Macromolecules **2003,** *36,* 1047−1053

Synthesis and Chemical Properties of π-Conjugated Poly(imidazole-2,5-diyl)s

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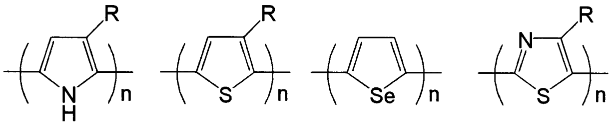
Received July 15, 2002; Revised Manuscript Received November 15, 2002

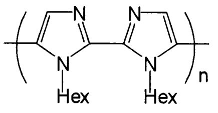
ABSTRACT: Poly(*N*,*N*′-dihexyl-2,2′-biimidazole-5,5′-diyl), **PBIm(NHex)**, poly(*N*,*N*′-dimethoxymethyl-2,2′-biimidazole-5,5′-diyl), **PBIm(NMOM)**, and poly(*N*-methylimidazole), **PIm(NMe)**, were prepared by dehalogenative polycondensation using a zerovalent nickel complex. **PBIm(NHex)**, **PBIm(NMOM)**, and **PIm(NMe)** showed number-average molecular weights, M_n's, of 15000, 12000, and 8200 (GPC; poly(methyl methacrylate) standards), respectively, and **PBIm(NHex)** gave an [η] value of 0.24 dL g^{-1} in formic acid. **PBIm(NHex)** showed a UV−vis absorption peak at 308 nm in $CHCl_3$, which was shifted by 97 nm to a longer wavelength from that of *N*-hexylimidazole. Powder XRD data of **PBIm(NHex)** and **PIm(NMe)** supported formation of a stacked structure in the solid. Films of polymers received electrochemical oxidation at about 1.0 V vs Ag^+/Ag. Deprotection of **PBIm(NMOM)** afforded poly(2,2′-imidazole-5,5′-diyl) which showed UV−vis peaks at 320 nm in film and at 350 nm in formic acid, respectively. **PBim(NHex)** formed a copper(II) complex in reaction with $CuCl_2$, which was followed by UV−vis spectroscopy.

Introduction

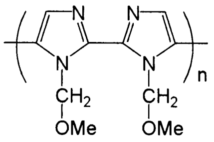
π-Conjugated polymers are the subject of many recent papers.[1] π-Conjugated poly(heterocycle)s constituted of recurring five-membered rings have especially attracted attention, and various five-membered ring π-conjugated polymers such as poly(pyrrole)s, poly(thiophene)s, poly(selenophene)s, poly(thiazole)s, poly(silole)s, poly(thiophene-1,1-dioxide)s, and their derivatives have been synthesized.



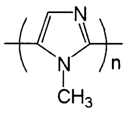
Imidazole is an interesting building block for π-conjugated polymers because of its attractive chemical properties (e.g., acid−base reactions and metal-complex forming reactivity)[2,3] and high importance in biosystems.[3] Recently use of low-molecular-weight imidazoles as basic compounds for electrically conducting materials (e.g., solid electrolytes) has also been actively investigated.[2d,e] Non-π-conjugated polymers with imidazole groups in the side chain have long been studied, especially as polymer catalysts.[4] However, synthesis of π-conjugated poly(imidazole)s containing the imidazole unit in the main chain and revealing their chemical properties[2f] have received much less attention. Herein we report preparation of new π-conjugated polymers consisting of the imidazole unit.



PBIm(NHex)
Hex = *n*-C_6H_{13}

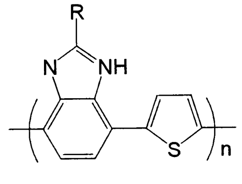


PBIm(NMOM)



PIm(NMe)

Although several π-conjugated polymers consisting of benzimidazoles,[5] e.g.



have been reported, the polymer consisting of the π-conjugated imidazole unit will give more direct information on the role of the imidazole unit in the π-conjugated polymer.

Experimntal Section

Materials. Bis(1,5-cyclooctadiene)nickel(0),[6] 2,2′-biimidazole,[7] and alkylated imidazoles and 2,2′-biimidazoles[8] were prepared according to the literature. 2,2′-Bipyridyl (bpy) was purchased from Tokyo Chemical Industry Co. Ltd.

Synthesis of Monomers. 2,5-Dibromo-*N*-methylimidazole was prepared following a literature method.[9] 5,5′-Dibromo-*N*,*N*′-dialkyl-2,2′-biimidazoles were prepared as follows.

N-Bromosuccinimide (2.4 g, 14 mmol) was added to an anhydrous chloroform solution (10 mL) of *N*,*N*′-dimethyl-2,2′-biimidazole (1.1 g, 7.0 mmol) under vigorous stirring under air. After 2 h, the reaction mixture was neutralized with NaOH(aq), and the product was extracted with chloroform.

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10.1021/ma0211232 CCC: $25.00

After being washed with water, the extract was dried over $MgSO_4$, condensed under vacuum, and purified by column chromatography on SiO_2 (eluent = 1:1 mixture of ethyl acetate and chloroform) and recrystallization from hexane to obtain 1.4 g (yield = 64%) of white 5,5′-dibromo-*N*,*N*′-dimethyl-2,2′-biimidazole. ^1H NMR ($CDCl_3$): δ 7.11 (s, 2H), 3.96 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 130.9, 128.4, 106.7, 33.8. Anal. Calcd for $C_8H_8Br_2N_4$: C, 30.03; H, 2.52; N, 17.51; Br, 49.94. Found: C, 29.85; H, 2.15; N, 17.56; Br, 50.09.

