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Preparation of Head-to-tail π-Conjugated Poly(thiophene–pyridine) and Polypyrimidine by Organometallic Polycondensation

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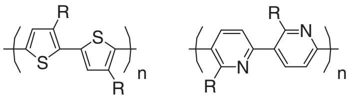
The metalation of Br–ThPy–Br (Th: thiophene-2,5-diyl; Py: pyridine-2,5-diyl) and 2-iodo-5-bromopyrimidine with *i*-PrMgCl proceeds regioselectively. The cross-coupling polycondensation of regioselectively metalated intermediates gives head-to-tail π-conjugated poly(thiophene–pyridine) and polypyrimidine, respectively, and their packing structures in the solid state and optical data are discussed.

The synthesis of regioregular π-conjugated heteroaromatic polymers by cross-coupling polymerization is important for controlling the solid structures and electrical and optical properties of π-conjugated polymers.[1,2] Head-to-tail-type poly(3-alkylthiophene-2,5-diyl) (HT-P3RTh)[1,2] and poly(6-alkylpyridine-2,5-diyl) (HT-P6RPy)[3] (Chart 1) have been prepared via the regioselective metalation[1–4] of dihalo starting materials (e.g., via XMg–$C_4HS(R)$–X, X = halogen) and cross-coupling polymerization using Ni(II) catalysts.

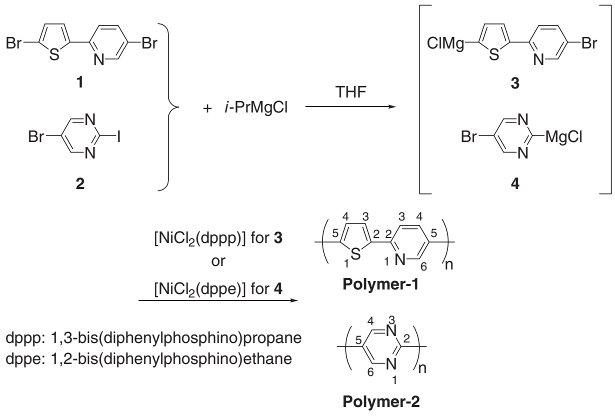
Here, we report on the selective metalation of the following dihalo compounds with *i*-PrMgCl and the utilization of the metalated intermediates for the synthesis of new head-to-tail-type π-conjugated polymers.

Reactions of **1** and **2** with *i*-PrMgCl[4] gave the intermediates **3** and **4** (Scheme 1). The hydrolysis of the formed intermediates gave only H–Th–Py–Br and 5-bromopyrimidine, respectively, and no Br–Th–Py–H or 2-iodopyrimidine was detected in the hydrolysis products by ^{1}H NMR spectroscopy. The selective formation of **3** was also supported by the production of the following boron compound **5** (Chart 2) from **3** in good yield.[5] These results support the selective metalation of **1** and **2** by *i*-PrMgCl. The use of 2,5-dibromopyrimidine, instead of **2**, did not lead to the selective formation of **4**.



HT-P3RTh **HT-P6RPy**

Chart 1.

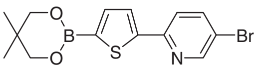


Scheme 1.

The addition of diphosphine complexes of nickel to **3** and **4** in THF gave **Polymer-1** and **Polymer-2**, respectively.[5] On the other hand, the zerovalent-nickel-complex ([Ni(0)L_m])-promoted dehalogenative polycondensation of dihaloaromatic compounds usually gives head-to-head-rich regiorandom polymers,[6] and such polymers, i.e., **Polymer-1′**[7] and **Polymer-2′**,[8] were previously prepared by the dehalogenative polycondensation of **1** and 2,5-dibromopyrimidine, respectively.

