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ELECTRICALLY CONDUCTING AND THERMALLY STABLE π-CONJUGATED POLY(ARYLENE)S PREPARED BY ORGANOMETALLIC PROCESSES

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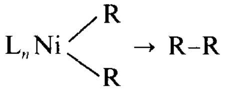
CONTENTS

1. INTRODUCTION

Diorganonickel(II) complexes NiR_2L_n undergo reductive coupling reactions to give R–R,[1-13]



$$L_nNi\begin{matrix}R\\R\end{matrix} \rightarrow R\text{–}R \qquad (1)$$

and this coupling reaction has been utilized to carry out nickel-catalyzed C–C coupling reactions between Grignard reagent and organic halide (eq. 2),[14-16] and dehalogenation coupling of organic halides with zinc (eq. 3).[17-19]

$$\mathrm{RMgX} + \mathrm{R'X} \xrightarrow{\text{Ni-complex}} \mathrm{R{-}R'} + \mathrm{MgX_2} \tag{2}$$

$$2\mathrm{RX} + \mathrm{Zn} \xrightarrow{\text{Ni-complex}} \mathrm{R{-}R} + \mathrm{ZnX_2} \tag{3}$$

In addition to the coupling reactions expressed by eqs 2 and 3, Ullmann type coupling of organic halides using a zero-valent nickel complex itself as a dehalogenation reagent[20-25]

$$2\mathrm{RX} + \mathrm{NiL}_n \rightarrow \mathrm{R{-}R} + \mathrm{NiX_2} \tag{4}$$

has been developed.

On the other hand, Pd-complexes catalyze the following C–C coupling reactions, which are also considered to proceed through organotransition metal compounds,

$$\mathrm{RC{\equiv}CH} + \mathrm{R'X} + \mathrm{Et_2NH} \xrightarrow{\text{Pd complex}} \mathrm{RC{\equiv}CR'} + \mathrm{Et_2NH_2X} \qquad (5)^{26,27}$$

$$\mathrm{PhC{\equiv}CMgBr} + \mathrm{PhI} \xrightarrow{\text{Pd complex}} \mathrm{PhC{\equiv}CPh} + \mathrm{MgBrI}. \qquad (6)^{28}$$

We have applied the transition metal-promoted C–C coupling found by us to the polycondensation of dihaloaromatic compounds,

Method I

$$n\mathrm{X{-}Ar{-}X} + n\mathrm{Mg} \rightarrow [\mathrm{X{-}Ar{-}MgX}] \xrightarrow{\text{Ni-complex}} \left(\!-\mathrm{Ar}-\!\right)_n \qquad (7)^{29,30}$$

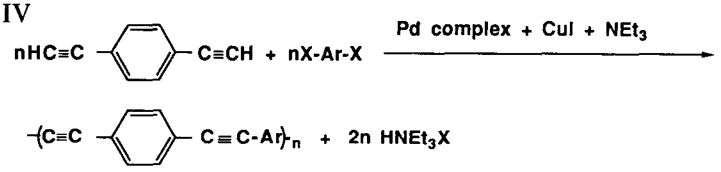
Method II

$$n\mathrm{X{-}Ar{-}X} + n\mathrm{Zn} \xrightarrow{\text{Ni-complex}} \left(\!-\mathrm{Ar}-\!\right)_n \qquad (8)^{31}$$

Method III

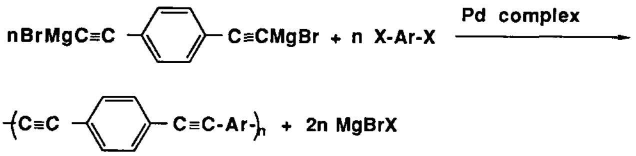
$$n\mathrm{X{-}Ar{-}X} + n\mathrm{Ni(0)L}_m \rightarrow \left(\!-\mathrm{Ar}-\!\right)_n \qquad (9)^{32-34}$$

Method IV



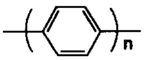
(10)[35]

Method V

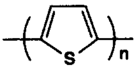


(11)[35]

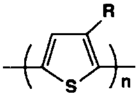
to prepare the following electrically conducting and thermally stable π-conjugated aromatic polymers, and related polymers.



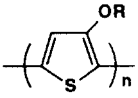
poly(p-phenylene)
PPP



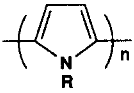
poly(thiophene
2,5-diyl)
PTh



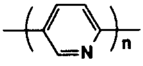
poly(3-alkylthiophene-
2,5-diyl)
PRTh



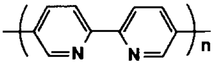
poly(3-alkoxy-
thiophene-
2,5-diyl)
PORTh



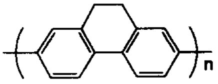
poly(N-alkyl-
pyrrole-2,5-diyl)
PRPyrro



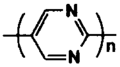
poly(pyridine-
2,5-diyl)
PPy



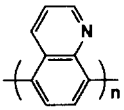
poly(2,2'-bipyridine-
5,5'-diyl)
PBpy



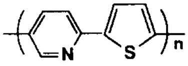
poly(dihydrophenan-
threne-2,7-diyl)
PH_2Ph



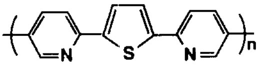
poly(pyrimidine-
2,5-diyl)
PPyrim



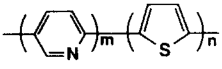
poly(quinoline-
5,8-diyl)
PQ
and its anologues



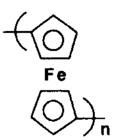
Copoly 1
and its analogues



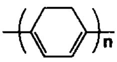
Copoly 2



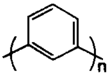
Copoly 3
and its analogues



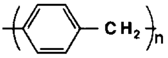
poly(ferrocene-
1,1'-diyl)
PFc



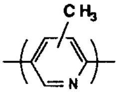
poly(1,3-cyclo-
hexadiene-
1,4-diyl)
PCyh



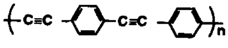
poly(m-phenylene)
PMP

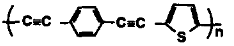


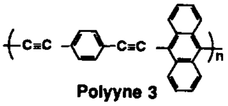
poly(α,p-xylylene)
Pxy

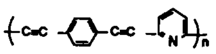


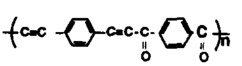
PMePy


Polyyne 1


Polyyne 2


Polyyne 3

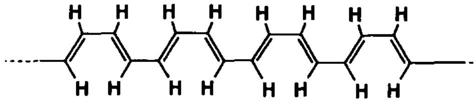

Polyyne 4

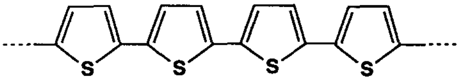

Polyyne 5


Polyyne 6

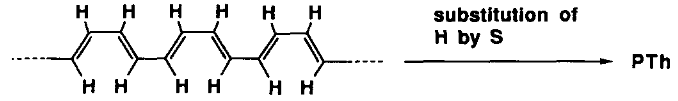
Among the polymers, PTh,$^{36-41}$ PRTh,$^{39,40,42-44}$ PRPyrro,$^{45-47}$ PPy,$^{32,48-50}$ PBpy,$^{51-53}$ PH_2Phen,^{33} PPyrim,^{54} PQ^{55} and its analogues, PCyh,^{56} Copoly's 1–3,$^{57-59}$ PMePy,^{60} and Polyyne 1–6^{35,61} were first prepared by the transition metal-promoted polycondensations, Methods I–V, (by us except for PRPyrro). Some π-conjugated poly(arylene)s (e.g. PPP^{29,30} and PFc) with high crystallinity and well-defined bonding between the monomer units were also first prepared by this polycondensation. PTh^{41} and PRTh^{43,44} (as materials) as well as the polycondensation Method I were patented by our institute; PPy^{32} and PBpy^{51} as well as the polycondensation Methods II^{31} and III^{34} are under patent application.

PTh is the first π-conjugated electrically conducting polymer consisting of 5-membered heteroaromatic rings. It has a π-conjugation system similar to that of poly(acetylene), which has the most simple π-conjugation system and highly electrically conducting properties, but shows only low chemical stability.


cis-poly(acetylene)


PTh

Formal substitution of hydrogens of *cis*-poly(acetylene) affords PTh, which is expected to have high chemical and thermal stability due to the aromaticity of the recurring monomer unit. However, this substitution of H of



poly(acetylene) by S cannot be achieved by usual chemical methods. On the other hand, application of Methods I–III to 2,5-dihalothiophene clearly affords PTh. PTh prepared about 15 years ago^{36,37} still remains chemically unchanged in air at room temperature.

After PTh was reported to have high chemical and thermal stability,[36,37] other various electrically conducting π-conjugated polymers consisting of 5-member heteroaromatic rings (e.g. polypyrrole[62]) were synthesized.

In this review, we will describe results of the polycondensation, structure of the polymers, and chemical and physical properties of the various π-conjugated polymers shown above.

2. SYNTHETIC PROCEDURES

2.1. *Synthesis through Grignard reagent*

Various dihalo- as well as polyhaloorganic compounds can be polymerized according to the following reaction (eq. 12).

$$\text{X–R–X} + \text{Mg} \rightarrow [\text{X–R–MgX}] \xrightarrow{\text{transition metal compounds}} -\!\!\left(\text{R} \right)\!\!-_n \qquad (12)$$

R: arylene or α, ω-alkanediyl. Transition metal: nickel, palladium, iron, chromium, cobalt, copper, etc.

Results of the polymerization of dihaloaromatic compounds are shown in Table 1.[29,30] As shown in Table 1, nickel compounds serve as the best catalyst among the transition metal complexes tested. When copper complexes are employed, the polymerization expressed by eq. 12 is applicable to the polymerization of α, ω-dihaloalkane (e.g. 1,6-dibromohexane)

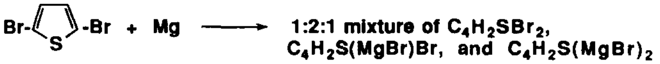
$$\text{Br(CH}_2)_6\text{Br} + \text{Mg} \rightarrow [\text{Br(CH}_2)_6\text{MgBr}] \xrightarrow{\text{Cu complex}} -\!\!\left(\text{CH}_2 \right)\!\!-_{6n} \qquad (13)$$

to afford poly(methylene) or poly(ethylene) (Mw = ca. 5000),[63] which shows very sharp v(C–H) absorption bands comparable to those of Ziegler–Natta poly(ethylene).

The polymerization proceeds very smoothly at room temperature and at warm (e.g. reflux temperature of THF) conditions. Analysis of the products of the reaction of X–R–X and Mg revealed that the reaction of Br–C_6H_4–Br mainly affords mono-Grignard reagent Br–C_6H_4–MgBr,[30] whereas those of Br$(CH_2)_6$Br and 2,5-dibromothiophene yield a 1 : 1 mixture of Br$(CH_2)_6$Br and BrMg$(CH_2)_6$MgBr[63] and a 1 : 2 : 1 mixture of $C_4H_2SBr_2$, C_4H_2S (MgBr)Br, and C_4H_2S $(MgBr)_2$,[39] respectively.

$$\text{Br-C}_6\text{H}_4\text{-Br} + \text{Mg} \longrightarrow \text{Br-C}_6\text{H}_4\text{-MgBr} \qquad (14)$$

$$\text{Br(CH}_2)_6\text{Br} + \text{Mg} \longrightarrow \text{1:1 mixture of Br(CH}_2)_6\text{Br and BrMg(CH}_2)_6\text{MgBr} \qquad (15)$$



(16)

The polymerization can also be carried out by using pseudo halides such as tosylates,[63]

$$\text{Y–R–Y} \xrightarrow{\text{Organometallic process}} \text{polymer (Y = halogen, OTs, etc.).}$$

TABLE 1. Dehalogenation polymerization of haloaromatic compounds with magnesium in the presence of transition metal catalysts*

No.	Monomer	Catalyst†	Solvent‡	Time (h)	Yield§ (%)	Remarks
1	*p*-Dibromobenzene	none	THF	4.0	0	
2	*p*-Dibromobenzene	$NiCl_2$(bpy)	THF	4.0	95	
3	*p*-Dibromobenzene	$NiCl_2$(bpy)	THF	6.0	94	‖
4	*p*-Dibromobenzene	$NiCl_2$(bpy)	Bu_2O	4.5	68	
5	*p*-Dibromobenzene	$NiBr_2(PPh_3)_2$	THF	4.0	64	
6	*p*-Dibromobenzene	$PdCl_2$(bpy)	THF	4.0	95	
7	*p*-Dibromobenzene	$FeEt_2(bpy)_2$	THF	6.0	18	
8	*p*-Dibromobenzene	$CrMrCl_2(THF)_3$	THF	7.0	11	
9	*p*-Dibromobenzene	Ni(cod)$(PPh_3)_2$	THF	4.0	86	
10	*p*-Dibromobenzene	$NiCl_2$	THF	4.0	83	
11	*p*-Dibromobenzene	$FeCl_2$	THF	4.0	76	
12	*p*-Dibromobenzene	$FeCl_3$	THF	4.0	68	
13	*p*-Dibromobenzene	$CoCl_2$	THF	4.0	77	
14	*p*-Dibromobenzene	$NiCl_2$(bpy)	THF	6.0	60	
15	*p*-Diiodobenzene	$NiCl_2$(bpy)	THF	4.0	50	
16	*m*-Dichlorobenzene	$NiCl_2$(bpy)	THF	6.0	92	
17	Bis(*p*-bromophenyl)ether	$NiCl_2$(bpy)	THF	5.0	60	
18	Bis(*p*-bromophenyl)ether	$NiBr_2(PPh_3)_2$	THF	9.0	39	
19	α,*p*-Dichlorotoluene	$NiCl_2$(bpy)	THF	7.0	69	
20	2,5-Dibromopyridine	$NiCl_2$(bpy)	THF	8.0	62	
21	2,5-Dibromopyridine	$NiBr_2(PPh_3)_2$	THF	8.0	64	
22	2,5-Dibromopyridine	$NiCl_2$	THF	8.0	23	
23	9,10-Dibromoanthracene	$NiCl_2$(bpy)	THF	6.0	22	
24	1,3,5-Trichlorobenzene	$NiCl_2$(bpy)	THF	15		
25	1,3,5-Trichlorobenzene	$NiCl_2$(bpy)	Diglyme	10.5	72	
26	Hexachlorobiphenyl	$NiCl_2$(bpy)	THF	15.0		
27	2,5-Dibromothiophene	$NiCl_2$(bpy)	THF	5.0	78	
28	2,5-Dibromothiophene	$NiCl_2$(bpy)	THF + *n*-Bu_2O (1:4)	5.0	48	
29	2,5-Dichlorothiophene	$NiCl_2$(bpy)	THF	4.0	40	
30	3-Methyl-2,5-dibromothiophene	$NiCl_2$(bpy)	THF	8.0	86	
31	3-Methyl-2,5-dibromothiophene	$NiCl_2$(dpp)	THF	10.0	79	
32	2,4-Dibromothiophene	$NiCl_2$(bpy)	THF + *n*-Bu_2O (1:4)	5.0	58	

* Under reflux except for No. 3.

† bpy = 2,2′-bipyridine; PPh_3 = triphenylphospine; cod = 1,5-cyclooctadiene; dpp = 1,3-bis-(diphenylphosphino)propane; Me = methyl; Et = ethyl.

‡ THF = tetrahydrofuran, Bu_2O = dibutyl ether under reflux.

§ Based on the amount of carbon taken into the polymer.

‖ At 0°C.