5,5′-Dibromo-*N*,*N*′-dihexyl-2,2′-biimidazole was prepared analogously from 1.2 g (3.9 mmol) of *N*,*N*′-dihexyl-2,2′-biimidazole, and *N*-bromosuccinimide (1.4 g, 7.8 mmol) and purified by chromatography on SiO_2 (eluent = chloroform) and recrystallization from methanol. Yield: 1.7 g (94%). ^1H NMR ($CDCl_3$): δ 7.1 (s, 2H), 4.4 (t, 4H), 1.2−1.7 (m, 16H), 0.86 (t, 6H). ^{13}C NMR ($CDCl_3$): δ 138.5, 128.7, 105.5, 46.1, 31.2, 30.2, 26.1, 22.5, 13.9. Anal. Calcd for $C_{18}H_{28}Br_2N_4$: C, 46.97; H, 6.13; N, 12.17; Br, 34.72. Found: C, 46.57; H, 6.09; N, 12.09; Br, 34.94.

5.5′-Diiodo-*N*,*N*′-dimethoxymethyl-2,2′-biimidazole was prepared by modifying a literature method.[10]

A hexane solution of butyllithium (1.53 M, 10.5 mL; 16.1 mmol) was added dropwise to an anhydrous THF (100 mL) solution of tetramethylpiperidine (2.7 mL, 16 mmol) at −78 °C under nitrogen. After this was stirred for 30 min, an anhydrous THF (50 mL) solution of *N*,*N*′-dimethoxymethyl-2,2′-biimidazole (1.6 g, 7.3 mmol) cooled to −78 °C was added dropwise to the reaction mixture at −78 °C. After the reaction was stirred for 1 h at −78 °C, a THF (20 mL) solution of iodine (4.1 g, 16 mmol) was added. After this mixture was stirred for 2 h at −78 °C, water was added, and the product was extracted with a mixture of hexane and THF. The extract was washed with water and an aqueous solution of $Na_2S_2O_3$, dried over $MgSO_4$, and condensed under vacuum. Purification by column chromatography on SiO_2 (eluent = a 1:1 mixture of ethyl acetate and chloroform) and recrystallization from methanol gave a white solid of the product in 52% yield (1.8 g). ^1H NMR ($CDCl_3$): δ 7.24 (s, 2H), 5.90 (s, 4H), 3.26 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 140.3, 136.4, 76.5, 73.8, 56.0. Anal. Calcd for $C_{10}H_{12}I_2N_4O_2$: C, 25.34; H, 2.55; N, 11.82. Found: C, 25.23; H, 2.46; N, 11.74

Synthesis of Polymers. 5,5′-Diiodo-*N*,*N*′-dimethoxymethyl-2,2′-biimidazole (1.5 g, 3.2 mmol) was added to an anhydrous DMF (50 mL) solution of $Ni(cod)_2$ (1.4 g, 5.2 mmol) and bpy (0.81 g, 5.2 mmol) under nitrogen. After the reaction was stirred for 48 h at 60 °C, the formed brown powder was washed with aqueous ammonia (three times) and dried under vacuum to yield 540 mg (77%) of poly(*N*,*N*′-dimethoxymethyl-2,2′-biimidazole-5,5′-diyl). **PBIm(NMOM)**. ^1H NMR ($CDCl_3$): δ 7.1−7.6 (2H), 5.8(br, about 3H), 3.2−3.8 (br, 6H). Anal. Calcd for $(C_{10}H_{12}N_4O_2)_n$: C, 54.54; H, 5.49; N, 25.44. Found: C, 52.92; H, 5.54; N, 24.38; I, 0.96. The polymer may contain hydrated water. E.g., Anal. Calcd for $H(C_{10}H_{12}N_4O_2{\cdot}0.1H_2O)_{50}I$: C, 53.48; H, 5.48; N, 24.95; I, 1.13.

PBIm(NHex) and **PIm(NMe)** were prepared analogously.

PBim(NHex). ^1H NMR (CF_3COOD): δ 7.8−8.3 (m, 2H), 4.38 (br, 4H), 0.8−1.9 (m, 22H). ^{13}C NMR ($CDCl_3$): δ 139.6, 131.0, 128.1, 122.4, 122.0, 47.5, 45.4, 31.1, 26.1, 22.6, 13.9. Anal. Calcd for $(C_{18}H_{28}N_4)_n$: C, 71.96; H, 9.39; N, 18.65. Found: C, 70.98; H, 9.34; N, 18.45; Br, 0.00.

PIm(NMe). ^1H NMR (CF_3COOD): δ 7.8−8.3 (m, 2H), 3.7−4.2 (m, 3H). Anal. Calcd for $(C_4H_4N_2)_n$: C, 59.99; H, 5.03; N, 34.98. Found: C, 58.09; H, 4.95; N, 32.51; Br, 0.40.

Use of 5,5′-dibromo-*N*,*N*′-dimethyl-2,2′-biimidazole as the monomer in a similar dehalogenative polymerization also gave a brown polymer. However, the product contained a considerable amount of Br. ^1H NMR (CF_3COOD): δ 7.7−8.3 (m, 2H), 3.9−4.1 (m, 6H). Anal. Calcd for $Br(C_8H_8N_4)_{14}Br$: C, 56.00; H, 4.70; N, 32.65; Br, 6.65. Found: C, 55.42; C, 4.79; N, 32.07; Br, 6.65.

Deprotection of **PBIm(NMOM)** was carried out according to a literature method.[11] **PBIm(NMOM)** (0.20 g, 0.90 mmol monomer unit) was treated with a mixture of LiBr (2.6 g, 30 mmol) and $BF_3{\cdot}OMe_2$ (10 mL, 110 mmol) in acetic anhydride (53 mL) for 48 h at room temperature. Crashed ice was added to the reaction mixture under cooling in an ice bath, and the reaction mixture was nuetralized with an aqueous solution of NaOH. The precipitate was separated by filteration, washed with water (twice), methanol (twice), formic acid (twice), water (twice), and methanol (twice) in this order, and dried under vacuum.

