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π-Conjugated and Light Emitting Poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl)s and Their Analogues Comprised of Electron-Accepting Five-Membered Rings. Preparation, Regioregular Structure, Face-to-Face Stacking, and Electrochemical and Optical Properties

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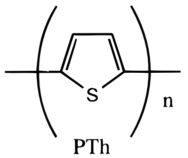
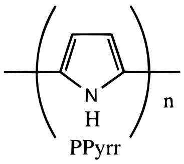
Poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl)s (PRBTz, alkyl = methyl (PMeBTz), butyl (PBuBTz), and heptyl (PHepBTz)) and their analogues comprised of 33−150 thiazole rings have been prepared by organometallic polycondensation, and their chemical and physical properties are compared with those of π-conjugated poly(thiophene-2,5-diyl) (PTh) and poly(pyridine-2,5-diyl) (PPy). Electrochemical n-doping of PRBTz takes place at $E° = -1.77$ to -2.30 V vs Ag/Ag$^+$ and is accompanied by the appearance of a new absorption band in the near-infrared. PMeBTz assumes a relatively stiff structure in solution and shows a large refractive index increment of 0.55 cm^3 g^{-1}; powder X-ray diffraction analysis of PMeBTz supports a face-to-face type stacking of the polymer chains in the solid state. All of the polymers show photoluminescence in solutions and in the solid, and an electroluminescence device using PMeBTz as the emitting layer gives emission of light at $\lambda_{max} = 680$ nm with 100 cd m^{-2} at 8 V. A thin film of PMeBTz gives an optical third-order nonlinear susceptibility $\chi^{(3)}$ of 2.5×10^{-11} esu, which is larger than observed with PTh and PPy films, and comparison of the $\chi^{(3)}$ value with that (0.3×10^{-11} esu) of nonregioregular poly(4-methylthiazole-2,5-diyl) (PMeTz) reveals the importance of the regioregular structure of PMeBTz to give the larger $\chi^{(3)}$ value.

Introduction

The electronic, optical, and electric properties of π-conjugated poly(arylene)s have been the subject of many papers.[1] Among the poly(arylene)s, those made up of recurring five-membered rings [e.g., poly(thiophene-2,5-diyl) (PTh),[2] poly(pyrrole-2,5-diyl) (PPyrr),[3] and their derivatives (e.g., alkyl derivatives)[4]] have received much attention because of their interesting chemical and physical properties. They are considered to take coplanar structures and to form highly extended π-conjugated


PTh


PPyrr

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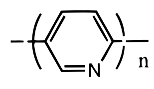
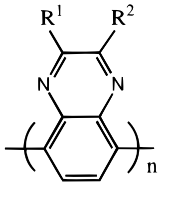
systems owing to their less sterically hindered structures compared with those of poly(arylene)s constituted of six-membered rings [e.g., poly(*p*-phenylene), PPP].

PTh and PPyrr are made up of "electron-excessive"[5] heterocyclic units and are susceptible to chemical and electrochemical oxidation (or p-doping). On the other hand, it has been recently reported that π-conjugated polyheterocycles containing electron-withdrawing imine nitrogen(s) (e.g., poly(pyridine-2,5-diyl) PPy[6a,b] and poly(quinoxaline-5,8-diyl) derivatives P[5,8-Qx(R^1R^2)]) show electron-accepting properties and are susceptible to reduction (or n-doping).[6c–j]

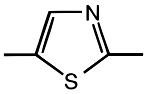


PPy



P(5,8-Qx(R^1R^2))

However, despite many examples of six-membered-ring poly(arylene)s with imine nitrogen(s), analogous π-conjugated polymers composed of recurring five-membered heterocyclic units have received much less attention. Here we report the preparation of new π-conjugated five-membered-ring poly(arylene)s containing the imine nitrogen



thiazole[7]

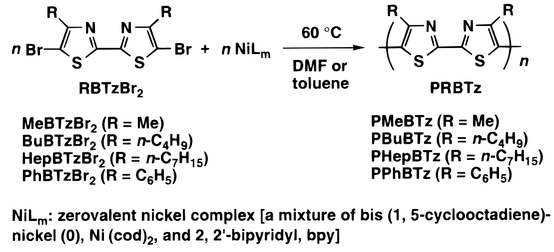
and their redox and optical properties in comparison with those of other π-conjugated polyheterocycles described above.

Stacking of planar π-conjugated polymer molecules in the solid state has attracted the attention of chemists for several years,[4b,d,g] and this paper is also concerned with the stacking of regioregular polythiazoles and the effect of the stacking on optical and electrochemical properties of the polymer. Part of the results have been reported in the form of a communication.[8]

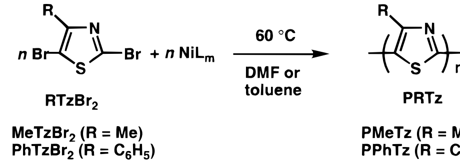
Curtis and co-workers separately reported the preparation of poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl)s and found thermochromism in a film of poly(4,4′-nonyl-2,2′-bithiazole-5,5′-diyl).[9]

Results and Discussion

Preparation. Dehalogenative polycondensation[2,6a–d] of 4,4′-dialkyl-5,5′-dibromo-2,2′-bithiazole ($RBTzBr_2$) with a zerovalent nickel complex gives the corresponding poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl) (PRBTz) in high yields (eq 1). Use of 2,5-dibromothiazole derivatives, $RTzBr_2$, affords another type of polymer (eq 2).

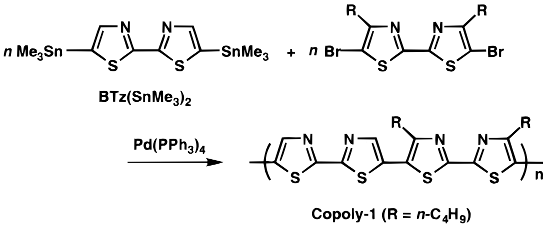


(1)



(2)

On the other hand, the following copolymer is obtained by using a Stille reaction:[10]



(3)

Table 1 summarizes the results of polymerization and basic optical data of the polymers.[11] In most cases the polymerization expressed by eqs 1 and 2 is carried out in DMF similarly to the previously reported Ni(0) complex-promoted polycondensation;[2d,6a–d] however, use of toluene[12a,b] as the solvent in eqs 1 and 2 also gives PBuBTz (run 3 in Table 1) and PMeTz, respectively.