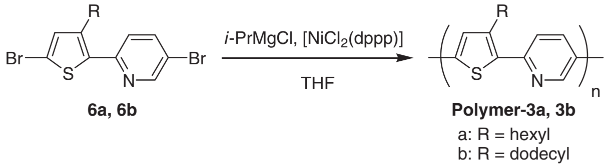
Polymer-1 was soluble in HCOOH and showed an intrinsic viscosity [η] of 0.58 dL g^{-1} (dL = 100 mL) in HCOOH. The Suzuki cross-coupling polycondensation of **5** using [Pd(PPh_3)$_4$] and K_2CO_3 in THF gave **Polymer-1** with a smaller [η] of 0.16 dL g^{-1}. **Polymer-2** was soluble in H_2SO_4 and partly soluble in HCOOH; however, it was insoluble in the other solvents tested. The MALDI-TOF-Mass spectrum of **Polymer-2** showed peaks in the range from $m/e = 450$ corresponding to $n = 6$ in $(C_4H_2N_2)_n$ to $m/e = 1200$ ($n = 15$).

The ^{1}H NMR spectra of **Polymer-1** and **Polymer-1′** (cf., Figure S1 in Supporting Information[5]) clearly differ from each other owing to the difference in microstructure between the two polymers. Because **Polymer-1** has only aromatic protons, detailed analysis of its ^{1}H NMR spectrum was difficult. However, the following hexyl polymer (**Polymer-3a** (Scheme 2)[5]) synthesized analogously gives rise to a simple ^{1}H NMR spectrum (Figure 1), supporting the formation of a regioregular polymer. In particular, the appearance of the α-CH_2 signal, which is often used for evaluating the regioregularity of π-



5

Chart 2.



Scheme 2.

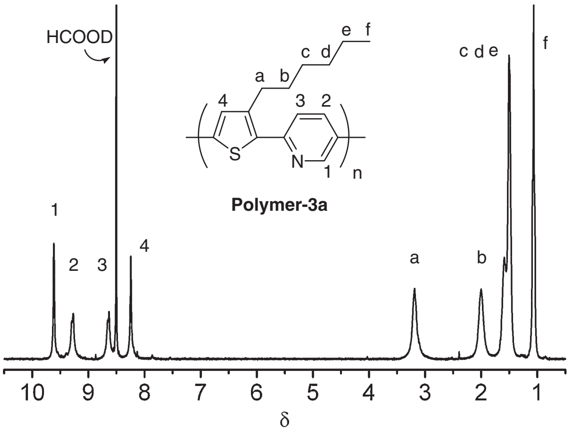


Figure 1. ^{1}H NMR spectrum of **Polymer-3a** in DCOOD.

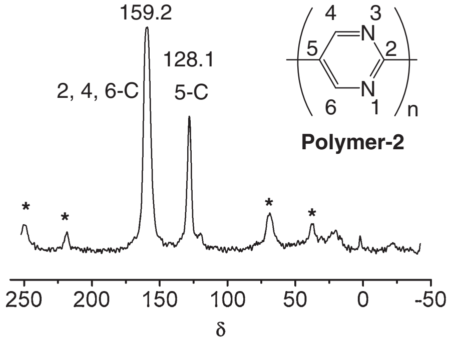


Figure 2. CP/MAS solid ^{13}C NMR spectrum of **Polymer-2**. Peaks with * are spinning side bands.

conjugated polymers with an alkyl side chain,[1–3,9] as a single peak supports the regioregular structure of **Polymer-3a**; regioirregular polymers usually show split α-CH_2 signals. The ^{1}H NMR spectrum of **Polymer-3a** is compared with that of a regioregular alternating π-conjugated copolymer of alkylthiazole (Tz(R)) and thiophene.[9] **Polymer-3b** also gives rises to a simple ^{1}H NMR spectrum, which indicates its regioregular structure.

Polymer-3a and **Polymer-3b** are soluble in *o*-dichlorobenzene and 1,1,2,2-tetrachloroethane. **Polymer-3a** and **Polymer-3b** showed M_w (weight-average molecular weight) of 11000 and 56000 with polydispersity indexes of 3.6 and 3.1, respectively, in GPC analysis at 140 °C (vs. polystyrene standards, eluent: 1,2,4-trichlorobenzene).