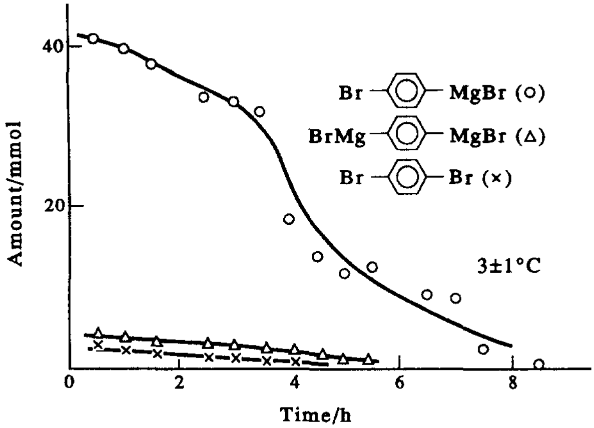
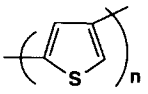


FIG. 1. Time course of the polymerization of p-$C_6H_4Br_2$ (50 mmol) monitored by consumption of monomers.[30] In THF (50 ml) at 3 ± 1°C. ○: p-BrC_6H_4MgBr; △: p-$C_6H_4(MgBr)_2$; ×: p-$C_6H_4Br_2$. Catalyst = $NiCl_2$ (bpy) 50 mg).

The time course of the polymerization of Br–C_6H_4–Br, as monitored by the consumption of the chemical species at low temperature (3°C), is shown in Fig. 1.

Color and thermal stability of poly(arylene)s prepared by this method are shown in Table 2. As shown in Table 2, π-conjugated PPP, PTh and PRTh show absorption in the visible region due to the π–π^* transition, whereas non-conjugated PMP, $-(C_6H_4OC_6H_4)_n-$, $-(C_6H_4CH_2)_n-$, and poly(thiophene-2,4-diyl)



are white or colorless.

In the case of poly(acetylene), introduction of a substituent usually affords white or colorless $-(CH{=}CR)_n-$ in which the π-conjugation is essentially destroyed due to the steric effect of the R group. On the other hand, introduction of a substituent in the five-membered-ring π-conjugated polymers does not cause the destruction of the π-conjugation, due to the presence of less steric repulsion between the R group and the five-membered ring.[42]

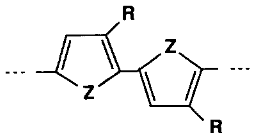


TABLE 2. Properties of poly(arylene)s

No.*	Polymer	Color	*Mp* (°C)
2	$+p\text{-}C_6H_4+_n$(PPP)	light yellow	550 dec
6	$+p\text{-}C_6H_4+_n$	light yellow	550 dec
14	$+p\text{-}C_6H_4+_n$	light yellow	550 dec
17	$+m\text{-}C_6H_4+_n$(PMP)	white	190–200† 280–295‡
18	$+C_6H_4CH_2+_n$	white	230–235† >400‡
26	$+C_6H_3+_n$	brown	290 dec
28	poly(thiophene-2,5-diyl) (PTh)	reddish brown	116§ ca. 320‖
31	poly(3-methylthiophene-2,5-diyl) (PRTh)	reddish brown	ca. 300‖
33	poly(thiophene-2,4-diyl)	white	ca. 320‖

* Numbers correspond to those in Table 1.

† For fraction soluble in hot toluene.

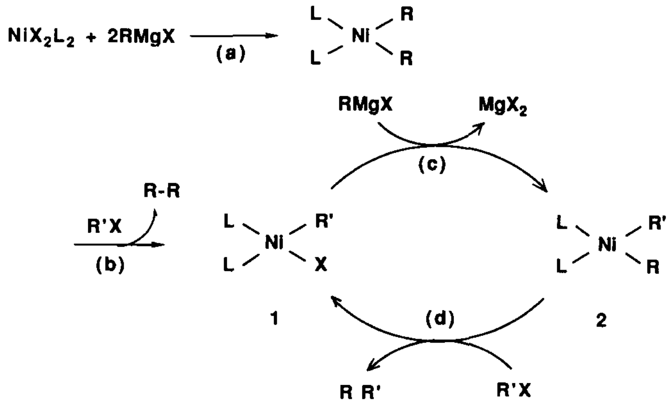
‡ For fraction insoluble in hot toluene.

§ For fraction soluble in hot $CHCl_3$ softening point.

‖ For fraction insoluble in hot $CHCl_3$.

Based on this finding, a number of 3-substituted poly(thiophene-2,5-diyl)s[39,40,42–44,64–66] and poly(pyrrole-2,5-diyl)s[67–70] have been synthesized, and their electrical, chemical, and physical properties have been investigated.

The basic condensation reaction (eq. 2) for the polycondensation (eq. 12) is considered to proceed through the following organonickel-mediated catalytic cycle involving: (a) formation of NiR_2L_2 by the reaction of NiX_2L_2 with RMgX; (b) reaction of NiR_2L_2 with R′X to yield R–R and $NiR'(X)L_2$; (c) alkylation of $NiR'(X)L_2$ with RMgX to yield $NiR(R')L_2$; and (d) elimination of R–R′ with formation of $NiR'(X)L_2$ in the reaction of $NiR(R')L_2$ with R′X.[14,30]



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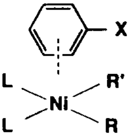
In the mechanism the starting complex NiX_2L_2 is converted into the active species $NiR'(X)L_2$ by reactions (a) and (b). The catalytic formation of R–R′ then proceeds through the key intermediates $NiR'(X)L_2$.

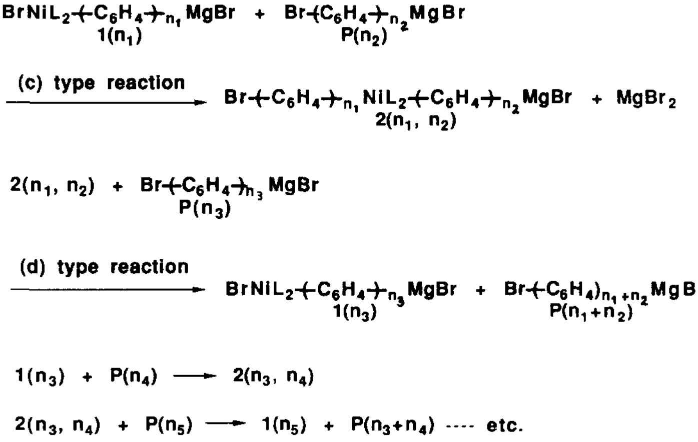
As for the coupling of R and R′ groups on Complex 2 (reaction d), coordination of the aromatic halides R′X to Ni



may take place to facilitate the coupling reaction, since coordination of a π-accepting ligand on diorganonickel(II) complexes strongly enhances the reductive coupling of the organic groups on Ni.[1]

If the same mechanism shown above can be applied to the present polymerization of $p\text{-}C_6H_4Br_2$, it seems to proceed as follows: where P(*n*) stands for the polymer having *n* phenylene units and P(1) represents the monomer $p\text{-}BrC_6H_4MgBr$ which is the main product of the reaction between $p\text{-}C_6H_4Br_2$ and Mg. $1(n_1)$, $2(n_1,\ n_2)$.... represent intermediate nickel complexes 1 and 2 having phenylene groups bonded to nickel.

Figures 2 and 3 show IR spectra of some of the prepared poly(arylene)s, and Fig. 4 shows X-ray diffraction patterns of some of the poly(arylene)s. The IR spectrum of poly(*p*-phenylene) prepared by the present method is essentially the same as those of poly(*p*-phenylene)s prepared by other methods such as oxidative cationic polymerization of benzene (Kovacic's method[71,72]). The out-of-plane vibration of *p*-phenylene units, δ(*para*), in poly(-phenylene)s prepared



$$\underset{1(n_1)}{\mathrm{BrNiL_2(C_6H_4)_{n_1}MgBr}} + \underset{P(n_2)}{\mathrm{Br(C_6H_4)_{n_2}MgBr}}$$

$$\xrightarrow{\text{(c) type reaction}} \underset{2(n_1,\ n_2)}{\mathrm{Br(C_6H_4)_{n_1}NiL_2(C_6H_4)_{n_2}MgBr}} + \mathrm{MgBr_2}$$

$$2(n_1,\ n_2) + \underset{P(n_3)}{\mathrm{Br(C_6H_4)_{n_3}MgBr}}$$

$$\xrightarrow{\text{(d) type reaction}} \underset{1(n_3)}{\mathrm{BrNiL_2(C_6H_4)_{n_3}MgBr}} + \underset{P(n_1+n_2)}{\mathrm{Br(C_6H_4)_{n_1+n_2}MgBr}}$$

$$1(n_3) + P(n_4) \longrightarrow 2(n_3,\ n_4)$$

$$2(n_3,\ n_4) + P(n_5) \longrightarrow 1(n_5) + P(n_3+n_4) \text{ ---- etc.}$$

Scheme 1.

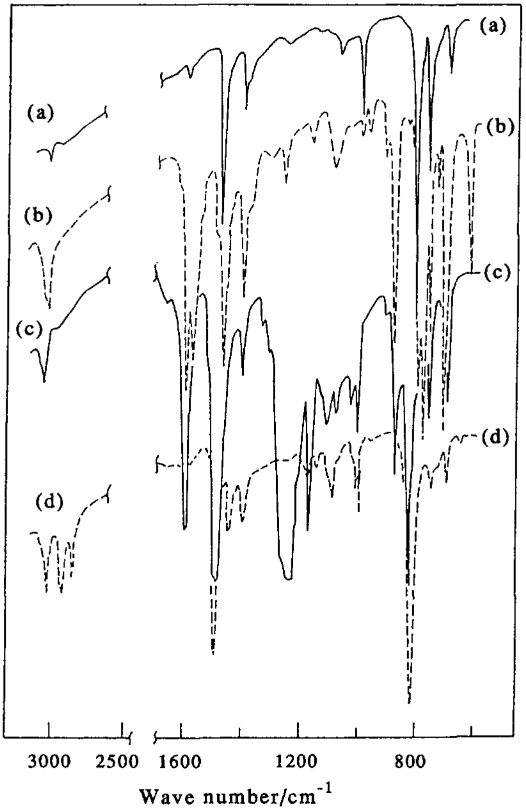
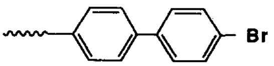
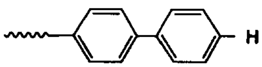


FIG. 2. IR spectra of (a) poly(p-phenylene) (PPP) prepared from p-$C_6H_4Br_2$; (b) poly(m-phenylene) (PMP); (c) poly(oxybiphenylene); (d) poly(phenylenemethylene).[30]

under various conditions appears in the region 805 ± 5 cm^{-1}. Weak v(C–Cl), v(C–Br), and v(C–I) bands of terminal p-halophenyl groups are observed at 1085, 1065, and 1055 cm^{-1}, respectively, in the IR spectra of poly(p-phenylene)s prepared from the corresponding p-dihalobenzenes. In addition to the δ(*para*) band at 805 ± 5 cm^{-1} assignable to the p-phenylene units, the IR spectrum of poly(p-phenylene) shows two out-of-plane vibration bands due to terminal phenyl groups at 760 cm^{-1} (δ(mono$_1$)) and 690 cm^{-1} (δ(mono$_2$)).[71] These IR spectroscopic data suggest that the poly(p-phenylene) has both p-halophenyl and phenyl groups as the terminal groups:





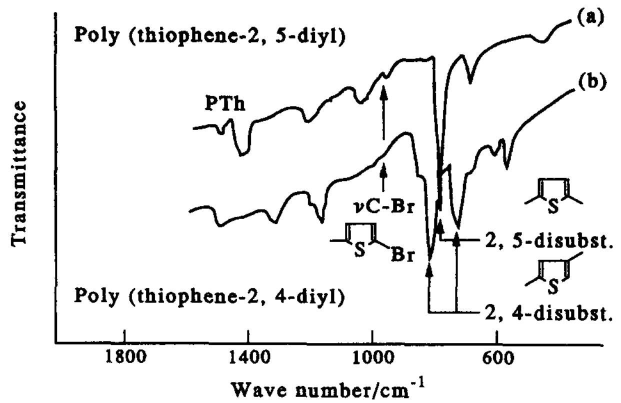


FIG. 3. IR spectra of (a) poly(thiophene-2,5-diyl) PTh; and (b) poly(thiophene-2,4-diyl) prepared from 2,5-dibromothiophene and 2,4-dibromothiophene, respectively.[39]

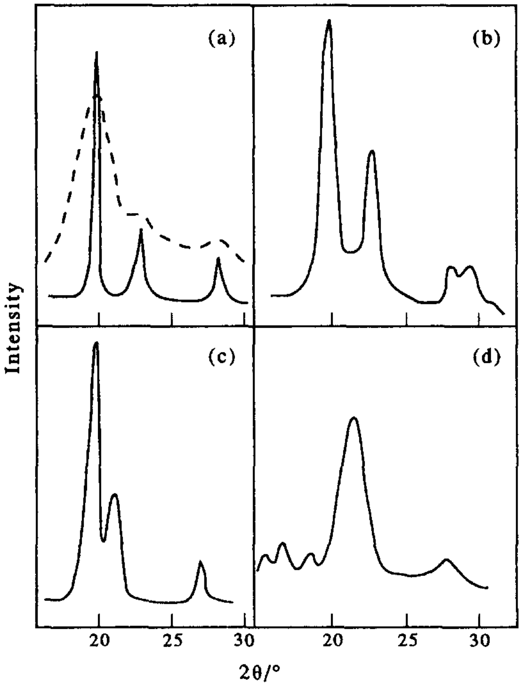


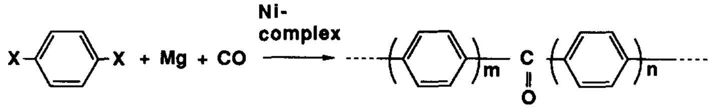
FIG. 4. Powder X-ray diffraction patterns (CuK$_\alpha$) of (a) poly(*p*-phenylene) (PPP); (b) poly(oxybiphenylene); (c) poly(phenylene-methylene); and (d) poly(*m*-phenylene) PMP.[30] Data of PPP prepared by oxidation of benzene by CuCl$_2$ in the presence of AlCl$_3$[71,72] are also shown by a broken line in (a).

The fact that the intensities of the bands due to the terminal phenyl group ($\delta(\text{mono}_1)$ and $\delta(\text{mono}_2)$) are much greater than that of v(C–X) band suggests that the proportion of the terminal group bearing the halogen is not high.

Kovacic and Oziomek took the relative intensity of $\delta(para)$ to that of $\delta(\text{mono}_1)$, and $\delta(\text{mono}_2)$, $A(\delta(para))/\{A(\delta(\text{mono}_1)) + A(\delta(\text{mono}_2))\}$ (A = absorbance of the peak), as a measure for the degree of polymerization.[71,72] The value $A(\delta(para))/\{\text{A}(\delta(\text{mono}_1)) + A(\delta(\text{mono}_2))\}$ for poly(p-phenylene) prepared from dibromobenzene with various catalysts lies between 1.92 (No. 2, Table 1) and 3.85 (No. 7, Table 1). This indicates that poly(p-phenylene)s obtained by this method have relatively high degrees of polymerization, comparable to those of polymers prepared by Kovacic and Oziomek through oxidative cationic polymerization of benzene.[71]

The IR spectrum of PTh gives rise to a different absorption pattern from that of poly(thiophene-2,4-diyl) in the out-of-plane δ(CH) vibration region (Fig. 3). PTh can be also prepared through electrochemical[73,74] and chemical[74,75] oxidation of thiophene, and PTh's thus prepared may contain some of the thiophene-2,4-diyl unit, as shown by comparison of their IR spectra with those shown in Fig. 3.