IR, NMR, and Solution Properties. The IR and ^1H NMR data of the polymers agree with the polymer structures shown above. The IR spectra of PRBTz resembles those of the monomers except for the ν(C−Br) absorption bands, which are not observable in the IR spectra of the polymers. The IR spectrum of PMeTz

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[11] Use of 2,5-dibromothiazole in eq 2 also gives a polymeric material with an [η] value of 0.062 dL g^{-1} and λ_{max} at 421 nm in HCOOH. However, its IR spectrum shows very broadened absorption bands, and characterization of the material was not possible. Blocking of the 4-position of highly reactive thiazole[7] with the R group seems to be necessitated.

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Table 1. Preparation of Polymers

run	polymer[a]	yield, %	mol wt[b]	[η],[c] dL g^{-1}	ρ_v[d]	λ_{max}, nm in solution[c]	film[f]	PL,[e] λ_{max}, nm in solution[c]	PL,[e] λ_{max}, nm film
1	PMeBTz	68	3200 (LS)	0.60 (TFA)	0.10	425 (TFA) (ϵ = 18 000)	498[g,i] (425)[h]	562 (TFA) ($\Phi = 1.1 \times 10^{-2}$)	680 (670)[h]
2	PBuBTz	79	21000 (LS)	0.39 (DCA)	0.018	418 (TFA) (ϵ = 19 000) 405 ($CHCl_3$)[k]	560[i]	570 (TFA) ($\Phi = 1.6 \times 10^{-2}$)	580 (460)[j] 680 (560)[j]
3	PBuBTz[a]	84		0.85 (DCA)		422 (TFA) (ϵ = 20 000)	560[i]	570 (TFA) ($\Phi = 1.3 \times 10^{-2}$)	580 (460)[j] 680 (580)[j]
4	PHepBTz	79	11000 (GPC)	0.14 ($CHCl_3$)		420 (TFA) (ϵ = 15 000) 405 ($CHCl_3$) (ϵ = 12 000)	433	572 (TFA) ($\Phi = 1.7 \times 10^{-2}$) 561 ($CHCl_3$) ($\Phi = 5.5 \times 10^{-2}$)	544
5	PPhBTz	48				421 (TFA) (ϵ = 11 000) 371 ($CHCl_3$) (ϵ = 10 000)	382		
6	PMeTz	70		0.16 (HCOOH)		420 (HCOOH) (ϵ = 3900) 416 (TFA) (ϵ = 3500)	420	572 (HCOOH)	
7	PPhTz	71		0.13 (HCOOH)		446 (HCOOH) 434 (NMP) 458 (TFA) (ϵ = 5400)	437	567 (HCOOH)	
8	Copoly-1[a]	83		0.23 (TFA)		462 (TFA) (ϵ = 35 000)	438 455[h]	576 (HCOOH)	

[a] In DMF at 60 °C for runs 1, 2, and 4−7. In toluene at 60 °C for run 3. In toluene at 90−100 °C for run 7. [b] Method is shown in the parentheses. LS = light-scattering method. GPC = gel permeation chromatography (polystyrene standard). [c] Solvent for measurement is given in parentheses. TFA = CF_3COOH. DCA = $CHCl_2COOH$. NMP = *N*-methyl-2-pyrrolidone. ϵ = absorption coefficient (in cm^{-1} M^{-1}; molarity is based on the repeating unit). Φ = quantum yield. [d] Degree of depolarization. [e] Photoluminescence. [f] On a glass plate or an ITO glass plate. Examples (on ITO glass) are shown in Supporting Information. [g] 498 ± 7 nm. [h] Vacuum-deposited film. [i] The λ_{max} value varies with preparation conditions of the film.[15] [j] The position of photoluminescence depends on wavelength of irradiated light given in the parentheses (in nm). [k] For a $CHCl_3$-soluble part.

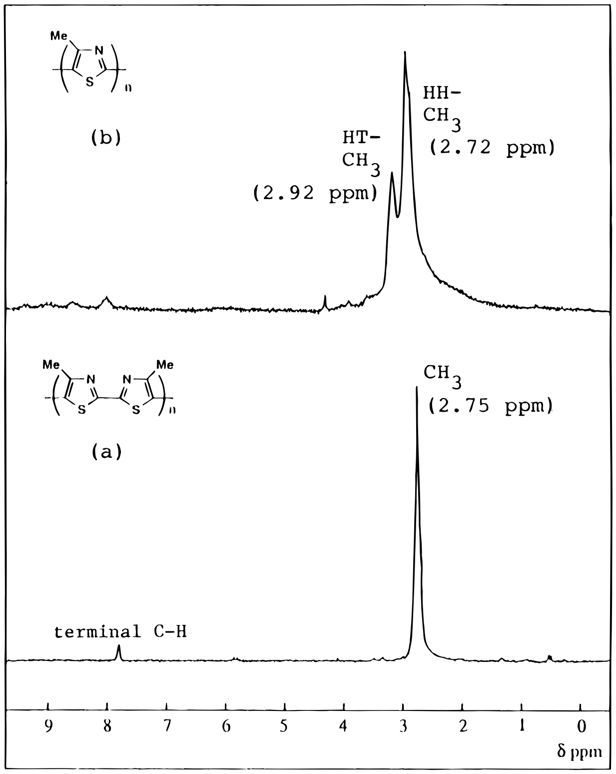
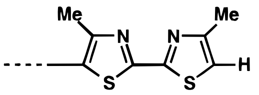


Figure 1. ^{1}H NMR spectra of (a) PMeBTz and (b) PMeTz in trifluoroacetic acid-*d*$_1$.

gives somewhat broadened absorption bands compared with those of PMeBTz, which may be ascribed to the presence of both the head-to-tail HT and head-to-head HH units in PMeTz. The IR signals of PRBTz and Copoly-1 are sharp.

Figure 1 shows the ^{1}H NMR spectra of PMeBTz and PMeTz. As shown in Figure 1, PMeBTz gives a sharp CH_3 signal at δ 2.75 ppm, whereas the ^{1}H NMR spectrum of PMeTz exhibits two signals at δ 2.72 and 2.92 ppm assigned to the CH_3 groups in the HH and HT units, respectively. An additional signal of PMeBTz (part a of Figure 1) at δ 7.78 ppm is assigned to aromatic H in the terminal thiazole ring:



The peak area of the terminal aromatic H agrees with the observed molecular weight of 3200 (run 1 in Table 1), if both the polymer ends have the H-terminated unit, which is considered to be formed from Ni-terminated polymer ends.[2d,6a] Introduction of a longer alkyl substituent at the thiazole ring enhances the solubility of the monomer and leads to an increase in the molecular weight of the polymer,[13] thus giving PBuBTz and PHepBTz with molecular weights of 21 000 (150 thiazole rings) and 11 000 (61 thiazole rings), respectively (runs 2 and 4).