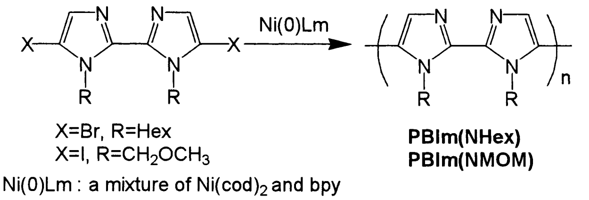
Measurements. IR, NMR, and UV−vis spectra were recorded on a JASCO IR-810 spectrometer, a JEOL EX-400 spectrometer, and a JASCO Ubset-35 or a Shimadzu UV-2100 PC spectrometer, respectively. Photoluminescence spectra were obtained by using a Hitachi F-4010 spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW 1000 X-ray diffractometer with Cu Kα radiation. Viscosity was measured with an Ubbelohde viscometer. Gel permiation chromatography (GPC) was carried out on a Waters 150-C gel permeation chromatograph using two Shodex HFIP-806 M columns (poly(methyl methacrylate) standards; eluent = hexafluoro-2-propanol). Elemental analyses were carried out with a LECO CHNS-932 analyzer or a Yanaco CHN Cordon MT-5 analyzer (C, H, and N) and a Yanaco YS-10 SX-Elements microanalyzer. Thermal analysis was performed with a Shimidzu TA-50 WS thermal analyzer equipped with a Shimadzu DSC-50 calorimeter and a Shimadzu TGA-50 analyzer.

X-ray Diffraction Analysis of 5,5′-Dibromo-*N*,*N*′-dimethyl-2,2′-biimidazole. Crystal data: $C_8H_8Br_2N_4$, M_r = 319.99; monoclinic; $P2_1/n$(No. 14); $a = -6.454(3)$, $b = 6.77(4)$, and $c = 11.741(2)$ Å; $\beta = 92.59(2)$ °; $V = 512.8(4)$ Å^3; $Z = 2$; $\mu = 78.92$ cm^{-1}; $F(000) = 308$; $D_{calc} = 2.072$ Mg m^{-3}; 2θ range = 6.0−55°; *hkl* ranges, $0 \leq h \leq 8$, $-8 \leq k \leq 0$, $-14 \leq l$ 15; number of unique reflections = 1287; number of used reflections $(I > 3\sigma(I)) = 629$; number of variables = 64. The final $R(F_0)$ and $R_w(F_0)$ values were 0.078 and 0.094, respectively; $R = \Sigma||F_0|| - |F_c|/\Sigma|F_0|$; $R_w = \Sigma\omega|F_0 - F_c|^2/\Sigma\omega|F_0|^2]^{1/2}$; weighting scheme $\omega = [\{\sigma(F_0)\}^2]^{-1}$. The unit cell parameters were obtained with $18.4 \leq 2\theta \leq 24.6°$.

Intensities were collectd on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) and the ω-2θ method. Empirical absorption correction (ψ-scan method) of the collected data was applied. Calculations were carried out by using the program package teXan on a VSX-II computer. Atomic scattering factors were taken from the literature.[12]

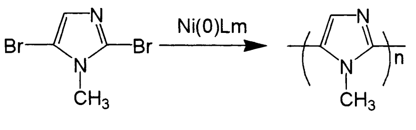
Results and Discussion

Preparation of Polymers by a Dehalogenative Polycondensation. The following dehalogenative polycondensation of 2,5-dihaloimidazoles with a zerovalent nickel complex[1c,5] (a mixture of bis(1,5-cyclooctadiene)-nickel(0), $Ni(cod)_2$, and 2,2′-bipyridyl, bpy) gave the corresponding polymers. The monomers were synthesized by halogenation of the corresponding biimidazoles and 1-methylimidazole as described in the experimental part. Molecular structure of 5,5′-dibromo-*N*,*N*′-dimethyl-2,2′-biimidazole determined by X-ray crystallography is exhibited in Figure 1.



PBIm(NHex)
PBIm(NMOM)

(1)



(2)

PIm(NMe)

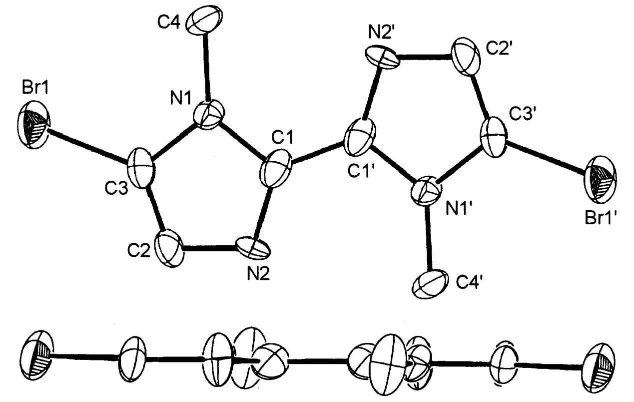


Figure 1. Molecular structure of 5,5′-dibromo-*N*,*N*′-dimethyl-2,2′-biimidazole. Views from two directions are depicted. Selected bond lengths (Å) and angles (deg): C1−C1′ 1.46(4), N1−C4 1.39(2), C3−Br1 1.86(2); N1−C1−C1′ 121(1), N1−C1−C1′−N1′ 180, N1−C1−C1′−N2′ 2(3).

The obtained polymers showed only low or no halogen content, indicating that the dehalogenative polycondensation proceeded smoothly. **PBIm(NHex)**, **PBIm(NMOM)**, and **PIm(NMe)** showed M_n values of 15 000, 12000, and 8000 in GPC analysis. **PBIm(NHex)** and **PIm(NMe)** gave inherent viscosities [η] of 0.24 and 0.14 dL g^{-1}, respectively, in HCOOH. IR spectra of the polymers were reasonable for their structures. For example, the IR spectrum of **PBIm(NHex)** (chart b in Figure 2) resembles that of the corresponding monomer (chart a in Figure 2), except for changes of the absorption pattern in the range of aromatic ν(C−Br) peaks (1100−1200 cm^{-1}).[13] Use of 5,5′-dibromo-1,1′-dimethyl-2,2′-biimidazole in the polymerization also gave the corresponding polymer, **PBIm(NMe)**, whose IR spectrum and XRD pattern were very similar to those of **PIm(NMe)**, however, **PBIm(NMe)** showed a fairly high Br content (6.6%) (cf. Experimental Section). The polymerization expressed by eq 1 did not proceed well for R = −COO-*t*-C$_4$H$_9$ and R = −SiMe$_3$.

