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# Synthesis and Chemical Properties of $\pi$-Conjugated Poly(9,10-dialkyl-9,10-dihydrophenanthrene-2,7-diyl) and a Related Polymer

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$\pi$-Conjugated poly(9,10-dioctyl-9,10-dihydrophenanthrene-2,7-diyl) and a related polymer were prepared by dehalogenative organometallic polycondensation using the corresponding dibromo compound. The polymers are photoluminescent and show a tendency to self-assemble.

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$\pi$-Conjugated polymers and oligomers are the subject of many papers.[1] Fluorenes, especially 9,9-dialkylfluorenes, are important building blocks of $\pi$-conjugated polymers and oligomers,[2] and utilization of fluorene (Flu)-based $\pi$-conjugated polymers, PFlu(9,9-R) (Chart 1), for electronic and optical devices has been actively investigated.

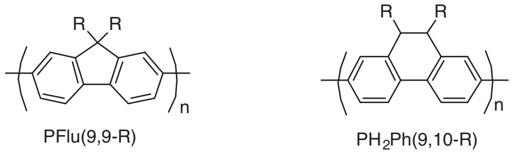
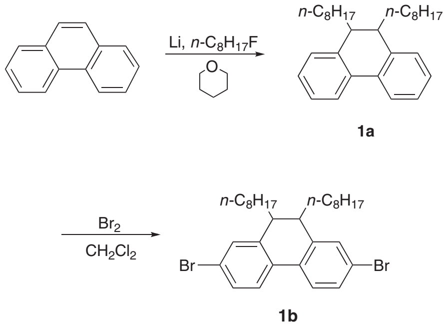


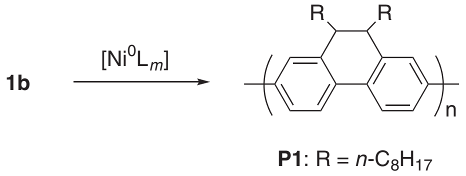
**Chart 1.**

In spite of many studies on Flu-based $\pi$-conjugated polymers, use of a 9,10-dihydrophenanthrene ($H_2$Ph) unit as the building block of $\pi$-conjugated polymers has received less attention. We now report (1) synthesis of 2,7-dibromo-9,10-dihydrophenanthrene with two alkyl substituents at the 9- and 10-positions and (2) organometallic polycondensation of the dibromo compound to $H_2$Ph-based $\pi$-conjugated polymers. The obtained polymer, P$H_2$Ph(9,10-R), essentially has a poly(*p*-phenylene)-type electronic system similar to that of PFlu(9,9-R). Analogous polymers with two OR groups at the 9- and 10-positions of P$H_2$Ph were previously reported from our group;[3] however, the P$H_2$Ph(9,10-R) polymers with alkyl groups have not been reported. Revealing chemical properties of P$H_2$Ph(9,10-R) will make the characteristics of the $H_2$Ph-based $\pi$-conjugated polymer, in comparison with that of the Flu-based polymer, more clear. The monomer **1b** was prepared by bromination of **1a**.

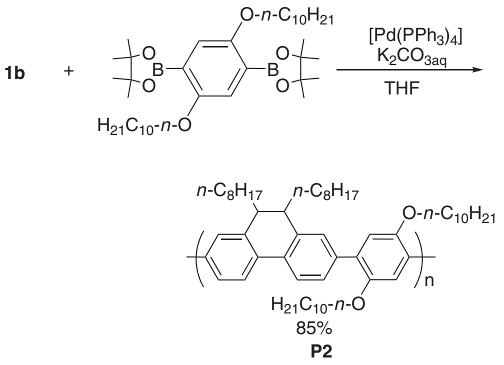
**1a** was prepared according to a method reported by Yus and co-workers (Scheme 1).[4] The reaction of **1a** with an excess amount of $Br_2$ in dichloromethane at room temperature gave **1b** in 57% isolated yield.[5] The $^1$H NMR spectrum of **1b** shows a simple pattern, indicating that **1b** is not a mixture of *trans* and *cis*-isomers. Liquid-chromatographic separation of **1b** using chiral columns (e.g., CHIRAPAC AS-RH) gave 1:1 two peaks,[5] revealing that **1b** was a 1:1 mixture of (*R,R*)- and (*S,S*)-isomers. These results support *trans*-configuration of **1a** and postulated *trans*-alkylation of phenanthrene with Li and RF.[4]



**Scheme 1.**



$[Ni^0L_m]$:a mixture of bis(1,5-cyclooctadiene)nickel(0), 2,2'-bipyridyl, and 1,5-cyclooctadiene