A large [η] value of PMeBTz ([η] = 0.60 dL g^{-1}; run 1 in Table 1) for its molecular weight and the large degree of depolarization[14] of PMeBTz (ρ_v = 0.10; run 1 in Table 1) suggests that PMeBTz assumes a stiff structure in

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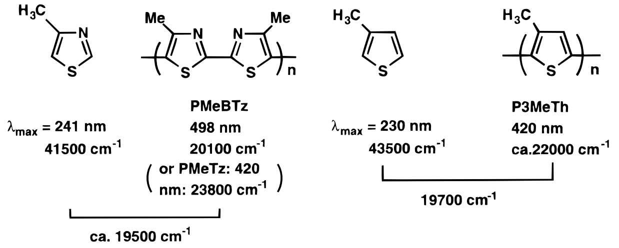
(13) PBuBTz and PHepBTz are not soluble in the polymerization solvent, DMF (cf. Supporting Information). However the Ni-promoted polycondensation usually proceeds even in seemingly insoluble precipitate of the polymer when the polymer has a side chain like alkyl group and its crystallinity is not high.[2d,6a]

(14) (a) Kubota, K.; Urabe, H.; Tominaga, Y.; Fujime, S. *Macromolecules* **1984**, *17*, 2096. (b) Kubota, K.; Chu, B. *Biopolymers* **1983**, *22*, 1461. (c) Zero, K.; Aharoni, S. M. *Macromolecules* **1987**, *20*, 1957.

Scheme 1. Shift of UV−Visible Absorption Band from That of the Monomeric Compound



the solution. The ρ_v value is comparable to that of stiff poly(*p*-benzamide).[14c] PBuBTz has a lower ρ_v value of 0.018, indicating that the polymer has a less stiff structure in solution, probably due to steric repulsion between the alkyl substituents and/or twisting out of the π-conjugated plane. PMeBTz shows a large refractive index increment of $\Delta n/\Delta c = 0.55$ cm^3 g^{-1} in trifluoroacetic acid when irradiated with 6328 Å light (He−Ne laser), whereas PBuBTz shows a smaller $\Delta n/\Delta c$ value of 0.43 cm^{-3} g^{-1}.

PMeBTz and PBuBTz are soluble in acidic solvents such as trifluoroacetic acid and dichloroacetic acid and insoluble or slightly soluble in the other organic solvents tested. On the other hand, PHepBTz is soluble in $CHCl_3$. Drying the solutions of the polymers, including the acidic solutions, under vacuum gives solvent-free polymer films as judged from the IR spectra of the films. It has recently been reported, based on ^{15}N NMR spectroscopy, that trifluoroacetic acid has considerably weaker ability to protonate nitrogen in an aromatic heterocycle compared with the ability to protonate an amine nitrogen.[12c]

UV−Visible Spectrum and Solid Structure. By forming a long π-conjugation system, the $\pi-\pi^*$ absorption bands of methylthiazole ($\lambda_{max} = 241$ nm) and α,α′-dimethylbithiazole (356 nm) are shifted to a longer wavelength (e.g., $\lambda_{max} = 498$ nm for a PMeBTz film;[15] run 1 in Table 1). The degree of red-shift (ca. 20 000 cm^{-1}) is comparable to those observed with thiophene-PTh (ca. 21 000 cm^{-1})[1,2b] and 3-methylthiophene[4a]−poly(3-methylthiophene-2,5-diyl) (P3MeTh, 19 700 cm^{-1})[4a] couples. Scheme 1 shows UV−visible data of films of the polymers and their corresponding monomers.

CPK molecular model analysis indicates that PMeBTz, PTh, and P3MeTh[4a] all can take a coplanar structure. Among these π-conjugated poly(arylene)s which can form a coplanar structure, PMeBTz has the highest solubility, therefore this polymer will contribute to better understanding of the electrochemical and optical properties of planar π-conjugated poly(arylene)s. It has recently been established by X-ray diffraction that a HH type tetramer of 3-methylthiophene, $(MeTh)_4$, which can be regarded as a model compound of P3MeTh with the HH sequence, takes a fully coplanar conformation in the solid state.[17a]

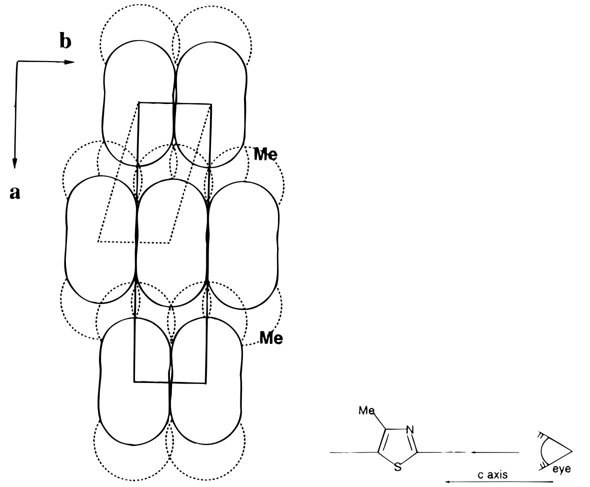


Figure 2. Two-dimensional molecular packing mode (seen from the polymer chain axis: *c* axis) of PMeBTz determined by X-ray diffraction. The unit indicates the thiazole unit seen from the *c*-axis.

By introducing a longer alkyl chain such as butyl and heptyl groups, the absorption peak of the film of the polymer is shifted to shorter wavelength (runs 2−4 and 8), similar to the case of 3-substituted polythiophenes (P3RTh).[2d,4] Although PMeBTz and PMeTz show the absorption peak at almost the same position in trifluoroacetic acid (runs 1 and 6), they show the $\pi-\pi^*$ absorption band at different positions in films, suggesting that there exists an intermolecular $\pi-\pi$ interaction between regioregular PMeBTz molecules in the solid.

A powder X-ray diffraction spectrum of PMeBTz shows several distinct peaks, and its analysis indicates that neighboring PMeBTz molecules take a face-to-face packing mode in the solid as depicted in Figure 2.[18] The molecular plane of PMeBTz is parallel to the *ac* plane (*c* axis in the direction of polymer chain), and the polymer molecules are stacked in a layer parallel to the *bc* plane. The pendant methyl group penetrates into the space between two adjacent chains in the next layer.