PBIm(NHex) was soluble in HCOOH, CF$_3$COOH, (CF$_3$)$_2$CHOH, CHCl$_3$, and C$_6$H$_6$. **PBIm(NMOM)** was soluble in the acidic solvents, acetic anhydride, and CHCl$_3$; however, its solubility was not enough to determine its [η] value. **PIm(NMe)** was soluble in HCOOH, CF$_3$COOH, and (CF$_3$)$_2$CHOH; however, it was insoluble in nonacidic solvents tested. Figure 3 exhibits ^{1}H NMR spectrum of **PBIm(NHex)**; essentially the same ^{1}H NMR spectrum was obtained in CDCl$_3$. Splitting of the aromatic signal suggests the presence of rotational isomers, and ^{1}H NMR spectra of **PBIm(NMe)** and **PBIm(NMOM)** show similar splitting.[14] The position of the aromatic H$_a$ signal in Figure 3 agrees with those of reported biimidazoles.[2b,15] **PBIm(NMe)** afforded more complicated ^{1}H NMR due to the presence of head-to-tail and head-to-head units; the head-to-head units is considered to be the major unit since the dehalogenative polycondensation using Ni(0)Lm usually affords the head-to-head unit preferably.[1c,16a] **PBIm(NHex)**, **PBIm(NMOM)**, and **PIm(NMe)** showed 5 wt % loss temperatures at 334, 311, and 337 °C, respectively.

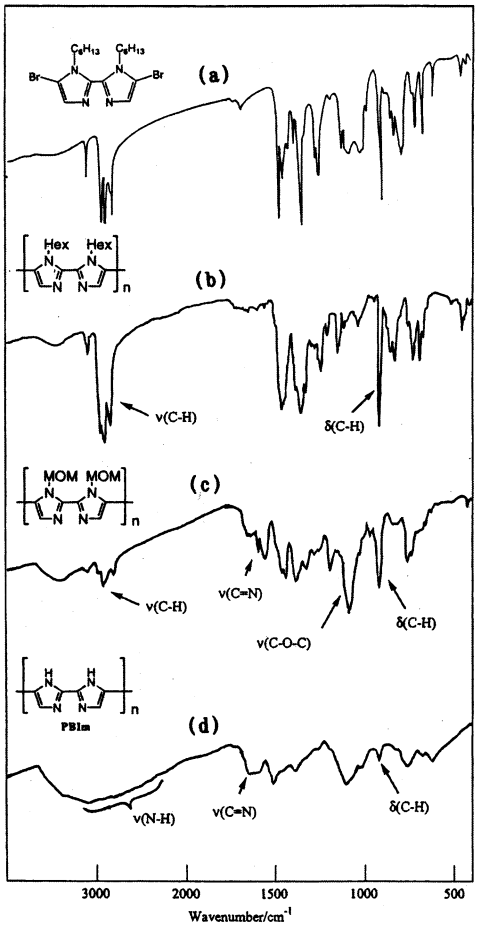


Figure 2. IR spectra of (a) *N*,*N*′-dihexyl-5,5′-dibromo-2,2′-biimidazole, (b) **PBIm(NHex)**, (c) **PBIm(NMOM)**, and (d) **PBIm**.

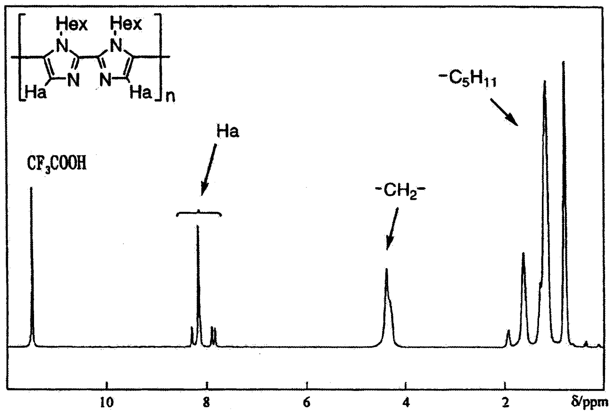
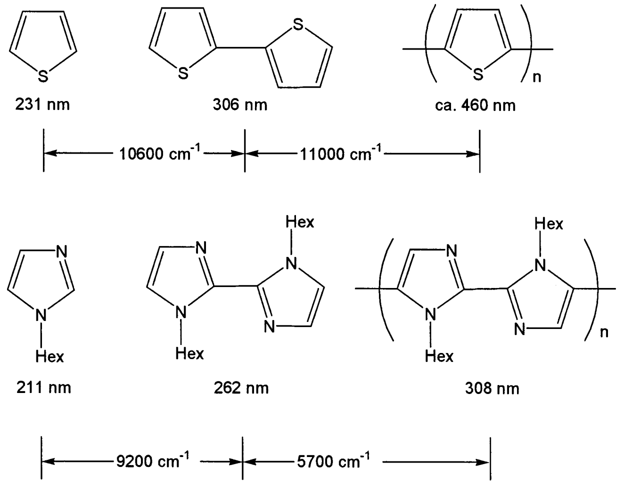


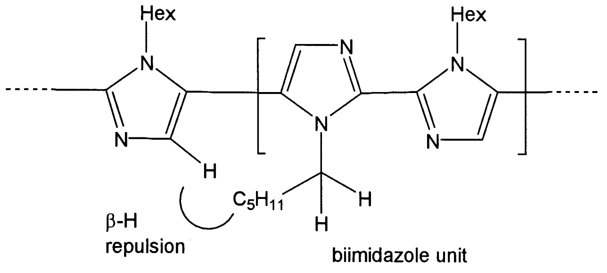
Figure 3. ^{1}H NMR spectra of **PBIm(NHex)** in CF$_3$COOD, 400 MHz.

