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Alternating copolymer of bithiophene and dialkylbithiazole and its tendency to align on the surfaces

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Abstract

New five-membered ring π-conjugated polymers composed of 2,2′-bithiophene and 4,4′-dialkyl-2,2′-bithiazole units were prepared. The polymers were soluble in 1,2-dichlorobenzene and showed a UV–vis peak at about 490 nm above 120 °C. Cooling the solution led to the appearance of new UV–vis peaks at 550 and 600 nm, which were considered to originate from self-assembled polymer molecules. Powder XRD (X-ray diffraction) data supported a well-stacked solid structure of the polymers and a highly ordered structure of a polymer film formed on a quartz glass substrate. These data revealed a strong tendency of the new polymers to self-assemble and to form an aligned structure on the surface of the substrates.

Keywords: Conjugated polymer; Molecular assembly; Polyaromatics

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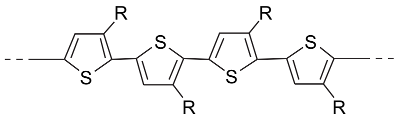
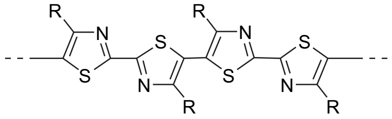
1. Introduction

π-Conjugated polymers are the subject of many studies [1–3]. Research studies of the application of such polymers to electronic and optical devices are actively carried out. In recent research studies, it is recognized that π-conjugated polymers often form a π-stacked molecular assembly and an aligned structure on the surface of the substrates [3–17]. Such molecular assembly and alignment on the surface are considered to be important for attaining better performance of electronic devices based on π-conjugated polymers [8,17].

π-Conjugated polymers composed of five-membered rings with side alkyl chains, e.g., head-to-tail (HT)-type poly(3-alkylthiophene) and head-to-head (HH)-type poly(4-alkylthiazole), exhibit a strong tendency to undergo molecular assembly and align on the surface of the substrates [4–17].



HT-P3RTh



HH-P4RTz

Herein, we report the synthesis of new π-conjugated polymers composed of bithiophene and bithiazole units,

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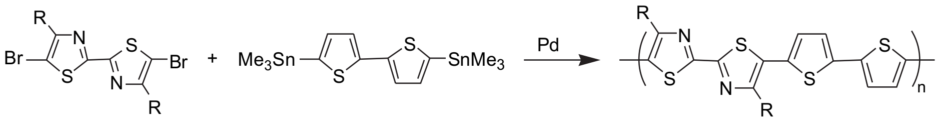


(1)

1 **2** **3a-3d**

1a (R = tridecyl)
1b (R = decyl)
1c (R = nonyl)
1d (R = heptyl)

their packing structure in solid, and their aligned structure on the surface of the substrates. Co-oligomers [18] and copolymers [14,19] of thiophene and thiazole have recently attracted interest, particularly in relation to the thin-film FET (field-effect transistor) functions of such donor(thiophene)–acceptor(thiazole) CT-type co-oligomers and copolymers.

2. Experimental

2.1. Materials and measurements

The monomers **1** [6,9–11] and **2** [20] and $Pd(PPh_3)_4$ [20] were prepared according to the literature.

UV–vis spectra were obtained with a Shimadzu UV-3100PC spectrometer and ^1H NMR spectra were recorded on a Jeol Lambda 300, JEOL JNM-ECA 400, and Bruker Avance DSX 300WB. GPC analysis was carried out using a Shimadzu LC-9A liquid chromatograph (eluent = chloroform at 40 °C) and a Waters 150CV (eluent = 1,2-dichlorobenzene at 140 °C) liquid chromatograph. Polymer films were prepared by casting a 1,2-dichlorobenzene solution of the polymer on a quartz glass plate (for optical measurements) or on a platinum plate (for electrochemical measurements).