The calculated density 1.65 g cm^{-3} is quite high but consistent with the observed value, 1.55 g cm^{-3} at 25 °C; polymers usually give somewhat lower density than that calculated based on their crystalline structures since they usually contain an amorphous part. It is reported that α-sexithiophene Th_6[17b] molecules are arranged locally in a packing mode similar to that of PTh, whereas the above-described HH type $(MeTh)_4$[17a] forms a face-to-face packed structure. Planar polymer molecules with side chains may prefer the face-to-face parallel packing. A resonable packing mode of PMeBTz

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[15] The peak position and shape of the absorption bands of films of PMeBTz, PBuBTz, PHepBTz, and Copoly-1 vary with subtle preparative conditions of films. For example the peak position of the PMeBTz film is in a range of 498 ± 7 nm. There is a trend that a thicker film (on a glass substrate) and films of PBuBTz with larger $[\eta]$ give the λ_{max} at a longer wavelength. These results suggest that the polymer film contains both an amorphous part and a crystalline stacked part, and the thicker film contains the crystalline part in a higher content (see the text). PL data also support this view. We have found that the λ_{max} position of a film of regioregular (HH/HT = 10/0; cf. Scheme 2)[4b] P3HexTh also varies with similar preparative conditions of the film. On the other hand it has been recently reported that poly(3-alkylthiophene-2,5-diyl)s P3RTh's such as P3HexTh show thermochromism in films and solutions, which is, at least partly, attributed to a degree of stacking of polymers depending on temperature.[4b,d,g,16] Recently similar thermochromism of a film of poly(nonylbithiazole)[9] has been reported.

[16] (a) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (b) Yue, S.; Berry, G. C.; MacCullough, R. D. *Macromolecules* **1996**, *29*, 933. (c) Yoshino, K.; Nakajima, S.; Gu, H. B.; Sugimoto, R.-I. *Jpn. J. Appl. Phys.* **1987**, *26*, L2046.

[17] (a) Barbarella, G.; Zambianchi, M.; Mongini, A.; Antolini, L. *Adv. Mater.* **1992**, *4*, 282. (b) Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J.-L.; Garnier, F. *Chem. Mater.* **1995**, *7*, 1337.

[18] C-centered orthorhombic unit cell with dimensions $a = 14.1$ Å and $b = 3.64$ Å, $c = 7.61$ Å, $\gamma = 90$ °.

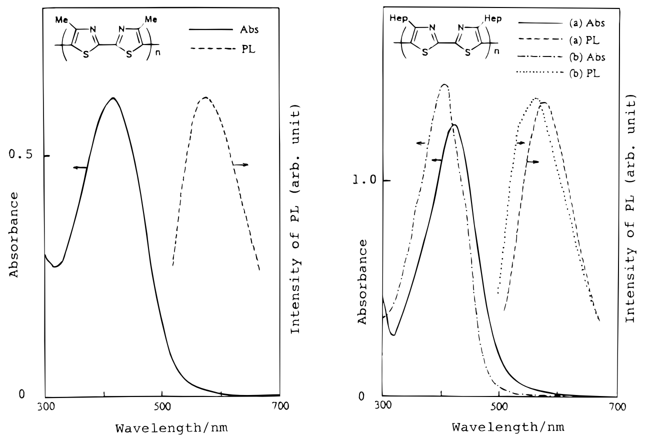


Figure 3. UV–visible (Abs) and photoluminescence (PL) spectra of PMeBTz (left) in CF_3COOH and PHepBTz (right) in CF_3COOH (a) and $CHCl_3$ (b).

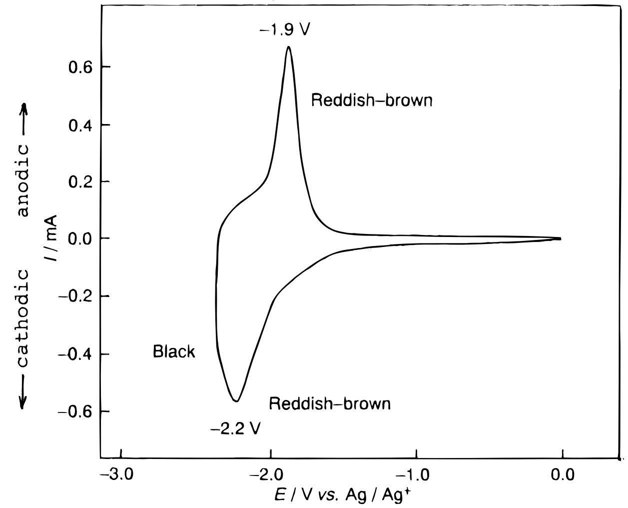
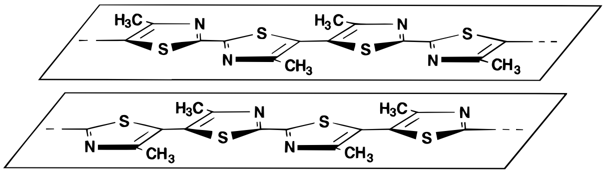


Figure 4. CV of PMeBTz in a MeCN solution of $[NEt_4][BF_4]$ (0.10 M) at 100 mV s^{-1}.

in view of the atomic van der Waals contacts is depicted below:



The PMeBTz molecules are considered to be stacked with a separation $b = 3.64$ Å[18] (Figure 2). The distance $b = 3.64$ Å is comparable to or somewhat smaller than that (3.79 Å)[4b] observed with regioregular HT type poly(3-hexylthiophene-2,5-diyl). A detailed X-ray analysis of PRBTz including PBuBTz and PHepBTz will be reported elsewhere.

