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Preparation of π-conjugated polymers consisting of 2-decylbenzimidazole and thiophene units and chemical properties of the polymers

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Abstract

Polycondensation by Stille coupling of 2-decyl-4,7-dibromobenzimidazoles and *N*-methyl-2-decyl-4,7-dibromobenzimidazole with 2,5-bis(trimethylstannyl)thiophene and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene gave the corresponding π-conjugated polymers, poly(2-decylbenzimidazole-4,7-diyl-thiophene-2,5-diyl) **1b**, poly(2-decylbenzimidazole-4,7-diyl-bithiophene-2,5-diyl) **1c** and poly(*N*-methyl-2-decylbenzimidazole-4,7-diyl-thiophene-2,5-diyl) **2b**, in 98–99% yields. The polymers **1b** and **2b** were fully soluble in CF_3COOH, and partially soluble in DMF (about 60 and 40% for **1b** and **2b**, respectively) and NMP (about 70 and 40%, respectively). The NMP soluble part of **1b** and DMF soluble part of **2b** gave values of 0.36 and 0.24 dl g^{-1} in NMP and DMF, respectively. The DMF soluble part of **1b**, **1c** and **2b** showed absorption peaks at about 458, 465 and 388 nm, respectively, in DMF. In an alkaline medium the absorption peaks of **1b** and **1c** are shifted to a longer wavelength by 92–101 nm; the observed shifts in the acidic medium and alkaline medium were much larger than those observed with usual benzimidazoles with low molecular weights. Packing structures of **1b**, **1c** and **2b** are discussed based on their XRD patterns.

Keywords: 2-Alkylbenzimidazole; Thiophene; Polycondensation

1. Introduction

Benzimidazole is an interesting building block for π-conjugated polymers (Chart 1), because it shows interesting chemical properties such as photoluminescence, solvatochromism, and metal-complex forming reactivity [1]. Preparation of homologues of benzimidazole and revealing their chemical and physical properties have also been paid too much attention[1] [2–4]. We previously reported preparation and chemical properties of poly(2-heptylbenzimidazole-4,7-diyl), P(4,7-Bim(Hep)), poly(2-phenyl-benzimidazole-4,7-diyl) [5] and poly(aryleneethynylene) type polymers consisting of 2-alkylbenzimidazole-4,7-diyl units [6].

Charge-transfer (CT-type) π-conjugated polymers have been attracting strong attention due to their unique optical and electronic properties, and have been the subject of many recent papers [7–13]. Benzimidazole bears an electron-withdrawing imine (C=N) nitrogen similar to pyridine and quinoxaline [7–10], and its homopolymer behaves as an electron-accepting molecule, which receives a facile electrochemical reduction [5]. On the other hand, thiophene is a typical electron-donating unit [7–13]. However, CT-type π-conjugated copolymers of 2-alkylbenzimidazoles with the electron-donating thiophene units have been limited. Under these circumstances, we have prepared the following polymers consisting of benzimidazole and the electron-donating thiophene units by fixing the alkyl side chain of the benzimidazole unit and the decyl group. Organometallic polycondensation using monomers **1a** and **2a** was applied to the preparation of the polymers reported in this paper. Herein we report results of the preparation of the polymers and their chemical properties. The present work is focused on the effect of the repeating unit of the polymer on its optical property and packing structure in the solid (Chart 2).

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[1] Our data using 2-heptylbenzimidazole in neutral (in DMF), protonated (in CF_3COOH), and deprotanated (in DMF containing a saturated amount of NaOH) states were essentially the same as those reported with 2-metylbenzimidazole.