PPP prepared by dehalogenation condensation gives rise to three main X-ray diffraction bands with good sharpness between 2θ = 18° and 30° (CuK_α). The three bands are regarded as associated with the diffractions from the *ab* planes (*c* axis is the direction of the polymer chain). PTh affords three main X-ray diffraction bands at almost the same 2θ values as those of PPP, and two-dimensional structures with the same *ab* parameters.[76–78] Unannealed PPP prepared by oxidation of benzene with CuCl_2–AlCl_3 (Kovacic's method) gives rise to somewhat broad X-ray diffraction bands (cf. broken line in Fig. 4a). Preparation of PPP in the presence of carbon monoxide gives PPP with some ketone groups in the chain.[79]



2.2. *Synthesis using zinc as the reducing reagent for Ni(II) complexes*

Table 3 summarizes results of Ni-catalyzed dehalogenation polycondensation of 2,5-dibromothiophene, 3-methyl-2,5-dibromothiophene, and p-diiodobenzene with zinc.[31] Palladium compounds also show

$$n\text{X–Ar–X} + n\text{Zn} \xrightarrow{\text{Ni- or Pd-catalyst}} \left(\text{Ar}\right)_n \qquad (17)$$

similar catalytic activity (run 3). PTh, PRTh (R = CH_3) and PPP thus prepared have essentially the same structures as those of the polymers prepared by other

TABLE 3. Ni- or Pd-catalyzed dehalogenation polycondensation of dihaloaromatic compounds with zinc[31]

Run no.	Monomer* (amount in mmol)	Catalyst (amount in mmol)	Amount of Zn in mmol	Additive (amount in mmol)	Solvent†	Temp. (°C)	Time (h)	Yield‡ (%)
1	$C_4H_2SBr_2$ (18)	$NiCl_2(dpe)$ (0,2)	54	None	HMPA	150	2	78
2	$C_4H_2SBr_2$ (18)	$NiBr_2(PPh_3)_2$ (1,8)	54	NEt_4I (36)	DMF	100	8	30
3	$C_4H_2SBr_2$ (18)	$PdCl_2$ (0,7)	65	NEt_4I (44) + PPh_3 (3)	Benzene	80	20	60
4	$C_5H_4SBr_2$ (42)	$NiBr_2(PPh_3)_2$ (1,3)	65	NEt_4I (87)	Benzene	80	5	62
5	$C_6H_4I_2$ (11)	$NiBr_2(PPh_3)_2$ (0,5)	30	NEt_4I (20) + PPh_3 (2)	DMF	150	18	66

* $C_4H_2SBr_2$, 2,5-dibromothiophene; $C_5H_4SBr_2$, 3-methyl-2,5-dibromothiophene; $C_6H_4I_2$, 1,4-diiodobenzene.

† HMPA, hexamethylphosphoric triamide; DMF, *N*,*N*-dimethylformamide.

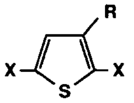
‡ Based on carbon recovered.

methods, as revealed by IR and X-ray diffractometry. Since the basic C–C coupling reaction (eq. 3) is applicable to organic halides with functional groups such as –COR and –CN and to reaction systems using polar solvents such as HMPA and DMF, the polycondensation can also be carried out by using 2,5-dibromothiophene with –CHO, –CH=NOH, or –CN substituents at the 3-position, which are sensitive to the Grignard reagent and cannot be polymerized by the X–R–MgX mediated method (eq. 12). However the *Mn* values of the products obtained using these unique monomers, so far, have not been high (*Mn* = 520–630).[80] On the other hand, Ueda and his coworkers[81,82] applied the Ni-catalyzed polycondensation using Zn, to the preparation of aromatic polyether-polyketones and poly(3-phenyl-2,5-thienylene) PRTh (R = C_6H_5) from the corresponding organic dihalides. Their polymers had [η] values of 0.50–0.87 dl g^{-1}.

2.3. *Synthesis by using Ni(0) complexes*

Since coupling reaction 4 proceeds under mild conditions, it can be applied to a wide range of aromatic compounds (e.g. those with carbonyl and cyano group) under various reaction conditions (e.g. in various solvents), and is the most direct and simple reaction among the Ni-based coupling reactions. Method III, expressed in reaction 9, is expected to provide a versatile means for molecular design and synthesis of electrically conducting π-conjugated polymers.

Polycondensation of the following dihaloorganic compounds affords π-conjugated polymers with well-defined linkages between the monomer units, to be suited to the investigation of crystal structure and doping processes of the polymers.[33]



R = H, X = Br (2,5-Br$_2$-Th)

R = H, X = Cl (2,5-Cl$_2$-Th)

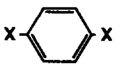
R = CH_3, X = Br (2,5-Br$_2$-MeTh)

R = n-C_6H_{13}, X = I (2,5-I$_2$-HexTh)

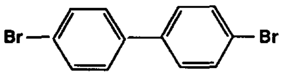
R = n-C_8H_{17}, X = I (2,5-I$_2$-OctTh)

R = n-$C_{12}H_{25}$, X = I (2,5-I$_2$-DodTh)

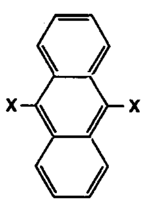
R = CN, X = Br (2,5-Br$_2$-CNTh)



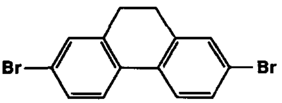
1,4-X$_2$-Ben
(X = Cl, Br, I)



4,4'-Br$_2$-diBen



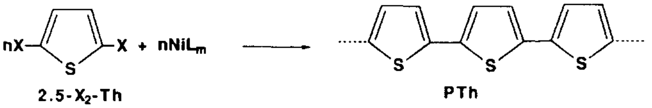
9,10-X$_2$-Anth
(X = Cl, Br)



2,7-Br$_2$-9,10-H$_2$Phen

Table 4 summarizes results of polymerization of 2,5-dihalothiophene, 1,4-dibromobenzene and related monomers. As the dehalogenating Ni(0)-complex, mixtures of bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$, and neutral ligand L were primarily employed.[33]

As shown in runs 1–6 in Table 4, the dehalogenation polycondensation of 2,5-Br$_2$–Th with a mixture of Ni(cod)$_2$ and PPh$_3$ proceeds smoothly in the temperature range 25 through 100°C. On mixing 2,5-Br$_2$–Th with the Ni(0)-complex, precipitation of reddish brown polymer starts immediately, and the best yield is attained at 60–80°C. The polymer obtained has the following π-conjugated PTh structure as revealed by its analytical data and comparison of its IR spectrum with that of the above described PTh.[39] Most of the obtained



(18)

PTh was unextractable by hot CHCl$_3$, indicating that most of the PTh had a molecular weight higher than 3000.[39] Even at short polymerization time (2 h, run 6), a quantitative yield is almost attained. However, PTh obtained after short polymerization time had a relatively high content of Br (3.9%), and the content of Br decreased to 1.8% (at 8 h at 60°C) and 0.7% (at 16 h at 60°C, run 3) with increasing polymerization time, revealing that the chain growth by coupling of the seemingly insoluble precipitate of PTh having a terminal C–Br bond, proceeded even after the formation of the precipitate. The CHCl$_3$-extractable fraction of PTh decreased from 3.2 to 1.2% with increase in the polymerization time from 2 to 16 h at 60°C.

Ni(PPh$_3$)$_4$ also affords PTh (run 7), however the yield is lower, indicating that the coordinatively saturated Ni(PPh$_3$)$_4$ has lower reactivity compared with the mixture of Ni(cod)$_2$ and PPh$_3$. Use of bpy, instead of PPh$_3$, affords similar results (runs 8 and 9). 2,5-Cl$_2$–Th shows lower reactivity than 2,5-Br$_2$–Th to afford lower yield (run 10). The CP-MAS ^{13}C-NMR spectrum of the present PTh (solid) shows two peaks at 136 and 125 ppm assigned to 2,5-carbon and 3,4-carbon atoms, respectively, and no other peak was observed.

Polymerization of 2,5-dihalo-3-alkylthiophenes, 2,5-X$_2$–RTh (R = CH$_3$, *n*-C_6H_{13}, *n*-C_8H_{17}, *n*-$C_{12}H_{25}$), gives the corresponding soluble poly(3-alkylthiophene-2,5-diyl)s PRTh's,[39,40,42–44, 64–66] which, in spite of the sterically large R group, are considered to have π-conjugation systems similar to that of PTh as judged from their reddish brown color and electrically conducting property.[42] On the other hand, in the case of substituted poly(acetylene)s $\left(\text{CH}=\text{CR}\right)_n$, the π-conjugation of poly(acetylene) is lost by substitution with R, and the polymer is generally white. CPK molecular models explain the difference in the results of

TABLE 4. Preparation of poly(thiophene-2,5-diyl), poly(*p*-phenylene) and related polymers by dehalogenation polycondensation of X–Ar–X with mixture of Ni(cod)$_2$ and neutral ligand L[33]

Run	Monomer (X–Ar–X)* (*concentration*, M)	Ligand†	Reaction conditions			Yield‡ (%)	Molecular weight§	
			Solvent	Temp. (°C)	Time		*Mn*	*Mw*
1	2,5-Br$_2$–Th (0.25)	PPh$_3$	DMF	100	16	92		
2	2,5-Br$_2$–Th (0.25)	PPh$_3$	DMF	80	16	100		
3	2,5-Br$_2$–Th (0.25)	PPh$_3$	DMF	60	16	100		
4	2,5-Br$_2$–Th (0.25)	PPh$_3$	DMF	40	16	80		
5	2,5-Br$_2$–Th (0.25)	PPh$_3$	DMF	25	24	74		
6	2,5-Br$_2$–Th (0.25)	PPh$_3$	DMF	60	2	100		
7	2,5-Br$_2$–Th (0.25)	Ni(PPh$_3$)$_4$‖	DMF	60	16	63		
8	2,5-Br$_2$–Th (0.25)	bpy	DMF	60	16	91		
9	2,5-Br$_2$–Th (0.25)	bpy	DMF	25	24	93		
10	2,5-Cl$_2$–Th (0.25)	PPh$_3$	DMF	60	16	55		
11	2,5-Br$_2$–3MeTh (0.25)	PPh$_3$	DMF	60	16	76		
12	2,5-I$_2$–3HexTh (0.13)	PPh$_3$	DMF	60	48	60		
13	2,5-I$_2$–3HexTh (0.25)	bpy	DMF	60	16	70		52,000
							(74,000)	(30,300)
14	2,5-I$_2$–3HexTh (0.13)	bpy	DMF	60	48	94		190,000
15	2,5-I$_2$–3HexTh (0.18)	bpy	toluene	60	48	60		
16	2,5-I$_2$–3OctTh (0.13)	bpy	DMF	60	48	80		
				10				

17	2,5-I_2–3OctTh (0.13)	bpy	DMF	30	48	80	(15,000)	(23,000)
18	2,5-I_2–3DodTh (0.13)	bpy	DMF	60	48	87		
19	2,5-Br_2–3CNTh (0.25)	PPh_3	DMF	60	16	91		
20	2,5-Br_2–3CNTh (0.25)	bpy	DMF	25	48	60		
21	1,4-Br_2–Ben (0.20)	PPh_3	DMF	60	16	26		
22	1,4-Br_2–Ben (0.20)	bpy	DMF	60	16	99		
23	1,4-Br_2–Ben (0.20)	bpy	DMF	30	24	95		
24	1,4-I_2–Ben (0.20)	bpy	DMF	60	16	91		
25	1,4-Cl_2–Ben (0.20)	bpy	DMF	60	16	92		
26	4,4′-Br_2–diBen (0.20)	bpy	DMF	60	48	95		
27	9,10–X_2–Anth (0.10)	PPh_3	THF	60	8	0 (complex)		
28	2,7-Br_2–9,10–H_2Phen (0.13)	bpy	DMF	60	24	90		

---

* 2,5-X_2–Th = 2,5-dihalothiophene; 2,5-I_2–3RTh = 2,5-diiodo-3-alkylthiophene (R: Hex = hexyl; Oct = octyl; Dod = dodecyl); 2,5-Br_2–CNTh = 2,5-dibromo-3-cyanothiophene; 1,4-X_2–Bz = 1,4-dihalobenzene; 2,7-Br_2–9,10-H_2Phen = 2,7-dibromo-9,10-dihydrophenanthrene.

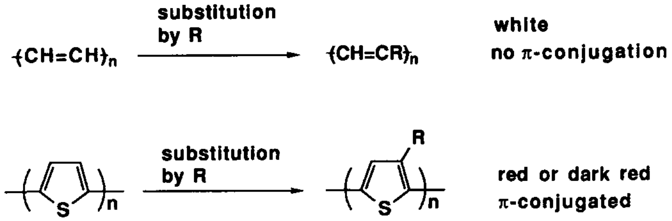
† PPh_3 = triphenylphosphine; bpy = 2,2′-bipyridyl.

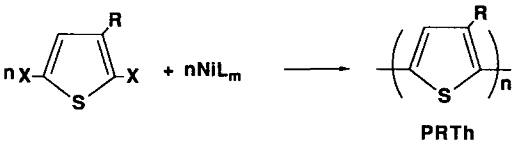
‡ Yield was calculated based on carbon recovered: (% carbon in polymer) × (weight of polymer)/(weight of carbon in monomer).

§ *Mn* = number average molecular weight; *Mw* = weight average molecular weight. The values without parentheses determined by a light scattering method, whereas the values in parentheses were determined by gel permeation chromatography (GPC).

‖ $Ni(PPh_3)_4$ was used instead of the mixture of $Ni(cod)_2$ and L.

substitution on poly(acetylene) and on PTh, containing a 5-membered ring.[42]





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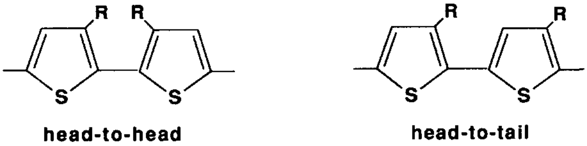
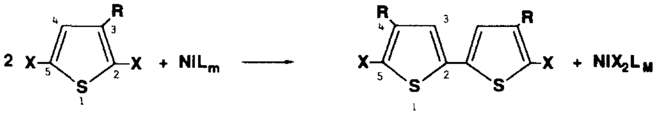
PRTh has been prepared by polycondensation *via* a Grignard intermediate,[42–45,64] oxidation of 3-alkylthiophene,[83–85] and electrochemical polymerization.[86–90] Comparison of ^{1}H-NMR spectra[90] of the variously prepared PRTh's reveals that the content of head-to-head junctions in PRTh prepared by the organometallic technique (methods using Ni(0) complex or the Grignard intermediate)



is considerably higher (ca. 60–70%) than that (ca. 10%) in PRTh's prepared by oxidation and electrochemical polymerization. In the ^{1}H-NMR spectrum of the present PRTh, the peak of the thiophene ring-attached-CH_2 protons $\delta 2.55$ ppm)[90] of the head-to-head unit is stronger than that ($\delta 2.8$ ppm) of the head-to-tail unit.

The high content of the head-to-head unit in PRTh prepared by the organometallic techniques suggests that the organometallic coupling reactions (eqs 2–4) proceed with some regio-selectivity; presumably the following 4,4′-dialkyl-5,5′-dihalo-2,2′-bithiophene is the major species formed in the initial step of the polycondensation.