UV—Vis Data. *N*,*N*′-Dihexyl-2,2′-biimidazole showed λ_{max} at 262 nm in chloroform, whereas **PBIm(NHex)** gave UV−vis absorption peaks at 308 nm (ϵ = 6000 M^{-1} cm^{-1} based on the imidazole unit) in chloroform and 310 nm in film, respectively. The absorption peaks of the dimer and the polymer locate at a longer wavelength compared with λ_{max} of *N*-hexylimidazole at 211 nm in CH$_3$OH. The degree of the shift (9200 cm^{-1}) to a longer wavelength observed with the dimer is comparable to that observed with 2,2′-bithiophene (10600 cm^{-1}). However, that observed with **PBIm(NHex)** (14900 cm^{-1}) is smaller compared with that observed with polythiophene (from 231 nm of thiophene to 460 nm[1c,16] of poly(thiophene) or 21 600 cm^{-1}) and poly(thiazole) (from 241 nm of thiazole to 502 nm of poly(thiazole)s corresponding to 22 600 cm^{-1} [1c]). The s-trans form of *N*,*N*′-dialkyl-2,2′-biimidazole seems to receive no significant steric repulsion due to lack of the *o*-hydrogen and takes a coplanar structure as depicted in Figure 1, and the biimidazole has an effectively π-conjugated electron

Chart 1. Comparison of UV−Vis Data of Thiophenes and 1-Hexylimidazoles



system as in 2,2′-bithiophene. However, in the polymer system, the biimidazole units will be somewhat twisted around the bond connecting the biimidazole units; this twisting is caused by the steric repulsion between the *N*-Hex group and the β-CH group of the neighboring biimidazole unit. **PBIm(NHex)** thus has a shorter effective π-conjugation length to give the $\pi-\pi^*$ absorption peak at a considerably shorter wavelength (308 nm) compared with poly(thiophene) (ca. 460 nm) and poly(thiazole)s (502 nm), **PBIm(NMOM)** showed the UV−vis peak at a somewhat longer wavelength of 323 nm in $CHCl_3$, compared with **PBIm(NHex)**.



The steric repulsion depicted above is considered to be similar to that observed with *N*-substituted polypyrroles, and it has been reported that introduction of substituent at nitrogen of polypyrrole retards formation of effective π-conjugated systems and leads to a shift of the UV−vis peak to a shorter wavelength compared with that of polypyrrole.[16e,f] In formic acid, the $\pi-\pi^*$ transition peak was shifted to a shorter wavelength and **PBIm(NHex)** (λ_{max} = 291 nm), **PBIm(NMOM)** (295 nm), and **PIm(NMe)** (292 nm) showed the peak at almost the same position. Protonation of the imine nitrogen of the polymer in HCOOH seems to lead to another β-hydrogen (N−H) repulsion between the NH^+ proton and the hexyl group; similar effect in HCOOH has been reported for polybenzimidazoles. [5d]

Since the UV−vis peak of **PBIm(NHex)** appears essentially at the same position in $CHCl_3$ (308 nm) and solid (film, 310 nm), occurrence of face-to-face intermolecular interaction in the solid, which will cause a bathochromic shift of the UV−vis peak as in cases of poly(thiophene) and poly(thiazole) with long alkyl chains,[17] is unlikely. Films of **PIm(NMe)** and **PBIm(NMe)** show UV−vis peaks at somewhat longer wavelength (325 and 330 nm, respectively) compared with their solutions, and analysis of their powder XRD data indicates formation of a stacked structure.

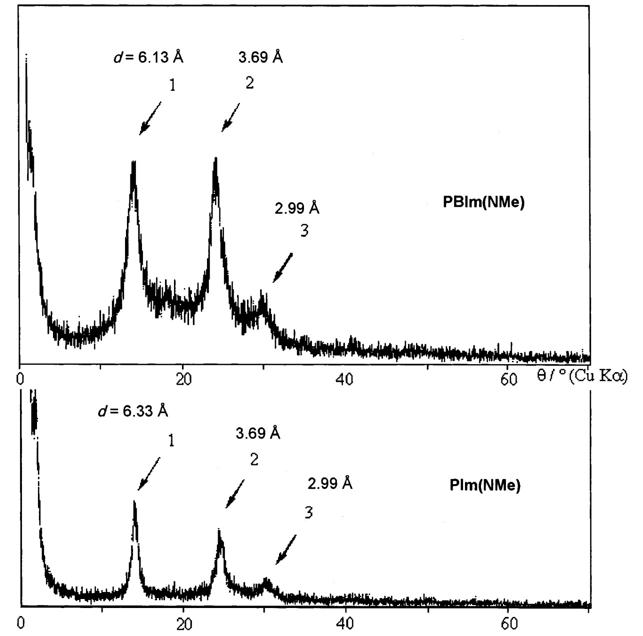


Figure 4. Powder XRD patterns of **PIm(NMe)** (bottom) and **PBIm(NMe)** (top).

