Macromolecules **2006,** *39,* 3959−3963 **3959**

Notes

Synthesis of New Thiophene-Based π-Conjugated Polymers for Investigation of Molecular Alignment on the Surface of Platinum Plate

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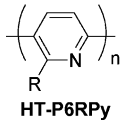
Received February 2, 2006
Revised Manuscript Received March 31, 2006

Introduction

Electronic devices using π-conjugated polymers are the subject of many papers.[1−4] Morphology of the π-conjugated polymer in cast or spin-coated film is considered to be an important factor to decide the device performances.[2] Recently, it has been demonstrated that some of π-conjugated polymers with alkyl side chains have a strong tendency to assume an ordered structure in cast films on various substrates, with the alkyl side chains oriented toward the surface of the substrate.[2,5−10] An example of such alignment of head-to-tail-type poly(3-alkylthiophene-2,5-diyl) (HT-P3RTh) is depicted in Figure 1; p-doped HT-P3RTh can also form such an ordered solid structure.[8b,c] Chart 1 shows reported examples of π-conjugated polymers which give such an ordered structure on the surface of the substrate.

One of the obvious features of such polymers is a large shift of the UV−vis peak to a longer wavelength in going from the solution to the solid state.[5−11] The shift (Δλ value in Chart 1) is usually larger than 50 nm, which suggests the presence of a strong intermolecular interaction between the polymer molecules and/or planarization effect of the π-conjugated polymer backbone in the solid.[5−16] In contrast, other polymers such as HT-poly(6-alkylpyridine-2,5-diyl) gives only a small UV−vis shift between the solution and film and does not assume such an ordered structure in cast film on substrates.[17] To obtain further information for the alignment of the π-conjugated polymer on the substrate, we have prepared the following thiophene-based π-conjugated polymers **4−12** listed in Chart 2 and examined whether the presence of the interaction between the polymer molecules and the large Δλ value are crucial for the formation of the aligned structure. For thiophene-based π-conjugated polymers with Th(R)−(aromatic unit)−Th(R) repeating units (e.g., PTh(R)ThTh(R) depicted in Chart 1), the synthesis of the polymers with various centered aromatic units such as pyridine-2,5-diyl[18a] and pyridazine-2,5-diyl[18b] has been reported.

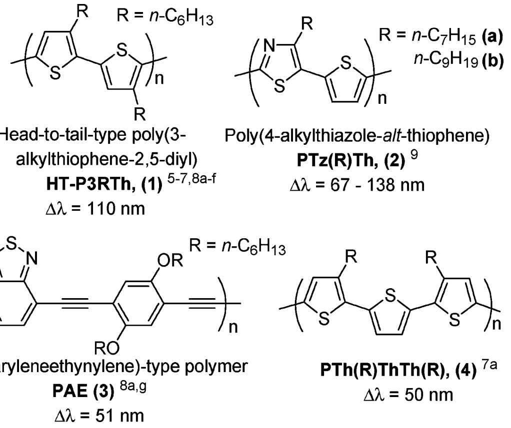


Δλ = 5 nm

HT-P6RPy

The synthesis of **4**,[11] **5**,[11,19] **6**,[20] **7**,[21] **8**,[22] **9**,[22,23] **10**,[24] **11**,[25] and **12**,[25b,26] in many cases by oxidative polymerization, has been reported. We have also synthesized by the organometallic polycondensations shown in Scheme 1.

Chart 1. Reported Examples of Linear π-Conjugated Polymers Which Show Stacking and Molecular Alignment Similar to That Depicted in Figure 1



Head-to-tail-type poly(3-alkylthiophene-2,5-diyl)
HT-P3RTh, (1) [5-7,8a-f]
Δλ = 110 nm

Poly(4-alkylthiazole-*alt*-thiophene)
PTz(R)Th, (2) [9]
Δλ = 67 - 138 nm

Poly(aryleneethynylene)-type polymer
PAE (3) [8a,g]
Δλ = 51 nm

PTh(R)ThTh(R), (4) [7a]
Δλ = 50 nm

Experimental Section

Measurements. ^{1}H NMR spectra, UV−vis spectra, and XRD patterns were recorded on a JEOL JNM-EX 400 spectrometer, a Shimadzu UV-3100 spectrometer, and a RIGAKU RINT2100 Ultima+/PC X-ray diffractometer, respectively. GPC analysis was performed with a Shimadzu liquid chromatography system with a Shodex 80 M column using chloroform as an eluent.