(20)

Easier oxidative addition of the 5-C–X bond to Ni(0)-complex than that of 2-C–X occurs because of the steric effect of R which explains the major formation of the symmetrical bithiophene derivative shown above, and thus explains the high content of the head-to-head junction in PRTh. Increase in polymerization time (cf. runs 13 and 14 in Table 4) leads to increase of molecular weight of poly(3-hexylthiophene-2,5-diyl). The weight-averaged molecular weight *Mw* of PRTh determined by the light scattering method roughly agrees with that determined by GPC method (polystyrene standard, cf. run 13). PRTh shows a π–π^* absorption band at 380–400 nm in $CHCl_3$. Both the present PTh and PRTh have good thermal stability; the TGA analysis under N_2 shows residual weight of 80% at 600°C and 81% at 400°C for PTh and PRTh ($R = n\text{-}C_{12}H_{25}$), respectively. Polymerization of 2,5-Br_2-CNTh (runs 19 and 20) gives the corresponding poly(3-cyanothiophene-2,5-diyl) whose IR spectrum shows $v(C{\equiv}N)$ vibration at $2200\,cm^{-1}$. This polymer is sparingly soluble in organic solvents.

Polymerization of 1,4-X_2-Ben and 4,4′-Br_2-diBen affords yellow and fluorescent PPP in high yield when it is carried out in the presence of bpy (runs 22–26). However, carrying out the polymerization in the presence of PPh_3 (run 21) affords PPP in only low yield. The difference between the two polymerizations may be attributed to the difference in the configuration of the intermediate nickel(II) complexes formed by using bpy and PPh_3. The polymerization is now assumed to proceed through oxidative addition of 1,4-X_2-Ben to a Ni(0) complex to form a (4-halophenyl)halonickel(II) complex $L_mNiX(C_6H_4X)$, disproportionation of $L_mNiX(C_6H_4X)$ to afford a di(4-halphenyl)nickel(II) complex $L_mNi(C_6H_4X)_2$, and reductive elimination of $XC_6H_4C_6H_4X$ from $L_mNi(C_6H_4X)_2$. A propagation process involving coupling between $X(C_6H_4)_XX$ and $X(C_6H_4)_yX$ is also accounted for by similar basic reactions.

$$\text{1,4-X}_2\text{-Ben} + \text{NiL}_m \xrightarrow[\text{addition}]{\text{oxidative}} \text{L}_m\text{NiX(C}_6\text{H}_4\text{X)} \qquad (21)$$

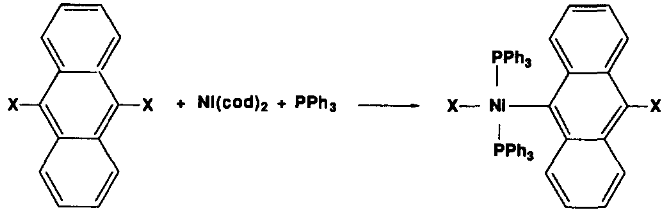
$$\xrightarrow{\text{disproportionation}} \text{Ni(C}_6\text{H}_4\text{X)}_2\text{L}_m + \text{NiX}_2\text{L}_m \qquad (22)$$

$$\Big\downarrow \begin{array}{l}\text{reductive}\\ \text{elimination}\end{array} \qquad (23)$$

$$\text{X-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-X}$$

Such basic reactions shown above have been well established in organometallic chemistry,[1-13,25] and it is known that tertiary phosphine ligands like PPh_3 usually afford *trans*-Ni(II) complex[91,92] whereas the bidentate bpy ligand definitely affords *cis*-Ni(II) complex. The reductive elimination usually proceeds more easily in the *cis*-type complex than the *trans*-type complex,[1-13,93-96] and the disproportionation reaction involving exchange of the anionic ligands X and C_6H_4X (eq. 22) also may proceed more easily in the *cis*-type complex.

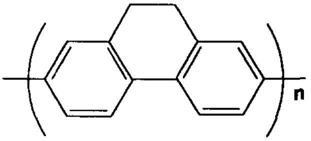
In the case of 9,10-X_2-Anth (run 27), its reaction with a mixture of $Ni(cod)_2$ and PPh_3 affords a complex corresponding to $L_mNiX(C_6H_4X)$, Complex 1, in high yield, and it has been revealed that the 10-C–X bond in Complex 1 is inert toward excess Ni(0) complex, presumably due to the steric hindrance of the bulky anthryl group and the decrease in electrophilicity of the 10-carbon in Complex 1, caused by back donation from nickel. Complex 1 has high thermal and chemical stability; it is stable not only in boiling toluene under air for several hours but also in hydrochloric acid (2 M) in a dispersion system. In the case of Complex 1, the steric effect[91] of the bulky anthryl group as well as partial formation of double bonds between nickel and the aromatic group[97] accounts for the high stability of the Ni–carbon bond. Due to the extremely high stability of the Ni–carbon bond, 9,10-X_2-Anth does not afford the polymer (run 27). Addition of bpy, instead of PPh_3, as the neutral ligand does not afford the polymer, either. Use of 2,7-Br_2-9,10-H_2Phen as the monomer (run 28) yields a yellow fluorescent polymer, PH_2Phen, which is partly soluble in $CHCl_3$ and N-methylpyrrolidone (NMP).



(24)

Complex 1a (X = Br)

Complex 1b (X = Cl)



PH_2Phen

The yellow color and the fluorescent property support that the obtained polymer has a π-conjugation system similar to that of PPP. The IR spectrum of the polymer shows peaks of two categories, one originating from the PPP-like structure (e.g. δ(CH) at 814 cm^{-1}) and another from the ethylene unit (e.g. v(CH) at 2930, 2890, and 2830 cm^{-1}). Use of BrCH=CHBr in combination with the mixture of Ni(cod)$_2$ and neutral ligand (PPh$_3$ or bpy) gives a black solid, whose IR spectrum is similar to that of *trans*-poly(acetylene),[98] showing a characteristic sharp absorption peak at 1010 cm^{-1}, whereas an attempt to polymerize BrCH=CHBr by nickel-catalyzed polycondensation with Mg (eq. 7) leads only to evolution of gas (presumable acetylene). Since the Ni(0) complex can be generated by electrochemical reduction[99,100] of the Ni(II) complex, and the Ullmann type C–C coupling (eq. 4) can be achieved using the electrochemically generated Ni(0)-complex,[101] the present polymerization can also be carried out electrochemically starting from the dihaloaromatic compounds as the monomer and Ni(II) complexes (e.g. [Ni(bpy)$_3$]Br$_2$) as the catalyst; details of the electrochemical polymerization will be reported elsewhere.

The PPP prepared by using the Ni(0) complex seems to have higher molecular weight than the PPP's prepared by the Ni-catalyzed Grignard-reagent mediated dehalogenation polycondensation of 1,4-X$_2$–Ben (eq. 7) and by the Kovacic method,[71,72] as judged from its IR spectrum and relatively low bromine content. The IR spectrum of the present PPP shows out-of-plane vibration at 804 ± 2 cm^{-1} (δ(*para*)) and those of the terminal phenyl unit at 760 (δ(mono$_1$)) and 690 cm^{-1} (δ(mono$_2$)). As described above, it is generally accepted that the following R value

$$R = \frac{A(\delta(para))}{A(\delta(\mathrm{mono}_1)) + A(\delta(\mathrm{mono}_2))} \qquad (25)$$

A: Absorbance

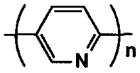
increases with the degree of polymerization of PPP.[30,71,72]

The IR spectrum of the present PPP shows very weak δ(mono$_1$) and δ(mono$_2$), and the R value for the present PPP (R value = 12.7) is much larger than those for PPP's reported by Kovacic and his coworkers[71] (R value = 4.6) and prepared by the Grignard reagent-mediated polycondensation of 1,4-1-Br$_2$Ben (R value = 1.9–3.9). This fact, together with the relatively low content of bromine, indicates that the present PPP has a relatively high degree of polymerization. The present PPP contains 2.7% of bromine. This bromine content corresponds to a molecular weight of 2960 (*DP* (degree of polymerization) of 38) and 5930 (*DP* of 76), if the polymer has bromine at one terminal unit or at both terminal units, respectively. If the present PPP has bromine at only one terminal unit, another terminal unit is regarded to be a phenyl group, which is considered to originate from the intermediate Ni(C$_6$H$_4$)-polymer species (cf. eqs 21–23) giving C$_6$H$_5$-polymer species during work up after polymerization. CP/MAS ^{13}C-NMR spectrum of the present PPP (solid) shows two peaks at 137 and 127 ppm assigned to 1,4-carbons and 2,3-carbons, respectively. No signal assignable to terminal carbon (C–X or C–H) was observable. As for poly(pyridine-2,5-diyl) (PPy) prepared analogously by using 2,5-dibromopyridine and Ni(0) complex, the polymer is soluble in formic acid and has a degree of polymerization of 20–50 (determined by light scattering method) depending on preparative conditions.[32,102]

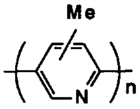
Various poly(arylene)s including the following polymers have been also prepare by dehalogenation polycondensation using Ni(0) complexes.

$$n\ X\text{-}Ar\text{-}X\ +\ n\ Ni(0)L_m \longrightarrow -\!(Ar)\!-_n\ +\ n\ NiX_2L_m \tag{26}$$

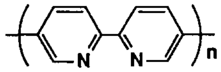
$-\!(Ar)\!-_n$:



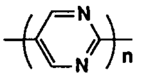
PPy Mw = 3,800



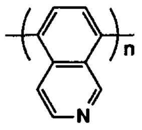
PRpy Mw = 12,000-27,000
[η] = 1.0-1.6



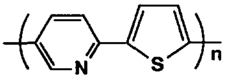
PBpy Mw = 3,200



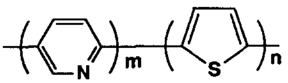
PPyrim Mw = 82,000



PQ and its analogues Mw = ca. 5,000-25,000



Copoly 1 Mw = 5,400



Copoly 3 Mw = ca. 5×10^4-5×10^6

2.4. *Synthesis by using Pd-catalyzed coupling reactions between aryl dihalides and diethynylarenes*

Table 5 summarizes results of the Pd-catalyzed polycondensation between

TABLE 5. Pd-catalyzed polycondensation between X–Ar–X and p-$C_6H_4(C{\equiv}CH)_2$ (A) or p-$C_6H_4(C{\equiv}CMgBr)_2$ (B)

Run	X–Ar–X†	Catalyst	Time (h)	Yield‡ (%)	Polymer obtained
		Method IV: Diacetylenic compound = A*			
1	$C_6H_4Br_2$	$Pd(PPh_3)_4$ + 2CuI	2	79	Polyyne-1
2	$C_6H_4I_2$	$Pd(PPh_3)_4$ + 2CuI	2	97	Polyyne-1
3	$C_4H_2SBr_2$	$Pd(PPh_3)_4$ + 2CuI	2	84	Polyyne-2
4	$C_{14}H_8Br_2$	$Pd(PPh_3)_4$ + 2CuI	2	93	Polyyne-3
5	$C_5H_3NBr_2$	$Pd(PPh_3)_4$ + 2CuI	2	95	Polyyne-4
6	$C_6H_4(COCl)_2$	$Pd(PPh_3)_4$ + 2CuI	3	64	Polyyne-5
		Method V: Diacetylenic compound = B§			
7	$C_6H_4I_2$	$Pd(PPh_3)_4$	2	97	Polyyne-1
8	$C_4H_2SBr_2$	$Pd(OAc)_2$ + $2PPh_3$	3	82	Polyyne-2
9	$C_6H_4(CH_2Cl)_2$	$Pd(OAc)_2$ + $2PPh_3$	3	72	Polyyne-6

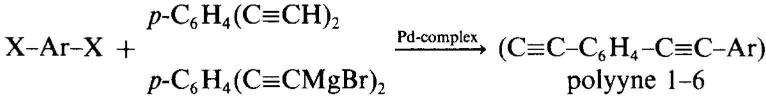
* Excess NEt_3 was added. In toluene under reflux. Amount of Pd catalyst = 0.01 mol per mol of X–Ar–X.

† $C_5H_3NBr_2$ = 2,6-Dibromopyridine; $C_6H_4(CH_2Cl)_2$ = p-Bis(chloromethyl)benzene.

‡ Yield based on the weight of carbon in the polymer (calculated from the weight and carbon content of polymer). Yield after removing toluene extractable fraction (see Experimental).

§ In THF under reflux. Amount of Pd catalyst = 0.01 per mol of X–Ar–X.

X–Ar–X and p-$C_6H_4(C{\equiv}CH)_2$ (Method IV, eq. 10) or p-$C_6H_4(C{\equiv}CMgBr)_2$ (Method V, eq. 11).[35]



$$\text{X–Ar–X} + \begin{matrix} p\text{-}C_6H_4(C{\equiv}CH)_2 \\ p\text{-}C_6H_4(C{\equiv}CMgBr)_2 \end{matrix} \xrightarrow{\text{Pd-complex}} \underset{\text{polyyne 1–6}}{(C{\equiv}C\text{–}C_6H_4\text{–}C{\equiv}C\text{–Ar})_n} \qquad (27)$$

Polyynes 1–6 are obtained in high yields. They, except for polyyne 5, show absorption in the visible region and strong fluorescence as summarized in Table 6. Marvel and his coworkers have expanded the Pd-catalyzed polymerization to the synthesis of similar polymers with the –C≡C– and arylene units.[103]

TABLE 6. Color and fluorescence of Polyynes 1–6

Polymer	Color	Fluorescence
Polyyne-1	yellow	bluish purple
Polyyne-2	yellow	bluish purple
Polyyne-3	red	green
Polyyne-4	light yellow	purple
Polyyne-5	white	none
Polyyne-6	yellow	purple

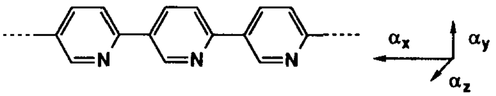
3. STRUCTURE

3.1. *Structures in the solid and solutions*

As shown in Fig. 4, PPP and related aromatic hydrocarbon π-conjugated polymers are crystalline. X-ray diffraction pattern of PTh also reveals high crystallinity of the polymer. PPP and PTh are considered to have rigidly linear rod-like structures.

In the case of PPy, it is soluble in formic acid, and its rigidly linear structure in the solution has been revealed by the large degree of depolarization (ρ_v = 0.31–0.33[32,49]) of polarized laser light.[104] On the other hand, PRpy ($R = CH_3$)[60] and PRTh ($R = n\text{-}C_6H_{13}, n\text{-}C_8H_{17}$)[33] in formic acid and $CHCl_3$, respectively, give a ρ_v value of 0, indicating that they take random coil structures in the solutions presumably due to the steric effect of the R group. Copolymers 1 and 3 also take the random coil structure in formic acid.

The theoretical limiting value of ρ_v for ideally linear molecules with strong anisotropy of polarizability ($\alpha_X \gg \alpha_y, \alpha_z$) of the molecule is 1/3, and observation of the limiting value for PPy indicates that the PPy molecules take the rigidly linear structure. PQ also takes such a rigid structure in formic acid.[55] Formic acid seems to mainly serve as a simple solvent for PPy, PMePy, and PQ and essentially seems not to form salts with these polymers, as judged by recovery of the original polymers by natural evaporation of formic acid from the solutions under air. Both the linear PPy and PQ and non-linear PRpy and PRTh show large specific refractive index increments ($\Delta m/\Delta c$ = 0.35–0.60 cm^3 g^{-1} [33,49]) compared with usual non-conjugated polymers ($\Delta n/\Delta c$ = 0.1–0.2 cm^3 g^{-1}) due to the presence of mobile π-electrons along the polymer chain.



