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π-Conjugated Polymers, $(\mathrm{Th(R)–CH=CH–Th(R)})_n$ (Th(R) = 3-Alkylthiophene-2,5-diyl; R = Octyl, Decyl, and Dodecyl): Preparation of Dibromo Monomers and the Polymers

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π-Conjugated polymers, $(\mathrm{Th(R)–CH=CH–Th(R)})_n$ (Th(R) = 3-alkylthiophene-2,5-diyl; R = octyl, decyl, and dodecyl), and their dibromo monomers have been prepared. The polymers show a tendency to self-assemble in solutions and in the solid state. X-ray diffraction data suggest that the polymers assume an interdigitation packing in the solid state.

π-Conjugated polymers are the subject of many papers,[1] and molecular assembly of π-conjugated polymers has attracted strong interest.[1–3] Self-assembled π-conjugated polymers show superior electronic[2] and optical[3] functionalities. For example, head-to-tail type poly(3-alkylthiophene-2,5-diyl) forms π-stacked molecular assembly and shows higher electrical conductivity[2a] and carrier mobility[2b] as well as larger Faraday rotation[3a] and third-order optical nonlinear susceptibility[3b] than regiorandom poly(3-alkylthiophene-2,5-diyl). π-Conjugated $(\mathrm{Th(R)–(\pi)–Th(R)})_n$ polymers also show a tendency to self-assemble,[1d,2c,4] and polymers having various (π) units have been prepared (Chart 1).[1,2c,4]

The poly(arylene vinylene) polymer, **P(Hex)** (R = hexyl) containing a vinylene (–CH=CH–) unit as the (π) unit was prepared by Professors Akagi and Shirakawa[5a] and Professor Holdcroft[5b] by oxidative polymerization of **H–Th(Hex)–CH=CH–Th(Hex)–H** (Hex = hexyl) (Chart 2). Later we reported preparation of the polymer by organometallic dehalogenative polycondensation of **Br–Th(Hex)–CH=CH–Th(Hex)–Br** with zerovalent nickel complex, $[\mathrm{Ni^0L}_m]$, and self-assembly of the polymer in the solid state.[4c]

$$n(\mathrm{Br–Th(Hex)–CH{=}CH–Th(Hex)–Br}) + n[\mathrm{Ni^0L}_m] \rightarrow (\mathrm{Th(Hex)–CH{=}CH–Th(Hex)})_n \qquad (1)$$

$[\mathrm{Ni^0L}_m]$:
a mixture of bis(1,5-cyclooctadiene)nickel(0) ($[\mathrm{Ni(cod)_2}]$), 2,2′-bipyridyl (bpy), and 1,5-cyclooctadiene (cod).

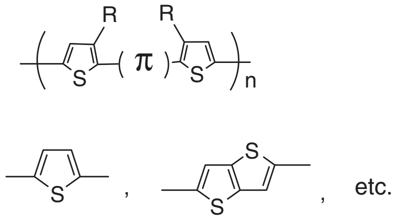

Chart 1. Examples of $(\mathrm{Th(R)–(\pi)–Th(R)})_n$ type polymers.[1d,2c,2d,4]

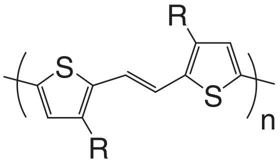

Chart 2.

To reveal the self-assembling behavior of the $\mathbf{(Th(R)–CH{=}CH–Th(R))}_n$ polymer in more detail, obtaining such polymers with various R groups is desired, and we now report the preparation of such polymers with R = octyl, decyl, and dodecyl groups at the thiophene unit. The polymers were prepared by organometallic dehalogenative polymerization (cf. eq 1); yields of **P(Oct)** (R = octyl), **P(Dec)** (R = decyl), and **P(Dod)** (R = dodecyl) were 63%, 72%, and 73%, respectively. The polymers are poly(thienylene vinylene) polymers; recently various poly(thienylene vinylene)s have been synthesized and application of the polymers to optoelectronic devices (especially for photovoltaic cells) is actively investigated.[6]

P(Oct), **P(Dec)**, and **P(Dod)** were soluble in hot (e.g., at 120 °C) halogenated hydrocarbons such as *o*-dichlorobenzene (*o*-DCBZ) and 1,1,2,2-tetrachloroethane. However, they were only partly soluble in halogenated hydrocarbons including chloroform at room temperature (r.t.) and not soluble in polar solvents such as DMF. *o*-DCBZ solutions of the polymers prepared in hot *o*-DCBZ did not cause apparent precipitation of the polymer for a while (several hours) after the solution was cooled to r.t.

