makromol. Chem. Rapid Commun.*, **14**, 833 (1993); i) T. Kanbara, N. Saito, and T. Yamamoto, *Macromolecules*, **24**, 5883 (1991); j) T. Kanbara, T. Kushida, N. Saito, I. Kuwajima, K. Kubota, and T. Yamamoto, *Chem. Lett.*, **1998**, 583; k) T. Maruyama, K. Kubota, and T. Yamamoto, *Macromolecules*, **26**, 4055 (1993); l) T. Yamamoto and K. Kizu, *J. Phys. Chem.*, **99**, 8 (1995); m) T. Kanbara and T. Yamamoto, *Chem. Lett.*, **1993**, 419; n) T. Yamamoto, S.-B. Kim, and B. K. Choi, *J. Polym. Sci.: Part B: Polym. Phys.*, submitted.

5) a) T. Yamamoto, K. Osakada, T. Wakabayashi, and A. Yamamoto, *Makromol. Chem., Rapid Commun.*, **6**, 671 (1985); b) T. Yamamoto, Japan Kokai Patent, 1986-233014; c) T. Yamamoto, A. Kashiwazaki, and K. Kato, *Makromol. Chem.*, **190**, 1649 (1989); d) M. Ueda and F. Ichikawa, *Macromolecules*, **23**, 926 (1990); e) M. G. Grab, A. E. Fering, B. C. Auman, V. Percec, M. Zhao, and D. H. Hill, *Macromolecules*, **29**, 7284 (1996).

6) a) N. Saito, T. Kanbara, T. Sato, and T. Yamamoto, *Polym. Bull.*, **30**, 285 (1993); b) N. Saito, T. Kanbara, Y. Nakamura, T. Yamamoto, and K. Kubota, *Macromolecules*, **27**, 756 (1994); c) N. Saito and T. Yamamoto, *Macromolecules*, **28**, 4260 (1995); d) T.

Yamamoto and N. Saito, *Macromol. Chem. Phys.*, **197**, 165 (1996); e) J.-F. Fauvarque, A. Digua, M.-A. Petit, and J. Savard, *Makromol. Chem.*, **186**, 2415 (1985); f) T. Yamamoto, N. Hayashida, and T. Maruyama, *Macromol. Chem. Phys.*, **198**, 341 (1997).

7) a) T. A. Skotheim, "Handbook of Conducting Polymers," Marcel Dekker, New York (1986), Vols. I and II; b) W. R. Salaneck, D. L. Clark, and E. J. E. Samuelsen, "Science and Applications of Conducting Polymers," Adam Hilger, New York (1990); c) A. G. MacDiarmid and A. J. Heeger, *NRL Memo, Rep.*, AD-A05816208 (1981); d) H. S. Nalwa, "Handbook of Organic Conductive Molecules and Polymers," John Wiley, Chickester (1997); e) T. A. Skotheim, R. I. Elsenbaumer, and J. R. Reynold, "Handbook of Conducting Polymers," 2nd ed, Marcel Dekker, New York (1997); f) J. Roncali, *Chem. Rev.*, **92**, 711 (1992); g) R. D. McCullough, *Adv. Mater.*, **10**, 93 (1998).

8) F. Ozawa, K. Kurihara, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **58**, 399 (1985); b) K. Osakada, R. Sakata, and T. Yamamoto, *Organometallics*, **16**, 5354 (1997); c) K. Osakada, R. Sakata, and T. Yamamoto, *J. Chem. Soc., Dalton Trans.*, **1997**, 1265.

9) a) K. Sanechika, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **57**, 752 (1984); b) K. Sanechika, T. Yamamoto, and A. Yamamoto, *Polym. Prepr. Jpn.*, **30**, 160 (1981); c) T. Yamamoto, M. Takagi, K. Kizu, T. Maruyama, K. Kubota, H. Kanbara, T. Kurihara, and T. Kaino, *J. Chem. Soc., Chem. Commun.*, **1983**, 797; d) T. Yamamoto, W. Yamada, M. Takagi, K. Kizu, T. Maruyama, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, and K. Kubota, *Macromolecules*, **27**, 6620 (1994); e) T. Yamamoto, K. Honda, N. Ooba, and S. Tomaru, *Macromolecules*, **31**, 7 (1998); f) D. L. Trumbo and C. S. Marvel, *J. Polym. Sci., Part A, Polym. Chem.*, **24**, 2311 (1986); g) H. Hayashi and T. Yamamoto, *Macromolecules*, **30**, 330 (1997); h) J. Li and Y. Pang, *Macromolecules*, **30**, 7487 (1997).

