Notes

Synthesis, Solid Structure, and Optical Properties of New Thiophene-Based Alternating π -Conjugated Copolymers Containing 4-Alkyl-1,2,4-triazole or 1,3,4-Thiadiazole Unit as the Partner Unit

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Introduction

There is currently much attention focused on π -conjugated polymers due to their interesting electronic and optical properties.¹

It is reported that five-membered ring heteroaromatic π -conjugated polymers such as regioregular head-to-tail poly(3-alkylthiophene-2,5-diyl)s (HT-P3RTh),² poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl)s (HH-P4RBTz),³ and alternating copolymers of 4-alkylthiazole and thiophene (PTz(R)Th)⁴ form a π -stacked solid structure assisted by side chain aggregation. Because of the formation of the π -stacked structure, they exhibit interesting optical and electronic properties in the solid.

Among the above shown polymers, PTz(R)Th (cf. Chart 1) is considered to have a charge-transfer (CT) electronic structure, because the alternating copolymer is constituted of electron-donating thiophene unit and electron-accepting thiazole unit.⁴ PTz(R)Th assumes a unique π -stacked structure in the solid assisted by the CT electronic structure.





To obtain further scope about the packing structure and chemical properties of such CT type alternating π -conjugated copolymers, we have synthesized new thiophene-based CT type alternating copolymers by choosing 4-alkyl-1,2,4-triazole and 1,3,4-thiadiazole as the electron-accepting five-membered ring unit. 1,2,4-Triazole, 1,3,4-thiadiazole, and 1,3,4-oxadiazole are typical electron-accepting compounds.^{5–7}



4-Alkyl-1,2,4-triazole 1,3,4-Thiadiazole 1,3,4-Oxadiazole

It is known that 1,3,4-oxadiazole-containing compounds are useful as an electron-transporting material to increase the quantum efficiency in OLEDs.⁸ π -Conjugated copolymers bearing thiophene and 1,3,4-oxadiazole alternating units were previously prepared by a cyclodehydration reaction of a precursor polymer.⁹ However, π -conjugated polymers consisting of the 4-alkyl-1,2,4-triazole and 1,3,4-thiadiazole units have received less attention.

We now report the synthesis, characterization, and solid-state structure of new thiophene-based alternating π -conjugated copolymers containing the 4-alkyl-1,2,4-triazole or 1,3,4-thiadiazole unit as the partner unit.

Results and Discussion

Synthesis. As shown in Scheme 1, new copolymers were prepared via palladium-catalyzed Stille crosscoupling reaction in good yields (76-92%). Synthetic procedures and spectroscopic and analytical data of the monomers and polymers are described in the Supporting Information. The polymers 2b-2e with long alkyl chains were partially (ca. 60-90%) soluble in CHCl₃, THF, and NMP; whereas **2a** with the propyl group was almost insoluble in these solvents. 2a-2c were completely soluble in hexafluoro-2-propanol and CF₃COOH. 2d and 2e were partly soluble in hexafluoro-2-propanol and completely soluble in CF₃COOH. The nonsubstituted polymer 4 was only partly (about 30%) soluble in CF₃COOH and was not soluble in other solvents tested. GPC analysis (eluent = hexafluoro-2-propanol (for 2a-2c) or CHCl₃ (for 2d and 2e; soluble part)) indicated that the polymers had number-average molecular weights $(M_n$'s) of 4100-8800, as exhibited in Table 1. The ¹H NMR spectra of 2b-2e in CDCl₃ gave a broad aromatic peak at about δ 7.6 due to the protons in the thiophene rings (Figure S1). Signals of alkyl protons appeared at normal positions and the peak area ratios agreed with the structure. Thermogravimetric analysis (TGA) indicated that the 5% weight-loss temperature $(T_{\rm d})$ of all the polymers was higher than 310 °C.

Optical Properties. As shown in Figure 1, the UV– vis spectrum of **2d** in CHCl₃ gives the lowest energy $\pi - \pi^*$ absorption maximum (λ_{max}) at 353 nm. The film of **2d** showed λ_{max} at a longer wavelength (375 nm) than that for the CHCl₃ solution, suggesting the presence of

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Table 1. Synthesis and Characterization of the Copolymers