P(Oct), **P(Dec)**, and **P(Dod)** showed number average molecular weights (M_n, vs. polystyrene standards) of 7700, 6500, and 8200 with $M_\mathrm{w}/M_\mathrm{n}$ values (M_w: weight average molecular weight) of 2.4, 2.2, and 2.1, respectively, in gel permeation (GPC) analysis using 1,2,4-trichlorobenzene as the eluent at 140 °C. Synthesis of the corresponding dibromo monomers, **M(Oct)**, **M(Dec)**, and **M(Dod)**, is described in the Experimental section.

The IR spectrum of **P(Oct)** shown in Figure S1 in Supporting Information (SI) resembles that of **M(Oct)** and previously synthesized **P(Hex)** indicating that the basic structure of **M(Oct)** is maintained. Because content of Br is negligible in elemental analysis of **P(Oct)**, the polymer with the structure shown above is thought to be obtained. ^{1}H NMR spectrum of the polymer (Figure S2 in SI) agrees with its structure.

As shown by curve (a) in Figure 1, the UV–vis spectrum of an *o*-DCBZ solution of **P(Oct)** shows a UV–vis peak at 561 nm[7] when an *o*-DCBZ solution prepared at 130 °C was cooled to r.t. and the UV–vis spectrum was measured just after cooling. As described above, this solution state was essentially

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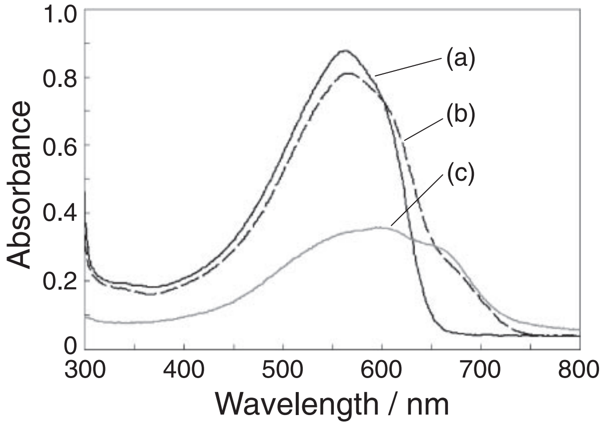

Figure 1. (a) and (b): UV–vis spectra of **P(Oct)** in *o*-DCBZ at r.t. The solution was obtained by dissolving **P(Oct)** in *o*-DCBZ at 130 °C and the spectra were measured at r.t.: (a) just after cooling to r.t.; (b) after 8 h (dashed line). (c) UV–vis spectrum of a film of **P(Oct)**; the film was made by casting an *o*-DCBZ solution of **P(Oct)** on a quartz glass plate. **P(Oct)** is partly soluble in $CHCl_3$, similar to **P(Hex)**,[4c] and a dilute pink $CHCl_3$ solution of **P(Oct)** shows a UV–vis peak at 505 nm.

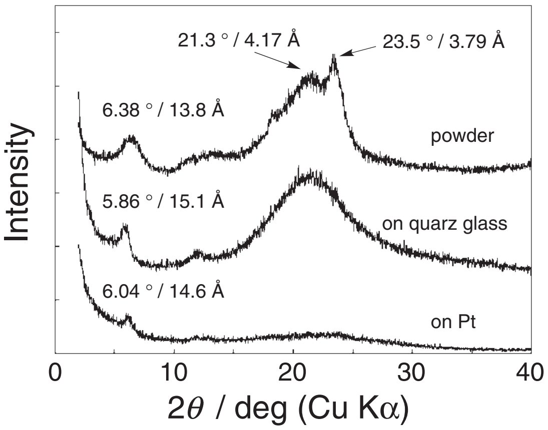

Figure 2. XRD patterns of **P(Oct)**. (top): Powdery sample. (middle): Cast film on a quartz glass plate. The broad peak at about 21° is due to diffraction from the glass plate. (bottom): Cast film on a Pt plate.

stable for a while. However, as shown by curve (b) in Figure 1, a new shoulder peak appears at about 670 nm after standing the solution at r.t. for 8 h. Cast film of **P(Oct)** gives rise to the UV–vis peak at the longer wavelength clearly.

Various π-conjugated polymers give an additional UV–vis peak at a longer wavelength, in addition to the UV–vis peak originating from the single polymer molecule when they self-assemble.[1–4] Electronic interaction between the π-conjugated polymers in the assembly is thought to bring about the new UV–vis absorption band. The UV–vis data of the polymer suggest self-assembly, and the following X-ray diffraction (XRD) data of the polymer support the formation of an ordered structure in the solid state.