Pv = 0.33,
$\alpha_x \gg \alpha_y, \alpha_z$

Since PPy takes the rigidly linear structure, it shows the following interesting optical properties:

(a) Painting of polymer film (e.g. film of poly(vinyl alcohol)) with a formic acid solution of PPy and ensuing removal of formic acid affords the polymer film with the linear PPy molecule in its surface region. Elongation of the polymer film leads to the alignment of the PPy molecules in the surface region (Fig. 5a), and irradiation of polarized light to the elongated polymer film (Fig. 5b) shows strong dichroism of the film (Fig. 6). When the direction of the oscillating electric field of the polarized light coincides with the direction of the elongation ($\theta = 0$ in Fig. 5b), the film absorbs the light strongly (Fig. 6(a)). On

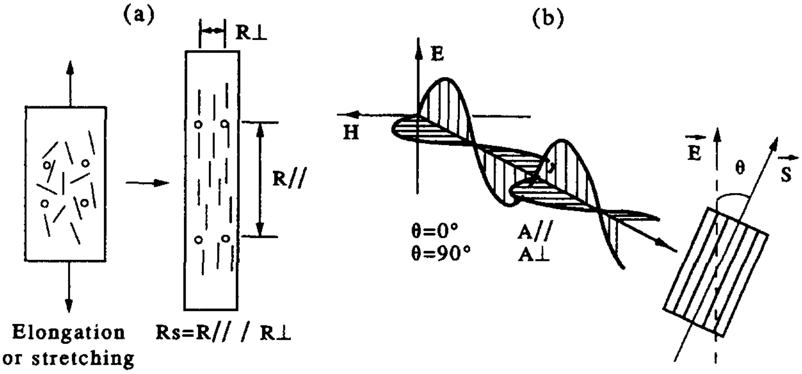


FIG. 5. (a) Stretching of polymer (e.g. poly(vinyl alcohol)) film containing the needle-like poly(pyridine-2,5-diyl) PPy molecules (the bars) in its surface region. (b) Irradiation of polarized light to the stretched film. Directions of the oscillating electric field of the polarized light and the stretching are shown by E and S, respectively.

the other hand, when the two directions are perpendicular to each other, the film absorbs the light only weakly (Fig. 6(b)).[105]

(b) PPy and PBpy molecules give excimer-like emission both in formic acid with relatively high concentration (e.g. 0.5 mol of monomer units dm^{-3}) and in the solid state when irradiated by UV light, whereas they show only normal monomeric fluorescence in a dilute (e.g. 2×10^{-6} mol of monomer unit dm^{-3})

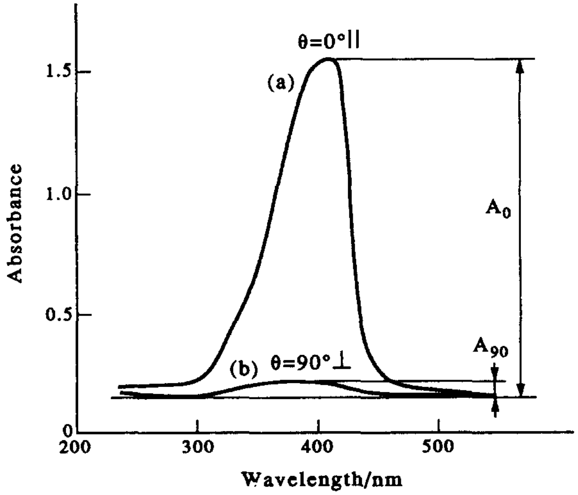
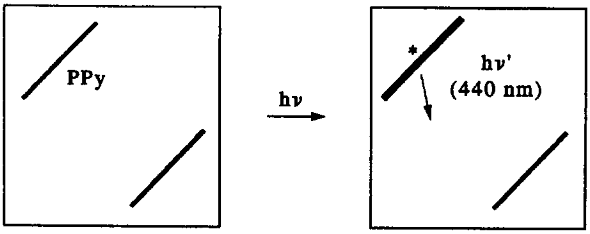
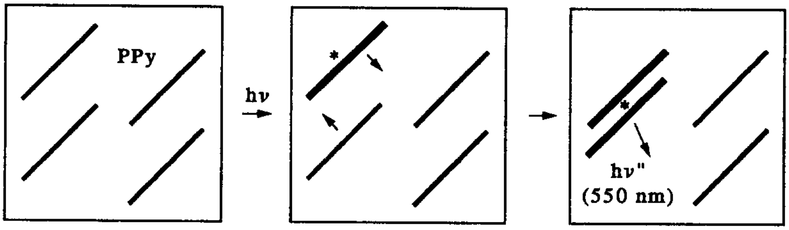


FIG. 6. Strong dichroism of the stretched poly(vinyl alcohol) film containing poly-(pyridine-2,5-diyl) (PPy) in its surface region. See Fig. 5. Measured at $\theta = 0°$ (a) and 90° (b), respectively.[102]



(a) At low concentration



(b) At high concentration

FIG. 7. Fluorescence of solutions containing a low concentration (a, e.g. 2×10^{-6} mol of monomer unit dm^{-3}) and a high concentration (b, e.g. 0.5 mol of monomer unit dm^{-3}) of poly(pyridine-2,5-diyl) (PPy).

formic acid solution of PPy.[51] As shown in Fig. 7, a photo-excited PPy molecule with an * mark will emit usual monomeric fluorescent light (λ_{max} = 440 nm) at the low concentration (Fig. 7a), whereas the photo-excited PPy molecule will form the excimer with the non-excited PPy molecule at the higher concentration (Fig. 7b) to show the excimer-like emission at λ_{max} of 550 nm. The linear structure of PPy seems to assist the formation of the excimer.

Because of the linear structure of PPP, PTh, PBpy, and PPy, vacuum evaporation of these polymers on substrates gives interesting oriented thin films of these polymers. Features of the vacuum evaporation and oriented structures of the thin films are as follows.

(i) The vacuum deposition was carried out by heating the sample in a tantalum boat at 200–350°C at 10^{-4}–10^{-5} Pa. It is reported that PPP with molecular weight of 1500–2000 corresponding to the phenylene unit of about 20 can be vaporized under vacuum.[106] Since thiophene and pyridine oligomers (e.g. α-terthiophene, bipyridine, etc.) have vapor pressure analogous to that of the corresponding benzene oligomers, we assume that PTh, PPy, and PBpy with about 20 aromatic units corresponding to the length of 8–10 nm can also be vaporized.

(ii) Figure 8 shows the electron diffraction (ED) patterns of the vacuum deposited PPP, PTh, and PBpy thin films (thickness = ca. 100 nm) on a carbon substrate.[33,107-109] The ED patterns are taken by irradiating the electron beam perpendicularly to the surface of the thin films, and the observed ED spots can

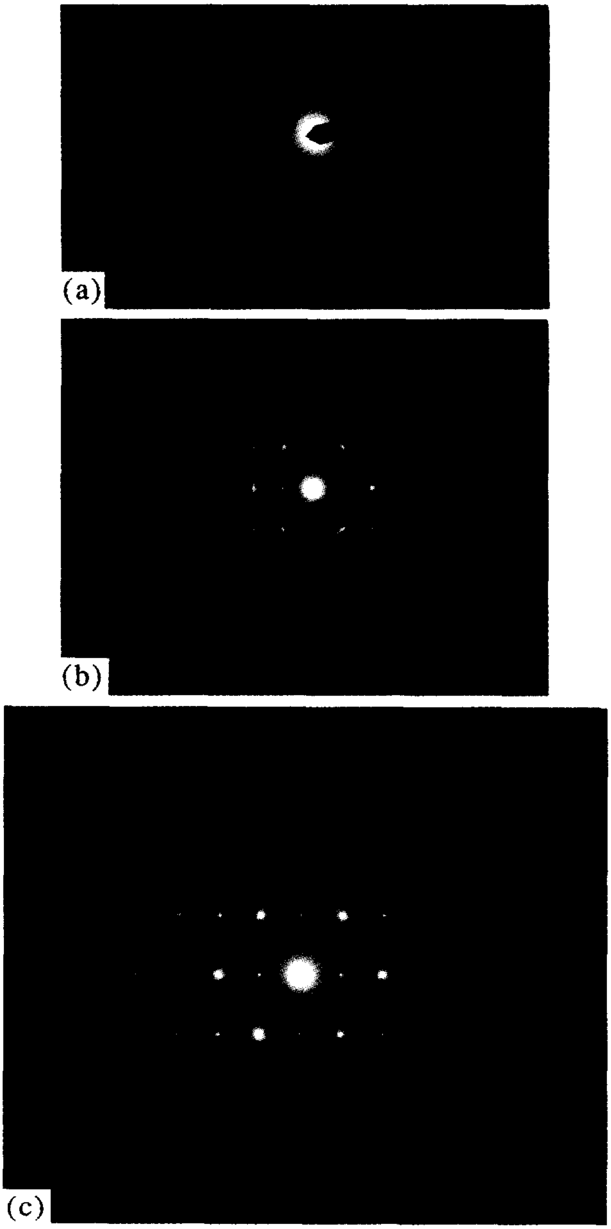


FIG. 8. Electron diffraction (ED) patterns of (a) poly(2,2′-bipyridine-5,5′-diyl) (PBpy); (b) poly(thiophene-2,5-diyl) (PTh); and (c) poly(*p*-phenylene) (PPP) deposited on carbon substrate under vacuum.[108]

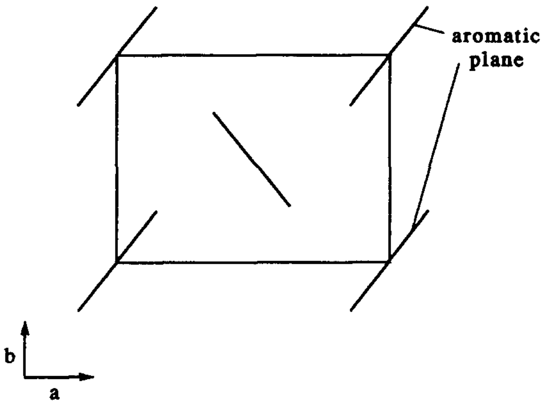


FIG. 9. Packing model for orthorhombic crystals of poly(arylene)s. The direction of the polymer chain is assigned to the *c* axis, and the aromatic plane of the monomer unit is shown by the bar.

be reasonably assigned by assuming the orientation of the polymer molecules perpendicularly to the surface of the substrate. The cross stripe ED spots are considered to be assigned to the diffraction concerning the *ab* plane (Fig. 9, *c* axis is the direction of the polymer chain) of orthorhombic crystals of poly(arylene). It is reported that PPP,[77,78] PTh,[110,111] poly(ethylene),[112] and poly(acetylene)[113] take such orthorhombic or similar crystalline structures. Comparison of the values of *ab* crystalline parameters of these polymers determined by the previously reported X-ray diffractometry and the present ED patterns is shown below and is reasonable in view of the size of the monomer unit.[108]

	PBpy	PPP	PTh	poly(ethylene)	poly(acetylene)
a(nm)	0.81	0.78	0.78	0.76	0.76
b(nm)	0.57	0.56	0.56	0.49	0.44

Molecular models for the perpendicular orientation of PPP and PTh are shown in Fig. 10.

(iii) The vacuum deposition of PPP on metal substrates also affords the oriented thin films, which show the ED patterns similar to those shown in Fig. 8. However, the number of the clearly observed ED spots varies depending on the kind of substrates, and the order of orientation judged from the number of the observable ED spots is as follows.

Order of orientation:

$$\mathrm{C} > \underbrace{\mathrm{Al} > \mathrm{Cu}}_{\text{nontransition metal}} > \underbrace{\mathrm{Ag} > \mathrm{Au}}_{\text{transition metal}} \qquad (28)$$

Number of observable diffraction spots at 150°C:

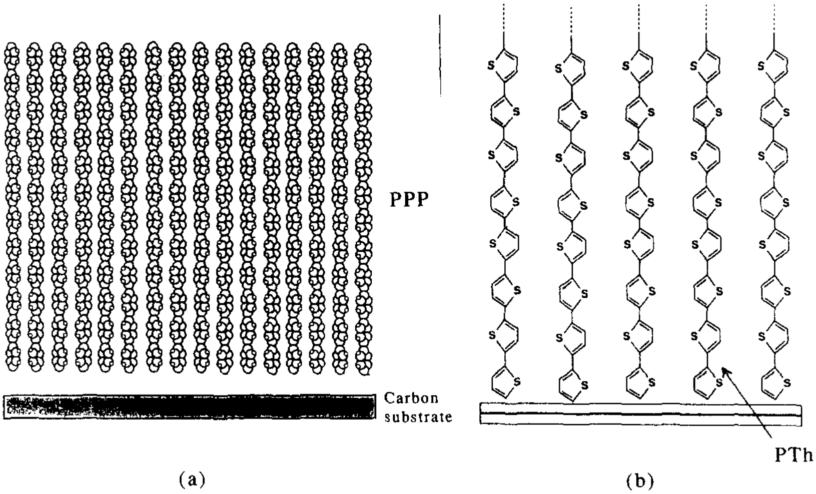


FIG. 10. Models for the perpendicular orientation of (a) poly(p-phenylene) (PPP) and (b) poly(thiophene-2,5-diyl) (PTh). Twisting of the monomer units around the bonds between the monomer units is omitted for simplification.

	66	26	10	10	10
At r.t.:					
	37	(12*)	9	7**	3†

*Separation from spots from aluminum oxides is difficult.
†Only dim spots were observed.

As for orientation or alignment of liquid crystalline molecules on substrate, it is generally recognized that the liquid crystalline molecules stand upright on the substrate when the surface energy or adhesive energy between the liquid crystalline molecules and the substrate is smaller than that between the liquid crystalline molecules themselves.[114] On the contrary, when the former energy is larger than the latter energy, the liquid molecules tend to be oriented in parallel with the surface of the substrate. The trend observed for the order of the perpendicular orientation of PPP (eq. 28) also seems to be accounted for on the basis of surface energy or strength of interaction between PPP and the substrate. It has been reported that heat of wetting H_w of carbon, aluminum, and copper in benzene, which corresponds to the monomer unit of PPP, increases in the order of

$$\mathrm{C}(H_\mathrm{W} = \text{ca. } 0.11\,\mathrm{J/M^2})^{115} < \mathrm{Al}(H_\mathrm{W} = \text{ca. } 0.20\,\mathrm{J/M^2})^{116} < \mathrm{Cu}(H_\mathrm{W} = 0.88\,\mathrm{J/M^2}).^{115} \tag{29}$$

The large H_W value of Cu seems to originate from π-coordination of benzene to

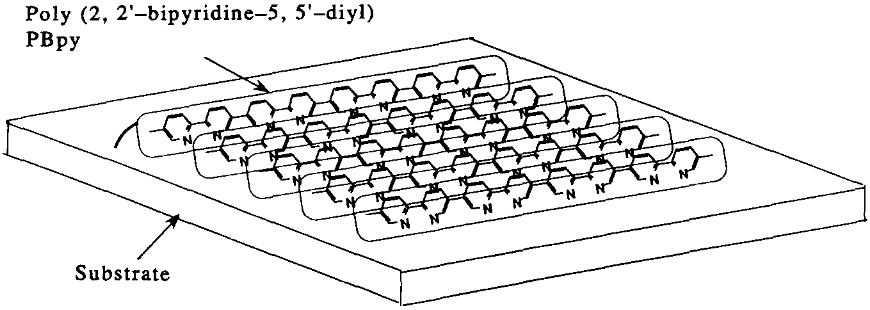
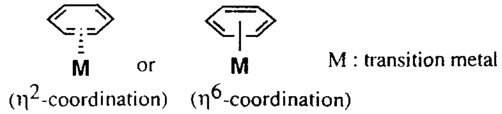


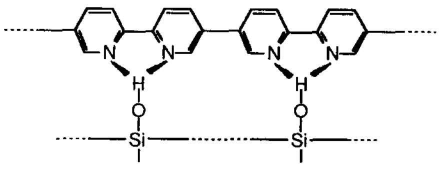
FIG. 11. Model for the parallel orientation of poly(arylene) on the surface of polar substrate.

transition metal,



and a number of π-benzene complexes of various transition metals including Cu and Ag have been isolated.[117] Thus, the higher order of the orientation of PPP on the carbon substrate seems to be attributable to the weaker interaction of the PPP molecule with carbon than the interaction with metals.