				UV–vis λ_{max} , nm			
polymer	yield, %	$\mathrm{mol}\ \mathrm{wt}^a$	$T_{ m d},^c$ °C	$\overline{\text{in solution}^d}$	film ^f	$\operatorname{PL}\lambda_{\operatorname{em}},^d\operatorname{nm}$	$\Phi,^g \%$
2a	84	8800 (2.0)	312	320^{e}	366	465^{e}	b
2b	80	7500(2.0)	352	356	368	479	21
2c	76	4100 (2.9)	381	356	375	459	27
2d	83	8600 (1.9)	373	353	375	458	29
$2\mathbf{e}$	92	7200 (1.9)	331	343	366	449	23
4	86	b	322	409^e	437	535^e	b

^{*a*} Number-average molecular weight (M_n) estimated from GPC. The values in parentheses are polydispersity index (M_w/M_n) . Eluent = hexafluoro-2-propanol for **2a**-**2c** (vs poly(methyl methacrylate) standards); CHCl₃ for **2d** and **2e** (vs polystyrene standards). ^{*b*} Not determined. ^{*c*} 5% weight-loss temperature measured by TGA. ^{*d*} Solvent = CHCl₃ unless otherwise noted. ^{*e*} In CF₃COOH. ^{*f*} Formed on a quartz glass plate by casting. ^{*g*} PL quantum yield (Φ) was calculated by comparing with the standard of quinine sulfate (ca. 10⁻⁵ M solution in 0.5 M H₂SO₄, having Φ of 54.6%).



Figure 1. (a) UV–vis and (b) PL spectra of 2d in CHCl₃. (c) UV–vis spectrum of the film of 2d.

an intermolecular interaction due to stacking of the polymer molecules in the solid.^{2,4,10} **2a**-**2e** were photoluminescent both in solution and in film. The photoluminescence (PL) spectrum of **2d** in CHCl₃ gave the peak at 458 nm (Figure 1b), which essentially agreed with the onset position of the absorption band as usually observed with π -conjugated polymers. The PL quantum yield of **2d** ($\Phi = 29\%$) was comparable to those of 1,3,4oxadiazole-containing π -conjugated polymers.^{9,11} UVvis and PL data of the copolymers are included in Table 1.

Solid Structure. The molecular ordering of 2a-2ein the solid was investigated by powder X-ray diffraction (XRD) measurements and density functional theory (DFT)¹² computation approach. In the XRD patterns of 2a-2e shown in Figure 2, the strong peaks observed in the low-angle region ($d_1 = 10.3-22.8$ Å) seem to be assignable to a distance between the conjugated main chains separated by the alkyl side chains, as previously proposed for π -conjugated polymers with alkyl side chains (e.g., HT-P3RTh and HH-P4RBTz).^{2,10}



Figure 2. Powder XRD patterns of 2a-2e and 4.

The interchain d_1 -spacing reasonably increases upon elongation of the side chain from the *N*-propyl (**2a**) to the *N*-hexadecyl (**2e**) group. As shown in Figure 3a, plots of the d_1 -spacing against the number of carbons in the alkyl group give a linear line with a slope of 0.96 Å/carbon, which is smaller than the height of the $-CH_2-$ unit (1.25 Å/carbon). In the case of previously reported HT-P3RTh, HH-P4RBTz, and PTz(R)Th (cf. Chart 1), similar plots gave a slope of about 1.8 Å/carbon, and an end-to-end packing in the solid was proposed.^{2,4,10} The much smaller slope of 0.96 Å/carbon observed with **2a**-**2e** suggests that they assume an interdigitation packing mode, which is depicted in Figure 3b. The presence of alternating *syn-anti* conformation (cf. Figure 3b) between the 1,2,4-triazole and



Figure 3. (a) Plots of the d_1 value vs the number of carbons in the alkyl group of **2a**-**2e**. (b) Schematic diagram of twodimension interdigitation packing structure for **2a**-**2e** with the interchain spacing (d_1) . The polymer molecules are considered to form a stacked assembly.

thiophene units in 2a-2e allows the formation of the interdigitation packing structure. Although the N atom at the 4-position is formally considered to take an sp³-like structure around the atom, participation of the lone pair electrons of N atom in the aromatization of the ring suggests that the N atom at the 4-position takes an sp²-like structure. Actually, N atoms in analogous compounds such as *N*-alkylcarbazole form a planar structure around the atom as revealed by X-ray crystal-lography.¹³