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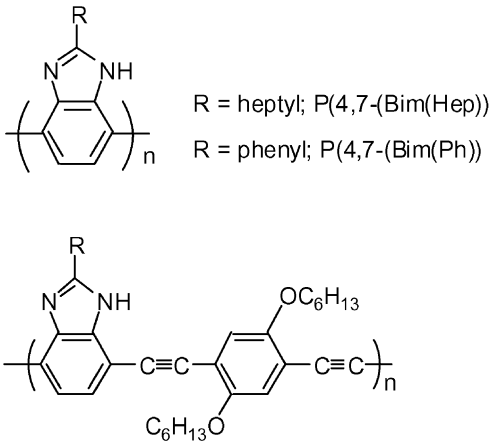


Chart 1. Examples of reported π-conjugated polymers consisting of benzimidazole.

2. Experimental

2.1. Materials

1,4-Dibromo-2,3-diaminobenzene [14], 2,5-bis(trimethylstannyl)thiophene [15], 5,5′-bis(trimethylstannyl)-2,2′-bithiophene [16], and $Pd(PPh_3)_4$ [17] were prepared according to the literature. Undecanoic acid was purchased from Aldrich Chemical.

2.2. Monomer synthesis

4,7-Dibromo-2-decylbenzimidazole (**1a**) was prepared by reaction of 2,3-diamino-1,4-dibromobenzene with undecanoic acid, in a manner similar to that previously reported [5]. Yield 55%. ^{1}H NMR ($CDCl_3$) 9.33 (br, 1H, NH), 7.27 (s, 2H, Ph), 2.96 (t, 2H, $J = 8.0$ Hz, CH_2), 1.85 (m, 2H, CH_2), 1.36 (m, 14H, CH_2), 0.88 (t, 3H, $J = 6.8$ Hz, CH_3). Data from elemental analyses of monomers and copolymers are summarized in Table 1.

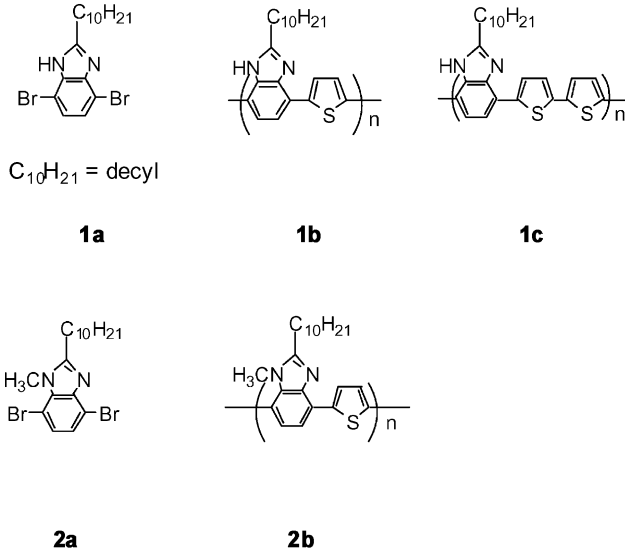


Chart 2. Monomers and polymers reported in this work.

N-Methyl-2-decyl-4,7-dibromobenzimidazole **2a** was prepared by reaction of **1a** with iodomethane. To a solution of **1a** (1.26 g, 3 mmol) in 15 cm^3 of THF at room temperature were added NaH (0.11 g, 4.5 mmol) and MeI (0.32 g, 4.5 mmol) in this order. After stirring for 1 h at room temperature, the reaction mixture was evaporated, and the residue was washed with diluted hydrochloric acid and water. The resulting solid was collected by filtration and dried under vacuum. Yield 0.98 g (76%). ^{1}H NMR ($CDCl_3$) 7.24 (d, 1H, $J = 8$ Hz, Ph), 7.20 (d, 1H, $J = 8$ Hz, Ph), 4.05 (s, 3H, N–CH_3), 2.91 (t, 2H, $J = 8$ Hz, CH_2), 1.83–1.75 (m, 2H, CH_2), 1.48–1.26 (m, 14H, CH_2), 0.88 (t, 3H, $J = 16$ Hz, CH_3).

