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Basic Information on Nonsubstituted Polyphenylene and Polythiophene Obtained via Solubilization of Polymers

Takakazu Yamamoto,*,[†] Masahiro Abe,[†] Biyao Wu,[†] Byoung-Ki Choi,[†] Yosuke Harada,[†] Yasuo Takahashi,[‡] Kentaro Kawata,[‡] Shintaro Sasaki,[§] and Kenji Kubota[||]

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, Sankyo Organic Chemicals Co., Ltd., 3-13-1 Kuji, Takatsu-ku, Kawasaki 213-0032, Japan, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi 923-1292, Japan, and Faculty of Engineering, Gunma University, Tenjincyo, Kiryu 376-8515, Japan

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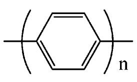
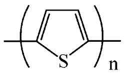
ABSTRACT: Basic information on the molecular weights and structures of poly(*p*-phenylene) **PPP**, poly(*m*-phenylene) **PMP**, poly(thiophene-2,5-diyl) **PTh**, and related copolymers has been obtained. **PPP**s prepared by a Ni-catalyzed dehalogenative polycondensation of *p*-$C_6H_4Br_2$ with Mg (**PPP**(Ni)) and an oxidative polymerization of benzene using $CuCl_2$ (**PPP**(Cu)) became soluble in DMF after nitration. The nitration proceeded essentially without crosslinking, and GPC analysis gave M_n values of 8300 and 6100 for nitrated **PPP**(Ni) and **PPP**(Cu), respectively. Light scattering analysis indicated that nitrated **PPP**(Ni) and **PPP**(Cu) assumed a rather stiff structure in DMF with ρ_v (degree of depolarization) in the range of 0.12−0.13. **PMP** and **PTh** also became soluble in DMF after nitration, and GPC analysis of nitrated **PMP** and **PTh** gave M_n values of 5500 and 8500, respectively. Light scattering analysis of nitrated **PTh** gave a ρ_v of 0.33, which indicated that the polymer had a stiff structure in DMF. Copolymers of *p*-phenylene (PP) and *m*-phenylene (MP) were soluble in organic solvents when the content of the PP unit was about 20%, and a soluble fraction with an M_n of 12 100 was obtained. Light scattering analysis indicated that the copolymer assumed an essentially random coil-like structure in THF. To the contrary, copolymers of 2,5-thienylene (2,5-Th) and 2,4-thienylene (2,4-Th) were insoluble in organic solvents presumably due to their essentially linear and stiff structure.

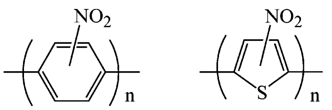
Introduction

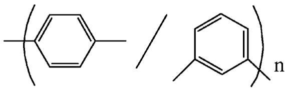
π-Conjugated polymers are the subject of many recent papers. Poly(*p*-phenylene) **PPP** and poly(thiophene-2,5-diyl) **PTh** are fundamental π-conjugated polymers.[1] Their various derivatives such as poly(9,9-dialkylfluorene)s, head-to-tail type poly(3-alkylthiophene), and poly(ethylenedioxythiophene) have been synthesized, and their chemical and physical properties have actively been investigated. However, the chemical and physical properties of basic nonsubstituted **PPP** and **PTh** have not been sufficiently clarified because of the insolubility of the polymers in solvents.


PPP


PTh

We have found that the nitration of **PPP** and **PTh** gives soluble nitrated polymers essentially without crosslinking. Using these soluble nitrated polymers, we have obtained molecular weight information on the original polymers and have confirmed a linear, stiff structure of the polymers. In addition to the solubilization of **PPP** and **PTh** by nitration, we have found that copolymers of *p*-phenylene (PP) and *m*-phenylene (MP) are soluble in organic solvents when the content of the PP unit is in the range of about 10−30%. The copolymers, **PP(a/b)**s, are thermally stable and light-emissive materials.


Soluble in organic solvents

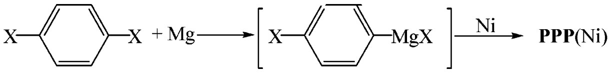

Soluble in THF, $CHCl_3$, etc. when PP/(PP+MP) is in the range of 0.1 - 0.3

PP(a/b)

Herein, we report results obtained using solubilized **PPP** and **PTh**, soluble **PP(a/b)**s, and related polymers. Some of the results have been reported in letters.[2]

Results and Discussion

Preparation of PPP. Two types of **PPP** were prepared; one was prepared by a Ni-catalyzed dehalogenative polycondensation of *p*-$C_6H_4X_2$ using Mg as the dehalogenating reagent,[3] and the other was obtained by an oxidative polymerization of benzene with $CuCl_2$ according to Kovacic's method.[4] **PPP** can also be prepared by various other routes including (i) the polyaddition of 1,3-cyclohexadines and the thermolysis of the obtained polymer,[5a,b] (ii) the electrochemical oxidative polymerization of benzene,[5c,d] and (iii) the oraganometallic polycondensation of 1,4-dihalobenzene using a zero-valent nickel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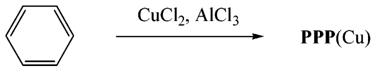
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* Corresponding author. E-mail: tyamamot@res.titech.ac.jp.

[†] Tokyo Institute of Technology.

[‡] Sankyo Organic Chemicals Co., Ltd.

[§] Japan Institute of Science and Technology.

[||] Gunma University.

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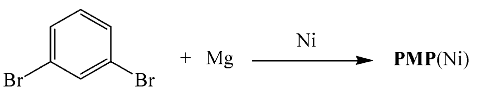
Table 1. Preparation of PPP(Ni), PMP(Ni), and PP(a/b) by Dehalogenative Polycondensation of $C_6H_4X_2$

run		monomer[a] p:m	catalyst[b]	solvent[c]	yield, %	M_n[d]	DP[e]
				X = Br			
1[f]	**PPP**(Ni)	10:0	$NiCl_2$(bpy)	Bu_2O+THF (ca. 5:1)	68	3400	45
2		10:0	$NiCl_2$(dppf)+dppf (1:1)	THF+CPME+TL (1:8:8)	80	5200	68
3	**PMP**(Ni)	0:10	$NiCl_2$(dppf)+dppf (1:1)	THF+CPME+TL (1:8:8)	80	3400	45
4	**PP(a/b)**	1:9	$NiCl_2$(dppp)	THF+TL(1:3)	75	3000	39
5		2:8	$NiCl_2$(dppp)	THF+TL(1:3)	80	2200	29
6		2:8	$NiCl_2$(dppp)	THF+TL(1:3)	80	3000	39
7		2:8	$NiCl_2$(dppf)+dppf(1:1)	THF+TL(1:3)	91	3250	43
8		2:8	$NiCl_2$(dppf)+dppf(1:1)	CPME	85	4000	53
9		2:8	NiCl(dppf)+dppf(1:1)	THF+CPME(1:16)	90	4000	53
10[g]		2:8	$NiCl_2$(dppf)+dppf(1:1)	THF+CPME+TL (1:8:8)	fraction $A = 37\%$	1800	24
					fraction $B = 53\%$	5400	71
				X = Cl			
11		2:8	$NiCl_2$(dppf)+dppf(1:1)	THF	89	4100	54

[a] The ratio of p-$C_6H_4X_2$ to m-$C_6H_4X_2$. [b] bpy = 2,2′-bipyridyl. dppp = 1,3-bis(diphenylphosphino)propane. dppf = 1,1′-bis(diphenylphosphino)ferrocene. Catalyst per monomer = 1 mol %. [c] Bu_2O = dibutyl ether. CPME = cyclopentyl methyl ether. TL = toluene. [d] M_n = number average molecular weight (GPC, polystyrene standards). M_n in runs 1−3 was estimated from the GPC data of nitrated polymers. [e] DP = degree of polymerization. [f] Data from ref 3a. A THF solution of a product between p-$C_6H_4Br_2$ and Mg was condensed and Bu_2O was added. [g] This experiment was carried out at a 1.93:8.07 ratio of p-$C_6H_4Br_2$ and m-$C_6H_4Br_2$. Copolymerization in a 2:8 ratio of p-$C_6H_4Br_2$ to m-$C_6H_4Br_2$ on a large scale (p-$C_6H_4Br_2$ = 77.9 g ; m-$C_6H_4Br_2$ = 311.4 g) gave essentially the same results.

complex.[1] However, because of the ease of handling the polymerization system and the long history of the above-mentioned dehalogenative polycondensation and oxidative polymerization methods, research has focused on two types of **PPP** prepared according to eqs 1 and 2.