Materials. 2-Bromo-3-hexylthiophene,[27] 3,3′-dihexyl-2,2′-bithiophene,[19] 3,3′′-dihexyl-2,2′;5′,2′′-terthiophene,[11] 3,4-dihexylthiophene,[28] 2,5-dibromo-3,4-dihexylthiophene,[21] 5,5′-diiode-3,3′-dihexylbithiophene,[11] 5,5′′-diiode-3,3′′-dihexyl-2,2′;5′,2′′-terthiophene,[11] Pd(PPh$_3$)$_4$,[29] bis(1,5-cyclooctadiene)nickel (Ni(cod)$_2$),[11] and polymers **4**[11] and **5**[11] were prepared according to the literature.

Preparation of Monomers and Their Precursors. Preparation of 5,5′-Dibromo-3,3′-dihexyl-2,2′-bithiophene: Monomer for Polymer 6. NBS (2.43 g) was added to a 3,3′-dihexyl-2,2′-bithiophene (2.17 g) in dry THF (50 mL) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The reaction solution was poured into water, and the product was extracted with hexane and purified by column chromatography on SiO$_2$ (eluent = hexane) to yield 2.96 g (92%) of 5,5′-dibramo-3,3′-dihexyl-2,2′-bithiophene as a light yellow liquid. ^{1}H NMR (CDCl$_3$): δ 7.09 (s, 2H), 2.45 (t, 4H), 1.31 (m, 16H), 0.88 (m, 6H). Calcd for C$_{20}$H$_{28}$Br$_2$S$_2$: C, 48.79; H, 5.73; Br, 32.46; S, 13.02. Found: C, 48.90; H, 5.89; Br, 32.73; S, 13.14.

Preparation of other monomers is described in the Supporting Information.

Polymerization. Preparation of Poly(3,3′-dihexyl-2,2′-bithiophene-*alt*-thiophene): Polymer 6. Pd(PPh$_3$)$_4$ (0.139 g) was added to a mixture of 5,5′-dibromo-3,3′-dihexyl-2,2′-bithiophene (0.591 g) and 2,5-bis(trimethylstannyl)thiophene (0.492 g) in a dry DMF (20 mL) at room temperature. The reaction mixture was stirred for 16 h at 90 °C. The reaction solution was poured into methanol, and the precipitate was washed with dilute hydrochloric acid, aqueous ammonium, and water. The product was dissolved in a small amount of chloroform, and the solution was poured into a