(iv) In contrast to the vacuum deposition of poly(arylene)s to the non-polar carbon and metal substrates, similar vacuum deposition of coordinating PBpy and PTh to polar substrates like glass plate, which has acidic Si–O–H groups leads to another type of orientation of the PBpy molecule, orientation along the direction of the surface.[118,119] A model for the horizontal orientation is shown in Fig. 11. Coordination of the arylene unit to the polar group accounts for such a type of orientation, e.g.



PBPy

2,2′-Bipyridine usually takes the *s-trans* structure.[120,121] However, in acidic media it takes the *s-cis* structure[122] by interaction with the acidic proton. Because of the horizontal orientation, the vacuum deposited PBpy and PTh films are SHG (second harmonic generation)-active.[118,119]

Vacuum deposition of the linear PBpy and PTh on a rubbed polyimide film leads to orientation of the polymer molecules along the direction of rubbing.[108]

The polyimide film containing the vacuum deposited polymer molecules shows dichroism, which is accounted for by assuming the orientation of the polymer molecules along the direction of rubbing.

3.2. *Structures of doped polymers*

Doping of π-conjugated polymers causes changes of the crystal structures of the polymers,[123–127] usually including expansion of the distance between the polymer chains and disordering of the polymer molecules.

We now describe reversible changes of chemical and crystallographical structures of PTh during iodine-doping and undoping. The present PTh prepared by the organometallic techniques has highly crystalline linear structure with well-defined linkage between the monomer units and is suited for the change of the structures.

Figures 12 and 13 show changes of IR spectrum and X-ray diffraction pattern of PTh during the iodine-doping and undoping with hydrazine, respectively.[33] The doping causes profound change in the IR spectrum even at relatively low doping level (iodine/PTh = 16–40 wt %, spectra b and c in Fig. 12) presumably due to the change in the electronic state of PTh. The iodine doping causes broadening of the X-ray diffraction peaks at the relatively low doping level, however, at 16 wt % of iodine per PTh (pattern b in Fig. 13) no new peak is observable.

At 40 wt % of iodine per PTh (pattern c in Fig. 13), a small broad rise at about $2\theta = 9°$ (CuKα) appears in addition to the broadening of the diffraction peaks. At 69 wt % of iodine (pattern d), the peak at about $2\theta = 9°$ due to partial formation of new structure becomes distinct, and when PTh is extensively doped (saturation doping) with iodine (120 wt %, pattern e) the X-ray diffraction pattern is entirely changed, demonstrating formation of new structure.

The four X-ray diffraction peaks observed for the extensively iodine-doped PTh at $2\theta = 8.8, 18.0, 27.0$, and $36.1°$ correspond to d values of 1.00, 0.49, 0.33, and 0.25 nm. The appearance of the X-ray diffraction peaks at $d = a/n$ ($a = 1.00$ nm, $n = 1, 2, 3, 4$) indicates a one dimensional crystalline order with a period of 1.00 nm.

Based on the X-ray diffraction data as well as resonance Raman and ^{129}I Mössbauer data,[128] PTh doped to saturation with iodine is proposed to have the packing structure shown in Fig. 14. In Fig. 14, the length of the four thiophene-2,5-diyl units [Th_4] roughly fits the length of $[I\text{–}I\text{–}I \cdots I\text{–}I]^-$, and the 120 wt % of iodine per PTh corresponds to about 5 : 8 molar ratio between $[I\text{–}I\text{–}I \cdots I\text{–}I]^-$ and Th_4. Observed strength ratios between the four new X-ray diffraction peaks of the PTh doped to saturation (Fig. 13e) roughly agrees with calculated values based on this 5 : 8 molar ratio.

The IR and powder X-ray diffraction pattern (curves f in Figs 12 and 13) after the undoping of the iodine-doped PTh with hydrazine, are essentially the same

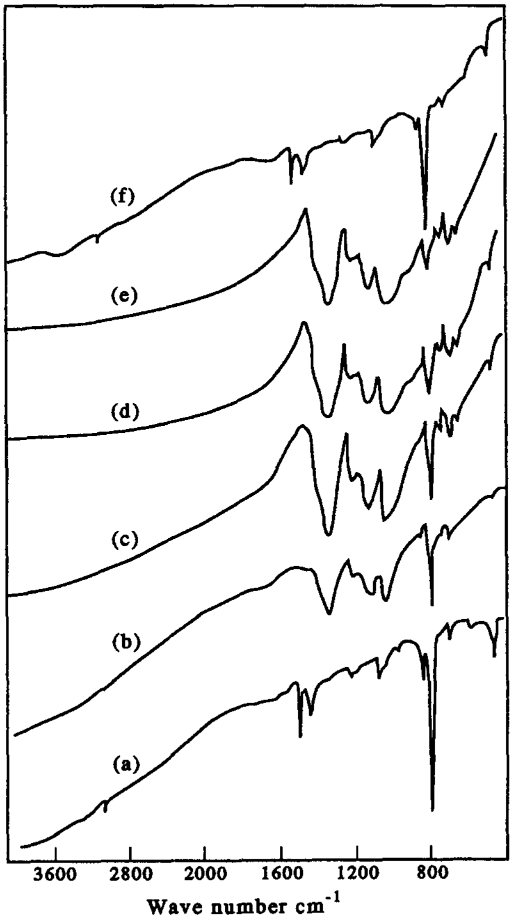


FIG. 12. Change of IR spectrum of poly(thiophene-2,5-diyl) (PTh) on doping with iodine and undoping with hydrazine.[33] (a) Original PTh; (b) iodine/PTh (wt/wt) = 0.16; (c) iodine/PTh = 0.40; (d) iodine/PTh = 0.69; (e) iodine/PTh = 1.20 (saturation doping); and (f) undoped with hydrazine.

as those of original PTh, revealing a good reversibility of the doping–undoping processes. Doping and undoping of PTh with $FeCl_3$ and hydrazine, respectively, are also reversible in view of the change in the IR spectrum, however, they are irreversible in view of the change in the X-ray diffraction pattern.

4. PROPERTIES

4.1. *Thermal stability*

As described above, PPP and other poly(arylene)s have good thermal stability

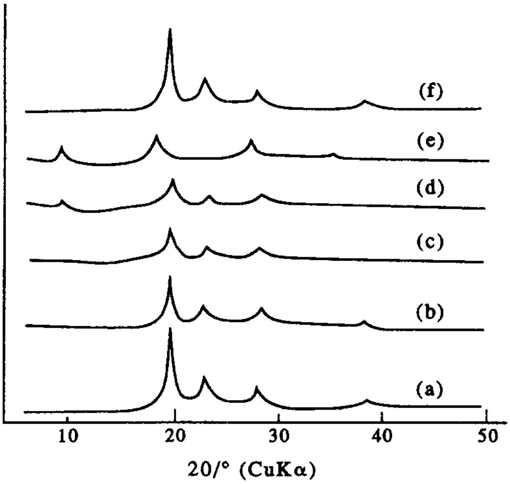


FIG. 13. Change of powder X-ray diffraction pattern of PTh on doping with iodine and undoping with hydrazine.[33] (a)–(f): as in Fig. 12.

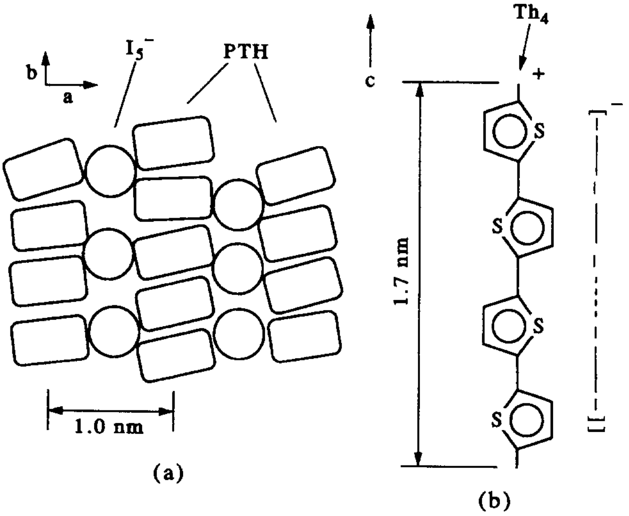


FIG. 14. Structure of PTh doped to saturation with iodine.[33]

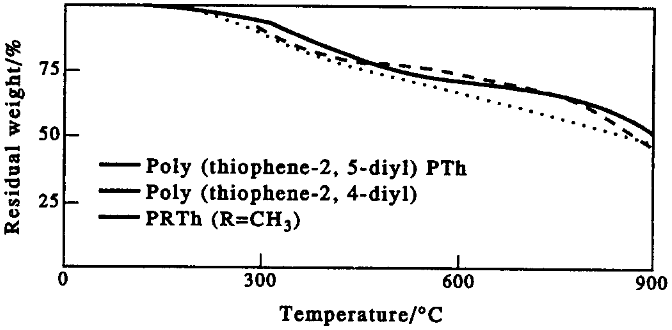


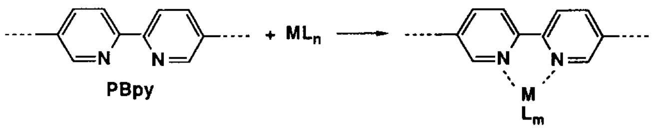
FIG. 15. Thermogravimetric analysis of poly(thiophene-2,5-diyl) (PTh), poly(thiophene-2,4-diyl), and poly(3-methylthiophene-2,5-diyl) (PRTh) ($R = CH_3$) under N_2.[39]

(Table 2). Examples of TGA curves for PTh, poly(thiophene-2,4-diyl), and Br($R = CH_3$) under N_2 are shown in Fig. 15. Heating the fluorescent yellow PPP at 350°C causes some color change to brown.

4.2. *Chemical properties*

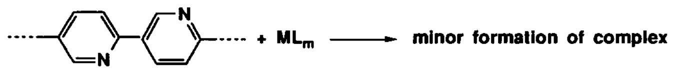
The above mentioned poly(arylene)s have high stability toward oxygen and moisture in air in contrast to high sensitivity of poly(acetylene) under air. No observable change in IR spectra has been observed for PPP and PTh stored under air for more than 15 and 13 years, respectively.

PBpy forms complexes with various metal salts and complexes,[52]



(30)

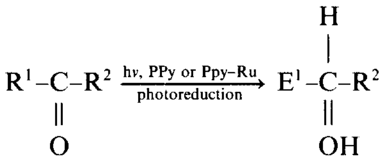
and some of the complexes show catalytic activity and unique electrochemical properties. In contrast to PBpy, Ppy has only a weak coordinating ability toward the metal compounds,[52] presumably due to the head-to-tail units of Ppy which are considered to be the main components of Ppy.



(31)

However, Yanagida and his coworkers reported that PPP–Ru[131,132] and PPy–Ru[133] systems show good visible-light-driven photocatalytic activity, e.g.

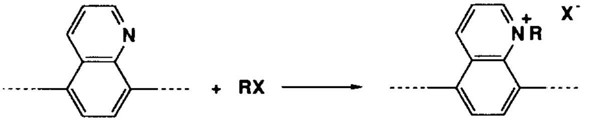
$$H_2O \xrightarrow[\text{photoreduction}]{h\nu,\ \text{PPy–Ru}} H_2 \qquad (32)$$



$$\underset{\displaystyle O}{\overset{}{R^1\text{-}\underset{\|}{C}\text{-}R^2}} \xrightarrow[\text{photoreduction}]{h\nu,\ \text{PPy or Ppy-Ru}} E^1\text{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{\overset{|}{\underset{\|}{C}}}}\text{-}R^2 \qquad (33)$$

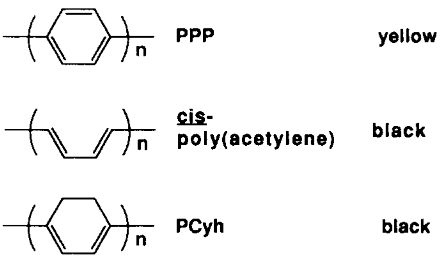
Formation of an adduct of Cu(II) with PTh and CV (cyclic voltammetry) data of the PTh–Cu complex are also reported.[129,130]

PQ and its analogues can be quaternized with organic halides.[134]

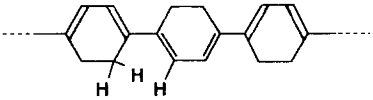


(34)

PCyh has a structure with similarities to those of both PPP and poly(acetylene).



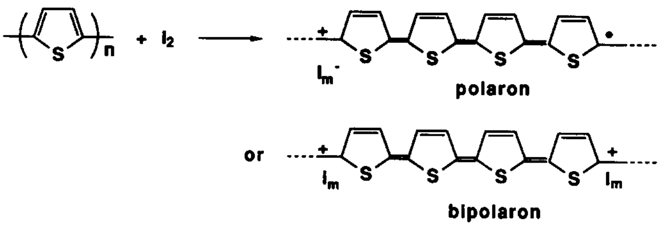
The color (black) of PCyh indicates the formation of an effective π-conjugation system along the polymer chain, presumably due to the coplanarity of the polymer chain in the following *s-cis* conformation.



In this conformation, the $=C\text{–}H$ hydrogen of the diene unit can get between the $\text{-}CH_2$ hydrogens of the $\text{-}CH_2\text{-}CH_2\text{-}$ unit, to form the planar polymer chain. In the case of PPP, coplanarity of the polymer chain is not possible due to the steric repulsion between the *o*-hydrogens. PCyh is air-sensitive and oxidized by oxygen in air, similarly to poly(acetylene); the high sensitivity of PCyh and poly(acetylene) seems to be related to the effective π-conjugation of the polymers.

4.3. *Electrically conducting properties*

4.3.1. *Chemical doping* — Conversion of π-conjugated polymers into electrically conducting materials by chemical doping has been widely investigated, and a number of books have been published concerning the electrically conducting π-conjugated polymers.[135-142] Chemical doping by adding electron-acceptor (e.g. iodine, $FeCl_3$, AsF_5, etc.) or electron donor (e.g. Na, Li, etc.) to the polymer is considered to generate positive carrier (hole) or negative carrier (electron) in the π-conjugated system, and models for such carriers (soliton, polaron, bipolaron, etc.) have been given, e.g.



(35)

(36)

In the case of PTh prepared by the above described organometallic technique, reactions with I_2 and $FeCl_3$ produce I_5^- and a mixture of $FeCl_2$ and $FeCl_4^-$, respectively:

$$\text{PTh} + 2\text{FeCl}_3 \rightarrow \text{doped-PTh}^+ \cdots \text{FeCl}_4^- + \text{FeCl}_2 \qquad (37)$$

as proved by Raman and Mössbauer spectroscopy.[128,143,144]

The formation of I_5^-, $FeCl_2$ and $FeCl_4^-$ supports the generation of the positive carrier in the polymer chain (*p*-type conductor) *via* electron transfer from the polymer to the electron acceptors. This *p*-type conducting property has been physically confirmed by measuring, e.g. Seebeck effect[145] and Hall effect. On the other hand, *n*-type conducting materials are obtained by Na doping of the π-conjugated polymers.