Data of PPP(Ni). Runs 1−3 in Table 1 show results of the preparation of **PPP**(Ni) and **PMP**(Ni) by the Ni-catalyzed polycondensation[1,3,6] (eqs 1 and 3) of the corresponding dibromobenzene using Mg as the dehalogenating reagent.

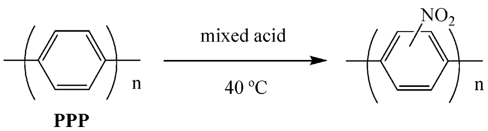


(3)

The **PPP**(Ni) shown in run 1 was prepared using $NiCl_2$(bpy) (bpy = 2,2′-bipyridyl) as the catalyst, as previously reported,[3a] and the recently developed $NiCl_2$(dppf)[7] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) was used to prepare the **PPP**(Ni) shown in run 2 and the **PMP**(Ni) shown in run 3.

Both the obtained polymers were insoluble in organic solvents, and the degree of the polymerization was estimated from GPC data of nitrated polymers and the degree of the nitration (number of the $-NO_2$ group per the benzene ring), which was calculated from a N/C molar ratio obtained from elemental analysis; for details, see the Experimental Section.

The nitration of **PPP**(Ni) shown in run 1 in Table 1 with a mixed acid proceeded smoothly at 40 °C in a heterogeneous system, and the nitrated polymer exhibited strong IR peaks at 1520 and 1340 cm^{-1}, characteristic of the NO_2 group (cf. Figures S1 and S2 in Supporting Information). After the nitration, the polymer became soluble in DMF and DMSO, and the estimation of the molecular weight of the polymer by GPC became possible.



PPP

(4)

Because both the nitrated samples obtained after 0.5 and 4 h showed the same M_n (number-average molecular weight) value of 5400 with the same M_w/M_n (M_w = weight-average molecular weight) value of 1.7 and gave essentially the same GPC trace (cf. Figure S3 in Supporting Information), the nitration was considered to proceed without crosslinking. The nitrated polymer samples obtained after the 0.5 h and 4 h nitrations showed the same degree of nitration (1.0 nitro group/p-phenylene unit). These data suggest that the nitration of the p-phenylene unit in **PPP** suppresses the reactivity of the p-phenylene ring toward further nitration due to steric reasons and/or a decrease in the nucleophilicity of the p-phenylene ring toward NO_2^+. From the M_n value and the degree of nitration, the M_n value of the original **PPP** was estimated to be 3400, as shown in run 1 in Table 1.

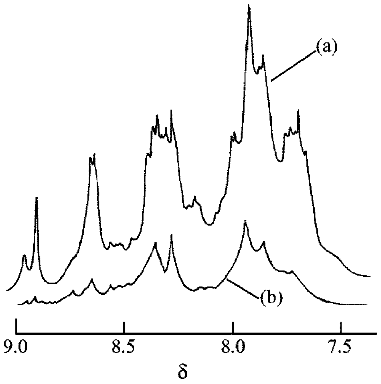


Figure 1. ^1H NMR spectra of (a) nitrated **PPP**(Ni) and (b) nitrated **PPP**(Cu) in DMSO-d_6.

Light scattering analysis[8] of the nitrated **PPP**(Ni) in DMF gave an M_w value of 54 000, revealing that the nitrated **PPP**(Ni) aggregated in DMF. Light scattering analysis by scattered light intensity measurement gives an M_w value of the aggregated polymer molecules.[8] The light scattering analysis was carried out with a static DMF solution of the nitrated **PPP**(Ni), and the aggregation is considered to occur in such a static solution. On the contrary, the GPC analysis was carried out with a fluid DMF solution of the nitrated **PPP**(Ni), and the aggregation is considered to be broken off in the fluid solution. The light scattering analysis afforded a ρ_v (degree of depolarization) value of 0.13 and a hydrodynamic radius (R_h) of 18 nm. The ρ_v value indicated that the nitrated polymer had a rather stiff structure in DMF, similar to aromatic polyamides such as Kevlar, which showed an analogous ρ_v value.[8c]

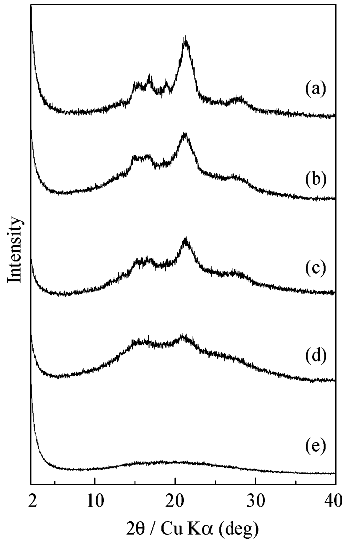


Figure 2. XRD patterns of (a): **PMP**(Ni) and (b−d): nitrated **PMP**(Ni)s. Nitration time: (b) 1 h, (c) 4 h, and (d) 8 h. Analysis of the XRD data shown by curve (a) revealed a helical structure for **PMP**(Ni).[12] PMP polymers are known to give helical structures.[12] For a nitration time of 1 h, the nitrated **PMP**(Ni) shows XRD curve (b) similar to curve (a); however, after dissolving the nitrated **PMP**(Ni) in THF and performing reprecipitation in MeOH, this nitrated **PMP**(Ni) did not show a distinct XRD peak (cf. curve (e)).

As shown in run 2 in Table 1, the use of $NiCl_2$(dppf) and a mixed solvent gave **PPP**(Ni) a larger M_n value of 5200, corresponding to a degree of the polymerization (DP) of 68. **PPP**(Ni) was a crystalline polymer;[1,9] however, it became amorphous after nitration, and the powder XRD (X-ray diffraction) pattern of the nitrated polymer showed one broad diffraction peak at 2θ(Cu Kα) = 22°. The packing structure[9] of **PPP**(Ni) has been analyzed, i.e., by a linked-atom Rietvelt whole-fitting method.[10]

Data of PPP(Cu). The nitration of **PPP**(Cu)[4] (cf. eq 2) also proceeded smoothly, and the nitrated **PPP**(Cu) showed an M_n of 6100. The nitrated **PPP**(Cu) showed a wider molecular distribution of an M_w/M_n of 3.8 than that ($M_w/M_n = 1.7$; cf. Figure S3 in Supporting Information) of nitrated **PPP**(Ni).

From the M_n value of the nitrated polymer, the M_n of **PPP**(Cu) was estimated to be 3830 (or DP of about 50). The chain length of **PPP** was previously discussed on the basis of the relative intensities of IR out-of-plane δ(C−H) peaks at 760 and 690 cm^{-1},[4] and **PPP**(Ni) and **PPP**(Cu) were considered to have an analogous chain length.[3a] The M_n data obtained using **PPP**(Ni) and **PPP**(Cu) supported this view.