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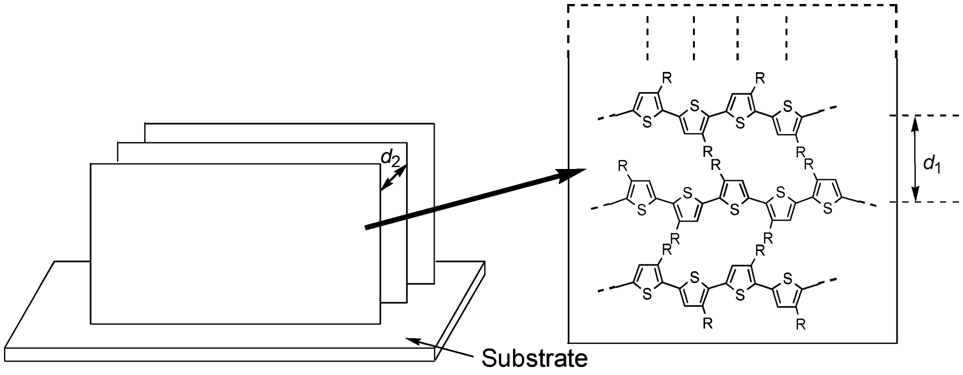
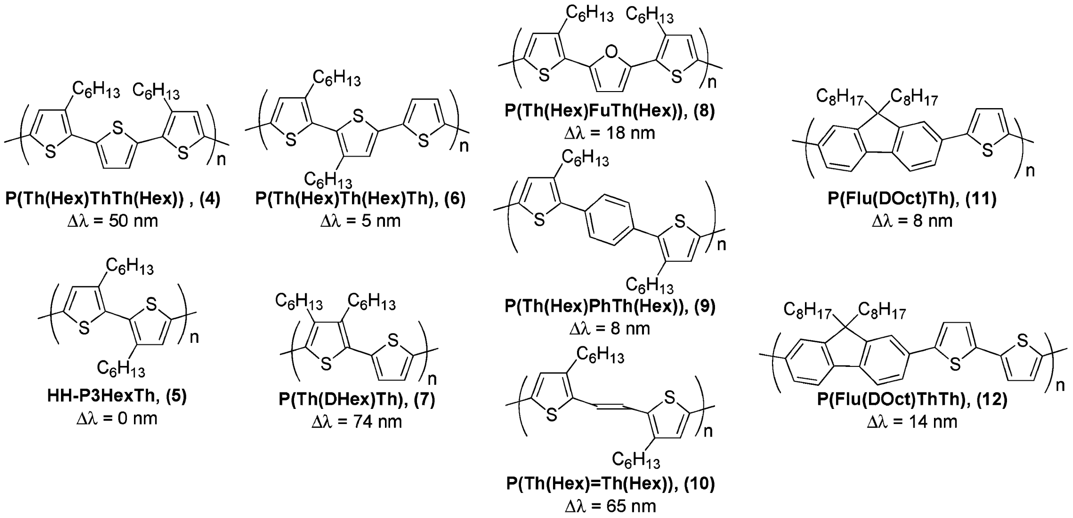
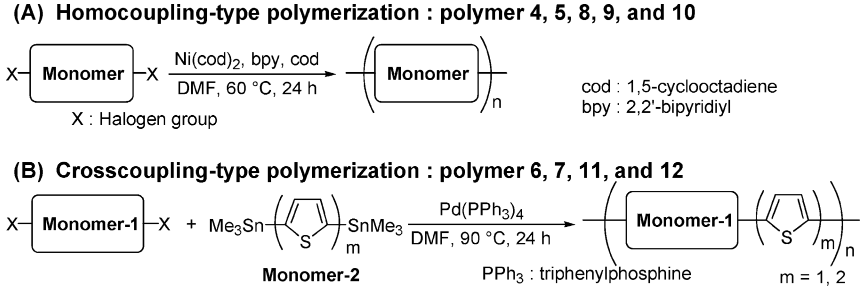


Figure 1. Alignment of HT-P3RTh film on a substrate.

Chart 2. New Thiophene-Based π-Conjugated Polymers 6−12 and Previously Reported Polymers 4 and 5



Scheme 1



large amount of methanol to yield 0.498 g (87%, chloroform soluble part) of polymer **6** as a yellow powder. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.15 (s, 2H), 7.02 (s, 2H), 2.54 (t, 4H), 1.70 (m, 4H), 1.30 (m, 12H), 0.89 (t, 6H). Calcd for $(C_{24}H_{30}S_3)_n$: C, 69.51; H, 7.29; S, 23.20. Found: C, 69.45; H, 7.39; S, 22.47.

Polymers **7**−**12** were prepared analogously via organometallic polycondensation, and characterization of the polymer is described in the Supporting Information.

Results and Discussion

Synthesis of Polymers. Results of the polymer synthesis are summarized in Table 1. They were characterized by IR, ^{1}H NMR, and GPC. They were soluble in organic solvents, and their cast films on Pt and glass plates were obtained from their chloroform solutions.