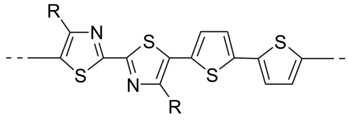
2.2. Synthesis of the polymers *3a–3d*

A mixture of **1a** (1.04 g, 1.5 mmol), **2** (0.74 g, 1.5 mmol), and $Pd(PPh_3)_4$ (0.053 g, 0.045 mmol) in anhydrous DMF (30 cm^3) was stirred for 48 h at 80 °C. The mixture was poured into an aqueous solution of KF, and the precipitated polymer was collected by filtration. The polymer was washed with aqueous ammonia, water, and methanol, and dried under vacuum to obtain 0.83 g (80%) of dark purple **3a**. ^1H NMR (300 MHz, 1,2-dichlorobenzene-d_4) δ: 7.09 (4H), 3.03 (4H), 1.95 (4H), 1.16–1.61 (40H), 0.89 (6H). Anal. Calcd for $(C_{40}H_{58}N_2S_4\cdot 0.3H_2O)_{11}(C_{32}H_{54}N_2S_2\text{-}Br)_2$: C, 67.80%; H, 8.50%; N, 4.08%; Br, 1.79%; S, 17.24%. M_n (number average molecular weight) = 8870. Found: C, 66.90%; H, 8.11%; N, 4.01%; Br, 1.82%; S, 17.82%. $M_n = 8600$; M_w/M_n (M_w = weight average molecular weight) = 3.0.

The polymers **3b**, **3c** and **3d** were prepared analogously; **3b**: $M_n = 8500$; $M_w/M_n = 2.4$, **3c**: $M_n = 7000$; $M_w/M_n = 3.0$, **3d**: $M_n = 6000$; $M_w/M_n = 2.1$.

3. Results and discussion

According to Pd-catalyzed polycondensation, the following copolymers were obtained in high yields.



	yield	M_n
3a (R = n-$C_{13}H_{27}$)	80%	8600
3b (R = n-$C_{10}H_{21}$)	81%	8500
3c (R = n-C_9H_{19})	99%	7000
3d (R = n-C_7H_{15})	88%	6000

At room temperature, the copolymers were not soluble in the tested organic solvents. However, they became soluble in 1,2-dichlorobenzene at elevated temperatures (approximately above 120 °C). Consequently, the characterization of the copolymers by NMR spectroscopy, the determination of their molecular weight by GPC, the preparation of cast films, and the determination of the basic optical properties of the copolymers in 1,2-dichlorobenzene and cast film became possible.

Fig. 1 shows the ^1H NMR spectrum of **3a**, which agrees with the molecular structure. Because the ^1H NMR spectrum does not show a peak of the terminal-$SnMe_3$ group at about δ 0.3 [21], **3a** is considered to have the thiazole–Br group as the major terminal group and the obtained M_n and Br content (cf. Section 2) agree with the assumption that **3a** has the polymer-Br group as the main terminal group. In the Pd-catalyzed Stille-type polycondensation shown in Eq. (1), the stannyl compound has a higher reactivity than the bromo compound [21], and this is consistent with the presence of the polymer-Br group as the main terminal group.

Fig. 2 shows the UV–vis spectra of **3a** in 1,2-dichlorobenzene and cast film. At 160 °C and 140 °C, **3a** is completely soluble in 1,2-dichlorobenzene and gives an absorption peak

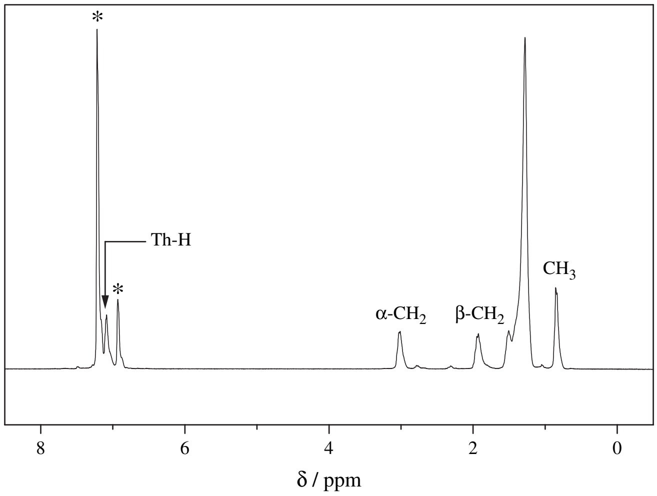


Fig. 1. ^1H NMR of **3a** in 1,2-dichlorobenzene-d_4 at 140 °C. Peaks at δ 6.94 and 7.19 marked by * are due to solvent impurities; they are assigned to 4-H and 3-H of 1,2-dichlorobenzene, respectively. The Th(thiophene)-H is overlapped with the impurity peak. The Th-H peak is observed at δ 7.09.