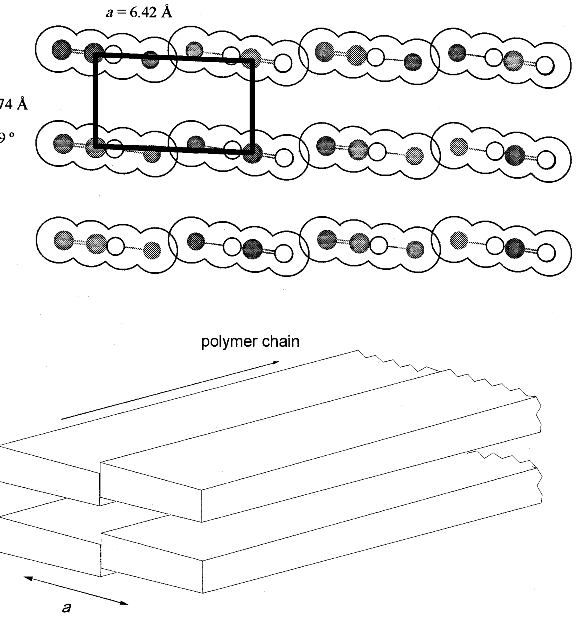


Figure 5. Packing model of **PBIm(NMe)**. The white and dark circles represent nitrogen and carbon atoms, respectively. Upper figure shows the packing seen from the direction of the polymer main chain (*c* axis). The cross section of one polymer chain is compared with a view of the corresponding monomer (cf. Figure 1) seen from the direction of the Br end. The two circles shown at the ends of the cross section of polymer chain (upper figure) represent the CH_3 group. Simulation was carried out with parameters of a = 6.42 Å, and b = 3.74 Å, and γ = 99°

Packing Structure of the Polymer. Powder XRD patterns of **PIm(NMe)** and **PBIm(NMe)** show clear peaks as exhibited in Figure 4; both the polymers give peaks at almost the same positions. The linked-atom Rietveld analysis[18] of the XRD pattern indicates that the polymer assumes a packing structure depicted in Figure 5. Use of the lattice constants shown in Figure 5 gives a simulated XRD pattern which agrees well with

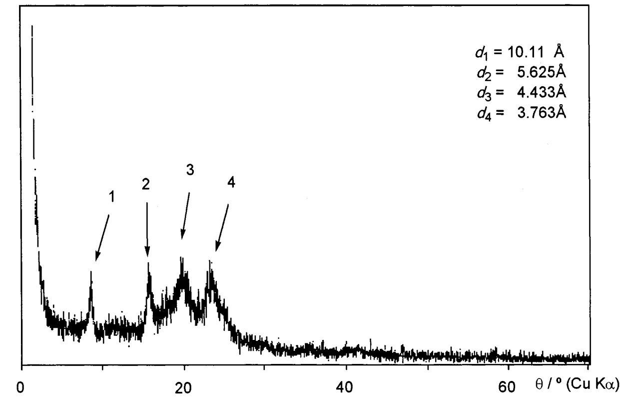
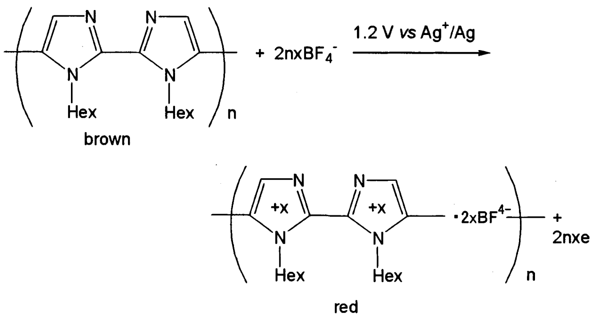


Figure 6. Powder XRD patterns of **PBIm(NHex)**.

the observed XRD pattern. The powder XRD pattern of π-conjugated polymers mainly give information about the two-dimensional packing and only minor information along the *c* axis direction of the polymer chain. **PBIm(NHex)** gives rise to a powder XRD pattern exhibited in Figure 6. In many cases, π-conjugated poly(heterocycle)s having alkyl or alkoxy side chains give a peak at a low angle region, and the peak is assigned to a distance between poly(heterocycle) main chains separated by the side chains.[1,17a,b] The d_1 peak at 10.11 Å observed with **PBIm(NHex)** may also be assigned to the distance between the poly(biimidazole) main chains separated by the hexyl groups. Among five-membered ring heterocycles, thiazole seems to have a stronger tendency to form π-stacking than thiophene[17b,c] and the π-stacking ability of imidazole seems not so strong as that of thiazole.

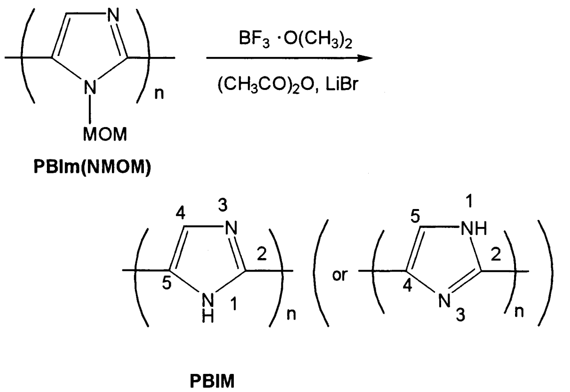
Electrochemical Response. All of the polymers were electrochemically active and received electrochemical oxidation. For example, a cast film of **PBIm(NHex)** on a Pt plate underwent electrochemical oxidation with peak oxidation potential of 1.2 V vs Ag$^+$/Ag and doping level (charge stored per the imidazole unit; *x* in eq 3) of 0.3 in an acetonitrile solution of 0.10 M [NEt$_4$]BF$_4$.



(3)

According to the oxidation, color of the polymer film changed from brown to red. Electrochemical dedoping of the polymer, however, did not take place easily presumably due to strong interaction of the anion (BF$_4^-$) with nitrogen(s) of the imidazole units (possibly by coordination of BF$_4^-$ to the biimidazole nitrogens). The electrochemical oxidation of **PBIm(Hex)** requires a higher potential than those of poly(thiophene)s (ca. 0.5 V vs Ag$^+$/Ag)[1,16c,19] and poly(pyrrole)s (ca. 0 V vs Ag$^+$/Ag)[1,20a] due to the presence of electron-accepting imine nitrogen.