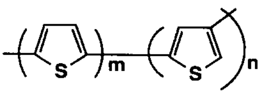
The electrical conductivity (σ) of PTh prepared using the Ni(0)-complex as the reactant (eq. 9) has been measured with:

(a) a disk prepared by pressing a powder of iodine- or $FeCl_3$-doped PTh, and

(b) the above described vacuum deposited film on a glass substrate.

Figure 16(a) shows the dependence of the σ-value on the amount of iodine taken up by PTh, whereas Fig. 16(b) shows the change of the σ-value with the exposure time of the vacuum deposited PTh film to the vapor of iodine.

PRTh, PORTh, PRPyrro, and other related polymers are also converted into electrically conducting materials by reaction (doping) with iodine. Copolymers containing thiophene-2,5-diyl and thiophene-2,4-diyl units



show electrical conductivity when doped with iodine. However their electrical conductivity was much smaller than that of the PTh–iodine adduct.[38,40]

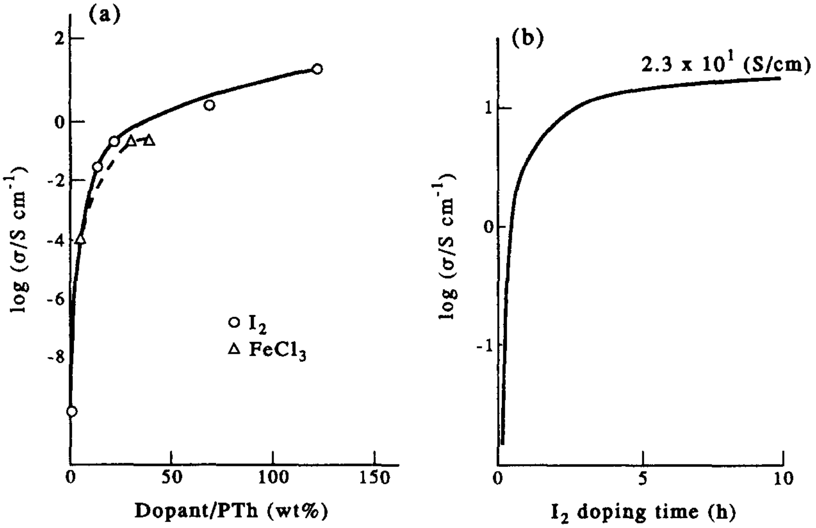
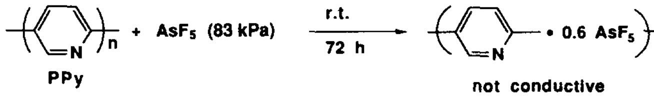


FIG. 16. (a) Dependence of the electrical conductivity (σ) of poly(thiophene-2,5-diyl) (PTh) on the amount of dopant.[33] (b) Change of the σ-value of the vacuum deposited PTh film with time of exposure to the vapor of iodine.

In contrast to PTh, PRTh, PORTh, PRPyrro, and related polymers which are constituted of electron-rich aromatic rings,[146] PPy, PBpy, PPyrim, and PQ, which are constituted of electron-deficient aromatic rings,[146] do not show electrically conducting properties when treated with electron acceptors like iodine. However, they are converted into electrical conductors when treated with electron donors like Na.

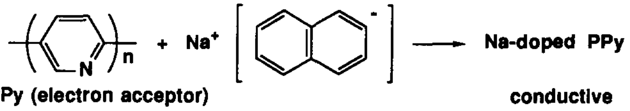
For example, treatment of PPy with iodine, BF_3, or AsF_5 gives adducts with electron acceptors or Lewis acids,[48,49] e.g.



(38)

however, the adducts are not electrically conductive ($\sigma = 1 \times 10^{-11}$ S cm^{-1} for the adduct with AsF_5 and 4.3×10^{-7} S cm^{-1} for $(C_5H_3N \cdot 0.46I)_n$). This is in sharp contrast to the highly electrically conducting property of AsF_5-doped PPP.[135-142] In the case of PPy, AsF_5 seems to form the adduct through the lone pair electrons of the nitrogen of PPy. This type of adduct formation seems to give only a minor effect on the 6π electron system and not to generate the carriers in the π-conjugation system. On the other hand, PPP does not have such lone pair electrons and the interaction of the Lewis acid with PPP takes place through the π-electrons, giving a profound influence for the π-conjugation system to generate the positive carrier (hole). It is generally accepted in the field of organic chemistry that pyridine shows electron-donating Lewis base nature, originating from the lone pair electrons of nitrogen, while its 6π-conjugation system has an electron-deficient character.[146]

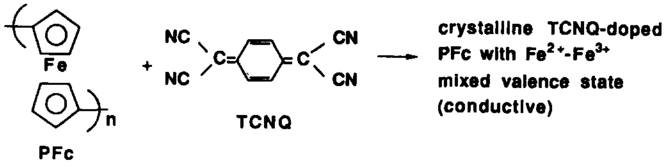
Doping of yellow PPy with sodium naphthalide gives reddish purple Na-doped PPy with an electrical conductivity of $1.2 \times 10^{-1}\,\mathrm{S\,cm^{-1}}$ as measured with pressed powder.



(39)

The electron accepting property of PPy account for this. PBpy, PPyrim, PQ, and related polymers comprised of π-deficient heterocycles show analogous doping behaviors.

PFc has electron-donating properties and forms various adducts with electron acceptors including iodine, tetracyanoquinodimethane (TCNQ), and 2,3-dichloro-5,6-dicyano-1,4-quinone,[147,148] PFc is partly oxidized by the electron accepting TCNQ to form a $\mathrm{Fe^{2+}}$–$\mathrm{Fe^{3+}}$ mixed valent material, which shows electrical conductivity of $4.1 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ (the monomer unit: TCNQ = 1 : 0.64).[148] Mössbauer spectra of the PFc–TCNQ adduct reveal the presence of $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ species at -193°C and a rapid electron exchange between $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ on Mössbauer time scale (10^{-7} s) at room temperature; e.g.



(40)

$$\underset{\text{PFc–TCNQ}}{---\underset{\text{(a)}}{\mathrm{Fe}^{2+}}-\underset{\text{(b)}}{\mathrm{Fe}^{3+}}-\underset{\text{(c)}}{\mathrm{Fe}^{2+}}-\underset{\text{(d)}}{\mathrm{Fe}^{3+}}---}\ \underset{\substack{\text{time scale}\\ 10^{-7}\,\mathrm{s}}}{\overset{\text{electron exchange}}{\rightleftharpoons}}\ ---\underset{\text{(a)}}{\mathrm{Fe}^{3+}}-\underset{\text{(b)}}{\mathrm{Fe}^{2+}}-\underset{\text{(c)}}{\mathrm{Fe}^{3+}}-\underset{\text{(d)}}{\mathrm{Fe}^{2+}}--- \qquad (41)$$

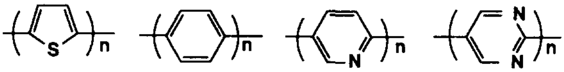
the electrical conducting property of the PFc–TNCQ adduct may be attributed to the rapid exchange of electrons between the $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ species.

Polyyne 3 becomes an electrically conducting material ($\sigma = 4 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$) when exposed to iodine vapor.[35]

4.3.2. *Electrochemical doping* – PRTh, PPy, PBpy, PPyrim, PQ and its analogues, Copoly 1–3, PMePy, and several other polymers prepared by the above-described organometallic technique are soluble in solvents. Painting electrodes (e.g. metal, ITO, and carbon) with the polymer solution and ensuing removal of solvent affords polymer-coated electrodes suited to electrochemical analysis. The vacuum evaporation of PPP, PTh, PPy, and PBpy on metal, ITO, and carbon substrates also affords good electrodes for the electrochemical analysis of polymers (e.g. cyclic voltammetry for the polymer).[149] The electrochemical analysis of the polymer film electrodes reveals the following electrochemical properties of the polymers.

(a) Redox potential (vs Ag/Ag^+) of the π-conjugated polymers varies as follows,[54,149]

Increase in ease of oxidation (oxidation at small Ep) ←

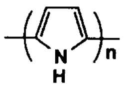


	PTh	PPP	PPy (PBpy, PQ)	PPyrim
$E_p(V)^a$	0.49 red → blue[c]	1.18 yellow → bluish yellow	no	no
$E_n(V)^b$		-2.6 (from ref. 150)	-2.11 yellow → purple	-1.70 reddish yellow → purple

→ **Increase in ease of reduction (reduction at small En)**

a E_p = 1/2 (p-doping potential + p-undoping potential) vs. Ag/Ag^+.
b E_n = 1/2 (n-doping potential + n-undoping potential) vs. Ag/Ag^+.
c Color change accompanying the doping.

If we take into account the lower E_p value of poly(pyrrole-2,5-diyl) (PPyrro)



PPyrro

(E_p = -0.3 V)[48,151-155]

of the above described poly(arylene)s, the ease of oxidation and reduction of poly(arylene)s appears to reflect the ease of oxidation (abstraction of electron) and reduction (addition of electron) of the arylene monomer unit, which is in the following order.[48,156,157]

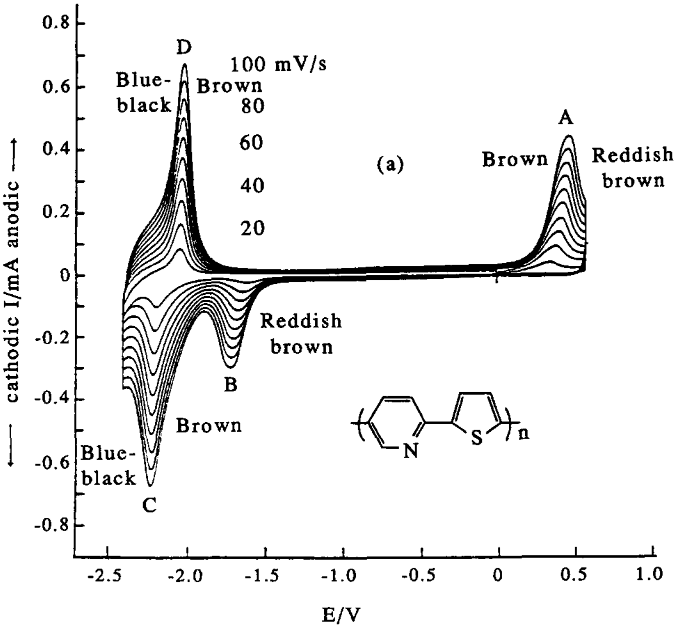
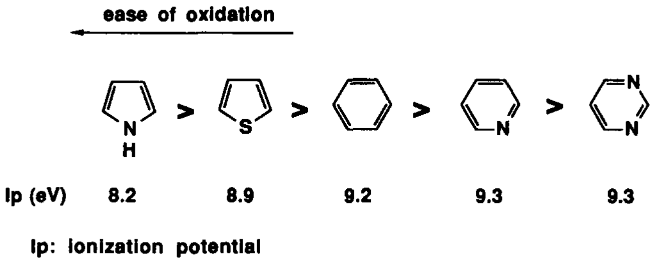
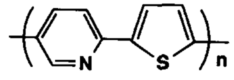


FIG. 17. Cyclic voltammogram of Copoly 1.[57] Potential: vs Ag/Ag$^+$. A, *p*-doping; B, *p*-undoping; C, *n*-doping; D, *n*-undoping.



(b) In the case of copolymers consisting of electron-donating thiophene units and electron-accepting pyridine units, e.g.



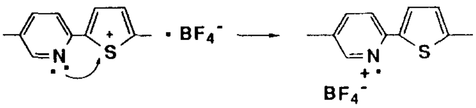
Copoly 1

their CV shows a large difference between *p*-doping potential and *p*-undoping potential as shown in Fig. 17, and the large difference is accounted for by an EC (electronic-chemical) process involving shift of a lone pair electron from the nitrogen of the pyridine ring to the *p*-doped thiophene ring.[57–59]

TABLE 7. Position of the absorption bands of poly(arylene)s prepared by organometallic methods

No.	Poly(arylene)	Solvent	λ_{max}/nm	Ref.
1	PTh (soluble part)	$CHCl_3$	420	39
2	poly(thiophene-2,4-diyl) (soluble part)	$CHCl_3$	290	39
3	65:35 copolymer of thiophene-2,5-diyl and thiophene-2,4-diyl	$CHCl_3$	ca. 400	39
4	PRTh ($R = n\text{-}C_6H_{13}$)	$CHCl_3$	370	158
5	PPy	HCOOH	373	51
6	PBpy	HCOOH	373	51
7	PMePy	HCOOH	310–340*	60
8	PPyrim	H_2SO_4	361	54
9	PQ	HCOOH	322, 343	55
10	Copoly 1	HCOOH	490	57
11	Copoly 2	HCOOH	430	57

* Depending on the position of the Me group.

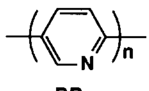


4.4. *Optical properties*

4.4.1. *UV-visible absorption* — The above described π-conjugated poly(arylene)s give rise to strong π–π* absorption bands. Examples of positions of the absorption bands are shown in Table 7.

The positions of the π–π* absorption bands of PTh (No. 1 in Table 7) and PRTh (No. 4) are comparable to those of PTh and PRTh prepared by the other methods (e.g. oxidation of thiophene and 3-alkylthiophene).[74,135-142,159] Poly(thiophene-2,4-diyl), having no extensively π-conjugated system, shows the absorption only in the UV region (No. 2). Change of the position of the absorption peak is much less sensitive (No. 3) to the change of the monomer composition of copolymers consisting of thiophene-2,5-diyl and thiophene-2,4-diyl monomer units than is change of the electrical conductivity of the copolymers with change of the monomer composition.[39]

PPy gives rise to a relatively sharp absorption peak at about 370 nm, and the λ_{max} value is comparable to that (ca. 380 nm measured in the solid state) of PPP prepared by the organometallic method. The position of λ_{max} of PPy is virtually independent of the degree of polymerization (*DP*) in a *DP* range of 16–50.

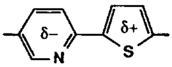


λ_{max} = 372 ± 3 for n = 16-50

PPy

The introduction of the alkyl group R to PTh and PPy causes a shift of the π–π^* absorption band to lower wavelength, which implies lower degree of π–conjugation in the R-substituted poly(arylene)s.

It may be expected that Copoly 1 gives rise to a UV-visible absorption peak at a middle position between the absorption peaks of PTh and PPy. However, the absorption band of Copoly 1 with λ_{max} at 490 nm (No. 9 in Table 7) rather shows a red shift compared with those of PTh and PPy, presumably due to intramolecular charge transfer.

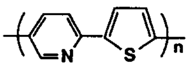


4.4.2. *Fluorescence, electroluminescence, and non-linear optical properties* — The π-conjugated poly(arylene)s and polyynes described above generally show strong fluorescence and several data are given in Table 6. Linear poly(arylene)s like PPy give rise to excimer-like emission as shown in Fig. 7.

Fluorescent (photoluminescent) materials are expected to have electroluminescent properties. Actually PTh[160] and PRTh[161] films do show electroluminescent properties. An Al/PTh/ITO electric junction prepared with PTh prepared by the organometallic method gives a i–V (current–voltage) curve which is accounted for by assuming the presence of a Schottky barrier between Al and PTh (*vide infra*), and the electric junction emits visible light centered at about 550 nm when direct current voltage of 25 V is applied.[149,160]

As described above, PBpy and PTh molecules arranged along the direction of the surface of the glass substrate (Fig. 11) are SHG (second harmonic generation) active. On the other hand some of the π-conjugated poly(arylene)s show another type of non-linear optical property, THG (third harmonic generation).