As shown in Figure 2, the powder XRD pattern of **P(Oct)** gives rise to a peak at $d_1 = 13.8$ Å. π-Conjugated polymers with long side chains often show such a peak in a low angle region when they self-assemble, and d_1 is thought to correspond to the distance between the polymer main chains separated by the long side chains.[1–4]

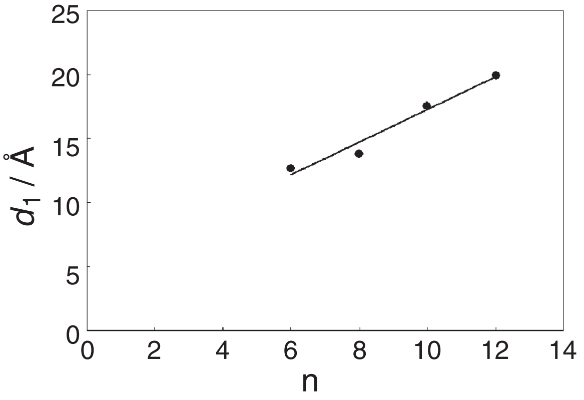

Figure 3. Plots of d_1 vs. number of carbon (n) in the R side chain. The data at $n = 6$ are from Ref. 4c. Powdery samples.

The d_2 peak at 3.79 Å may be assigned to a π-stacking face-to-face distance of thiophene-based π-conjugated polymers.[1,2,4c] The broad peak at about 4.2 Å corresponds to side-to-side distance between loosely packed alkyl side chains.[1,2] A packing model of **(Th(R)–CH=CH–Th(R))$_n$** is shown in Figure S3 in SI.

P(Dec) and **P(Dod)** give similar XRD data with $d_1 = 17.5$ and 19.8 Å, respectively, with powdery samples. However, cast film of **P(Dod)** does not show distinct XRD peak (Figure S4 in SI), suggesting that the molecular organization of **P(Dod)** during the casting and drying processes is difficult. As shown in Figure S5 in SI, UV–vis spectrum of a film of **P(Dod)** does not show the shoulder peak at a longer wavelength (ca. 650–670 nm) clearly.

Plots of d_1 vs. number of carbons in the alkyl side chain give a linear correlation shown in Figure 3.

The plots give a straight line with a slope of about 1.2 Å/carbon, which is comparable to the height of the $-CH_2-$ unit along linear alkyl chains (1.25 Å/carbon).[1,2,4] and suggests an interdigitation packing (Figure S3 in SI) of the polymer in the solid state. Some (Th(R)–(π)–Th(R))$_n$ polymers also assume such an interdigitation packing in the solid state.[2c,2d] As described above, a series of (Th(R)–CH=CH–Th(R))$_n$ π-conjugated polymers have been prepared and their self-assembling behavior has been revealed. These results are expected to contribute to design of new functional π-conjugated polymers.

Experimental

Synthesis of the Dibromo Monomers, M(R)s. The dibromo monomers were prepared in a way similar to that applied for the preparation of their hexyl analog.[4c]

M(Oct): A THF (20 mL) solution containing 2-bromo-3-octylthiophene (910 mg, 3.3 mmol), 1,2-bis(tributylstannyl)-ethylene (1.0 g, 1.65 mmol), and $[Pd(PPh_3)_4]$ (ca. 20 mg, 0.017 mmol) was stirred for 3 days at 80 °C. After cooling to r.t., an aqueous solution of KF and aqueous ammonia were added, and the product was extracted with hexane. The extract was dried over Na_2SO_4, and purification by column chromatography on SiO_2 (eluent: hexane) gave a yellow solid of

H–Th(Oct)–CH=CH–Th(Oct)–H in 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, $J = 5.1$ Hz, 2H), 6.99 (s, 2H), 6.84 (d, $J = 5.1$ Hz, 2H), 2.65 (t, $J = 7.5$ Hz, 4H), 1.59 (m, 4H), 1.33 (m, 20H), 0.87 (t, $J = 6.8$ Hz, 6H). Anal. Calcd for $C_{26}H_{40}S_2$: C, 74.94; H, 9.67; S, 15.39%. Found: C, 75.17; H, 9.46; S, 15.35%. Ni complex-catalyzed coupling reaction[4c,5b] between 1,2-dichloroethylene and a Grignard reagent of 2-bromo-3-octylthiophene also gave the product; however, the yield was lower (19%: cf. SI).

A THF (10 mL) solution containing **H–Th(Oct)–CH=CH–Th(Oct)–H** (760 mg, 1.83 mmol) and NBS (650 mg, 3.65 mmol) in 10 mL of THF was stirred at r.t. for 15 h. After addition of an aqueous solution of $NaHSO_3$, the product was extracted with hexane. The extract was dried over Na_2SO_4 and purification by column chromatography on SiO_2 (eluent: hexane) gave a yellow solid of **M(Oct)** in 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80 (s, 2H), 6.76 (s, 2H), 2.56 (t, $J =$ 7.5 Hz, 4H), 1.55 (m, 4H), 1.29 (m, 20H), 0.88 (t, $J = 6.8$ Hz, 6H). Anal. Calcd for $C_{26}H_{38}Br_2S_2$: C, 54.36; H, 6.67; S, 11.16%. Found: C, 54.40; H, 6.83; S, 11.23%. HRMS (FAB): *m*/*z* 572.0782, Found: 572.0779.