**Scheme 2.**

From **1b**, the following $\pi$-conjugated polymers, yellowish green **P1** and Chinese yellow **P2**, were prepared by using a zero-valent Ni complex[1–3] at 60 °C in DMF and the Suzuki-type polycondensation[1] in THF at 70 °C, respectively; yields of **P1** and **P2** were 71 and 85%, respectively, after work-up of the polymers (Scheme 2).[5] GPC analysis (140 °C, eluent: 1,2,4-trichlorobenzene) of **P1** showed $M_n$ (number average molecular weight) and $M_w$ (weight average molecular weight) of 4600 and 13000, respectively. GPC analysis (40 °C, eluent: THF) of **P2** showed $M_n$ of 12800 with $M_w/M_n$ of 2.8. **P1** and **P2** had high

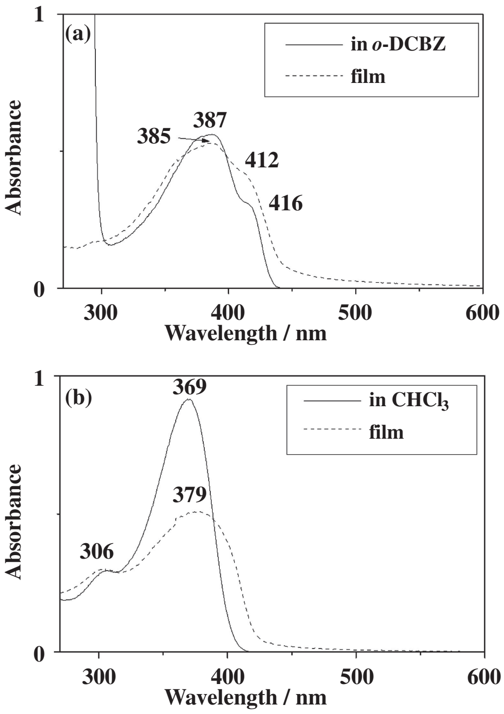


**Figure 1.** UV–vis spectra of (a) **P1** and (b) **P2** in solutions and in films. UV–vis spectrum of **P1** in chloroform essentially agrees with that in *o*-DCBZ.

thermal stability with 5% weight loss temperatures at 420 and 408 °C, respectively.

IR and $^1$H NMR data of **P1** and **P2** were reasonable for the structures of the polymers.[5] **P1** was soluble in chloroform, THF, and 1,2-dichlorobenzene (*o*-DCBZ). **P2** was soluble in chloroform and THF.

Figure 1 shows UV–vis spectra of **P1** and **P2** in solutions and films. **P1** and **P2** essentially have an electronic system of poly(*p*-phenylene) (PPP) and their UV–vis peaks appear near that of PPP ($\lambda_{max}$ = about 375 nm) as shown in Figure 1. In addition to the main peak at about 390 nm, **P1** gives rise to a shoulder peak at about 415 nm both in *o*-DCBZ and chloroform, and the shoulder peak becomes stronger in the film. For the shoulder peak of **P1** in *o*-DCBZ, it disappeared on raising temperature to 110 °C. Intermolecular electronic interaction of $\pi$-conjugated polymers often causes shifts of UV–vis absorption to a longer wavelength,[1,6,7] and the UV–vis data suggest that molecular aggregation of **P1** in *o*-DCBZ occurs at room temperature and in film and the molecular aggregation in *o*-DCBZ is resolved at elevated temperatures. PFlu(9,9-Oct) (Oct: octyl) gives rise to a $\pi$–$\pi^*$ transition peak at 386 nm and does not show such a shoulder peak in chloroform.[6] These results suggest that $PH_2Ph$(9,10-R) has a stronger tendency to self-assemble than PFlu(9,9-R).

The UV–vis spectrum of **P2** in chloroform does not show such a shoulder peak, presumably due to twisting of the polymer main chain caused by steric repulsion between the $–OC_{10}H_{21}$ groups and the polymer main chain. However, film of **P2** gives rise to a UV–vis shoulder peak, suggesting the molecular assembly of the polymer in the solid state.