2.3. Polycondensation

The polycondensation of **1a** and **2a** with 2,5-bis(trimethylstannyl)thiophene or 5,5′-bis(trimethylstannyl)-2,2′-bithiophene was carried out using $Pd(PPh_3)_4$ as a catalyst in DMF at 90 °C (Scheme 1, Pd-catalyzed synthesis of the polymers).

For example, **2b** was prepared by the reaction of **2a** (0.38 g, 1.0 mmol) and 2.5-bis(trimethylstannyl)thiophene (0.44 g, 1.0 mmol) in the presence of a catalytic amount of $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in 10 cm^3 of DMF at 90 °C for 48 h under N_2. The obtained polymer was washed with diluted hydrochloric acid (3 times), NH_4OH (once), warm water, and MeOH (3 times) in this order. The yellow powder of polymer **2b** was collected by filtration and dried under vacuum. Yield 99%. ^{1}H NMR ($CDCl_3$) 8.327–8.21 (m, 1H, Ph-H), 7.65–7.58 (m, 1H, Ph-H), 7.30–7.12 (m, 2H, Th-H), 3.63–3.55 (m, 3H, N–CH_3), 2.91 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 1.57–1.26 (m, br, 14H, CH_2), 0.87 (m, 3H, CH_3) (cf. Fig. 1).

Polymer **1b** was prepared analogously. Yield 98%. Polymer **1c** was obtained similarly from **1a** and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene. Yield 98%.

2.4. Measurements

IR, NMR, and UV–vis spectra were recorded on a JASCO IR-810 spectrometer, a JEOL EX-400 spectrometer, and JASCO Ubset-35 or 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 PW1000 X-ray diffractometer with Cu Kα radiation. Viscosity was measured with an Ubbelohde viscometer. Gel permeation chromatography (GPC) was carried out on a Tohso HLC-8020 gel permeation chromatograph (polystyrene standards; eluent = DMF containing 0.01 M LiBr). Elemental analyses were carried out by Dr Y. Hayashi of our laboratory with a LECO CHNS-932 analyzer or a Yanaco CHN Cordon MT-5 analyzer (C, H and N) and a

Table 1
Elemental analytical data of the monomers and polymers

Compound	Formula	Found					Calcd				
		C (%)	H (%)	N (%)	S (%)	Br (%)	C (%)	H (%)	N (%)	S (%)	Br (%)
1a	$C_{17}H_{24}N_2Br_2$	49.22	5.83	6.71	–	38.72	49.06	5.81	6.73	–	38.40
2a	$C_{18}H_{26}N_2Br_2$	50.43	5.95	6.41	–	37.33	50.25	6.09	6.51	–	37.15
1b	$(C_{21}H_{26}N_2S{\cdot}0.8H_2O)_n$	71.63	7.67	7.68	9.21	0.21	71.98	7.94	7.99	9.15	–
1c	$C_{25}H_{28}N_2S_2{\cdot}H_2O)_n$	68.72	6.43	6.00	13.76	0	68.45	6.89	6.39	14.62	–
2b	$(C_{22}H_{28}N_2S{\cdot}1.5H_2O)_n$	68.80	7.80	6.99	7.84	0	69.61	8.23	7.38	8.44	–

Yanaco YS-10 SX-Elements Microanalyzer (Br and S; with about 0.1% accuracy for the Br analysis). Thermal analysis was performed with a Shimadzu TA-50 WS thermal analyzer equipped with a Shimadzu DSC-50 calorimeter and Shimadzu TGA-50 analyzer.

3. Results and discussion

3.1. Preparation

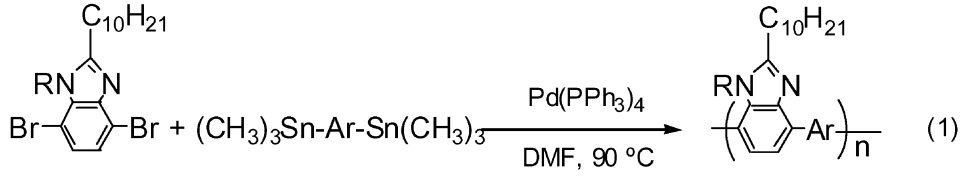
The polycondensation of **1a** and **2a** with bis(trimethylstannyl)thiophenes, according to Stille coupling reaction (Eq. (1)), gives the corresponding polymers in high yields (98–99%).