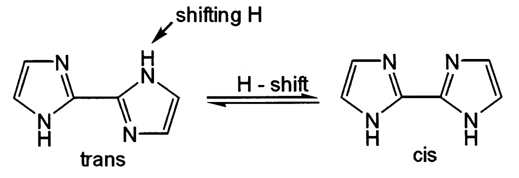
Deprotonation of PBIm(NMOM). Treatment of **PBIm(NMOM)** with BF$_3$·O(CH$_3$)$_2$[11] led to deprotection of the imidazole unit.



(4)

According to the reaction, about 90% of the imidazole unit was deprotected as estimated from ^{1}H NMR data shown in Figure 7. In the ^{1}H NMR spectrum of **PBIm(NMOM)**, the $-CH_2-O-$ peak gives a somewhat smaller area compared with a calculated area, although the peak appears at a reasonable position near the peak position of $-CH_2-O-$ hydrogens in 5,5′-diiodo-*N*,*N*′-dimethoxymethyl-2,2′-biimidazole (δ 5.90; cf. the experimental part) and *N*,*N*′-dimethoxymethyl-2,2′-biimidazole (δ 5.86). Similar phenomena were reported for α-CH$_2$ or $-O-CH_2-$ group bonded to the main chain of π-conjugated polymers such as poly(hexylthiophene)[17b] and branched poly(ethylene dioxythiophene)s;[20b] the unusual ^{1}H NMR data were considered to originate from lowering of free motion of the side chain attached to the rigid polymer chain and/or special electronic state of the π-conjugated polymer.[17b,20b]

The IR spectrum of the deprotected polymer (Figure 2d) shows a broad absorption band in a range of about 2300−3300 cm^{-1} which is characteristic of the hydrogen-bonded NH group. It is reported that 2,2′-biimidazole shows such a broad IR absorption band characteristic of the hydrogen-bonded compounds.[7] The obtained polymer, **PBIM**, was hardly soluble in organic solvents, similar to 2,2′-biimidazole, and showed minor solubility in acidic organic solvents such as HCOOH and CF$_3$COOH. The presence of the intermolecular hydrogen bonding explains the low solubility. Since hydrogen atom in imidazole can easily shifts between two N atoms, **PBIM** is considered to consist of the imidazole-2,5-diyl unit and imidazole-2,4-diyl unit as shown in eq 4. For 2,2′-biimidazole, the H shift brings about only a formal trans−cis isomerization and the π-conjugation along the two ring is not lost.



(5)

However, when the π-conjugated biimidazole systems is expanded, such H shift will break the π-jonjugation system partly, e.g., Chart 2. Appearance of the UV−vis peak at 320 nm in cast and dried (in a vacuum) film of **PBIm** suggests that the effective π-conjugation length of **PBIm** along the polymer chain is not so long despite removing the sterically demanding MOM substituent (**PBIm(NMOM)**: $\lambda_{max} = 323$ nm, vide ante). Containing the imidazole-2,4-diyl unit may be the reason for the short effective π-conjugation length.

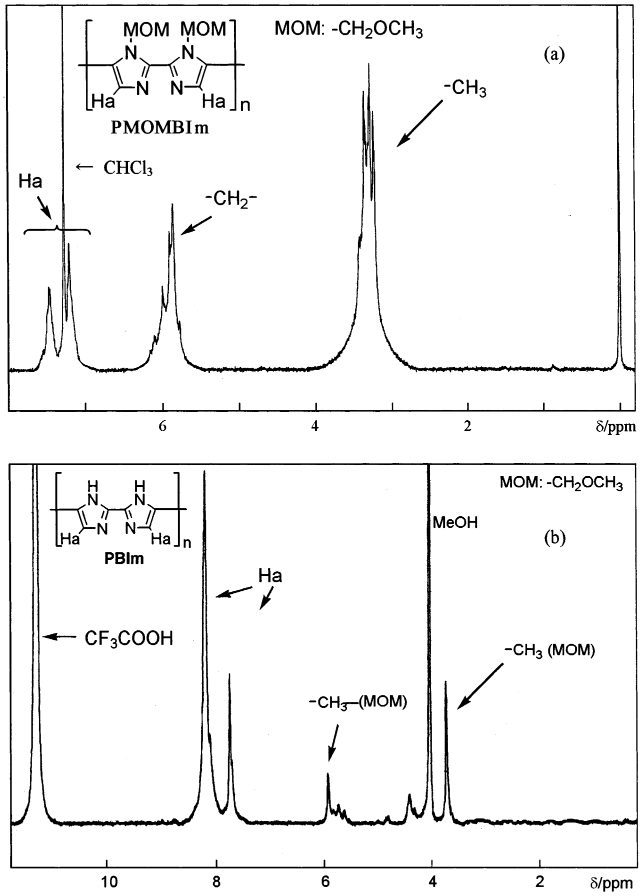
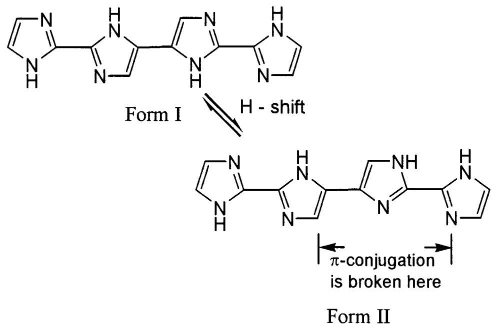


Figure 7. ^{1}H NMR spectra of (a) **PBIm(NMOM)** in $CDCl_3$ and (b) deprotected product in CF_3COOD. For Figure 7a, measurement of the FT ^{1}H NMR spectrum at interval times of 4.5 and 10 s for the 90° pulse gave the same spectrum.