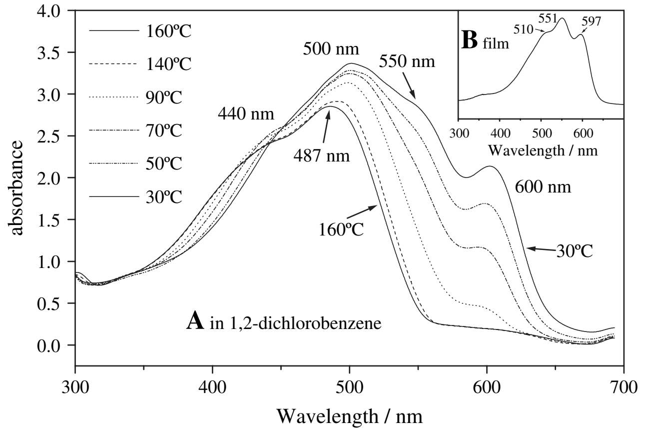


Fig. 2. UV–vis spectra of **3a** in (A) 1,2-dichlorobenzene at various temperatures and (B) cast film (inset). The film was prepared by casting a 1,2-dichlorobenzene solution of **3a** on a quartz glass plate. The inset shows the UV–vis spectrum of a cast film.

at 487 nm, which is assigned to the absorption by a single polymer molecule. The absorption peak locates at a longer wavelength than that of HT-P3RTh ($\lambda_{max} = 450$ nm [6]). As shown in Fig. 2, lowering temperature leads to the appearance of new absorption peaks at about 550 and 600 nm, which essentially agree with the absorption peaks of the film of **3a** and are assigned to the absorption of light by colloidal stacked molecules of **3a**. The shift of the UV–vis absorption peak to a longer wavelength is explained by the coplanarization of the polymer main chain and/or by the presence of intermolecular electronic interaction in the colloidal particles. Similar phenomena have been observed when a chloroform solution of HT-P3RTh is cooled below 0 °C [6]. At about 100 °C, the precipitation of some brown polymer particles started. The occurrence of the self-assembly of **3a** at temperatures higher than that of well-known HT-P3RTh suggests a strong tendency of **3a** for self-assembly.

Fig. 3 shows examples of powder X-ray diffraction patterns of the polymers. The XRD pattern of **3a** gives d_1, d_2, and d_3 peaks at $d_1 = 18.2$, $d_2 = 3.6$, and $d_3 = 4.5$ Å. The second and third peaks (200 and 300 peaks) of the d_1 peak are also observed at $d = 18.2$ Å/n ($n = 2, 3$).

For various π-conjugated polymers with long alkyl side chains, a similar d_1 peak has been observed, and d_1 is considered to correspond to the distance between π-conjugated main chains [1,4,6,12–17] separated by alkyl side chains. For **3a**, a packing model is depicted in Fig. 4. The number