The decyl and dodecyl homologs were prepared analogously.

H–Th(Dec)–CH=CH–Th(Dec)–H: In 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, $J = 5.2$ Hz, 2H), 6.99 (s, 2H), 6.84 (d, $J = 5.2$ Hz, 2H), 2.65 (t, $J = 7.5$ Hz, 4H), 1.58 (m, 4H), 1.30 (m, 28H), 0.87 (t, $J = 6.8$ Hz, 6H). Anal. Calcd for $C_{30}H_{48}S_2$: C, 76.20; H, 10.23; S, 13.56%. Found: C, 76.17; H, 10.31; S, 13.49%.

M(Dec): In 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (s, 2H), 6.75 (s, 2H), 2.56 (t, $J = 7.5$ Hz, 4H), 1.56 (m, 4H), 1.29 (m, 28H), 0.88 (t, $J = 6.8$ Hz, 6H). Anal. Calcd for $C_{30}H_{46}Br_2S_2$: C, 57.14; H, 7.35; S, 10.17%. Found: C, 57.41; H, 7.57; S, 10.30%.

H–Th(Dod)–CH=CH–Th(Dod)–H: In 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, $J = 5.1$ Hz, 2H), 6.99 (s, 2H), 6.83 (d, $J = 5.1$ Hz, 2H), 2.64 (t, $J = 7.6$ Hz, 4H), 1.57 (m, 4H), 1.30 (m, 36H), 0.88 (t, $J = 6.7$ Hz, 6H). Anal. Calcd for $C_{34}H_{56}S_2$: C, 77.21; H, 10.67; S, 12.12%. Found: C, 76.91; H, 10.89; S, 11.89%.

M(Dod): In 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (s, 2H), 6.75 (s, 2H), 2.56 (t, $J = 7.5$ Hz, 4H), 1.54 (m, 4H), 1.29 (m, 36H), 0.88 (t, $J = 6.8$ Hz, 6H). HRMS (FAB): *m*/*z* 684.2034, Found: 684.2015.

Preparation of Polymers, P(R)s. Polymers were prepared by dehalogenative polycondensation of **M(R)** in a way similar to that applied for the preparation of **P(Hex)**.[4c] Polymerization was carried out under inert gas using standard Schlenk techniques.

P(Oct): A mixture of **M(Oct)** (600 mg, 1.05 mmol), $[Ni(cod)_2]$ (495 mg, 1.8 mmol), bpy (280 mg, 1.8 mmol), and cod (110 mg, 1.0 mmol) in 40 mL of dry DMF was stirred for 24 h at 60 °C. The reaction mixture was poured into HCl-acidic methanol and the precipitate was collected by filtration. The powder was washed with diluted hydrochloric acid, aqueous ammonia, an aqueous solution of a disodium salt of ethylenediaminetetraacetic acid, and water, and dried to obtain a black powder of **P(Oct)** in 63% yield. The ^{1}H NMR spectrum in 1,1,2,2-tetrachloroethane-d_2 at 130 °C indicated that the thiophene-H and vinylene-H were overlapped (Figure S2 in SI). ^{1}H NMR (500 MHz at 130 °C, $CDCl_2CDCl_2$): δ 6.93 and 6.92 (overlapped, 4H), 2.63 (4H), 1.65 (4H), 1.37 (ca. 20H[8]), 0.88 (6H).

GPC analysis of the polymer was carried out at Tosoh Analysis and Research Center with a HLC-8121GPC/HT apparatus (with RI detector) and using 1,2,4-trichlorobenzene as the eluent at 140 °C and a TSKgel GMH_{HR}-H(20)HT column; $M_n = 7700$, $M_w = 19000$, and M_z (z average molecular weight) $= 32000$.

P(Dec) and **P(Dod)** were prepared analogously.

P(Dec): In 72% yield. GPC data (140 °C, 1,2,4-trichlorobenzene): $M_n = 6500$, $M_w = 14000$, and $M_z = 30000$.

P(Dod): In 73% yield. GPC data (140 °C, 1,2,4-trichlorobenzne): $M_n = 8200$, $M_w = 17000$, and $M_z = 33000$.

Supporting Information

Additional synthetic results, spectroscopic (IR, UV–vis, and ^{1}H NMR) data of **M(Oct)** and polymers, XRD patterns, and a packing model. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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7 The UV–vis peak position is comparable to those reported for poly(vinylene thienylene)s.[5b,6]

8 This peak of the CH_2 groups and a peak of a small amount of water contained in the solvent overlapped (Figure S2 in SI).