UV−Vis and XRD Data. Figure 2 depicts UV−vis spectra of polymers **4**−**12** in chloroform and in the cast film. The UV−vis data are also listed in Table 1. Among the polymers with the Th(R)(π-unit)Th(R) recurring unit, **10** shows the UV−vis peak at the longest wavelength of 518 nm; on the other hand, most of other polymers such as **4**[11] and a polymer with a pyridazine-2,5-diyl[18b] unit as the (π-unit) give the UV peaks at about 450 nm. The band gap of **10** (1.96 eV) estimated from the onset position (ca. 630 nm) of the UV−vis absorption band is considerably smaller than that (2.24 V)[24] reported with the polymer prepared by oxidative polymerization using FeCl$_3$. As exhibited in Figure 2, UV−vis peaks of films of polymers **4**, **7**, and **10** show a large shift (>50 nm) to a longer wavelength from the UV−vis peaks observed in the solution. The subpeak of the polymer **7** solution at 550 nm suggests the presence of a small amount of colloidal particles, similar to the case of HT-P3RTh.[13] Other polymers did not exhibit such a large shift. Polymer **8** has a structure similar to that of polymer **4**; however, the small structural difference between polymers **4** and **8** brings about such a significant difference. As has been discussed, the large UV−vis peak shift between the solution and film is associated with the formation of stacked structure assisted by

Table 1. Synthetic Results and UV−Vis Data of Polymers 4−12 and Related Polymers

polymer[a]	M_n[b]	M_w/M_n[b]	λ_{max}/nm (in $CHCl_3$)	λ_{max}/nm (film)[c]	Δ/nm[d]	alignment in the film[e]
4	12 000	1.30	459	509, 589*	50	aligned
5	48 000	2.90	389	389	0	not aligned
6	34 000	2.13	426	431	5	not aligned
7	35 000	1.81	434	508, 545*	74	aligned
8	2300	1.65	471	489	18	not aligned
9	3500	2.15	406	414	8	not aligned
10	2500	1.20	518	583	65	aligned
11	2400	2.00	422	430	8	not aligned
12	3400	2.70	446	460	14	not aligned
HT-P3HexTh (**1**)	24 000	2.06	450	520*, 560, 610*	110	aligned
PTz(Hep)Th (**2a**)[f]	−[g]	−[g]	467	504*, 534, 592*[h]	67	aligned
PTz(Non)Th (**2b**)	2200	1.20	467	561*, 605	138	aligned
PAE (**3**)	10 000	3.48	517	530*, 568	51	aligned

[a] $CHCl_3$-soluble part. [b] Evaluated from GPC analysis. [c] Cast from $CHCl_3$ solution on a glass; the value with an asterisk is for the subpeaks. [d] Δ (nm) = [λ_{max}(film)] − [λ_{max}(in solution)]. [e] Judging from powder and film of XRD patterns. [f] CF_3COOH-soluble part. [g] Not measured. [h] Cast from CF_3COOH.