Figure 1 exhibits ^1H NMR spectra of nitrated **PPP**(Ni) and **PPP**(Cu). The two spectra are similar. The rather complicated ^1H NMR patterns of the nitrated **PPP**s suggest that the nitration did not proceed regioselectively (e.g., to give a head-to-tail controlled polymer).

Light scattering analysis of the nitrated **PPP**(Cu) in DMF showed an M_w of 61 000, which indicated that the polymer molecules also aggregated in DMF. The light scattering analysis gave a ρ_v value of 0.12 and an R_h of 17 nm. Although **PPP**(Cu) was considered to have some irregular components, such as fused aromatic units[11] formed during the cationic polymerization of benzene, the large ρ_v value revealed that **PPP**(Cu) also had essentially a linear structure.

Data of PMP(Ni). The nitration of **PMP**(Ni) also proceeds with mixed acid in a heterogeneous dispersion system at a somewhat slower reaction rate than that of **PPP**. The nitrations for 1, 4, and 8 h at 40 °C gave degrees of nitration of 57%, 73%, and 98% per *m*-phenylene unit, respectively. GPC data of the nitrate **PMP**(Ni)s at 1 and 8 h gave the same degree of polymerization (the number of *m*-phenylene rings) of 45 as determined by GPC analysis, and this indicated that the nitration did not cause crosslinking.

PMP(Ni) assumes a helical structure in solid,[12,13] and the powder XRD pattern of nitrated **PMP**(Ni) shown in Figure 2 reveals that the helical structure is essentially maintained at a lower nitration degree of 57%; however, the helix structure is lost at 98% degree of the nitration attained in the heterogeneous system. The nitrated **PMP**(Ni)s were also soluble in organic solvents such as THF, DMF, and DMSO; however, they were insoluble in chloroform. GPC data of the nitrated **PMP**(Ni) revealed that the original **PMP**(Ni) had a degree of polymerization of 45, as shown in run 3 in Table 1.

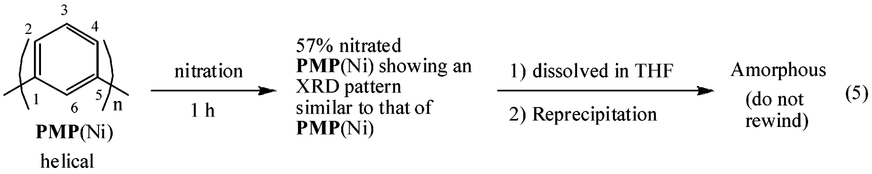
When the nitrated **PMP**(Ni) with a 57% degree of nitration was dissolved in THF and reprecipitated in methanol, the reprecipitated polymer became amorphous, as shown in Figure 2e. These results revealed that the helical structure of nitrated **PMP**(Ni) is not stable and that rewinding the helix structure from the solution is not possible. However, the helical structure of the original **PMP**(Ni) is considered to be stable because it has been reported that crystallization of oligomic C_6H_5-(*m*-C_6H_4)$_8$-C_6H_5 from a solution gives a single crystal in which C_6H_5-(*m*-C_6H_4)$_8$-C_6H_5 molecule forms a helical structure.[13] The nitro group attached to **PMP**(Ni) seems to prevent the helical structure from being rewound.

The formation of helixes from *m*-phenylene- or *m*-pyridine-linked oligomers and polymers are the subject of recent interest.[12−14] The 3-position of **PMP**(Ni) in solid form (cf. Scheme 1) is at the outside edge of the helix,[12,13] and the nitration seems to proceed preferentially at the 3-position because of the steric reasons and the *m*-orientating effect of the phenyl group at the 1- and 5-positions.

In solid form, **PMP**(Ni) has a lower density (ρ = 1.24 g cm^{-3})[12] than **PPP**(Ni) (ρ = 1.39 g cm^{-3}) owing to the requirement of additional space to form the helical structure. After 57% nitration, the density increased to ρ = 1.44 g cm^{-3}. The reprecipitated polymer shown in Scheme 1 gave a higher density of 1.51 g cm^{-3}, presumably because of loss of the additional space required to form the helical structure. The 57% nitrated **PMP**(Ni)s before and after the reprecipitation gave essentially the same IR and analytical data.

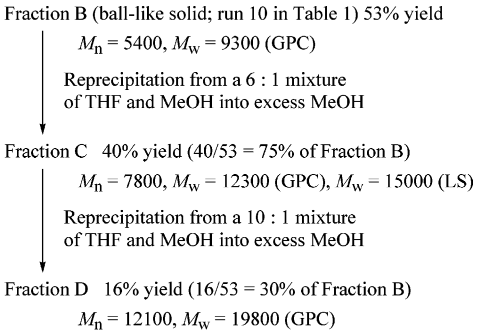
Preparation of Soluble PP(a/b). The use of mixtures of *p*-dibromobenzene and *m*-dibromobenzene in Ni-catalyzed

Scheme 1. Nitration of PMP(Ni) with Helical Structure in Solid and Loss of Helical Structure in Solution.



PMP Polymers Are Known to Give Helical Structures.[12,13]

Scheme 2. Fractionation of PP(a/b) (PP Unit (a):MP Unit (b) = 2:8)



Fraction B (ball-like solid; run 10 in Table 1) 53% yield

$M_n = 5400$, $M_w = 9300$ (GPC)

Reprecipitation from a 6 : 1 mixture of THF and MeOH into excess MeOH

Fraction C 40% yield (40/53 = 75% of Fraction B)

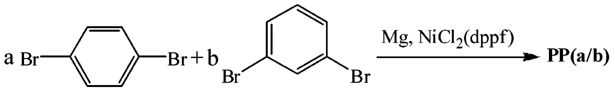
$M_n = 7800$, $M_w = 12300$ (GPC), $M_w = 15000$ (LS)

Reprecipitation from a 10 : 1 mixture of THF and MeOH into excess MeOH

Fraction D 16% yield (16/53 = 30% of Fraction B)

$M_n = 12100$, $M_w = 19800$ (GPC)

dehalogentive polycondensation using Mg gave the corresponding copolymers in high yields.



(6)

The copolymers showed IR peaks at about 1000 and 1595 cm^{-1} (cf. Figure S6 in Supporting Information), which are characteristic of the PP (*p*-phenylene) and MP (*m*-phenylene) units, respectively. A comparison of the intensities of the IR peaks at 1000 and 1595 cm^{-1} for **PPP**(Ni), **PMP**(Ni), and **PP(a/b)**s indicated that the composition of the copolymer agreed with the feeding ratio of *p*-dibromobenzene and *m*-dibromobenzene; ^{1}H NMR data of **PP(2/8)** also support this view, as described below. The IR peak near 1470 cm^{-1} shifted to a larger wavenumber with increase in the content of the PP unit; **PP(2/8)**, **PP(5/5)**, **PP(7/3)**, and **PPP**(Ni) showed the peak at 1466, 1469, 1473, and 1479 cm^{-1}, respectively.

When the fraction of *m*-dibromobenzene in the fed monomer was lower than 0.7 or higher than 0.9, the obtained polymer was not soluble in organic solvents. However, the **PP(a/b)** became soluble in THF and chloroform when the fraction of *m*-dibromobenzene was in a range of about 0.7−0.9; the copolymer was partly soluble in DMSO, DMF, and toluene.