1b and **2b** were fully soluble in CF_3COOH and partly soluble in DMF, NMP, formic acid, THF and $CHCl_3$. **1c** had lower solubility and was only partially soluble in CF_3COOH, DMF, and NMP. Since the soluble part and insoluble part gave the same IR spectrum, a portion of the obtained polymer with lower molecular weight was considered to dissolve in the solvent. The GPC analysis (eluent = DMF containing LiBr) indicated that the DMF soluble part (about 60, 20, and 40% for **1b**, **1c**, and **2b**, respectively) of **1b**, **1c** and **2b** had number average molecular weights, M_n, of about 5500, 2800 and 3100, with weight average molecular weights, M_w, of 5900, 3200, and 3600, respectively. About 70, 20, and 40% of **1b**, **1c**, and **2b** were soluble in NMP. The NMP soluble part of **1b** and the DMF soluble part of **2b** gave $[\eta]$ values of 0.36 and 0.24 dl g^{-1} in NMP and DMF at 30 °C, respectively.

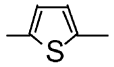
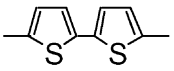
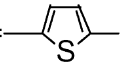
All monomers and polymers were characterized by elemental analysis as well as by IR and ^{1}H NMR spectroscopy. Analytical data shown in Table 1 indicate that the polymers are hydrated, similar to previously reported polymers of 2-alkylbenzimidazole [5,6]. The presence of hydrophilic nitrogen and sulfur atoms seems to lead to the hydration of the polymer, and the degree of the hydration may be related to the volume of space formed for the water molecule. A part of the discrepancy between the observed and calculated values may be due to high thermal stability of the polymer. All IR spectra of the polymers give absorption peaks characteristic of the thiophene units [18] at about 1490, 1440 and 800 cm^{-1}. IR spectra of **1b** and **1c** clearly show a ν(N–H) peak at 3450 cm^{-1}. All polymers were thermally stable, and the thermogravimetric analysis of **1b**, **1c** and **2b** showed 5 wt% loss temperature at 343, 417 and 344 °C, respectively. DSC analysis showed no clear peak in a temperature of −100 to 300 °C.

3.2. ^{1}H NMR analysis

As depicted in Fig. 1, the ^{1}H NMR spectra of the polymers **1b** and **2b** are reasonable for the structure. In the ^{1}H NMR spectrum of **1b**, the N–H peak appears more clearly than those of the previously reported



1a: R = H
2a: R = CH_3

1b: R = H, Ar = 
1c: R = H, Ar = 
2b: R = CH_3, Ar = 

Scheme 1.