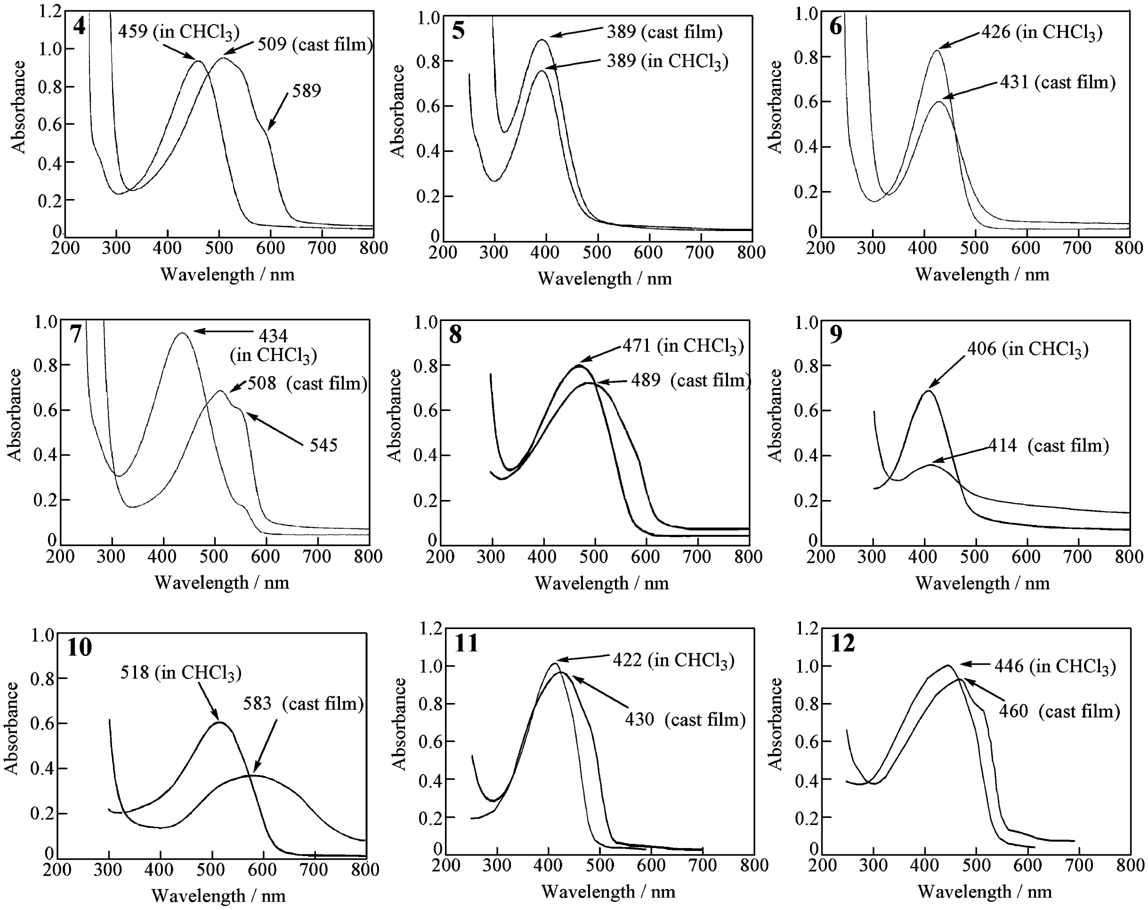


Figure 2. UV−vis spectra of the obtained polymers **4**−**12**. Measured with chloroform solutions and films on a glass plate.

side-chain aggregation[30] and may be related to the tendency for the polymer to be aligned on the surface of the substrate. Figure 3 exhibits XRD patterns of polymers **4**, **7**, and **10**, obtained with powdery samples and with film samples. The data shown in Figure 3 reveal that polymers **4**, **7**, and **10** assume ordered structures in the powder to give distinct XRD peaks. The d_1 = 12.7, 23.8, and 12.6 Å peaks of polymers **4**, **7**, and **10**, respectively, seem to be assignable to a distance between the polymer chains separated by the alkyl side chains (cf. Figure 1).

The d_1 value seems to reflect the space allotted for the alkyl chain. The number density of the alkyl chain in polymer **7** is higher than that in polymers **4** and **10**; consequently, polymer **7** gives the longest d_1. The d_1 values of **4** and **10** are considerably shorter than that (16.7 Å)[13a] of HT-P3RTh. The lower number density of the alkyl group in **4** and **10** may make it possible for the polymer to assume an interdigitation packing; on the other hand, HT-P3RTh is considered to assume an end-to-end packing which gives a longer d_1 value. In contrast, **7** gives a longer d_1 value than that of HT-P3RTh. It has recently reported that some π-conjugated polymers can take a doubly running packing structure.[31] If **7** takes such a doubly running structure as depicted in Figure S7 in the Supporting Information, it explains the long d_1 of **7**.