10) a) H. A. Dieck and R. F. Heck, *J. Organomet. Chem.*, **93**, 259 (1975); b) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **16**, 4467 (1975); c) K. Soga, M. Ohgisawa, and T. Shiono, *Makromol. Chem., Rapid Commun.*, **10**, 503 (1989).

11) a) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986); b) A. Suzuki, *Acc. Chem. Res.*, **15**, 178 (1982); c) A. Suzuki, *Pure Appl. Chem.*, **57**, 1749 (1985); d) M. Kosugi, M. Koshiba, H. Sano, and T. Migita, *Bull. Chem. Soc. Jpn.*, **58**, 1075 (1985); e) T. Mizoroki, K. Mori, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **44**, 581 (1971); f) R. F. Heck and J. P. Nolley, *J. Org. Chem.*, **37**, 2320 (1972).

12) a) M. Remmers, M. Schize, and G. Wegner, *Macromol. Rapid Commun.*, **17**, 239 (1996); b) Q.-S. Hu, D. Vitharana, G. Liu, V. Jain, and L. Pu, *Macromolecules*, **29**, 5075 (1996); c) M. Bochmann and J. Lu, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 2493 (1994); d) T. Kanbara, Y. Miyazaki, and T. Yamamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 999 (1995); e) T. Yamamoto, Z. -H. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, Y. Nakamura, T. Fukuda, B.-L. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, and S. Sasaki, *J. Am. Chem. Soc.*, **118**, 10389 (1996); f) K. Tamao, S. Yamaguchi, Y. Ito, Y. Matsuzaki, T. Yamabe, M. Fukushima, and S. Mori, *Macromolecules*, **28**, 8668 (1995); g) H. Nishide, T. Kaneko, S. Torii, Y. Kuzumaki, and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, **69**, 499 (1996); h) W.-K. Chan and L. Yu, *Macromolecules*, **28**, 6410 (1995); i) Z. Peng, A. R. Gharavi, and L. Yu, *J. Am. Chem. Soc.*, **119**, 4622 (1997); j) A. D. Schluter and G. Wegner, *Acta Polym.*, **44**, 59 (1993); k) M. Bochmann and K. Kelly, *J. Chem. Soc., Chem. Commun.*, **1989**, 532; l) Z. Bao, W. K. Chan, and L. Lu, *J. Am. Chem. Soc.*, **117**, 12426 (1995).

13) a) T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, and A. Yamamoto, *J. Am. Chem. Soc.*, **102**, 3758 (1980); b) T. Yamamoto, J. Ishizu, and A. Yamamoto, *J. Am. Chem. Soc.*, **103**, 6863 (1981); c) T. Yamamoto, S. Miyashita, S. Komiya, T. Ito, and A. Yamamoto, *Organometallics*, **1**, 808 (1982); d) M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, *J. Organomet. Chem.*, **30**, 279 (1971); e) D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, **36**, 269 (1979); f) G. W. Parshall, *J. Am. Chem. Soc.*, **96**, 2360 (1974); g) T. Yamamoto, T. Kohara, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **54**, 1720 (1981).

14) a) T. Yamamoto, K. Sanechika, and A. Yamamoto, Japan Kokai Patent, 47421 (1981); Japan Patent 120926 (1984) and Japan Patent 1236581 (1984); b) T. Yamamoto, K. Sanechika, and A. Yamamoto, Japan Kokai Patent 147426 (1983) (applied: 26 February 1981); Japan Patent 1258016 (1985) and Japan Patent 1262404 (1985); c) U.S. Patent 4521589 (1985).

15) a) T. Yamamoto, K. Sanechika, and A Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 9 (1980); b) K. Sanechika, T. Yamamoto, and A. Yamamoto, *Polym. Prepr. Jpn.*, **27**, 966 (1979); c) T. Yamamoto, K. Sanechika, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 1497 and 1503 (1983); d) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992).