Chart 2. Possible Route for Formation of the Imidazole-2,4-diyl Unit



If the imidazole-2,4-diyl is incorporated in **PBIm**, this polymer is considered to have a π-conjugation system similar to that of a copolymer of thiophene-2,5-diyl and thiophene-2,4-diyl. It has been reported that incorporation of the thiophene-2,4-diyl unit in polythiophene leads to a shift of the π–π* absorption peak to a shorter wavelength.[22] MOPAC PM3 calculation indicated that the HOMO–LUMO transition energy in form II was by 0.27 eV (or about 2200 cm^{-1}) larger than that in form I, supporting the assumption described above.

Protonation of **PBIm**, however, caused a shift of the peak to a longer wavelength. The UV–vis peaks of **PBIm** in the film was shifted to 350 nm in HCOOH, and the direction of the shift caused in HCOOH was reverse to those observed with **PBIm(NHex)**, **PBIm-(NMOM)**, and **PIm(NMe)** (vide ante). This may be due to change(s) of electronic state of the polymer by protonaion or due to formation of a π-conjugated framework similar to that of polypyrrole, which is considered to assume a coplanar polymer chain.

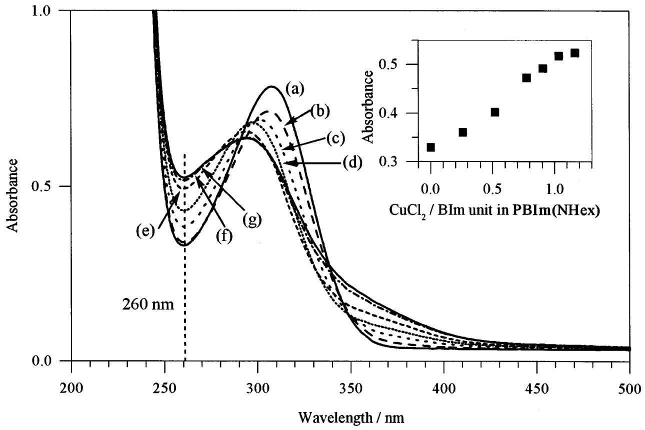
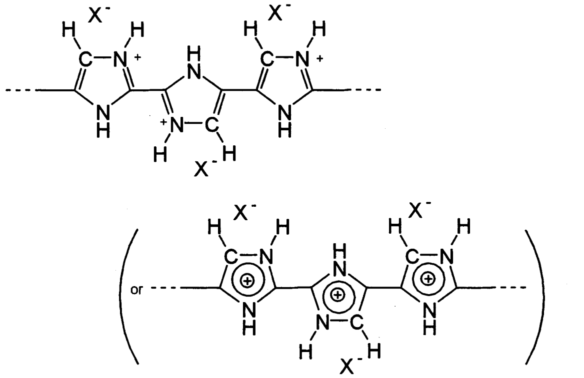


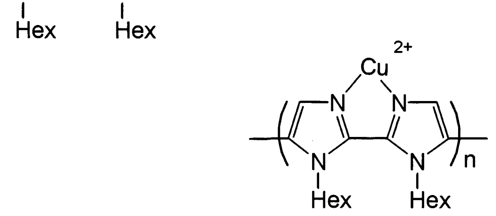
Figure 8. Changes in UV–vis spectrum on addition of an acetnitrile solution of $CuCl_2$ to a $CHCl_3$ solution of **PBIm-(NHex)**. Solvent = 3:0.5 (v/v) mixture of $CHCl_3$ and CH_3CN Concentration of **PBIm(NHex)** = 4.3×10^{-5} M. Concentration of $CuCl_2$/M = (a) 0, (b) 1.1×10^{-5}, (c) 2.2×10^{-5}, (d) 3.3×10^{-5}, (e) 3.9×10^{-5}, (f) 4.4×10^{-5}, and 5.0×10^{-5}. The inset shows changes of the absorbance at 260 nm depending on the amount of $CuCl_2$ added. The absorbance is saturated at about a 1:1 molar ratio between $CuCl_2$ and the BIm unit in **PBIm-(NHex)**, suggesting smooth formation of a 1:1 complex between Cu^{2+} and the BIm unit in **PBIm(NHex)**.



(6)

As described above, various poly(imidazole)s can be prepared via the organometallic polycondensation and **PBIm** exhibits unique solvatochromism in the acidic medium.

Function as Ligand. Biimidazoles are typical chelating ligand.[2] As exhibited in Figure 8, addition of $CuCl_2$ to a $CHCl_3/CH_3CN$ solution of **PBIm(NHex)** leads to a change in the UV–vis spectrum, suggesting occurrence of the following chelate complex forming reaction.



(7)

It is known that Cu^{2+} usually has the highest coordinating ability among the first-row transition metal ions and forms various stable chelate complexes. Plots of the absorbance at 260 nm in Figure 8 vs the amount of Cu^{2+} per mole of the BIm unit in **PBIm(NHex)** give a curve saturating at Cu^{2+}/BIm = about 1, suggesting that a smooth complex formation reaction proceeds in the system. The shift to a shorter wavelength on the complex formation may be due to increase in the steric hindrance which disturbs the full π-conjugation along the polymer chain. Fe^{3+} seems to have only weak coordinating ability toward **PBIm(NHex)**, since addition of $FeCl_3$ did not cause obvious UV−vis changes.

Conclusion

New π-conjugated polymers consisting of imidazole units have been obtained. They have expanded π-conjugated systems along the main chain. The polymer is electrochemically active and the polymer with *N*-methyl or *N*-hexyl groups assumes a stacked structure in the solid. **PBIm(Hex)** forms a metal complex with copper. The obtained results are expected to contribute to better understanding of π-conjugated poly(heterocycle)s constituted of five-membered ring units.

Acknowledgment. We are grateful to Dr. T. Maruyama of our university (now in The Yokohama Rubber Co., Ltd.) for helpful discussion and experimental support. Authors express great acknowledgment to Dr. M. Takeuchi of Showa Denko K.K. for the GPC analysis.

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MA0211232