In contrast to regioregular PMeBTz, regioirregular PMeTz gives only one broad powder X-ray diffraction peak at about 2θ (Cu Kα) = 25°, indicating that PMeTz does not take such a well-stacked structure as shown in Figure 2. The shift of the UV–visible absorption peak of crystalline PMeBTz in the solid state (cf. Figures 5 and 7 shown later) to a longer wavelength, compared with the absorption peak of the amorphous film of PMeTz, seems to be attributable to the presence of the intermolecular π–π interaction in the case of PMeBTz. A similar shift has been reported for regioregular head-to-tail (HT) type P3HexTh and regioirregular P3HexTh.[4b,g]

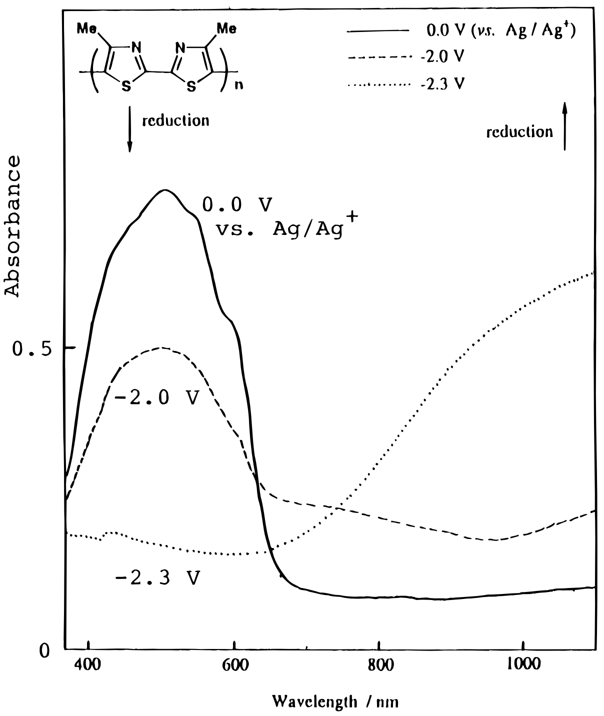


Figure 5. Changes in the absorption spectrum of a film of PMeBTz on an ITO glass electrode during electrochemical n-doping (reduction) in a CH_3CN solution of $[NEt_4]BF_4$ (0.10 M). The changes in absorption spectrum are reversible.

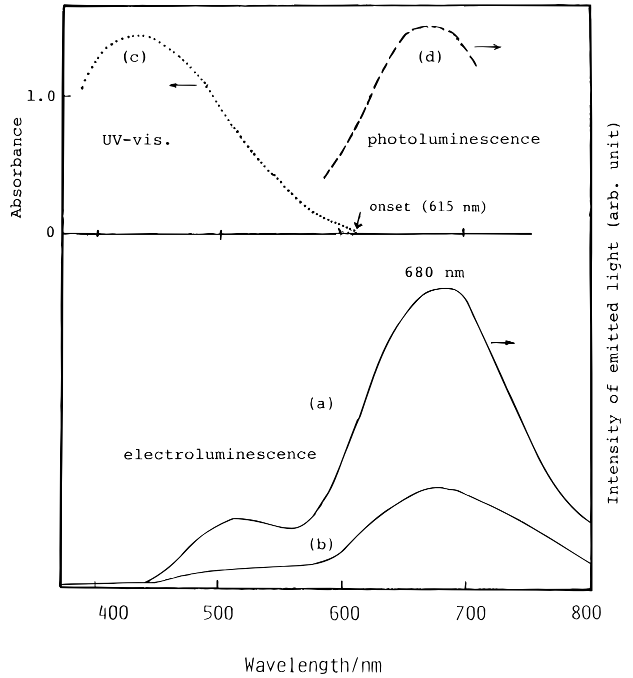


Figure 6. Electroluminescence of type 3 device at (a) 100 mA cm^{-2} and (b) 20 mA cm^{-2}. Graphs (c) and (d) exhibit absorption and photoluminescence spectra of the vacuum deposited film of PMeBTz, respectively.

The UV–visible peaks (in the solid state) are shown in Scheme 2. The degree of the shift is larger in the case of P3HexTh, presumably due to higher stacking order of the HT type P3HexTh.[4b]

In solutions, both PMeTz and PMeBTz give an absorption peak (at about 420 nm) near the absorption

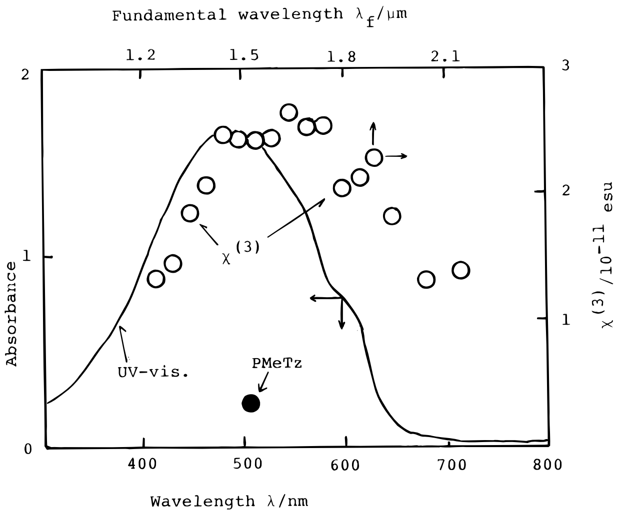


Figure 7. (a) UV–visible spectrum (–) and (b) dependence of the magnitude of $\chi^{(3)}$ against wavelength (○) of the PMeBTz film (thickness = ca. 0.2 μm). UV–visible data are based on λ and absorbance, whereas $\chi^{(3)}$ data are based on λ_f. Datum of the PMeTz film is shown by (●).

Scheme 2. Effect of Stacking on the UV–Visible Absorption (Data from the Film)

PMeTz(run 6)	PMeBTz (run 1)	regio-irregular (HT/HH = 3/7) P3HexTh	regioregular (HT/HH = 10/0) P3HexTh
420 nm	498 nm	431 nm	560 nm
23800 cm^{-1}	20100 cm^{-1}	23200 cm^{-1}	17900 cm^{-1}
ΔE =3700 cm^{-1}		ΔE =5300 cm^{-1}	

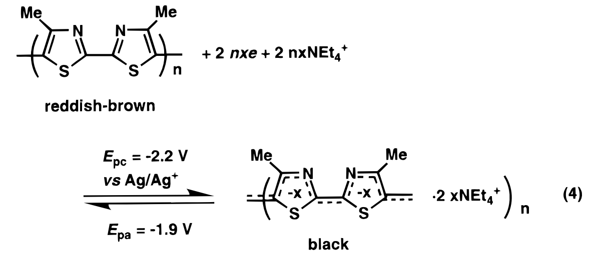
peak position of the amorphous PMeTz film. Similarly, in solutions (e.g., in $CHCl_3$ and CH_2Cl_2), both the regioirregular and regioregular P3HexTh's exhibit an absorption peak (at about 430 nm) near the absorption peak of the amorphous film of P3HexTh.[4b,g] These results also support the presence of an intermolecular $\pi-\pi^*$ interaction in the film of regioregular PMeBTz and P3HexTh. UV–visible data of PBuBTz in the solution and film (run 3) also suggest the presence of an intermolecular $\pi-\pi$ interaction in the solid state. The UV–visible spectrum of the film of PBuBTz exhibits a shoulder at about 450 nm, which seems to originate from an amorphous part of the film,[15] besides the main absorption band at 550 nm; the energy difference between the two absorption bands is about 4000 cm^{-1}. PMeBTz forms a Ru complex with $Ru(bpy)_2^{2+}$ (cf. Supporting Information).