The d_2 = 3.9 Å peak of polymer **4** is assigned to the stacking face-to-face distance between the polymer chains;[11] the d_2 peak is considered to be overlapped with the third-order 003 peak of d_1 and a broad peak at about 2θ = 22° (or d_3 = 4.2 Å), which is assigned to a side-to-side distance between loosely packed alkyl chains.[30] Polymers **7** and **10** seem to have the overlapped d_2 and d_3 peaks, too.

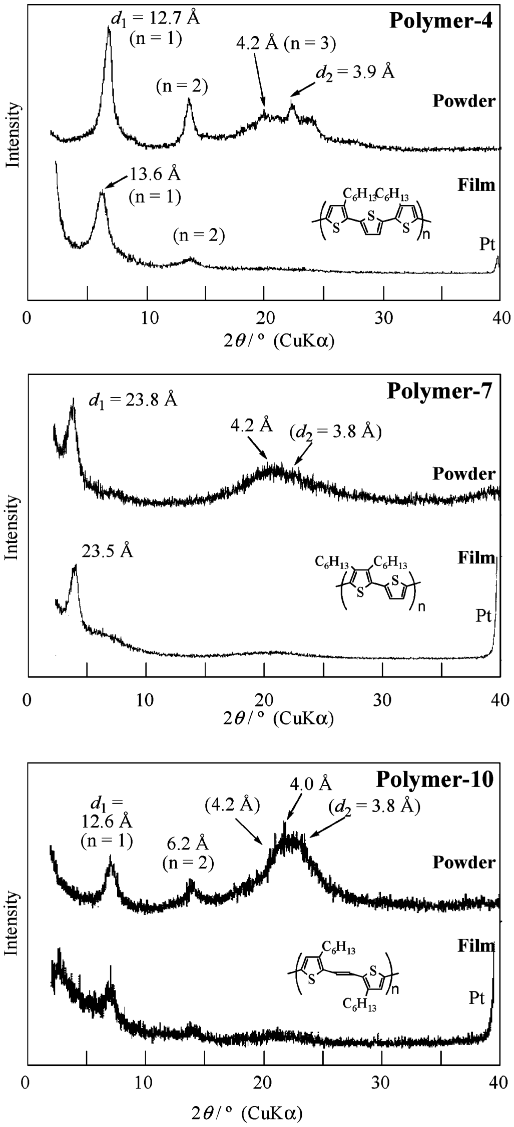


Figure 3. XRD patterns of polymers **4** (top), **7** (middle), and **10** (bottom), measured with powders and cast films on a Pt plate. For the cast film samples, the XRD pattern was measured at a reflection mode.[5a,8a]

The XRD patterns of the cast films on a Pt plate clearly exhibit disappearance of the d_2 and d_3 peaks, which is taken as the indication of molecular alignment of the polymers,[5−10] similar to the case of HT-P3RTh depicted in Figure 1. In contrast to cases of polymers **4**, **7**, and **10**, the other polymers, which show the only negligible or minor UV−vis shift between the solution and film, do not give distinct XRD peak as exhibited in the Supporting Information, except for polymer **9**. Polymer **9** seems to form a crystalline packing in the solid. However, the minor UV−vis shift of polymer **9** suggests that polymer **9** assumes a crystalline packing different from those of polymers **4**, **7**, and **10**, presumably due to the presence of the *p*-phenylene unit with four *o*-hydrogen atoms which will cause torsion of the main chain.

As described above, the stacking of the thiophene-based polymers and their alignment on the substrate are correlated with the UV−vis peak shift between the solution and film.

Supporting Information Available: Preparation and characterization of polymers **7**−**11** and their precursors; XRD patterns of polymers **5**, **6**, **8**, **9**, **11**, and **12** in their powder and film states and possible packing structure of **7** in the solid. This material is available free of charge via the Internet at http://pubs.acs.org.

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