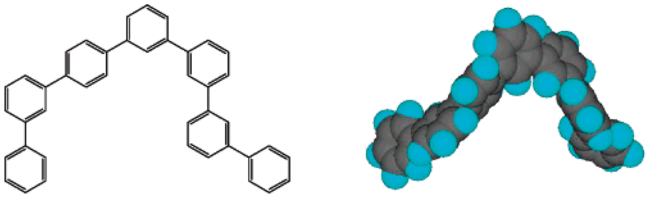
Runs 4−11 in Table 1 show results of the preparation of the soluble **PP(a/b)**s, particularly that with a PP:MP ratio of 2:8, under various conditions. NiCl$_2$(dppf) was also an effective catalyst for copolymerization, and dichloromonomers were also able to be used as shown in run 11. The soluble **PP(a/b)** obtained using NiCl$_2$(dppf) showed a DP value of about 50, as shown in Table 1.

Usually the polymerization gave a dispersion system containing the polymerization solution, and powdery **PP(a/b)** precipitated from the polymerization system. However, when the polymerization was carried out under the conditions shown for run 10, a solution portion and a ball-like curd were obtained. The ball-like curd (fraction B in run 10 in Table 1) was obtained in 53% yield based on the sum of fed *p*-$C_6H_4Br_2$ and *m*-$C_6H_4Br_2$ and showed an M_n value of 5400 corresponding to a DP of about 70.

The fractionation of fraction B based on solubility gave fractions C and D, which had higher M_n values.

Thus, 75% of fraction B, corresponding to 40% yield based on the sum of fed *p*-$C_6H_4Br_2$ and *m*-$C_6H_4Br_2$, was recovered as fraction C, and 30% of fraction B was recovered as fraction D, as shown in Scheme 2 (for detailed procedures, cf. the Experimental Section). Fractions C and D showed essentially the same solubility in THF and chloroform as fraction B; the IR spectra of fractions C and D were also essentially identical to that of fraction B. LS in Scheme 2 represents the light scattering method.

Chart 1. Bending Structure of a Co-oligomer of PP and MP



The soluble **PP(a/b)** was considered to be amorphous in solid form, and its powder XRD pattern of **PP(2/8)** (cf. Figure S8 in Supporting Information) exhibited only a broad background diffraction peak. A CPK molecular model for an oligomeric unit of **PP(a/b)** shows twisting and bending of the main chain, which seem to prevent the crystalline packing of **PP(a/b)** (Chart 1).

Fraction C (cf. Scheme 2) in THF showed an M_w of 15 000 in the light scattering analysis at room temperature (about 30 °C), which roughly agreed with the M_w of 12 300 estimated from GPC using chloroform as the eluent. A low ρ_v value of 0.007 obtained in the light scattering analysis revealed that the copolymer assumed an essentially random coil structure in the THF solution at room temperature.

When the THF solution was warmed to about 50 °C, very strong scattering of light occurred, and the Tyndall phenomenon was clearly observed when a He−Ne laser (632.8 nm) was irradiated. This result indicated that the aggregation of the copolymer occurred in the warm THF solution. The aggregation was reversible; cooling the solution to room temperature weakened the light scattering and the Tyndall phenomenon gradually disappeared. Delicate balance of intra- and/or intermolecular interaction forces (e.g., those originating from nonuniform distribution of charge along the polymer chain[15] and CH/π interaction[16]) seemed to bring about such phenomenon.

A chloroform solution containing **PP(2/8)** showed a UV−vis peak at 260 nm and a PL (photoluminescence) peak at 376 nm with a quantum yield of 60%. The UV−vis peak was between the UV−vis peaks of biphenyl ($\lambda_{max} = 256$ nm) and *p*-terphenyl ($\lambda_{max} = 265$ nm).

Thermogravimetric analysis (TGA) data indicated that the polymer was highly thermally stable and had residual weights of about 90% and 60% at 600 °C and 800 °C, respectively (cf. Figure S9 in Supporting Information). However, the thermal stability of **PP(2/8)** was somewhat lower than that of **PPP**(Ni), and the nitration of polyphenylenes decreased their thermal stability.

The electrochemical oxidation (or p-doping) of **PPP**(Ni) takes place at about 1.2 V vs Ag$^+$/Ag.[1] However, a cast film of **PP(2/8)** on a Pt electrode was electrochemically inert up to 1.2 V vs Ag$^+$/Ag, and an irreversible oxidation peak was observed at 1.58 V vs Ag$^+$/Ag as exhibited in Figure S12 in Supporting Information. After the electrochemical oxidation, the colorless polymer film became yellow and insoluble in organic solvents, implying that the electrochemical oxidative polymerization of the polymer occurred to give a polymer with a longer π-conjugated system via electrochemical coupling between the benzene rings. The electrochemical oxidative polymerization of benzene to give a film of **PPP** has been reported.[5c,d]

As a comparing experiment of the 2:8 copolymerization between *p*-dibromobenzene and *m*-dibromobenzene, a 1:8 polymerization between 4,4′-dibromobiphenyl and *m*-dibro-

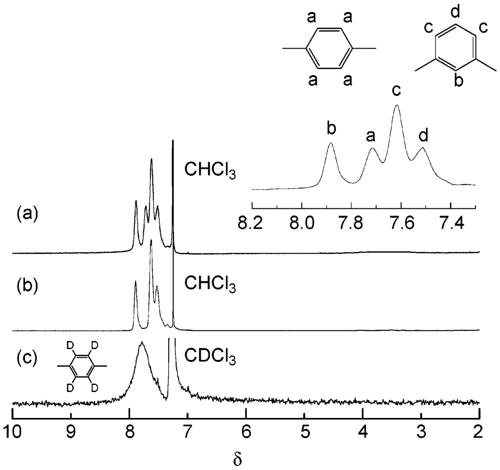
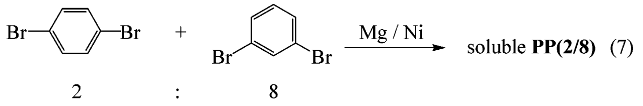
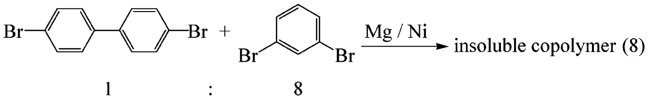


Figure 3. (a) ^{1}H NMR (400 MHz) spectrum of **PP(2/8)** (PP:MP = 2:8). (b) ^{1}H NMR (400 MHz) spectrum of **PP(2-*d*$_4$/8)**. (c) ^{2}H NMR (61.4 MHz) spectrum of **PP(2-*d*$_4$/8)**. Solvent = chloroform-*d*$_1$.

mobenzene was carried out, as shown in eq 8, under the same conditions applied for run 10 in Table 1. The copolymerization also gave a copolymer in a high yield (88%).



(7)

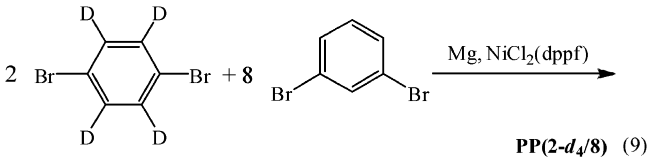


(8)

The IR spectrum of the polymer obtained by eq 8 gave almost the same intensity ratio between the 1000 cm^{-1} peak of the *p*-phenylene unit and the 1595 cm^{-1} peak of the *m*-phenylene unit as the IR spectrum of **PP(2/8),** indicating that the two polymers had essentially the same PP/MP unit ratio. However, in contrast to the good solubility of **PP(2/8)** in THF and chloroform, the 1:8 copolymer of 4,4′-dibromobiphenyl and *m*-dibromobenzene was not soluble in the solvents.