Photoluminescence PL. PMeBTz, PBuBTz, and PHepBTz all give photoluminescence PL in trifluoroacetic acid with their peaks at 562, 570, and 572 nm, respectively; PHepBTz exhibits photoluminescence at λ_{max} = 561 nm in $CHCl_3$. The peak positions of photoluminescence agree with onset positions of the absorption bands of the polymers (Figure 3), as usually observed with photoluminescent aromatic compounds.

As described above, the absorption peak of regioregular PMeBTz is shifted to a longer wavelength in the film (by about 80 nm), and this shift is accompanied by a shift in the onset of the absorption band to a longer wavelength by about 120 nm. This shift in the onset leads to a shift of the PL peak of PMeBTz at 562 nm to a longer wavelength (680 nm) by about 120 nm in the film, suggesting that the PL process in the film also involves an intermolecular $\pi-\pi$ interaction.

On the other hand, the film of regioirregular PMeTz shows a PL peak at about 570 nm near the onset of the unimolecular absorption band. A similar difference in the PL position is observed between films of regioirregular P3HexTh (PL peak = 590 nm) and regioregular P3HexTh (PL peak = 670 nm), although both the polymers give a PL peak at a similar peak position (555 and 577 nm, respectively) in $CHCl_3$. These data indicate that both the $\pi-\pi^*$ absorption and the PL in the polymer solids mainly take place through a multimolecular (not unimolecular) process due to the presence of the $\pi-\pi$ interaction.

Redox Behavior. Figure 4 shows the cyclic voltammogram (CV) of PMeBTz. Reduction (n-doping) of PMeBTz starts at ca. 1.5 V vs Ag/Ag$^+$ with a peak cathode potential E_{pc} of -2.2 vs Ag/Ag$^+$. Changing the scanning direction causes n-undoping with an anodic peak potential E_{pa} of -1.9 V vs Ag/Ag$^+$. The electrochemical processes can be expressed by eq 4 and the CV cycle shown in Figure 4 can be repeated more than five times with no observable change in the CV curve.



(4)

The redox potential, $E°$, obtained as an average of E_{pc} and E_{pa} [$E° = (E_{pc} + E_{pa})/2 = -2.05$ V vs Ag/Ag$^+$] appears at more positive value than those observed with PTh [$E°$(PTh) = -2.14 V[19] vs Ag/Ag$^+$] and P3MeTh [$E°$(P3MeTh) = -2.30 vs Ag/Ag$^+$],[20] revealing that the electrochemical reduction of PMeBTz is easier than those of PTh and P3MeTh.

Comparison of the $E°$ data of PMeTz and P3MeTh indicates that the introduction of the imine nitrogen to the thiophene ring also enhances the electron-withdrawing ability of the five-membered ring polymer, similarly to the case of the six-membered ring polymers, and leads to a shift of the $E°$ value by ca. 0.4 V. The degree of the shift of the $E°$ value is comparable to that (0.3–0.5 V) observed upon the introduction of the imine nitrogen to PPP and poly(naphthalenediyl) type polymers.[6c,19c]

Owing to the enhancement of their electron-withdrawing ability, PRBTz's and PRTz's are not susceptible to p-doping (oxidation) up to 0.6 V vs Ag/Ag$^+$, in contrast to facile p-doping of PTh at about 0.5 V vs Ag/Ag$^+$. Scanning beyond 0.6 V vs Ag/Ag$^+$ seems to cause degradation of PMeBTz, owing to the high reactivity of the thiazole ring.[7] The difference in the $E°$ value (by 0.20 V) between PMeBTz and PMeTz (Table 2) is attributed to the difference in the packing mode between the two polymers; the n-doping of amorphous PMeTz proceeds more easily.

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(19) (a) Zotti, G.; Shiavon, G. *J. Electroanal. Chem.* **1984**, *163*, 385. (b) Yamamoto, T.; Kanbara, T.; Mori, C.; Wakayama, H.; Fukuda, T.; Inoue, T.; Sasaki, S. *J. Phys. Chem.* **1996**, *100*, 12631; EP 1995-643118. (c) Yamamoto, T. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 997.

(20) Measured with a film of chemically prepared P3MeTh[4a] ($CHCl_3$ soluble part) prepared by casting on a Pt plate from $CHCl_3$ solution.

Table 2. CV Data of Polymers[a]

no.	polymer	E_{pc}	E_{pa}	$E°$
1	PMeBTz	−2.24	−1.87	−2.06
2	PBuBTz	−2.09	−1.95	−2.02
3	PHepBTz	−2.17	−1.99	−2.08
		−2.37	−2.22	−2.30
4	PMeTz	−1.93	−1.79	−1.86
5	PPhTz	−1.95	−1.58	−1.77
6	Copoly-1	−2.02	−1.81	−1.92

[a] E_{pc} = peak cathode potential vs Ag/Ag$^+$. E_{pa} = peak anode potential. $E° = (E_{pc} + E_{pa})/2$. Measured with a cast film on a Pt plate in a CH_3CN solution of $[NEt_4][BF_4]$ (0.10 M).

All of the other polymers are also n-doped with an $E°$ value of about −1.8 to −2.1 V vs Ag/Ag$^+$ and they are inert against p-doping. Although five-membered ring aromatic heterocycles are generally regarded as π-excess compounds,[5] the ionization potential (9.50 eV[7]) of thiazole is considerably larger than those of thiophene (8.87 eV) and pyrrole (8.20 eV),[21a] and MO calculations[22] indicate that the thiazole ring has a π-deficient nature. The CV data are summarized in Table 2. The electrochemical behaviors of molecules having large π-conjugation systems and those of polymer-modified electrodes have been the subject of recent interest.[21b−d]

The n-doping and undoping of PMeBTz are accompanied by color changes as shown in eq 4 and Figure 4. The color change can be followed spectroscopically by using a cast film on an ITO (indium−tin oxide) glass plate, and the results are shown in Figure 5. As shown in Figure 5, the strength of the original π−π* absorption band of PMeBTz at 505 nm decreases and a new broad absorption band toward the near-infrared appears on n-doping. It is known that similar new broad absorption bands appear on n- or p-doping of various π-conjugated poly(arylene)s, and the new absorption bands are considered to originate from formation of polarons or bipolarons.[1] The changes in the absorption spectrum are reversible, and application of the n-undoping potential recovers the original spectrum at 0 V vs Ag/Ag$^+$.