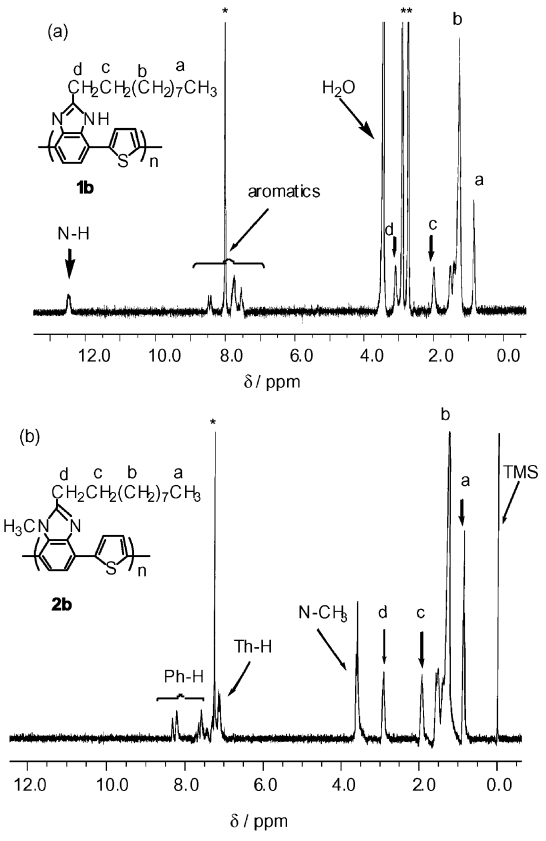


Fig. 1. ^{1}H NMR spectra of (a) **1b** in DMF-d_7 and (b) **2b** in $CDCl_3$. Peaks with a * mark are due to solvent impurities.

poly(2-hepthylbinzimidazole-4,7-diyl) [5] and related polymers including benzimidazole unit [19]. The sharper NH signal suggests that the hydrogen exchange between the NH group and H_2O is slower than those occurring with other polymers including the benzimidazole unit. Peak ratios observed for the NH aromatic and alkyl signals agree with the structure of **1b** and **2b**.

3.3. UV–vis data and acid–base reaction

Table 2 summarizes optical data of the polymers. The $\pi-\pi^*$ absorption peak of **1b** in DMF appears at 458 nm, which locates at a considerably longer wavelength than the absorption peak of poly(2-hepthylbenzimidazole-4,7-diyl), P(4,7-Bim(Hep)) [5] at 400 nm, and is somewhat shifted to a longer wavelength compared with that of poly(thiophene-2,5-diyl) at 430–450 nm [7]. Release of steric hindrance in P(4,7-Bim(Hep)) (cf. Chart 1) by introduction of the thiophene unit and contribution from the expected CT structure along the polymer chain account for the bathochromic shift. The polymer 1c with the bithiophene unit shows a similar effect, as shown in Table 2. Substitution of the NH hydrogen with the CH_3 group, as in **2b**, leads to a shift of the absorption peak of **1b** to a shorter wavelength by about 70 nm due to an increase in the steric hindrance.

In acidic solvents, the absorption maximum of the polymers shifted to a shorter wavelength. Scheme 2 depicts the acid–base reactions of **1b**, **1c**, and **2b**, as well as the shifts of the absorption peak according to the acid–base reaction.

Shifts of the $\pi-\pi^*$ absorption peak of π-conjugated polymers of benzimidazoles in CF_3COOH were also reported [5,19,20], and the degree of the shift (41–81 nm) observed for the protonation of **1b**, **1c**, and **2b** is comparable to that (about 80 nm) observed for the protonation of (P(4,7-Bim(Hep)) [5].

The shift observed in the protonation is considerably larger, compared with a reported shift (shift = about 5 nm) of protonation of 2-methylbenzimidazole [4] and 2-phenyl benzimidazoles [19], and suggests a severe effect of the protonation on the electronic state of the π-conjugated polymer chain. The CPK molecular model for a dimeric compound (Chart 3) (calculated based on CS Chem3D Pro) indicates that the benzimidazole–thiophene bond is somewhat twisted due to the repulsion between the thiophene ring and NH.