16) a) T. Yamamoto and K. Sanechika, *Chem. Ind. (London)*, **1982**, 301; b) Y. Miyazaki and T. Yamamoto, *Synth. Met.*, **64**, 69 (1994).

17) a) R. D. McCullough, R. D. Lowe, M. Jayaraman, and D. L. Anderson, *J. Org. Chem.*, **58**, 904 (1993); b) T. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, **117**, 233 (1995).

18) a) T. Yamamoto, M. Takeuchi, and K. Kubota, unpublished data; b) T. Yamamoto, in "Handbook of Organic Conductive Molecules and Polymers," ed by H. S. Nalwa, John Wiley, Chichester (1997), Vol. 2, p. 171.

19) a) T. Yamamoto, S.-B. Kim, and T. Yamamoto, *Chem. Lett.*, **1996**, 413; b) S.-B. Kim, K. Harada, and T. Yamamoto, *Macromolecules*, **31**, 988 (1998); c) T. Yamamoto and T. Okuda, *J. Electroanal. Chem.*, in press; d) T. Yamamoto and T. Kimura, *Macromolecules*, **31**, 2683 (1998); e) T. Yamamoto and K. Shiraishi, *Chem. Lett.*, **1998**, 895; f) T. Yamamoto, K. Sugiyama, T. Kanbara, H. Hayashi, and H. Etori, *Macromol. Chem. Phys.*, **199**, 1807 (1998); g) T. Yamamoto, N. Hayashida, T. Maruyama, and K. Kubota, *Chem. Lett.*, **1998**, 1125; h) N. Hayashida and T. Yamamoto, *Bull. Chem. Soc. Jpn.*, in press.

20) a) H. Hayashi and T. Yamamoto, *Macromolecules*, **31**, 6063 (1998); b) T. Yamamoto and T. Shimizu, *J. Mater. Chem.*, **7**, 1967 (1997); c) T. Yamamoto, T. Morikita, T. Maruyama, K. Kubota, and M. Katada, *Macromolecules*, **30**, 5390 (1997); d) Y. Muramatsu and T. Yamamoto, *Denki Kagaku*, **66**, 223 (1998); e) T. Yamamoto, Y. Xu, and H. Koinuma, *Chem. Lett.*, **1998**, 613; f) T. Yamamoto and B.-L. Lee, *Chem. Lett.*, **1998**, 1663; g) T. Yamamoto and M. Abla, *Synth. Met.*, in press.

21) a) T. Yamamoto, H. Suganuma, T. Maruyama, and K. Kubota, *J. Chem. Soc., Chem. Commun.*, **1995**, 1613; b) J. L. Nanos, J. W. Kampf, M. D. Curtis, L. Gonzalez, and D. C. Martin, *Chem. Mater.*, **7**, 2332 (1995).

22) a) T. Yamamoto, T. Kanbara, C. Mori, H. Wakayama, T. Fukuda, T. Inoue, and S. Sasaki, *J. Phys. Chem.*, **30**, 12631 (1996); b) T. Yamamoto and H. Etori, *Macromolecules*, **28**, 3371 (1995); c) T. Yamamoto, H. Saito, and K. Osakada, *Polym. Bull.*, **29**, 597 (1992); the reflection spectrum of PCyh indicates that it has an absorption peak at about 600 nm (T. Yamamoto and T. Fukuda,

unpublished data). The peak position locates near that of cis-polyacetylene ($\lambda_{\max} = 217$, 695 nm)[22d] The degree of the red shift (cf. Chart 2) from 1,3-butadiene ($\lambda_{\max} = 217$ nm) is estimated at 29400 cm^{-1}; d) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974) and **13**, 1943 (1975); e) M. Hatano, S. Kanbara, and S. Okamoto, *J. Polym. Sci.*, **51**, S26 (1961); f) H. W. Gibson and J. M. Pockan, *Macromolecules*, **15**, 242 (1982).