Among the poly(arylene)s, copolymers consisting of electron-donating thiophene rings and electron-accepting pyridine rings e.g.



Copoly 1

show large THG with $\chi^{(3)}$ value of

$$\chi^{(3)} = 1.5 \times 10^{-10}\,\text{esu} \qquad (42)$$

at a wavelength of 1.525 μm (3ω).[162] Figure 18 shows the dependence of the $\chi^{(3)}$

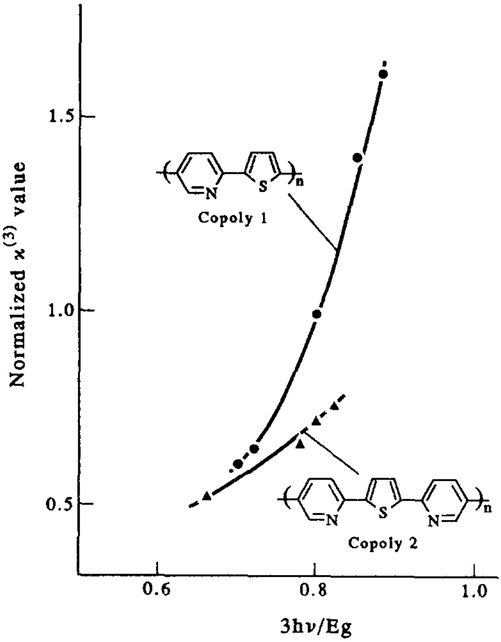


FIG. 18. χ^3 vs $h\nu$ normalized by optical band-gap energy for Copoly 1 and Copoly 2.[162]

value on wavelength normalized by the optical band-gap energy. Since Copoly 1 gives a mechanically strong thin film with smooth surface, it is suited to the making of optical devices based on THG.

5. APPLICATION

5.1. *Battery*

The poly(arylene)s prepared by organometallic methods serve as active materials and electrodes of galvanic cells (primary cells and secondary cells (batteries)). Usability of PTh,[163] poly(acetylene),[164] and PPP[165] as active materials and electrodes of polymer batteries was first reported at almost the same time (1981–1982).

For example, the following charging reactions (eqs 43–47) take place when a ZnI_2 solution is electrolyzed by using Zn and PTh as the negative and positive electrodes, respectively.

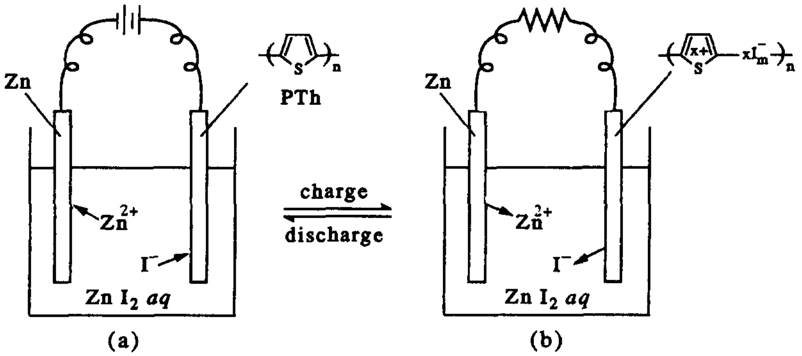
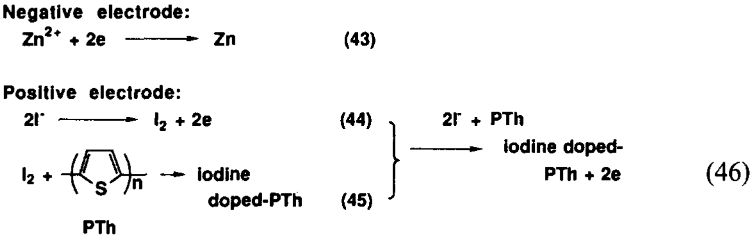


FIG. 19. Charging and discharging of $Zn|ZnI_2|PTh$ battery. The state (a) is charged to the state (b), which can go back into the state (a) by discharging.



$$ZnI_2 + PTh \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Zn + \text{iodine doped-PTh} \tag{47}$$

Since the iodine doped-PTh has electrically conducting properties and stores positive charge in the polymer chain, it serves as a good polymer electrode for a battery (Fig. 19). When the battery is discharged, a reverse reaction (cf. eq. 47) takes place. An example of the charge–discharge profile of the $Zn|ZnI_2|$ PTh battery is shown in Fig. 20.[166,167] As shown in Fig. 20, the charging and discharging proceeds smoothly with high current efficiency and energy efficiency.[166,167]

The charging reaction (eq. 46) at the positive electode is regarded as the electrochemical *p*-doping (or anion doping) of PTh, and such a battery can be expanded to various types of batteries using various metals, electrolytes, and polymer electrodes. Among the batteries, lithium batteries are especially important since they show high discharging voltage (ca. 3V).

$$Li^+ + e \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li \tag{48}$$

$$Y^- + \text{polymer} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} p\text{-doped polymer} + e \tag{49}$$

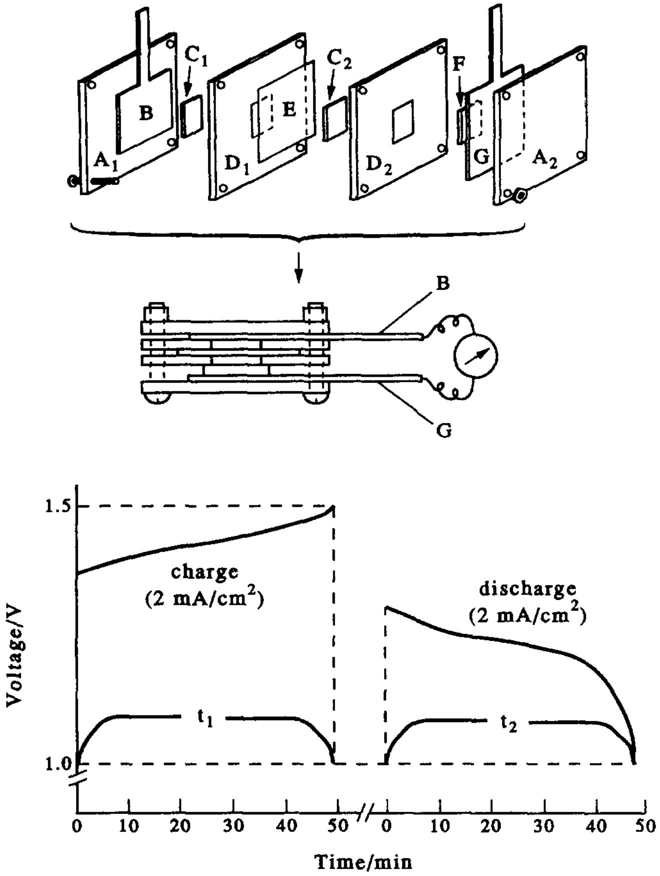


FIG. 20. Sketch of the test cell (Zn | ZnI_2 | PTh battery) and its charge–discharge curves (lower figure).[166] A_1 and A_2, board; B, negative electrode (Zn); C_1 and C_2, glass fiber (Toyo Roshi type GA 100, 10 × 10 mm) impregnated with an aqueous solution ($0.1\,cm^3$) of ZnI_2 ($0.5\,mol/dm^3$); D_1 and D_2, board with hole (10 × 10 mm); E, cation-exchange membrane; F, polymer-coated carbon fiber plate (10 × 10 mm); G, Pt-plate.

$$\text{LiY} + \text{polymer} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} \text{Li} + p\text{-doped polymer} \qquad (50)$$

$$Y = ClO_4^-,\ BF_4^-,\ \text{etc.}$$

The poly(arylene)s prepared by organometallic methods as well as electrochemical proceses are usable as positive electrodes of lithium batteries.[168]

On the other hand, the iodine–poly(arylene) adducts are useful as active materials of lithium–iodine solid electrolyte cells. Since the lithium–iodine solid electrolyte cell uses no solvent, one need not worry about the leakage of electrolytic solution from the cell, and the cell is suited for long-term use (e.g. cells for pacemakers).

$$2Li \rightarrow 2Li^+ + 2e \qquad (51)$$

$$I_2 + 2e \rightarrow 2I^- \qquad (52)$$

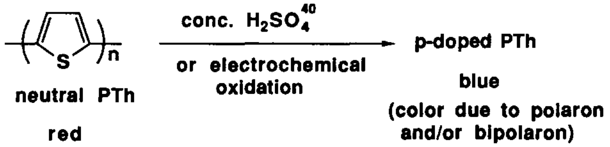
$$2Li + I_2 \xrightarrow[\text{(LiI)}]{\text{solid electrolyte}} 2LiI \qquad (53)$$

Iodine in the lithium-iodine solid electrolyte cell, however, is not used as pure iodine due to its very low electrical conductivity; iodine is used as an electrically conducting charge-transfer complex with an electron-donating polymer (e.g. poly(vinylpyridine)).[169]

Since the iodine adducts of the poly(arylene)s have much higher electrical conductivity than the iodine–poly(vinylpyridine) adduct, the iodine adducts of the poly(arylene)s are expected to serve as better active materials for the lithium–iodine solid electrolyte cells. Actually use of poly(arylene)s prepared by organometallic methods (e.g. PTh) as a partner for iodine affords an excellent lithium–iodine solid electrolyte cell. Structure of the cell and its discharging profile is shown in Fig. 21.[170] As shown in Fig. 21, the cell maintains a discharging voltage higher than 2.3 V up to 85.2% utilization of iodine.

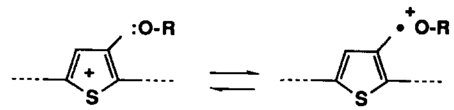
5.2. *Electrochromic display*

Doping of poly(arylene)s by chemical methods (e.g. with concentrated H_2SO_4 [40]) as well as electrochemical methods leads to a deep change of their color, which is interpreted as due to formation of polarons and/or bipolarons,[135-140] e.g.



(54)

In the case of PORTh, a shift of a lone pair electron of the OR group seems to occur in the *p*-doped state.[80]



(55)

Since the electrochemical oxidation (eq. 54) is reversible, preparation of electrochromic displays becomes possible[135] by using:

(i) ITO electrode coated with a poly(arylene) film prepared by a painting method (painting the ITO electrode with a solution containing poly(arylene) (e.g. PRTh)), and

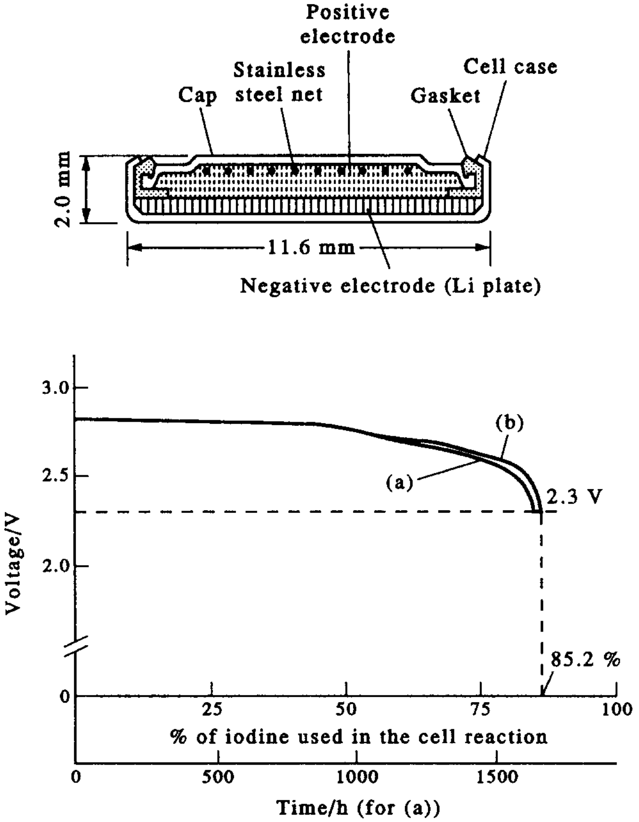


FIG. 21. Structure of the Li|LiI|I_2-PTh adduct cell and discharging profile of the cell. Positive electrode = I_2-PTh adduct. (a) Wt-% of iodine = 75% (weight of the adduct = 61.2 mg); (b) Wt-% of iodine = 50%.[170]

(ii) ITO electrode coated with a vacuum deposited film of poly(arylene) (e.g. PTh).

Examples of the color change accompanying the electrochemical redox reactions are shown in Section 4.3.2.

5.3. *Others*

The poly(arylene)s prepared or molecularly designed based on organometallic chemistry are now going to be used, or are intended to be used in the following various areas:

(a) Conductors or materials to remove static electricity. Various fibers, films,[171] and related materials coated with the conductive polymers are now industrialized. The polymers are to be used in electron beam lithography to avoid charge accumulation due to electrons from electron beam.[172] Recently industrial use of the polymers as electrodes of aluminum capacitor[173] as well as base layers for plating metals through holes in circuit boards has been established.

(b) Electrode and electochromism. The doping–undoping or redox property of the conductivy polymers has been utilized to store energy in batteries and to make electrochromic displays(ECD). Examples of the storage of energy in poly(arylene)s and electrochromism of poly(arylene)s are described above. Photo-assisted reduction of water and ketones has been reported.[131] Poly(iso-thianaphthene)[174–176] is expected to be usable as a transparent conducting material.

(c) Electric devices. Electric devices including diodes,[149,177–179] transistors,[180–182] and solar cells[183,184] have been made by using the π-conjugated conductive polymers. Among the polymers, poly(thiophene-2,5-diyl) and its derivatives are most widely used.

(d) Optical devices. As described above, π-conjugated poly(arylene)s show photoluminescent, electroluminescent and non-linear optical properties. Because of these interesting properties, the polymers are expected to support future industries producing highly effective optical telecommunication systems, photocomputer systems, photoconducting devices, and other optical devices.[141]

(e) Other. Since poly(arylene)s possess interesting π-conjugated electron systems along the polymer chain, appropriate molecular design of poly(arylene)s is expected to produce interesting materials, e.g. organic superconductors, organic ferromagnetic materials, molecular devices, etc.

6. CONCLUSION AND SCOPE

The basic C–C coupling reactions using transition metal complexes (e.g. eq. 1) found by us provide new polymerization methods (Methods I–V), which make it possible to make poly(arylene)s and poly(ethyne-diyl-arylene)s, $-(\mathrm{Ar})-_n$ and $-(\mathrm{C{\equiv}C{-}Ar})-_n$. The new polymerization methods have been especially developed to design electrically conducting and stable (chemically and thermally) poly(arylene)s, and various such poly(arylene)s including poly(thiophene-2,5-diyl), the first conductive polymer consisting of 5-membered heteroaromatic rings, poly(pyridine-2,5-diyl), and poly(3-alkylthiophene-2,5-diyl), the first conductive polymer having substituents, were first prepared by these techniques. The poly(arylene)s have well-defined bonding between the monomer units and are suited to reveal chemical (e.g. redox properties and coordinating properties), electrical and optical properties as well as chemical and physical (crystallographic) structures of poly(arylene)s. Some of the poly(arylene)s thus prepared have linear and rigid structures, and alignment of the polymers on the surface of substrate as well as in the surface region of polymer (e.g. poly(vinyl alcohol)) films is possible.[102,185] The poly(arylene)s are useful materials for making devices such as polymer batteries, electrochromic devices, electroluminescent devices, photoluminescent devices, etc. They are also industrially used as materials to remove static electricity and as electrodes. Some of the devices were first developed by us using the poly(arylene)s.

Thus, the basic pure organometallic reactions (e.g. eq. 1) have provided a basis to design electrically conducting and stable polymers, which show interesting electrical and optical properties. Such polymers are expected to support future industries.

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