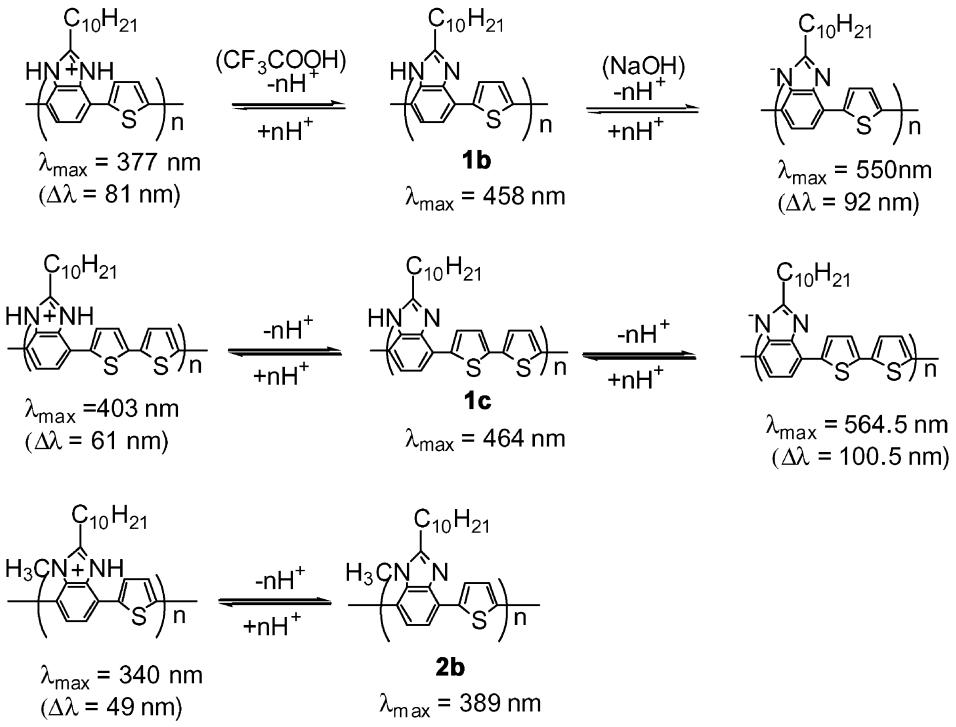
The two circles (○) in the central part of this figure represent two H atoms in the benzimidazole and thiophene units, respectively, to show the steric repulsion. The dihedral angle around the bond connecting the benzimidazole and thiophene units is estimated at about 30° from the CPK molecular model.

Protonation of the imine nitrogen at the 3-position will bring about an additional twist of the main chain to disturb the formation of an expanded π-conjugated system. A similar severe effect of protonation of benzimidazole unit on the π-conjugated system was reported for a

Table 2
Optical data of the copolymers

Compound	Absorption (λ_{max}/nm)				Photoluminescene (λ_{max}/nm)			Excitation[a] (λ_{max}/nm)			Quantum yield (%)	
	DMF[b]	TFA[c]	DMF–NaOH[d]	Film	DMF[b]	TFA[c]	DMF–NaOH[d]	DMF[b]	TFA[c]	DMF–NaOH[d]	DMF[b]	DMF–NaOH[d]
1b	458	377	516,550		528	480	582	455	375	560	25	ca. 8
1c	464	403	530,564		546	510	597	546	410	561	10.5	
2b	389	340	389	398	502	465		378	338		30	

[a] Peaks observed in the excitation spectrum.
[b] In DMF.
[c] In CF_3COOH.
[d] In alkaline DMF containing a saturated amount of NaOH.



Scheme 2.

poly(aryleneethynylene) type polymer containing a more bulky benzimidazole unit [19].

The UV–vis absorption bands of **1b** and **1c** were shifted to a longer wavelength in an alkaline medium, presumably due to deprotonation of NH to N^- in the imidazole ring (Scheme 2) of polymers **1b** and **1c**.

The degree of the shift (92–100.5 nm) to a longer wavelength is also considerably larger than that (about 10 nm) observed for deprotonation of 2-methylbenzimidazole by alkali [4]. The deprotonation will release the steric hindrance between the thiophene unit and the NH group, and make the formation of an extensively π-conjugated system possible. On the other hand, the UV–vis absorption band of **2b** in DMF is slightly affected by addition of NaOH to DMF, due to the absence of the active N–H.