23) a) Z.-H. Zhou, T. Maruyama, T. Kanbara, T. Ikeda, K. Ichimura, T. Yamamoto, and K. Tokuda, *J. Chem. Soc., Chem. Commun.*, **1991**, 1210; b) T. Kurihara, T. Kaino, Z.-H. Zhou, T. Kanbara, and T. Yamamoto, *Electronics Lett.*, **28**, 681 (1992); c) K. Kizu, T. Maruyama, and T. Yamamoto, *Polym. J.*, **27**, 205 (1995); d) T. Yamamoto, M. Shimura, K. Osakada, and K. Kubota, *Chem. Lett.*, **1992**, 1003; e) B.-L. Lee and T. Yamamoto, *Macromolecules*, in press; f) D. Komarudin, A. Morita, K. Osakada, and T. Yamamoto, *Polym. J.*, **30**, 860 (1998); g) T. Yamamoto, K. Sanechika, and H. Sakai, *J. Macromol. Sci. Chem.*, **A27**, 1147 (1990).

24) a) M. Karikomi, C. Kitamura, S. Tanaka, and Y. Yamashita, *J. Am. Chem. Soc.*, **117**, 6791 (1995); b) Q. T. Zhang and J. M. Tour, *J. Am. Chem. Soc.*, **120**, 5355 (1998).

25) T. Yamamoto, *J. Polm. Sci., Part A: Polym. Chem.*, **34**, 997 (1996).

26) a) N. Saito, T. Kanbara, T. Kushida, K. Kubota, and T. Yamamoto, *Chem. Lett.*, **1993**, 1775; b) T. Vahlenkamp and G. Wegner, *Macromol. Chem. Phys.*, **195**, 1933 (1994); c) T. Yamamoto, T. Kimura, and K. Shiraishi, *Macromolecules*, submitted.

27) T. Yamamoto, *J. Org. Synth. Chem. Jpn.*, **53**, 999 (1995).

28) Y. Saitoh and T. Yamamoto, *Chem. Lett.*, **1995**, 785.

29) a) T. Yamamoto, Y. Yoneda, and K. Kizu, *Makromol. Rapid Commun.*, **16**, 549 (1995); b) T. Yamamoto and B.-L. Lee, *Chem. Lett.*, **1996**, 65; c) T. Yamamoto and B.-L. Lee, *Chem. Lett.*, **1996**, 679; d) C. Davadoss, P. Bharathi, and J. S. Moore, *J. Am. Chem. Soc.*, **118**, 9635 (1996); e) M. R. Aktin, E. D. A. Stemp, C. Turro, N. J. Turro, and J. K. Barton, *J. Am. Chem. Soc.*, **118**, 2267 (1996).

30) a) N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, W. Yamada, M. Takagi, and T. Yamamoto, *Jpn. J. Appl. Phys.*, **34**, 3139 (1995); b) N. Ooba, M. Asobe, S. Tomaru, T. Kaino, W. Yamada, M. Takagi, and T. Yamamoto, *Nonlinear Optics*, **15**, 481 (1996).

31) K. Suruga, T. Fukuda, K. Ishikawa, H. Takezoe, A. Fukuda, T. Kanbara, and T. Yamamoto, *Synth. Met.*, **79**, 149 (1996).

32) a) H. Etori, T. Kanbara, and T. Yamamoto, *Chem. Lett.*, **1994**, 461; b) Y. Muramatsu and T. Yamamoto, *Chem. Lett.*, **1997**, 581; c) T. Yamamoto, Y. Muramatsu, T. Shimizu, and W. Yamada, *Macromol. Rapid Commun.*, **19**, 263 (1998); d) K. Yamamoto, T. Asada, H. Nishide, and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, **63**, 1211 (1990).

33) a) Y. Miyazaki and T. Yamamoto, *Chem. Lett.*, **1994**, 41; b) T. Yamamoto, M. Omote, Y. Miyazaki, A. Kashiwazaki, B.-L. Lee, T. Kanbara, K. Osakada, T. Inoue, and K. Kubota, *Macromolecules*, **30**, 7158 (1997).