The d_2 and d_3 peaks observed with **2a** in Figure 2 may be assigned to the side-to-side distance between the alkyl chains and the stacking distance between the polymer backbone chains, respectively. Comblike polymers having long alkyl side chains exhibit a sharp reflection of Bragg spacing 4.2 Å, indicating a formation of pseudohexagonal packing of the alkyl chains.¹⁴ The broadness of the XRD profile at 2θ = about 20° suggests that the side chain aggregation as well as the backbone π -stacking are not well controlled, compared with cases of HT-P3RTh and HH-P4RBTz. If the d_3 of 3.7 Å is taken as the stacking distance between the backbone chains of 2a-2e in the solid state, the packing model depicted in Figure 3b gives calculated density¹⁵ of 1.13, 1.07, 1.06, 1.02, and 1.00 g cm⁻³ for **2a** through **2e**, respectively. These calculated densities show good agreement with the observed values of 1.15, 1.08, 1.03, 1.00, and 0.97 g cm⁻³ within the experimental error, supporting the proposed packing structure. The alkyl group has an effective diameter of about 5 Å in the disordered state, and the aggregation will give a broad scattering at 2θ = about 20°. The relatively sharp d_2 and d_3 peaks of **2a** may indicate that **2a** forms a packing structure different from those of 2b-2e. However, the



Figure 4. Profiles of the potential energy vs the inter-ring dihedral angle (ω) for (a) **5**, (b) **6**, (c) **7**, and (d) **8** on ground-state calculated at the B3LYP/6-31G* level.

linear correlation exhibited in Figure 3a and the densities of the polymers suggest that 2a-2e have an isomorphous molecular geometry. For the copolymers with longer alkyl chains (2b-2e), the d_2 peak becomes intense while the d_3 peak becomes obscure with increase the side chain length, as exhibited in Figure 2. In these cases, the d_3 peak may be hidden under the overwhelming d_2 scattering. This supports the d_2 is attributable to the side chain aggregation. A polarized optical microscope (POM) image of 2d observed under crosspolarization conditions indicated formation of an ordered structure.

Usually π -conjugated polymers constituted of recurring five-membered rings (e.g., HT-P3RTh, HH-P4RBTz, and PTz(R)Th shown in Chart 1) are considered to assume an all *anti* conformation in the solid.^{2-4,10} However, in the proposed solid structure of **2a**-**2e**, the main chain is considered to include a *syn* conformation. The possibility of the inclusion of the *syn* conformation in the main chain of **2a**-**2e** is checked by the calculation at a B3LYP/6-31G* level using a simple model bicycle, 3-(2-thienyl)-4-ethyl-1,2,4-triazole (**5**). Figure 4 represents energy profiles of four kinds of dimeric model compounds **5**-**8**, calculated by rotating the bonding dihedral angle. Alemán and co-workers reported similar results for **7**.¹⁶ As depicted in Figure 4, the *anti* conformation is more stable in **6**-**8**. On the contrary, **5**



prefers the syn conformation and this may be taken as the origin of the inclusion of syn conformation of the postulated packing structure of 2a-2e. Delicate balance of charge distribution in the dimeric model compounds and o-hydrogen repulsion is considered to be the reason for the difference in the stabler form between 5 and the other compounds (6-8). However, the calculation is carried out with ideal isolated molecule in the gas phase at 0 K, and the calculated energy difference between the syn and anti conformations is not large. Consequently, the energy difference may not be the determining factor to control the syn and anti conformations; however, the results shown in Figure 4 affords additional support for the packing structure depicted in Figure 3.

The polymer 4 gives two XRD peaks at d = 5.5 Å and 3.5 Å. A packing model, which has an *ab* lateral packing

mode similar to those of HT-P3RTh ($R = CH_3$, cf. Chart 1) and HH-P4RBTz ($R = CH_3$),^{10,17} is depicted in the Supporting Information (Figure S4). The calculated density (1.79 g cm⁻³) according to the packing model agrees with the observed density (1.73 g cm⁻³) if one takes account of the presence of amorphous parts in the polymer solid. As depicted in Figure 4, **6** is considered to prefer rather the *anti* conformation, and **4** may assume all *anti* conformation similar to polythiophene.¹⁸ However, the energy difference between the *syn* and *anti* conformations also seems to be small, and the main chain of **4** may partly contain a *syn* joint, instead of the all *anti* conformation exhibited in Figure S4.

As described above, the new alternating π -conjugated copolymers between electron-donating thiophene and electron-accepting 1,2,4-triazole or 1,3,4-thiadiazole have been prepared, and the copolymer of 1,2,4-triazole is considered to assume the unique solid structures.

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Supporting Information Available: Text giving experimental details, characterization data, and computational details for the monomers and polymers and figures showing ¹H NMR spectra of 2b-2e, FT-IR spectra of 2a-2e and 4, TGA curves of 2a-2e under N₂, and a packing model of 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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