3.4. Photoluminescence

Table 2 includes photoluminescence data of the polymers. Their photoluminescence peaks appear at the onset position of the UV–vis absorption band as usually observed with π-conjugated aromatic compounds and polymers [21,22]. All polymers show medium or strong photoluminescence. The quantum yield (30%) of **2b** is somewhat higher than those of **1b** and **1c**. However, the quantum yield of **2b** is lower than those (61–88%) of low molecular weight *N*-alkylbenzimidazoles [4]. The results suggest the presence of quenching processes of the photoluminescence in the π-conjugated polymers. All the polymers showed strong photoluminescence in CF_3COOH. On the other hand, the intensity of the photoluminescence of **1b** and **1c** becomes weaker in alkaline DMF.

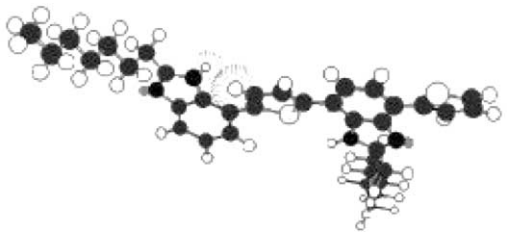


Chart 3. CPK molecular model for a dimeric compound.

3.5. XRD data

Fig. 2 exhibits XRD patterns of the polymers. They exhibit a small-angle reflection at $2\theta = 3.6^\circ$ ($d_1 = 25$ Å) (**1b** and **1c**) and $2\theta = 4.4^\circ$ ($d_1 = 20$ Å) (**2b**). The d_1 value is considered to correspond to the distance between the main chain layers separated by the decyl groups, similarly to cases of π-conjugated polymers with alkyl side chains [23–30]. The broad scattering around $2\theta \sim 22^\circ$ is mainly due to the disordered aggregation of the alkyl chains [31,32]. Regular face-to-face packing of the π-conjugated moieties generally gives rise to strong reflections with spacing 3.5–3.9 Å [27–30]. Even if they are going to overlap with the broad scattering, such a sharp reflection is not observed for the present polymers. These features indicate that the main chains as well as the alkyl chains are fairly disordered. As is schematically shown in Fig. 3,

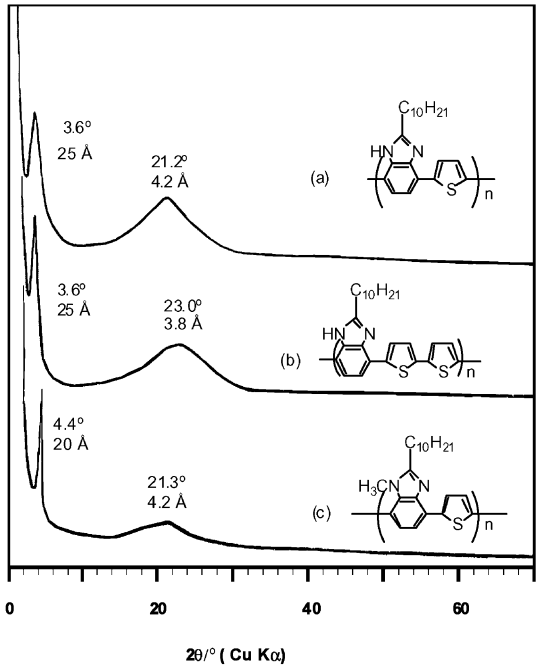


Fig. 2. XRD patterns of (a) **1b**, (b) **1c**, and (c) **2b**.

the layered structure consists of alternating stacking of main chain (high electron density) region and side chain (low electron density) region, although the segregation may not be well defined.