34) a) T. Miyamae, D. Yoshimura, H. Ishii, Y. Ouchi, T. Miyazaki, T. Koike, T. Yamamoto, and K. Seki, *J. Electron. Spectrosc.*, **78**, 399 (1996); b) T. Miyamae, M. Aoki, H. Etori, Y. Muramatsu, Y. Saito, T. Yamamoto, Y. Sakurai, K. Seki, and N. Ueno, *J. Electron Spectro. Relat. Phenom.*, **89-91**, 905 (1998).

35) a) T. Yamamoto, K. Sanechika, A. Yamamoto, M. Katada, I. Motoyama, and H. Sano, *Inorg. Chim. Acta*, **73f**, 75 (1983); b) F. Jonas and G. Heywang, *Electrochim. Acta*, **39**, 1345 (1994); c) A. O. Patil, Y. Ikenoue, N. Basescu, J. Chen, F. Wudl, and A. J. Heeger, *Synth. Met.*, **29**, 151 (1989);d) Y. Kudoh, M. Fukuyama, and S. Yoshimura, *Synth. Met.*, **66**, 157 (1994).

36) a) T. Yamamoto, T. Kanbara, and C. Mori, *Chem. Lett.*, **1990**, 1211; b) T. Yamamoto, T. Kanbara, and C. Mori, *Synth. Met.*, **38**, 399 (1990); c) T. Kanbara, C. Mori, H. Wakayama, T. Fukuda, Z.-H. Zhou, T. Maruyama, K. Osakada, and T. Yamamoto, *Solid State Commun.*, **83**, 771 (1992).

37) a) P. Ostoja, S. Guerri, S. Rossini, M. Servidori, C. Taliani, and R. Zamboni, *Synth. Met.*, **54**, 447 (1993); b) W. Porzio, S. Destri, M. Mascherpa, S. Rossini, and S. Brükner, *Synth. Met.*, **55-57**, 408 (1993); c) W. Pozzio, S. Destri, M. Mascherpa, and S. Brükner, *Acta Polym.*, **44**, 266 (1993); d) B. Xervet, S. Ries, M. Trotel, P. Alnot, G. Horowitz, and F. Garnier, *Adv. Mater.*, **5**, 461 (1993); e) C. Taliani and L. M. Blinov, *Adv. Mater.*, **8**, 353 (1996); f) A. J. Lovinger, D. D. Davis, A. Dodabalapur, and H. E. Katz, *Chem. Mater.*, **8**, 2836 (1996).

38) a) T. Yamamoto, *Chem. Lett.*, **1996**, 703; b) T. Yamamoto, T. Maruyama, H. Suganuma, M. Arai, D. Komarudin, and S. Sasaki, *Chem. Lett.*, **1997**, 139; c) T. Yamamoto, H. Suganuma, T. Maruyama, T. Inoue, Y. Muramatsu, M. Arai, D. Komarudin, N. Ooba, S. Tomaru, S. Sasaki, and K. Kubota, *Chem. Mater.*, **9**, 1217 (1997); d) L. Gonzalez Londa and D. C. Martin, *Macromolecules*, **30**, 1524 (1997); e) C. Yang, F. P. Orfino, and S. Holdcroft, *Macromolecules*, **29**, 6510 (1996); f) M. J. Winokur, P. Wamsley, J. Monlton, P. Smith, and A. J. Heeger, *Macromolecules*, **24**, 3812 (1991); g) J. Märdalen, E. J. Samuelsen, O. R. Gautun, and P. H. Carlsen, *Synth. Met.*, **48**, 363 (1992); h) T. Yamamoto, D. Komarudin, M. Arai, B.-L. Lee, H. Suganuma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda, and H. Matsuda, *J. Am. Chem. Soc.*, **120**, 2047 (1998); i) T. Yamamoto, B.-L. Lee, H. Suganuma, and S. Sasaki, *Polym. J.*, **30**, 83 (1998).