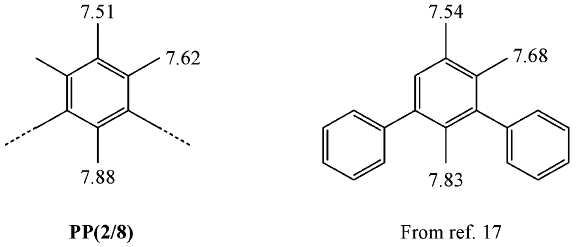
The insolubility of the copolymer obtained using eq 8 is considered to be due to the presence of a long and stiff part (e.g., *p*-quaterphenylene unit) in the polymer, and the results support the viewpoint that **PP(2/8)** is a random copolymer without a long oligomeric *p*-phenylene unit.

Figure 3 shows ^{1}H NMR and ^{2}H NMR spectra of **PP(2/8)** and **PP(2-*d*$_4$/8)** (PP-*d*$_4$:MP = 2:8), respectively. In the ^{1}H NMR spectrum of **PP(2-*d*$_4$/8)** shown in Figure 3b, the peak (a) at *δ* 7.71 observed with **PP(2/8)** (cf. the top part of Figure 3) clearly disappears, revealing that the peak (a) at *δ* 7.71 is assigned to the proton in the *p*-phenylene unit. ^{2}H NMR data shown in Figure 3c support the assignment. It is known that ^{1}H compounds and the corresponding ^{2}H compounds give a similar chemical shift in ^{1}H NMR and ^{2}H NMR, respectively, and the ^{2}H NMR peak is sometimes broadened due to interaction of the quadrupole moment of ^{2}H (spin quantum number of ^{2}H nucleus = 1) with the electronic field gradient.[17a] As shown in Figure 3, the ^{2}H NMR spectrum of **PP(2-*d*$_4$/8)** gives a ^{2}H NMR peak near the ^{1}H NMR peak at *δ* 7.71.

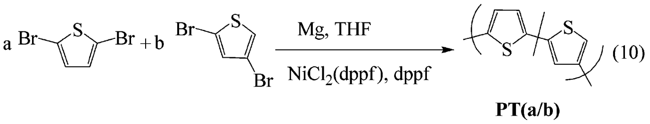


(9)

Chart 2. Comparison of *δ* Values of *m*-Phenylene (MP) Unit



Scheme 3. Preparation of Polythiophenes



(10)

From these NMR data, the ^{1}H NMR peak at *δ* 7.71 was assigned to the *p*-phenylene hydrogens, and the peaks at *δ* = 7.88, 7.62, and 7.51 were assigned to the *m*-phenylene hydrogens. The peak area ratios between these four peaks at *δ* = 7.88, 7.71, 7.62, and 7.51 in Figure 3a essentially agree with the 1:4 ratio between the *p*-phenylene (PP) and *m*-phenylene (MP) units in **PP(2/8)**. The broadening of the ^{2}H NMR peak of the *p*-C_6D_4 unit indicates the presence of strong electronic gradient or an electronic anisotropy around the *p*-C_6D_4 unit (e.g., between the planar direction and perpendicular direction toward the benzene ring). The half bandwidth of the ^{2}H NMR peak of the *p*-C_6D_4 unit is 17.7 Hz.

The assigned *δ* values agree with the reported *δ* values of *m*-diphenylbenzene (Chart 2).[17b]

The obtained **PP(2/8)** contained Br; however, treatment of the copolymer with $LiAlH_4$, in accordance with the method developed by Müllen,[18] gave a Br-free polymer. Because of the good solubility of **PP(2/8)**, chemical modification of the polymer in a solution system (e.g., Friedel−Crafts acylation in chloroform[19]) became possible.

Preparation of Polythiophenes and Results of Nitration. Poly(thiophene-2,5-diyl) **PTh**, poly(thiophene-2,4-diyl) **P(2,4-Th)**, and copolymers of 2,5-thiophene and 2,4-thiophene **PT-(a/b)** were prepared using the corresponding dibromomonomers, Mg, and $NiCl_2$(dppf). The polymers were obtained in high yields (83−95%) (Scheme 3).

Polythiophenes were essentially insoluble in organic solvents, although about 10% of **PT(2/8)** was soluble in $CHCl_3$. In contrast to the highly bent structure of **PP(a/b)** shown in Chart 1, **PT(a/b)** assumes a linear structure as depicted in Chart 3, and powder XRD patterns of **PT(a/b)**s revealed that **PT(a/b)** formed ordered structures in the solid as shown in Figure 4. These results explain the poor solubility of **PT(a/b)** in organic solvents.

Both **PTh** and **P(2,4-Th)** can form essentially a linear structure in the solid state as discussed below, even though the direction of S in each unit of the main chain of **P(2,4-Th)** may not be controlled (Chart 4). The linear structure and a *p*2*gg*-type packing structure of **PTh** in the solid has been reported).[20]

The powder XRD pattern of **P(2,4-Th)** shows two peaks at $2\theta = 13.6°$ ($d = 6.4$ Å) and 26.7° ($d = 3.34$ Å), with a broad background diffraction at about $2\theta = 22°$, as shown in Figures 4 and 5. The presence of only the two diffraction peaks suggests a simple packing structure of **P(2,4-Th)**, and the Rietveld

Chart 3. Linear Structure of a Co-oligomer of 2,5-Thienylene and 2,4-Thienylene

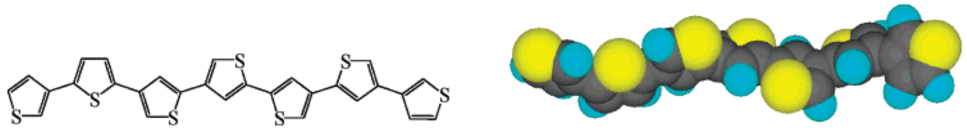
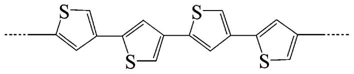


Chart 4. Linear Structure of P(2,4-Th)



analysis of the XRD pattern of **P(2,4-Th)** gives the packing structure depicted in Figure 5. The packing structure had a calculated density of 1.64 g cm^{-3}, which roughly agreed with the observed density of 1.59 g cm^{-3}; polymer materials usually show a lower observed density than calculated density due to the presence of amorphous parts.

PT(a/b) showed δ(C−H) IR peaks assigned to the 2,5-thienylene (2,5-Th) and 2.4-thienylene (2,4-Th) units at about 795 and 820 cm^{-1}, respectively, which were located near those of **PTh** and **P(2,4-Th)** at 790 and 818 cm^{-1}, respectively.[21] The position of the δ(C−H) IR peaks shifts with the composition of **PT(a/b)**, and the degree of the shift is larger for the δ(C−H) peak of the 2,5-Th unit as shown in Figure 6, suggesting that the δ(C−H) peak of the 2,5-Th unit is sensitive to π-conjugation length. The intensity of the two peaks indicated that the composition of **PT(a/b)** agreed with the feeding ratio of the two monomers. A portion of the thiophene polymers was soluble in chloroform, and the UV−vis and PL peaks of the soluble portion shifted to a longer wavelength with an increase in the content of the 2,5-thienylene unit, similarly to the case of previously reported polythiophenes.[21a]

The nitration of polythiophenes with mixed acid proceeded smoothly at 40 °C in a heterogeneous system, and **PTh-NO$_2$**, **P(2,4-Th)-NO$_2$**, and **PT(a/b)-NO$_2$** were obtained as black powders. Holdcroft et al. reported a similar nitration reaction of poly(3-hexylthiophene-2,5-diyl);[22] the nitration was considered to proceed without crosslinking on the basis of the molecular weight of the nitrated polymer.