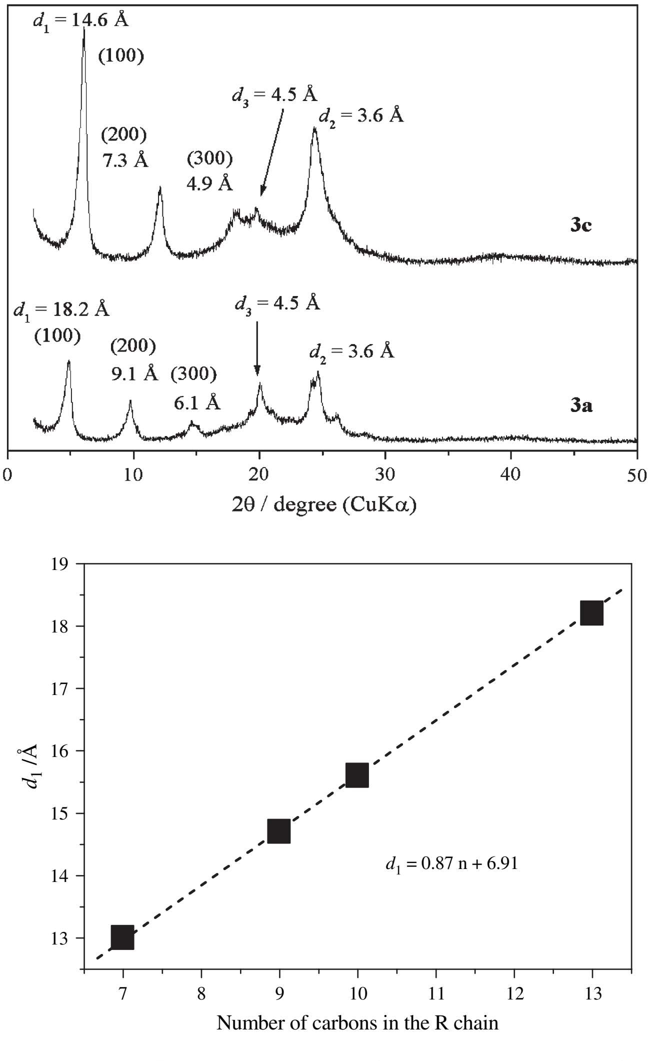


Fig. 3. Examples of powder XRD patterns of polymers (top panel) and d_1 vs. number of carbons in R chain plots (bottom panel).

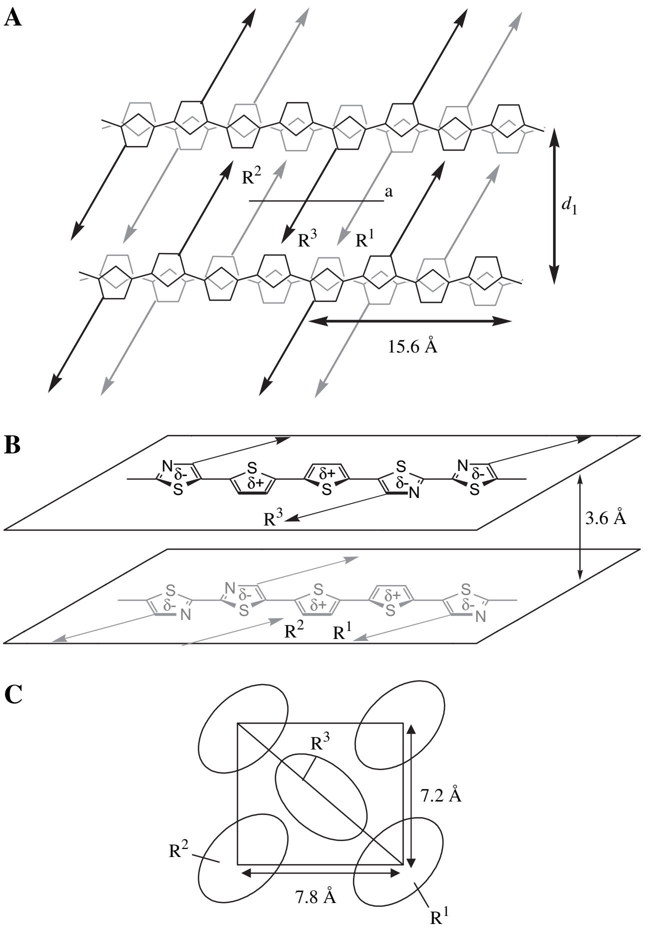


Fig. 4. Packing model of **3a** in the solid. (A) Two sheets with an interdigitation packing mode are shown. The polymer molecules in the lower layer are depicted in faint lines and letters, (B) layered structure, (C) side view of the packing of R chains on line a in (A); for R^1–R^3, see (A) and (B).