39) a) M. O. Wolf and M. S. Wrighton, *Chem. Mater.*, **6**, 1526 (1994); b) T. Maruyama and T. Yamamoto, *Inorg. Chim. Acta*, **238**, 9 (1995); c) S. S. Zhu and T. M. Swager, *J. Am. Chem. Soc.*, **119**, 12568 (1997); d) K. D. Ley, C. E. Whittle, M. D. Barberger, and K. S. Schanze, *J. Am. Chem. Soc.*, **119**, 3423 (1997); e) B. Wang and M. R. Wasielewski, *J. Am. Chem. Soc.*, **119**, 12 (1997); f) S. S. Zhu and T. M. Swager, *Adv. Mater.*, **8**, 497 (1996); g) K. Wärnmark, P. N. W. Baxter, and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, **1998**, 993; h) S. I. Yaniger, D. J. Rose, W. P. Mckenna, and E. M. Eyring, *Macromolecules*, **17**, 2579 (1984); i) J. Matsuda, K. Aramaki, and H. Nishihara, *J. Chem. Soc., Faraday Trans.*, **91**, 1477 (1995); j) H. Funaki, K. Aramaki, and H. Nishihara, *Synth. Met.*, **74**, 59 (1995); k) H. Nishihara, *J. Org. Synth. Jpn.*, **55**, 410 (1997); l) I. J. Spilner and P. Pellegrini, Jr., *J. Chem. Soc.*, **1965**, 3800; m) K. Sanechika, T. Yamamoto, and A. Yamamoto, *Polym. J.*, **13**, 255 (1981).

40) a) T. Kanbara and T. Yamamoto, *Macromolecules*, **26**, 1975 (1993); b) T. Yamamoto and T. Kanbara, U.S. Patent 5310829 (1994).

41) a) T. Yamamoto and N. Saito, *Chem. Lett.*, **1996**, 127; b) T. Yamamoto, B.-L. Lee, H. Hayashi, N. Saito, and T. Maruyama, *Polymer*, **38**, 4233 (1997).

42) a) S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac, and K. Yoshino, *J. Chem. Soc., Chem. Commun.*, **1985**, 474; b) S. Matsuoka, T. Kohzuki, Y. Kuwana, A. Nakamura, and S. Yanagida, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 679.

43) a) T. Maruyama and T. Yamamoto, *J. Phys. Chem. B*, **101**, 3806 (1997); b) Y. Sato and T. Yamamoto, Japan Patent Applied; c) Y. Sato, M. Kagatoni, T. Yamamoto, and Y. Souma, to be submitted to *Appl. Cat.*; d) Y. Sato and T. Yamamoto, Applied for Japan Patent.

44) a) M. Wakabayashi, Y. Miyazaki, T. Kanbara, K. Osakada, T. Yamamoto, and A. Ishibashi, *Synth. Met.*, **55/57**, 3632 (1993); b) T. Yamamoto and M. Wakabayashi, Eur. Patent Appl. EP 597234 (1994) and U.S. Patent 5561206 (1996); c) T. Yamamoto, M. Inami,

and T. Kanbara, *Chem. Mater.*, **6**, 44 (1994); d) T. Kanbara, M. Inami, and T. Yamamoto, *J. Power Sources*, **36**, 87 (1991).

45) a) T. Kanbara and T. Yamamoto, *Chem. Lett.*, **1993**, 1459; b) T. Yamamoto, T. Inoue, and T. Kanbara, *Jpn. J. Appl. Phys.*, **33**, L250 (1994).

46) a) T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **1981**, 187; b) D. MacInnes, Jr., M. A. Dury, P. J. Nigrey, D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, **1981**, 317; c) L. W. Schacklette, R. L. Elsenbaumer, R. R. Chance, J. M. Sowa, D. M. Ivory, G. G. Miller, and R. H. Baughmann, *J. Chem. Soc., Chem. Commun.*, **1982**, 361; d) T. Yamamoto, M. Zama, M. Hishinuma, and A. Yamamoto, *J. Appl. Electrochem.*, **17**, 607 (1987); e) T. Yamamoto, M. Zama, and A. Yamamoto, *Chem. Lett.*, **1985**, 563; f) M. Hishinuma, M. Zama, K. Osakada, and T. Yamamoto, *Inorg. Chim. Acta*, **128**, 185 (1987); g) T. Yamamoto, M. Zama, and A. Yamamoto, *Chem. Lett.*, **1984**, 1577.