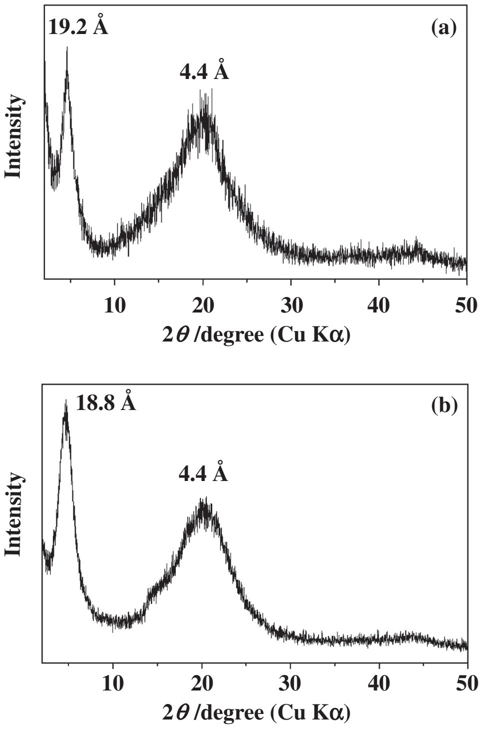


**Figure 2.** Powder XRD patterns of (a) **P1** and (b) **P2**.

Powder X-ray diffraction patterns of **P1** and **P2** showed distinct peaks as disclosed in Figure 2, revealing the formation of ordered structures in the solid state. The XRD patterns of **P1** and **P2** show a diffraction peak in a low-angle region. Many linear $\pi$-conjugated polymers with long side chains give rise to such a diffraction peak in a low-angle region, and the $d_1$ spacing for the peak is thought to correspond to a distance between $\pi$-conjugated polymer main chains separated by the long side chains.[1,7] The distance (1.92 nm) observed with **P1** is reasonable for end-to-end packing[5] of **P1**. The number density of the octyl side chains along the polymer main chain (one octyl group with effective diameter of about 0.42 nm/0.42 nm of the *p*-phenylene unit) supports the end-to-end (not an interdigitation) packing mode.[1,7]

In contrast to the formation of an ordered structure of **P1**, PFlu(9,9-Oct) gives an amorphous film and does not give a distinct XRD peak;[8] presumably due to the presence of the two alkyl groups deviating from the plane of the polymer main chain. In contrast, the two alkyl groups in **P1** may not deviate so much from the plane of the polymer main chain and make the molecular aggregation possible.

Various $\pi$-conjugated polymers consisting of 2,5-dialkoxy-1,4-phenylene units form molecular assembly because of a strong aggregation effect of the 2,5-dialkoxy-1,4-phenylene unit,[9] and observed $d_1$ of **P2** agrees with those (about 2 nm) observed with $\pi$-conjugated polymers constituted of the 2,5-bis(decyloxy)-1,4-phenylene unit.[9]

As described above, **P2** is believed to have a twisted main chain and exist as a single molecule in chloroform. However, in the solid state **P2** seems to assume a rather coplanar conformation in the self-assembled aggregate. The broad peak at about 0.44 nm observed for **P1** and **P2** is thought to arise from loosely packed alkyl side chains.

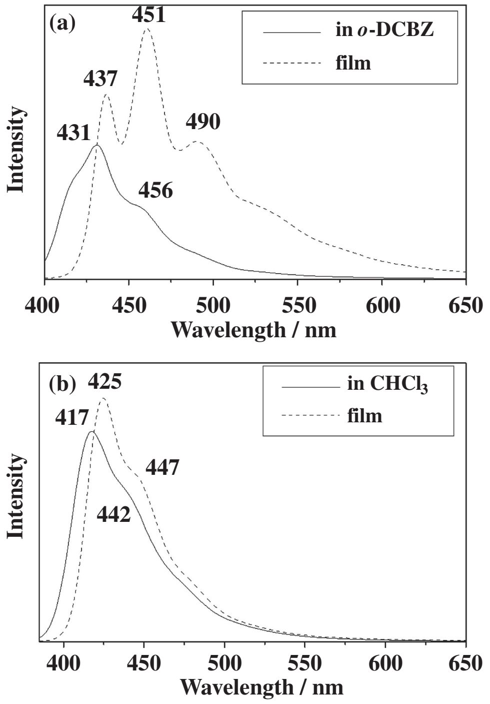


**Figure 3.** Photoluminescence spectra of (a) **P1** and (b) **P2**.

Figure 3 shows photoluminescence (PL) spectra of **P1** and **P2** in solutions and films. As usually observed with $\pi$-conjugated polymers, **P1** and **P2** show the PL peak near the onset position of the UV–vis absorption band. Quantum yields of PL of **P1** in $o$-DCBZ and **P2** in chloroform were 57% and 58%, respectively. The PL spectrum of the **P1** film was essentially unchanged after annealing at 150 °C, in contrast to shifts of PL peaks of PFlu(9,9-Oct) film to a longer wavelength after annealing at 150 °C. Obtaining **P1** with alkyl groups makes the difference in chemical properties between the 9-position of the Flu unit and 9,10-positions of the $H_2Ph$ unit clearer.

A cyclic voltammogram of **P1** film in a $CH_3CN$ solution of $(NBu_4)PF_6$ showed an oxidation (or p-doping) peak at 1.69 V vs. $Ag^+/Ag$. From the onset potential (1.1 V vs. $Ag^+/Ag$) of the oxidation peak,[10] the HOMO level of **P1** is estimated to be approximately $-5.8$ eV, which is similar to that ($-5.8$ eV) of PFlu(9,9-Oct).[11] Electrochemical oxidation of **P2** took place at a higher potential with an oxidation peak at 1.88 V vs. $Ag^+/Ag$. According to electrochemical oxidation, colors of **P1** and **P2** films changed: from yellowish green to purplish black for **P1** and from Chinese yellow to purplish black for **P2**. **P1** underwent electrochemical oxidation at higher potential by about 0.3 V than a related polymer[3] with $OSiBu_3$ (Bu: butyl) groups at the 9,10-positions. This is thought to be due to less electron-donating nature of the octyl group than the $OSiBu_3$ group.

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