In cases of **PPP**s, **PMP(Ni)**, and **PP(a/b)**, the nitration did not proceed, exceeding the degree of nitration of 1. However, in the case of the nitration of polythiophenes, the degree of nitration (number of the $-NO_2$ group per the thiophene ring) higher than 1 was sometimes attained, as shown in nos. 1 and 4 in Table 2. Highly electron excessive nature of the thiophene ring[23a] seems to make the nitration by electrophilic attack of NO_2^+ at the thiophene ring possible even after the first nitration.

All the nitrated polythiophenes were soluble in DMSO and DMF, and estimation of their molecular weights by GPC became possible. Table 2 summarizes results of the nitration reactions. The degree of nitration was calculated from the N/C molar ratio obtained in elemental analysis. The ^1H NMR spectrum of nitrated **PTh** exhibited peaks in a range of δ 8.2−8.8.

As shown in Table 2, the nitrated polymer showed M_n values of 5600−12 000, corresponding to DP values of 46−88. **PTh-NO$_2$**, **PT(8/2)-NO$_2$**, and **PT(2/8)-NO$_2$** gave intrinsic viscosities [η] of 0.15, 0.14. and 0.20 dL g^{-1}, respectively.

Light scattering analysis of **PTh-NO$_2$** (nitration time = 4 h), **PT(5/5)-NO$_2$**, and **PT(2/8)-NO$_2$** showed M_w values of 38 000, 75 000, and 135 000, with ρ_v values of 0.33, 0.31, and 0.27, respectively, in DMF. The M_w values larger than those estimated by GPC suggested the aggregation of the polymer molecules in DMF, and the large ρ_v values indicated that the polymers assumed a stiff structure. The ρ_v value provides information on the stiffness of the polymer, and an ideally stiff polymer has a ρ_v value of 1/3;[8] rigid poly(pyridine-2,5-diyl) has a similarly large ρ_v value.[23b] The UV−vis absorption band of nitrated polythiophenes became broad and showed a shoulder peak at about 350 nm in DMF. A PL spectrum of a DMF solution of **PT(2/8)** showed a peak at about 470 nm.

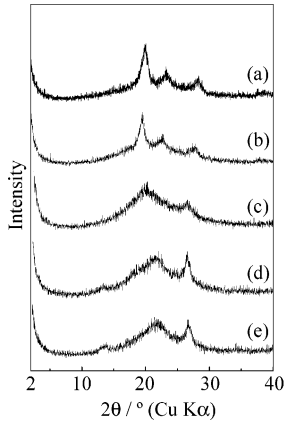


Figure 4. XRD patterns of (a) **PTh**, (b) **PT(8/2)**, (c) **PT(3/7)**, (d) **PT-(1/9)**, and (e) **P(2,4-Th)**.

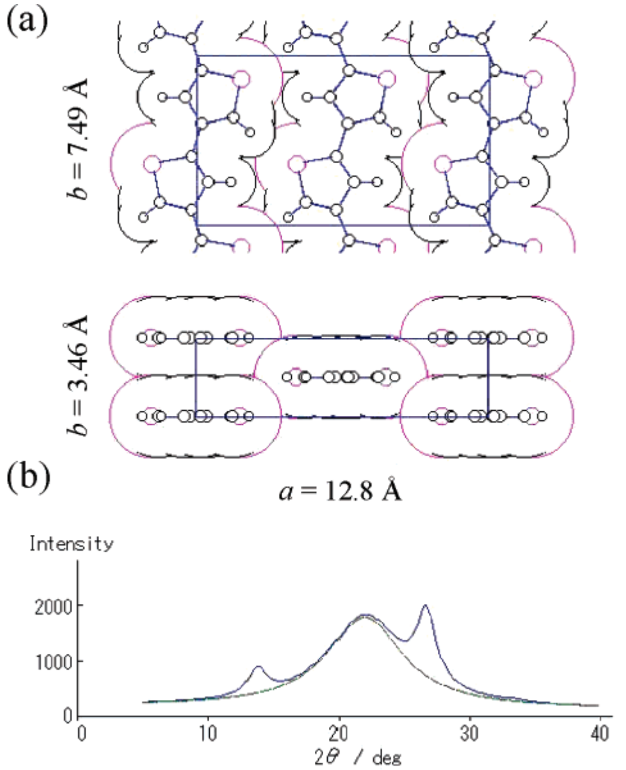


Figure 5. (a) Proposed *c*2*mm*-type packing structure of **P(2,4-Th)** and (b) the simulated XRD curve based on the packing structure. The observed XRD pattern of **P(2,4-Th)** is exhibited in Figure 4. In the simulated XRD curve, a broad background at about 2θ = 22° (d = ca. 4.0 Å) is added; this broad peak is considered to contain various interferences related to the 4.0 Å distance between various atoms (C, H, or S).

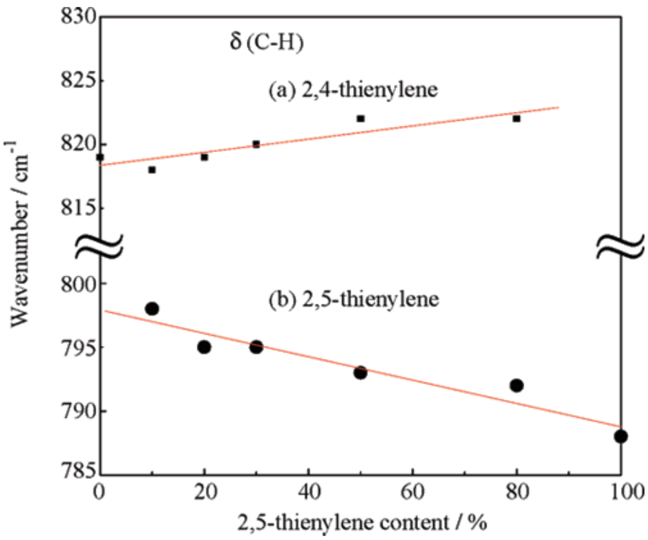


Figure 6. Changes in the positions of δ(C−H) out-of-plane vibrations for (a) the 2,4-thienylene unit at about 820 cm^{-1} and (b) the 2,5-thienylele unit at about 790 cm^{-1} depending on the composition of the 2,5-thienylene and 2,4-thienylene units in **PT(a/b)**.

Table 2. Results of the Nitration of Polythiophenes

no.	polymer	time /h	degree of nitration/%[a]	M_n[b] /10^3	M_w[b] /10^3	DP[c]
1	**PT(8/2)**	4	111	9.9	13	75
2	**PT(5/5)**	4	99	10	15	79
3	**PT(3/7)**	4	96	9.3	13	76
4	**PT(2/8)**	4	116	12	20	88
5	**PT(1/9)**	4	95	8.6	11	69
6	**PTh**	1	77	7.9	10	67
7	**PTh**	4	99	8.5	11	67
8	**PTh**[d] (Aldrich)	4	87	5.6	8.9	46
9	**P(2,4-Th)**	4	100	7.4	15	58

[a] NO_2 groups per thiophene unit; determined by N/C ratio obtained in the microanalysis (cf. the main text and the Experimental Section). [b] Determined by GPC (vs polystyrene standards; eluent = DMF containing 0.006 mol/L LiBr). M_n = number average molecular weight. M_w = weight average molecular weight. [c] Degree of polymerization calculated from M_n. [d] Commercially available **PTh** (cf. Experimental Section).

Conclusion

The nitration of **PPP**s, **PMP**(Ni), and **PTh** made the polymers soluble in organic solvents, and basic information on the molecular weights and stiff structures of **PPP**s and **PTh** was obtained. **PPP**(Ni) and **PPP**(Cu) showed similar molecular weights and stiffnesses. Copolymers of *p*-phenylene (PP) and *m*-phenylene (MP) were soluble in organic solvents when the content of PP was about 20%, and the polymer is a new thermally stable and photoluminescent material. These data give basic information on polyphenylenes and polythiophenes.