The changes in the absorption spectrum shown in Figure 5 are similar to those observed during n-doping of PPy,[6a] and films of the polymers including PBuBTz, PHepBTz, and Copoly-1 also give analogous changes in absorption spectra during the n-doping (see Supporting Information).

The polymers themselves are essentially insulators. However, n-doping of the polymers with sodium naphthalenide raises their electrical conductivity by an order of 10^5 to give semiconducting materials with an electrical conductivity of 7.7×10^{-5} to 9.8×10^{-4} S cm^{-1} (measured with compressed powders; cf. Supporting Information). On the other hand, iodine doping leads to only a minor change in the electrical conductivity of the polymer, and these results are consistent with the electron-accepting properties of the polymers.[6a]

Electroluminescent Diode. Light-emitting diodes (LEDs) using fluorescent π-conjugated polymers are now being actively investigated.[23] By using a vacuum deposition method,[19b] the following types 1−4 devices have been prepared: type 1 (+) ITO/PMeBTz (thickness = 30 nm)/Mg(Ag) (−); type 2 (+) ITO/PTh (10 nm)/PMeBTz (30 nm)/Mg(Ag) (−); type 3 (+) ITO/PTh (10 nm)/TPD (59 nm)/PMeBTz (15 nm)/Alq_3 (10 nm)/Mg-(Ag) (−).

The type 1 device is a simple device with a single-layer structure. On the other hand, in cases of the types 2 and 3 devices, PTh, TPD, and Alq_3 layers are inserted between the electrodes and the PMeBTz layer to introduce holes and electrons into the PMeBTz layer efficiently. PTh[6c,19b] and TPD[24] (*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine) are known as excellent hole-transporting materials, whereas Alq_3 (tris(8-quinolinolato)aluminum)[25] serves as an excellent electron-transporting material. It has recently been reported that such multiple-layer structures enhance light emission capability of LEDs.[23,25,26] All of the organic materials were vacuum deposited[19b] to avoid dust in the device, and curves observed with the types 1−3 devices show normal rectification of electric current by the LED devices:[23,25,26] the bias shown above (ITO is the (+) side) is a forward bias which gives much larger electric current than a reverse bias (ITO is the (−) side). Graphs a and b in Figure 6 depict the electroluminescence spectra of the type 3 device.

The IR spectrum of vacuum deposited PMeBTz is essentially identical with that of the original PMeBTz (cf. Supporting Information). The UV−visible spectrum (graph c in Figure 6) of vacuum deposited[27] PMeBTz exhibits an absorption peak at a somewhat shorter wavelength (λ_{max} = 425 mnm) than that of cast PMeBTz film (run 1 in Table 1) suggesting that the vacuum deposited PMeBTz molecules are in an amorphous state and do not form the well-stacked structure shown in Figure 2.[28] The onset of the absorption band of vacuum deposited PMeBTz film appears at 615 nm, which is shorter by 65 nm than that of the cast film of PMeBTz. The vacuum deposited PMeBTz film exhibits a photoluminescence PL at 670 nm (run 1 in Table 1 and graph d in Figure 6).

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(26) (a) Brown, A. R.; Greenham, N. C.; Burroughes, J. H.; Bradley, D. D. C; Friend, R. H.; Burn, P. L.; Kraft, A.; Holmes, A. B. *Chem. Phys. Lett.* **1992**, *200*, 46. (b) Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, L269.

(27) The following references and mass spectra in the references indicate that poly(arylene)s with molecular weight of up to about 2000 are sublimable. (a) Brown, C. E.; Kovacic, P.; Wilkei, C. A.; Cody, R. B., Jr.; Kinsinger, J. A. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 453. (b) Brown, C. E.; Kovacic, P.; Wilkei, C. A.; Cody, R. B.; Kein, R. E.; Kinsinger, J. A. *Synth. Met.* **1986**, *15*, 265. Poly(2-methylanthraquinone-1,4-diyl)[6d] can be evaporated up to molecular weight of about 5000 under vacuum.

Types 1 and 2 junctions show only weak electroluminescence. However, insertion of both the hole-transporting PTh and TPD layers and an electron-transporting Alq_3 layer (type 3 junction) enhances the electroluminescence (100 cd m^{-2} at 8 V and 75 mA cm^{-2}), presumably due to efficient injection of holes and electrons in the PMeBTz thin film through the TPD and Alq_3 layers, respectively.

As shown in Figure 6 (graphs a and b), the type 3 device gives the major electroluminescence at 680 nm, which is shifted from the onset (615 nm) of the $\pi-\pi^*$ absorption band of the vacuum deposited film of PMeBTz and agrees with the PL peak of the cast PMeBTz film.

A PL peak of the vacuum deposited PMeBTz film (graph d in Figure 6) also appears near the onset of the absorption band (or the PL peak position) of the crystalline cast PMeBTz film. These results suggest that even if the vacuum-deposited PMeBTz film is amorphous as discussed above, the photoactivated PMeBTz molecules form a locally stacked structure by an interaction with neighboring PMeBTz molecules, and the electroluminescence also involves a similar interaction.

A weak emission at about 500−550 nm is considered to be unimolecular light emission from the PMeBTz film or emission from Alq_3. As described above, PMeBTz (and also PMeTz) gives photoluminescence at about 560 nm in solutions and Alq_3 reportedly emits light at 550 nm.[25]

Optical Third-Order Nonlinear Susceptibility $\chi^{(3)}$. Optical third-order nonlinear properties of films of π-conjugated polymers are of recent interest,[1,29] and $\chi^{(3)}$ values of PTh containing S and PPy containing N have been reported. In addition, it has been reported that copolymers of pyridine and thiophene having an intramolecular CT structure give a much larger $\chi^{(3)}$ value compared with those of PTh and PPy homopolymers.[30]

Since the thiazole ring has a unique structure containing both S and N, estimation of the optical third-order nonlinear properties of the present polymers is intriguing. Comparison of the nonlinear optical properties of films of PMeBTz and PMeTz with different morphologies is also interesting.