Figure 2 shows the CP/MAS solid ^{13}C NMR spectrum of **Polymer-2**. A sharp signal at δ 128.1 is assigned to the 5-C carbon of the pyrimidine ring. 2-C, 4-C, and 6-C carbons show a single peak at δ 159.2. The ^{13}C NMR spectrum pattern of **Polymer-2** is similar to that of **Polymer-2′**.[8] However, the 5-C peak of **Polymer-2′** is broader (half width = 376 Hz) than that of **Polymer-2** (half width = 312 Hz), owing to the regio-irregular structure of **Polymer-2′**. On the other hand, for the head-to-head (HH)-type poly(pyrimidine-2,5-diyl) (**HH-PPyrim**) separately prepared from 2,2′-dichloro-5,5′-bipyrimidine,[10] the two ^{13}C NMR peaks are shifted upfield (155 and 126 ppm, respectively).

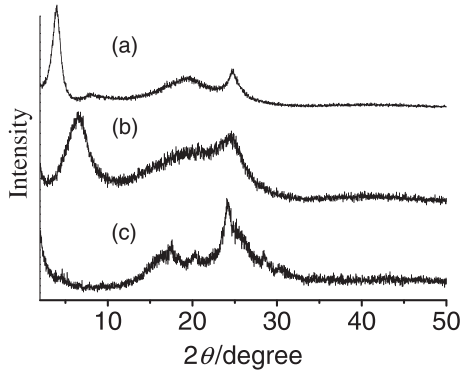


Figure 3. Powder XRD patterns of (a) **Polymer-3b**, (b) **Polymer-3a**, and (c) **Polymer-1**.

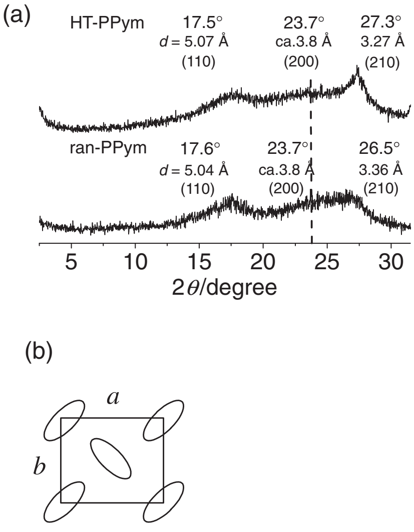


Figure 4. (a) Powder XRD patterns of **Polymer-2** and **Polymer-2′**. (b) Postulated herringbone packing of **Polymer-2**.[11]

Figure 3 shows the powder X-ray diffraction (XRD) patterns of **Polymer-1**, **Polymer-3a**, and **Polymer-3b**. As shown in Figure 3, the XRD patterns show distinct peaks supporting the notion that the polymers assume ordered structures in the solid state. The XRD pattern of **Polymer-1** is considerably different from that of **Polymer-1′** shown in Figure S2.[5]

The XRD patterns of **Polymer-3a** and **Polymer-3b** resemble those of regioregular π-conjugated aromatic polymers with long alkyl side chains,[1–3] including the regioregular alternating copolymer of Tz(R) and Th (see above).[9] The *d* space of the peak in a low-angle region is usually assigned to the distance between polymer chains separated by alkyl side chains. By increasing the length of an alkyl side chain from hexyl ($2\theta = 6.3°$, $d = 14$ Å) to decyl ($2\theta = 3.8°$, $d = 23$ Å), the *d* space increases reasonably.