Experimental Section

Materials and General Procedures. The dihalogenated monomers, $NiCl_2$(dppf), and dppf were used as purchased. Cyclopentyl methyl ether donated by Zeon Corporation was dried over a molecular sieve under N_2. Other solvents for the polymerization were distilled and stored under an inert gas (N_2 or Ar). Ni-catalyzed polymerization was carried out using the standard Schlenk techniques. **PPP**(Cu) was prepared as described in the literature.[4] Commercially available poly(2,5-thiophene-2,5-diyl), **PTh**, purchased from Sigma-Aldrich Inc. was also used in the nitration study.

Measurements. NMR and IR spectra were recorded on a JEOL EX-400 spectrometer (400 MHz for ^{1}H NMR and 61.4 MHz for ^{2}H NMR, respectively) and JASCO FT/IR-460 Plus spectrometer, respectively. IR spectra of mixtures of **PPP**(Ni) and **PMP**(Ni) in various ratios were measured, and absorbances of the peaks near 1000 cm^{-1} characteristic of the PP unit and 1595 cm^{-1} characteristic of the MP unit, respectively, were measured with the mixed samples; the two peaks gave comparable absorbances in a 1:1 mixture of **PPP**(Ni) and **PMP**(Ni). By comparing the IR spectrum of **PP(a/b)** with IR spectra of the mixtures of **PPP**(Ni) and **PMP**(Ni), the content of the PP and MP units in **PP(a/b)** was estimated. For example, **PP(3/7)** gave an absorbance of 0.48 at the peak near 1000 cm^{-1} and 0.91 at the peak near 1595 cm^{-1}, and the IR data roughly agreed with the 3:7 feeding ratio of *p*-dibromobenzene and *m*-dibromobenzene. Elemental analysis was carried out with a LECO CHNS-932 analyzer and a Yanaco YS-10 SX-Elements microanalyzer. Inductively coupled plasma emission spectrometry (ICP-AES) of Ni, Mg, and Li was carried out using a Shimadzu ICPS-8100 apparatus. GPC traces were obtained with a Shimadzu LC-9A chromatograph and a Tosoh HLC-8120GPC chromatograph using chloroform for **PP(a/b)** or DMF for nitrated polymers as the eluent. Thermogravimetric analysis was performed on Shimadzu TGA-50 and TA-50WS analyzers at a heating rate of 10 °C min^{-1}. UV−vis and PL spectra were measured with a Shimadzu UV-3100 spectrometer and a Hitachi F-4100 spectrophotometer, respectively. Cyclic voltammetry of cast films of the polymers on a Pt plate was performed in an acetonitrile solution containing $[NEt_4]PF_6$ (0.10 M) under N_2 using a Pt counter electrode, a Ag^+/Ag reference electrode, and a Toyo Technica Solartron SI 1287 electron interface. Light scattering analysis of the polymer solutions was carried out in a manner similar to that previously reported.[8b,23b] Powder XRD patterns were recorded on a Rigaku X-ray diffractometer.

Preparation of Polyphenylenes and Nitration of the Polymers. **PPP**(Ni) in run 1 in Table 1 was prepared as previously reported.[3a] The polymerization shown in run 1 was carried out in dibutyl ether with a high boiling point (142 °C) because use of the solvent with a higher boiling point was considered to give **PPP**(Ni) with a higher molecular weight. Other polyphenylenes were prepared similarly using the corresponding dihalobenzenes, nickel catalyst, and the solvent.[2] Reactions of Grignard reagents are usually carried out in ethereal solvents; however, addition of toluene to the Grignard reagent is also carried out.[24a−d] Cyclopentyl methyl ether (CPME) is a new ethereal solvent that has a high boiling point (106 °C) and can be dried easily.[24e]

The copolymerization between 4,4′-dibromobiphenyl and *m*-dibromobenzene (cf. eq 8) was carried out under the same conditions as those applied in run 10 in Table 1: yield of the polymer = 88%. In this case, the most part of the polymer was insoluble, as described above. A small part of the polymer was soluble in chloroform, and the soluble part gave an M_n of 1800 with an M_w/M_n ratio of 1.55.

Fractionation of the fraction B obtained in 10 in Table 1 and described in Scheme 2 was carried out as follows. To a THF (good solvent, 20 mL) solution of 3.71 g of fraction B (cf. Scheme 2 and run 10 in Table 1) under reflux, 3.5 mL of methanol (poor solvent) was added under reflux. When cooled to room temperature, a slurry was obtained. After removal of solution (about 5 mL) in the upper layer by decantation, the slurry was poured into 300 mL of methanol with stirring. The precipitated polymer was collected by filtration and dried under vacuum at 80 °C for 12 h to obtain 2.80 g of the fraction C. The amount of the fraction C gave 75% yield based on the amount of the fraction B and corresponded to 40% yield based on the total amount of the starting *p*-dibromobenzene and *m*-dibromobenzene monomers, as shown in Scheme 2. Similarly, the fraction D was obtained by dissolving the fraction C (2.80 g) in a mixture of THF (20 mL) and methanol (2 mL) under reflux and pouring the obtained slurry into 300 mL of methanol: yield = 1.12 g.

The IR spectra and XRD patterns of **PPP**(Ni) and **PMP**(Ni) agreed with those previously reported.[3a,9d,12] **PP(2/8)** (the fraction D in run 10 with M_n of 12 100 as shown in Scheme 2) contained 0.63% of bromine. Treatment of the polymer with $LiAlH_4$ was carried out as follows according to the method of Müllen.[18]

To a 100 mL Schlenk flask, $LiAlH_4$ (1.0 g, 26.3 mmol) and dry THF (20 mL) were added under N_2. A dry THF solution (30 mL) of **PP(2/8)** (fraction D, 300 mg, 3.94 mmol) was added dropwise, and the mixture was stirred under reflux for 12 h. After cooling to room temperature, the reaction mixture was poured into methanol. The polymer was recovered by filtration, and an aqueous solution of dimethylglyoxime (excess)[25] was added to the polymer powder. Aqueous ammonia was added to the solution to adjust the pH value to about 9, and the mixture was stirred at 60 °C overnight. The polymer was collected by filtration and washed with diluted hydrochloric acid, water, and methanol. The reprecipitation of a chloroform solution of the polymer into methanol and drying the recovered polymer for 24 h at 130 °C under vacuum gave **PP(2/8)**-$LiAlH_4$-treated (280 mg) without hydration. Anal. Calcd for $H(C_6H_4)_{160}H$: C, 94.69; H, 5.31. Found: C, 94.82; H, 5.60; Br, 0. Ni and Mg were not detected by the ICP-AES analysis. Drying the polymer for a shorter period or at a lower temperature gave samples containing water (e.g., 0.11 H_2O per the phenylene unit after drying for 12 h at 100 °C, as estimated from analytical data).