Figure 7 shows the dependence of the magnitude of the $\chi^{(3)}$ of the PMeBTz film on a glass substrate. As shown in Figure 7, the PMeBTz film gives a maximum $\chi^{(3)}$ of about $\chi^{(3)}{}_{max} = 2.5 \times 10^{-11}$ esu at a three-photon resonant region of PMeBTz [fundamental wavelength $\lambda_f(max) = 1500-1800$ nm; $\lambda_f(max)/3 = 500-600$ nm; fundamental wavelength λ_f = wavelength of light irradiated against the sample film]. The $\chi^{(3)}{}_{max}$ of π-conjugated molecules usually appears at the three-photon resonance region.[1,29,30] The $\chi^{(3)}{}_{max}$ value of PMeBTz is larger than those of the PTh and PPy films ($\chi^{(3)}{}_{max} = 0.7-0.9 \times 10^{-11}$ esu); however, it is smaller than that of copolymers of thiophene and pyridine having an intramolecular CT structure ($\chi^{(3)}{}_{max} = 4.9 \times 10^{-11}$esu).[30]

As shown in Figure 7, the absorption band of the PMeBTz film exhibits shoulders or subband structures with an energy separation of about 1600 cm^{-1}. Similar subband structures have been observed with films of vacuum-deposited α-oligothiophene Th_n[28a] and PTh,[31] and they have been assigned to coupling of the electronic transition with the ring vibration of the aromatic compounds. As for the vacuum deposited PTh film, it is also reported[31a] that the $\chi^{(3)}$ profile shows substructures originating from the shoulder subbands in the absorption band, and this is attributed to vibronic enhancement of $\chi^{(3)}$ which is sometimes observed with other organic molecular systems.[32] The $\chi^{(3)}$ profile of the PMeBTz film also seems to have similar substructures associated with the vibronic structure of the absorption band.

Although the PMeBTz film has a large $\chi^{(3)}$ value, a PMeTz film shows a much smaller $\chi^{(3)}$ value of 0.3×10^{-11} esu (Figure 7). The marked enhancement of $\chi^{(3)}$ in the PMeBTz film is apparently attributed to the shift of the absorption band to the longer wavelength due to the intermolecular $\pi-\pi$ interaction, since it is known that a narrower bandgap of a π-conjugated polymer brings about a larger $\chi^{(3)}$. However, formation of special electronic state(s) contributing to $\chi^{(3)}$ caused by the intermolecular $\pi-\pi$ interaction is also conceivable, and the study by using other polymer materials with similar stacked structures is considered to be important in the search for polymeric materials with large $\chi^{(3)}$ that are suited to the rapid switching of light.

Conclusions

A new class of π-conjugated polymers, poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl)s (PRBTz's) and their analogues, have been prepared by organometallic polycondensation, and their electrochemical and optical properties have been compared with those of polythiophenes PTh's and polypyridines PPy's. PMeBTz is crystalline and exhibits face-to-face stacking, and the importance of the stacked (or self-assembled) structure in the understanding of its optical and electrochemical properties has been demonstrated. For example, such stacking brings about a bathochromic shift of the $\pi-\pi^*$ absorption band, a similar shift of photoluminescence band, and large enhancement of the $\chi^{(3)}$ value. All of the polymers which contain the thiazole ring are electrochemically active against reduction (n-doping) due to the presence of the electron-withdrawing imine nitrogen; however, they are inert against oxidation. The polymers are photoluminescent and PMeBTz emits light in a multilayer structure on application of a dc voltage of about 8 V.

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(28) (a) In relation to this, we also have to take in a report that vacuum-deposited oligothiophene Th_n shows the absorption peak at shorter wavelength than that of Th_n in solution, since a similar hypsochromic shift may occur in the vacuum-deposited PMeBTz. For example, vacuum deposited Th_4 shows a $\pi-\pi^*$ absorption peak at 345 nm (Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1992**, *48*, 167), which is shifted from that (391 nm: Sease, J. W.; Zechmeister, L. *J. Am. Chem. Soc.* **1947**, *69*, 270) in benzene. (b) In addition, formation of well-packed structure in the vacuum deposited film requires selected conditions even for highly crystalline PPP and PTh without the alkyl substituent.[19b]

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Experimental Section

Materials. All solvents were dried, distilled, and stored under N_2. PTh's,[2,4] PPy's,[6a,b] Ni(cod)$_2$,[6a−d] Pd(PPh$_3$)$_4$,[33] RuCl$_2$(bpy)$_2$,[34] and the dibromo monomers (RBTzBr$_2$ (eq 1) and RTzBr$_2$ (eq 2))[35−37] were prepared according to the literature procedure. Stereoregular HT type R3HexTh was purchased from Rieke Metals, Inc.

Polymerization. Ni(cod)$_2$ (719 mg, 2.59 mmol) and bpy (419 mg, 2.59 mmol) were dissolved in 60 mL of DMF in a Schlenk tube under nitrogen. To the solution was added 5,5′-dibromo-4,4′-dimethyl-2,2′-bithiazole (700 mg, 1.98 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 32 h to yield a reddish-brown precipitate (run in Table 1). The precipitate was collected by filtration, washed with an aqueous solution of ammonia (four times), an aqueous solution of disodium ethylenediaminetetraacetate (twice), and methanol (three times) in this order, and dried under vacuum to obtain a reddish-brown powder of PMeBTz. Anal. Found: C, 48.3; H, 3.4; N, 13.7; Br, 0.9. $M_w = 3200$. Calcd for $(-C_8H_6N_2S_2\cdot 0.3H_2O-)_n$: C, 48.1; H, 3.3; N, 14.0. ^{1}H NMR (CF_3COOD, 90 MHz) δ 2.75 (3H, CH_3), 7.78 ppm (0.06 H, terminal-H). 4,4′-Dimethyl-2,2′-bithiazole gives its 5,5′-H peak at δ 7.62 ppm in CF_3COOD.

Other PRBTz's were prepared analogously. PBuBTz was also partly hydrated, however, PHepBTz became water-free by drying under vacuum.

Measurements. Measurements were carried out in manners similar to those previously reported.[6a−c,30a] The method to determine the quantum yield of PL is given in the Supporting Information.

Supporting Information Available: Experimental details and characterization data of polymers other than PMeBTz, solubility of polymers, experimental details of measurements and Ru complex formation, electrical conductivity of polymers, and UV−visible, IR, and NMR charts of selected polymers (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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