47) a) A. G. MacDiarmid, L. S. Yang, W. S. Haung, and B. D. Humphry, *Synth. Met.*, **18**, 393 (1987); b) J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986); c) E. Daifuku, *Kino Zairyo*, **8**, 17 (1988); d) T. Yamamoto and T. Matsunaga, "Polymer Battery," (in Japanese), Kyoritsu, Tokyo (1990).

48) e.g., K. Sanechika and A. Yoshino, Japan Kokai Tokkyo Koho 1985-253157; *Chem. Abstr.*, **104**, P152474 (1986).

49) a) T. Yamamoto and S. Sano, U.S. Patent 5273841 (1993); b) T. Yamamoto, T. Matsuzaki, A. Minetomo, Y. Kawazu, and O. Ohashi, *Bull. Chem. Soc. Jpn.*, **69**, 3461 (1996); c) T. Yamamoto, T. Nishiyama, G. Harada, and M. Takeuchi, to be submitted, *J. Power Sources.*

50) a) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, **347**, 539 (1990); b) D. Brown, A. J. Heeger, and H. Kroemer, *J. Electron Mater.*, **20**, 945 (1991); c) D. D. C. Bradley, *Synth. Met.*, **54**, 401 (1993); d) M. Ueda, Y. Ohmori, T. Noguchi, and T. Ohnishi, *Jpn. J. Appl. Phys.*, **32**, L921 (1993); e) C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **57**, 531 (1990).

51) a) T. Yamamoto, K. Sugiyama, T. Kushida, T. Inoue, and T. Kanbara, *J. Am. Chem. Soc.*, **118**, 3930 (1996);b) Eur. Patent 98105161. 8-2102 (1998).

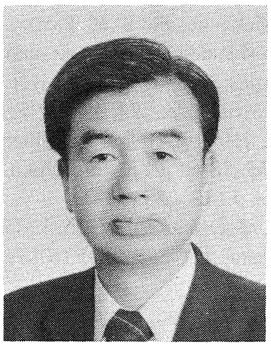
52) a) A. Tsumura, H. Koezuka, and T. Ando, *Synth. Met.*, **25**, 11 (1988); b) A. Tsumura, H. Fuchigami, and H. Koezuka, *Synth. Met.*, **41/4**, 1181 (1991); c) F. Garnier, G. Horowitz, X. Z. Peng, and D. Fichou, *Synth. Met.*, **45**, 163 (1991); d) J. G. Laquindanum, H. E. Katz, and A. J. Lovinger, *J. Am. Chem. Soc.*, **120**, 664 (1998).

53) a) T. Yamamoto, H. Wakayama, T. Kanbara, K. Sasaki, K. Tsutsui, and J. Furukawa, *Denki Kagaku*, **62**, 84 (1994).

54) a) D.-K. Moon, T. Maruyama, and K. Osakada, *Chem. Lett.*, **1991**, 1633; b) D.-K. Moon, K. Osakada, T. Maruyama, and T. Yamamoto, *Makromol. Chem.*, **193**, 1723 (1992); c) D.-K. Moon, M. Ezuka, T. Maruyama, K. Osakada, and T. Yamamoto, *Macromolecules*, **26**, 364 (1993); d) T. Yamamoto, *Chem. Lett.*, **1993**, 1211; e) T. Yamamoto and D.-K. Moon, *Makromol. Chem. Rapid Commun.*, **14**, 495 (1993); f) D.-K. Moon, M. Ezuka, T. Maruyama, K. Osakada, and T. Yamamoto, *Makromol. Chem.*, **194**, 3149 (1993); g) D.-K. Moon, K. Osakada, T. Maruyama, K. Kubota, and T. Yamamoto, *Macromolecules*, **26**, 6992 (1993).

55) a) C.-F. Liu, T. Maruyama, and T. Yamamoto, *Polym. J.*, **25**, 363 (1993); b) C.-F. Liu, D.-K. Moon, T. Maruyama, and T. Yamamoto, *Polym. J.*, **25**, 775 (1993); T. Yamamoto, S.-B. Kim, and M. Horie, to be submitted, *Jpn. J. Appl. Phys.*

56) T. Yamamoto and H. Hayashi, *J. Polym. Sci.: Part A: Polym. Chem. Ed.*, **35**, 463 (1997).



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