The nitrations of **PPP**(Ni) in run 1 in Table 1 and **PPP**(Cu) were carried out with a mixed acid (95% H_2SO_4:61% HNO_3:H_2O = 1:0.17:0.13 vol/vol) at 40 °C for 4 h. All the nitration reactions described in this paper proceeded heterogeneously with solid polymer and the aqueous solution. The nitrated product was poured into cold water, collected by filtration, washed with water and methanol, and then dried under vacuum; the yields of nitration of **PPP**(Ni) and **PPP**(Cu) were 94% and 98%, respectively. The degree of nitration of polyphenylenes was calculated from the N/C molar ratio. The nitrated **PPP**(Ni) gave a N/C molar ratio of (10.20/14.01)/(54.87/12.01) = about 1.0N/6C, corresponding to a degree of the nitration of about 1.0. The nitrated polymer seemed to contain hydration water. Anal. Calcd for $Br(C_6H_3NO_2{\cdot}0.4H_2O)_{45}Br$: C, 54.66; H, 2.90; N, 10.62; Br, 2.69. $M_n = 5600$. Found: C, 54.87; H, 2.50; N, 10.20; Br, 2.60. $M_n = 5400$. The end group of polyphenylenes (H or Br) seemed to depend on delicate polymerization conditions. The degree of the polymerization (DP) in Table 1 was calculated from the M_n value obtained from the GPC analysis and the degree of nitration. The nitrated **PPP**(Cu) gave a somewhat lower N/C molar ratio of (9.95/14.01)/(55.24/12.01) = 0.93N/6C: Anal. Found: C, 52.24; H, 2.28; N, 9.95.

The nitration of the *m*-phenylene unit in polyphenylenes seems to proceed at a slower reaction rate. The nitration of **PMP**(Ni) under the same conditions (with the mixed acid at 40 °C for 4 h) gave soluble nitrated **PMP**(Ni) with a somewhat lower degree of nitration. Analytical data of the original **PMP**(Ni): Anal. Calcd for $H_{1.7}(C_6H_4{\cdot}0.05H_2O)_{45}Br_{0.3}$: C, 92.91; H, 5.38; Br, 0.69. Found: C, 92.53; H, 5.50; Br, 0.79. Analytical data of the polymer obtained after nitration for 1 h (cf. Figure 2b) gave an N/C molar ratio of (7.28/14.01)/(65.68/12.01) = 0.57/6C, corresponding to a degree of the nitration of 0.57: Anal. Calcd for $H_{1.7}(C_6H_{3.43}(NO_2)_{0.57}{\cdot}0.35H_2O)_{45}Br_{0.3}$: C, 66.34; H, 3.87; N, 7.35; Br. 0.47; $M_n = 4600$. Found: C, 65.68; H, 3.51; N, 7.28; Br, 0.46. $M_n = 4700$. $M_w = 9800$. Analytical data of the polymer obtained after the nitration for 8 h (cf. Figure 2d) gave an N/C molar ratio of (10.73/14.01)/(56.31/12.01) = 0.98N/6C, corresponding to a degree of the nitration of 0.98: Anal. Calcd for $H_{1.7}(C_6H_{3.02}(NO_2)_{0.98}{\cdot}0.4H_2O)_{45}Br_{0.3}$: C, 56.31; H, 3.04; N, 10.73; Br, 0.42. $M_n = 5400$. Found: C, 55.42; H, 2.60; N, 10.23; Br, 0.42. $M_n = 5600$. $M_w = 11\,000$.

Preparation of Polythiophenes and Nitration of the Polymers. The preparation of polythiophenes was carried out using $NiCl_2$(dppf) as the catalyst in THF. A typical example is as follows. A THF (9 mL) solution of 2,5-dibromothiophene (435 mg, 1.8 mmol) and 2,4-dibromothiophene (1.02 g, 4.2 mmol) was prepared. A portion of the THF solution (0.5 mL) was added to Mg (146 mg, 6.0 mmol) in a 50 mL Schlenk tube under N_2, and the reaction mixture was stirred for 30 min at 70 °C. After cooling to room temperature, the rest of the THF solution (8.5 mL) was added, and the mixture was stirred for 3 h at room temperature. To the obtained red solution, $NiCl_2$(dppf) (45 mg, 0.06 mmol) and dppf (33 mg, 0.06 mmol) were added, and the reaction mixture was stirred for 1 h at room temperature. After further reaction for 8 h under reflux conditions, the reaction mixture was poured into a mixture of methanol (500 mL) and concd hydrochloric acid (3 mL). The crude polymer was recovered by filtration, washed with methanol, an aqueous solution of NaOH, water, and methanol in this order, and then dried under vacuum. Yield of **PT(3/7)** = 440 mg (80%). Anal. Calcd for $(C_4H_2S)_n$: C, 58.50; H, 2.46. Found: C, 58.67; H, 2.94. Other polythiophenes were prepared analogously. IR spectra of the polymers agreed with those prepared similarly using another type of Ni(II) complex as the catalyst.[21] Anal. for **PTh**: Found: C, 58.60; H, 2.70. Anal. for **PT(5/5)**: Found: C, 58.38; H, 2.98. Anal. for **P(2,4-Th)**: Found: C, 58.87; H, 2.99.

The nitration of the polythiophenes was also carried out using the mixed acid (95% H_2SO_4:61% HNO_3:H_2O = 1:0.17:0.13 vol/vol). An excess amount of the mixed acid was added to the polythiophene (82 mg for all the polythiophenes), and the mixture was stirred for 4 h at 40 °C. After cooling to room temperature, the mixture was poured into cold water. The nitrated polymer was collected by filtration, washed with water, and then dried under vacuum. The amounts of the obtained nitrate polythiophenes were: 93, 90, 92, 88, 89, 85, and 89 mg for the nitrated **PTh**, **PT(8/2)**, **PT(5/5)**, **PT(3/7)**, **PT(2/8)**, **PT(1/9)**, and **P(2,4-Th)**, respectively. The degree of nitration of polythiophenes was calculated from the N/C molar ratio, similar to the aforementioned polyphenylene cases. For example, analytical data of nitrated **PT(5/5)** gave an N/C molar ratio of (10.43/14.01)/(36.10/12.01) = 0.99N/4C, corresponding to a degree of the nitration of 0.99: Anal. Calcd for $(C_4H_{1.01}N_{0.99}O_{1.98}S{\cdot}0.4H_2O)_n$: C, 35.89; H, 1.36; N, 10.36. Found: C, 36.10; H, 1.58; N, 10.43. Analytical data of nitrated **P(2,4-Th)** gave an N/C molar ratio of (9.97/14.01)/(34.19/12.01) = 1.00N/4C, corresponding to a degree of nitration of 1.00: Anal. Calcd for $(C_4HNO_2S{\cdot}0.65H_2O)_n$: C, 34.61; H, 1.67; N, 10.09. Found: C, 34.19; H, 1.64; N, 9.97. GPC data are shown in no. 9 in Table 2. Sometimes the degree of nitration exceeded 1.00, indicating that more than one C−H group of the two C−H groups in the thiophene ring received the nitration. For example, analytical data of nitrated **PT(8/2)** gave an N/C molar ratio of (10.21/14.01)/(31.52/12.01) = 1.11N/4C corresponding to a degree of the nitration of 111%: Anal. Calcd for $((C_4HNO_2S)_{0.89}(C_4N_2O_4S)_{0.11}{\cdot}1.1H_2O)_{75}$: C, 31.63; H, 2.05; N, 10.24. $M_n = 9910$. Found: C, 31.52; H, 2.00; N, 10.21. $M_n = 9900$. The nitrated **PT(2/8)** also gave a degree of the nitration higher than 1.00 with an N/4C molar ratio of 1.16N/4C, corresponding to a degree of nitration of 116%. The degree of polymerization (DP) of polythiophenes shown in Table 2 was calculated from the M_n value determined by GPC analysis of the nitrated polythiophenes and the degree of nitration. **PTh** prepared in our laboratory gave a degree of nitration of 99% after the 4 h nitration and DP of 67 as shown in no. 7 in Table 2. The aforementioned commercially available **PTh** gave a somewhat lower degree of nitration of 87% (N/4C = 0.87) and DP of 46 with an M_w/M_n value of 1.59, as shown in no. 8 in Table 2.

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Supporting Information Available: IR, GPC, IR, XRD, TGA, NMR, UV−vis, and electrochemical data of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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