The comparison of the XRD patterns of **Polymer-2** and **Polymer-2′** shows differences, as shown in Figure 4. The XRD pattern of **Polymer-2** shows sharper XRD peaks than that of **Polymer-2′**. Linear π-conjugated polymers without side chains, e.g., poly(*p*-phenylene) and poly(thiophene-2,5-diyl), often

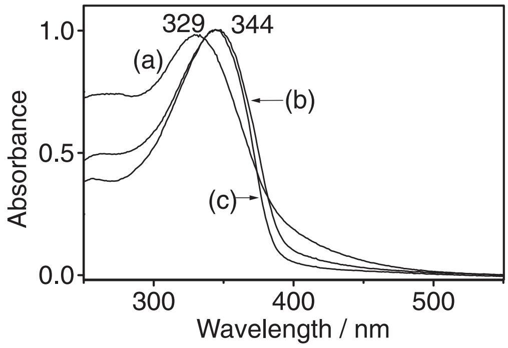
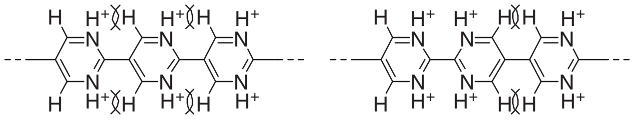


Figure 5. UV–vis spectra of (a) **Polymer-2**, (b) **HH-PPyrim**, and (c) **Polymer-2′** in concd H_2SO_4.



protonated **Polymer-2**

protonated **HH-PPyrim**

Figure 6. Postulated protonation of **Polymer-2** and **HH-PPyrim**.

assume herringbone packing in the solid state,[1] and the packing of **Polymer-2** may also be explained by the herringbone packing in view of its XRD pattern and density, as shown in Figure 4.[11]

Both **Polymer-1** and **Polymer-1′** showed a UV–vis peak at about 475 nm in HCOOH. **Polymer-1** obtained from **5** and with a smaller $[\eta]$ gave rise to a UV–vis peak at 455 nm in HCOOH. **Polymer-3a** showed a UV–vis peak at 438 nm in HCOOH. Figure 5 shows the UV–vis spectra of **Polymer-2** and related polymers in concd H_2SO_4. The π–π^* transition peaks of polypyrimidines appear at approximately 335 nm, which is considerably shorter than that (ca. 370 nm) of poly(*p*-phenylene).[1]

The protonation of the polymers seems to cause the twisting of the main chain, leading to the shift to a lower wavelength (Figure 6).[12] **Polymer-1** and **Polymer-3a** were photoluminescent. **Polymer-1** showed emission peaks at 525 and 552 nm with a quantum yield of 7% in HCOOH, and **Polymer-3a** gave rise to an emission peak at 518 nm with a quantum yield of 5% in HCOOH.

As described above, *i*-PrMgCl is useful for the regioselective metalation of dihalides of thiophene–pyridine compounds and pyrimidine, and new regiocontrolled π-conjugated polymers have been obtained by polycondensation utilizing the formed intermediate. Detailed analysis of functionalities of the obtained polymers is under way.

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11 If one assumes *a* and *b* dimensions of 7.4 and 6.9 Å, respectively, for the herringbone packing, *d* spaces of (110), (200), and (210) diffractions are calculated as 5.05, 3.7, and 3.26 Å, respectively, which agree with the observed diffraction peaks. If **Polymer-2** has a repeating height of 4.2 Å along the polymer chain, similarly to poly(*p*-phenylene),[1] the density of **Polymer-2** is calculated as $d_{\text{calcd}} = 1.21$ g cm^{-3}, which roughly agrees with the observed density $d_{\text{obs}} = 1.15$ g cm^{-3}. Polymers often give a lower observed density than the calculated density because they contain amorphous parts. The postulated *a* and *b* dimensions or the cross section ($S = 51$ Å^2) of the pyrimidine unit is larger than those of poly(*p*-phenylene) (**PPP**) ($a = 7.8$ Å and $b = 5.5$ Å; $S = 43$ Å^2)[1] and poly(2,2′-bipyridine-5,5′-diyl) (**PBpy**) ($a = 8.1$ Å and $b = 5.7$ Å; $S = 46$ Å^2),[6] thus giving the order: S (**Polymer-2**) > S (**PBpy**) > S (**PPP**). The importance of the presence of a lone pair of electrons for the determination of the effective cross section of the aromatic unit is suggested.

12 The repulsion between a lone pair of electrons[11] and *o*-H may also cause the shift to a shorter wavelength.