From the data of related compounds, the volumes of the component groups were evaluated to be about 150 $Å^3$ for benzimidazoles unit, 83 $Å^3$ for a thiophene unit, and 27 $Å^3$ for methylene group in the disordered state. By assuming the additivity, the volume V_u of the repeating unit was estimated. The values of the calculated density $M_u/N_A V_u$, 1.12 $(= 338.53/\{(150 + 83 + 27 \times 10) \times 10^{-24} \times 6.02 \times 10^{23}\})$ (**1b**), 1.20 (**1c**), and 1.11 g cm^{-3} (**2b**), were in good agreement with the observed values of 1.09 (**1b**), 1.25 (**1c**), and 1.03 g cm^{-3} (**2b**), where M_u is the molar mass of the repeating unit and N_A is Avogadro number. The number of the repeating units contained in each layer defined with an interfacial area A is given by $(A \times d_1)/V_u$. The apparent values of the area $A_s \equiv V_u/d_1$ admitted for a repeating unit are 20 $Å^2$ $(= (150 + 83 + 27 \times 10)Å^3/25\ Å)$ (**1b**), 23 $Å^2$ (**1c**), and 26 $Å^2$ (**2b**). For the extended planar conformation, the distance c for the repeating unit along the main chain is estimated at 7.9 Å (**1b**, **2b**) and 12.0 Å (**1c**), respectively, from the CPK molecular model and calculation. If we assume that the main chains with a thickness $t = 3.8$ Å are laid in the layer, the expected values of A_s should be greater than $A_s^c = c\,t = 30$ $Å^2$ (**1b**, **2b**) and 46 $Å^2$ (**1c**). The thickness of the side chain region, d_s, is given by $10 \times 27\ Å^3/A_s$ at most, 13 Å (**1b**), 12 Å (**1c**), and 10 Å (**2b**). Thus, the thickness of main chain region $d_m = d_1 - d_s$, which is about $d_1/2$ or more, is certainly longer than the lateral width of the extended main chain conformation. The single bonds at both sides of thiophene unit are not on a straight line, but form an angle of about 148° [33]. As a result of internal rotations about the single bonds, the main chains can be largely winding. In the cases of **1b** and **1c**, the fact $A_s \ll A_s^c$ suggests that the main chains are winding and probably entangled as shown in Fig. 3, or partly associated in side-by-side manner. The meander main chain conformation was supported by X-ray Fourier analysis of homologous polymer [34].

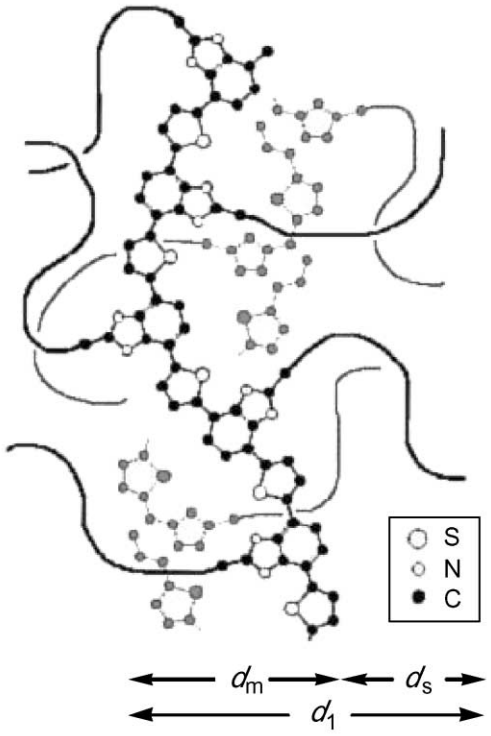


Fig. 3. A model of layered structure of **1b**. Two layers are shown.

In the case of **2b**, A_s is close to A_s^c. Therefore, the extent of meander is less. Replacement of the NH hydrogen with a methyl group seems to cause some structural difference due to the increase in the twisting angle between the benzimidazoles ring and thiophene ring.

As described above, three kinds π-conjugated polymers containing 2-decylbenzimidazole and thiophene units have been prepared. The polymers show the UV–vis absorption peak at a longer wavelength than the corresponding polymer constituted of only the 2-decylbenzimidazole or thiophene units. The acid–base reaction of the polymer brings about a very large shift of the UV–vis absorption peak due to the change of the electronic state of the π-conjugated system of the polymer. XRD data of the polymer suggest formation of an ordered structure where the π-conjugated main chains are separated by the decyl groups. The CH_3 group attached at the 2-decylbenzimidazole units affects the acid–base reaction and the packing structure of the polymer.

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