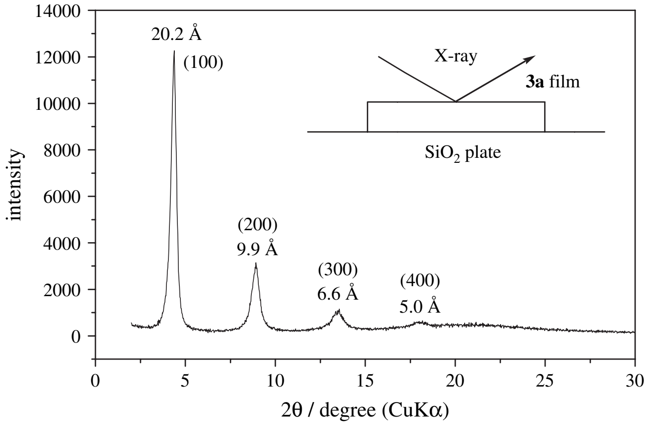


Fig. 5. XRD pattern of **3a** film cast on a quartz glass plate. Measured in a reflection mode.

density of the alkyl groups along the polymer main chain is smaller in **3a** than in HT-P3RTh, and **3a**–**3d** are considered to be capable of assuming an interdigitation packing mode as shown in Fig. 4; on the other hand, HT-P3RTh is considered to assume an end-to-end packing mode. Plots of d_1 vs. the number of carbons in the R chain give a straight line as shown in Fig. 3, and the slope of the straight line (0.87 Å/carbon) is smaller than the height of the CH_2 unit (1.25 Å), supporting the interdigitation packing model.

d_2 is considered to correspond to the sheet-to-sheet packing distance exhibited in Fig. 4, and d_2 is somewhat shorter than that (ca. 3.8 Å) observed with HT-P3RTh [4–6,17] which forms a similar stacked structure. These data imply better packing of **3a** than that of HT-P3RTh. The d_3 peak is assigned to the side-to-side packing distance between the alkyl side chains [22,23].

The packing model depicted in Fig. 4 gives the calculated densities [24] of 1.14, 1.15, 1.21, and 1.20 $\mathrm{g\,cm^{-3}}$ for **3a**, **3b**, **3c** and **3d**, respectively, which agree with the observed densities of 1.14, 1.12 1.21, and 1.20 $\mathrm{g\,cm^{-3}}$, respectively.

In contrast to the powder XRD pattern of **3a**, the XRD pattern of the cast film of **3a** on a quartz glass plate gives only n00 peaks at $d = 20.2$ Å/n ($n = 1, 2, 3, 4$), as shown in Fig. 5. A similar phenomenon has been reported for a cast film of HT-P3RTh [4,8,12,13,17], and has been taken as an indication of the molecular alignment of π-conjugated polymers on the surface of the substrates, with alkyl side chains oriented toward the surface of the substrate. Polymer **3a** is considered to assume a similar aligned structure on the surface of the quartz glass plate. The 200, 300, and 400 peaks in Fig. 5 are more distinct than those of HT-P3RTh, which implies a stronger tendency of **3a** to form a well aligned structure on the surface of the substrate. The d_1 observed in Fig. 5 is somewhat longer than the d_1 observed in Fig. 3, suggesting that the tilt angle of the R side chain toward the π-conjugated main chain differs between the bulk solid and the cast thin film.

The polymer was electrochemically active. The cast film of **1b** on a Pt plate showed an electrochemical oxidation (or p-doping) peak at 0.76 V vs. Ag^+/Ag and an electrochemical reduction (or n-doping) peak at −2.15 V vs. Ag^+/Ag. The oxidation peak is located at a higher potential than those of polythiophenes (ca. 0.60 V vs. Ag^+/Ag [1–3,25]). The higher oxidation potential of **1b** is considered to be due to an electron-accepting effect of the neighboring thiazole unit [11].

As described above, new π-conjugated five-membered ring polymers with the regioregularly added R side chains have been prepared, and the polymers show a strong tendency for self-assembly.

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[24] Calculated density of **3a** = (molecular weight of the repeating unit)/($15.6 \times 10^{-8} \times 18.2 \times 10^{-8} \times 3.6 \times 10^{-8} \times 6.0 \times 10^{23}$) = (700/613) = 1.14.
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