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Synthesis and Properties of Novel Optically Active Poly(thiophenyleneethynylene-phenyleneethynylene)s

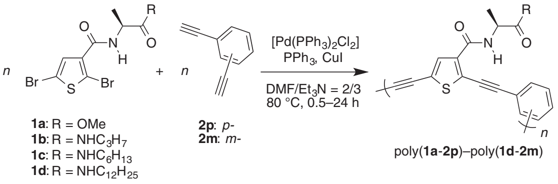
Yoshinori Otaki, Yu Miyagi, and Fumio Sanda*
Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering,
Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680

(E-mail: sanda@kansai-u.ac.jp)

The Sonogashira–Hagihara coupling polymerization of L-alanine-derived 2,5-dibromothiophene monomers **1a**–**1d** with *p*- and *m*-diethynylbenzenes **2p** and **2m** gave novel optically active poly(thiophenyleneethynylene-phenyleneethynylene)s poly(**1a**-**2p**)–poly(**1d**-**2m**). *p*-Phenylene-linked poly(**1b**-**2p**)–poly(**1d**-**2p**) bearing amide-amide side chains exhibited CD signals based on chiral aggregates, while the *m*-phenylene-linked counterparts poly(**1b**-**2m**)–poly(**1d**-**2m**) exhibited no evidence of the formation of secondary structures. Poly(**1a**-**2p**) and poly(**1a**-**2m**) bearing amide-ester side chains exhibited no CD signal as well.

Conjugated polymers gather much attention due to their excellent photo- and electric functions.[1] Among various conjugated polymers, polythiophenes have potential applications to field effect transistors,[2] organic thin film solar cells,[3] and light-emitting diodes.[4] Polythiophenes are also useful for chemo- and biosensors originating from the responsiveness of photoelectric properties to external stimuli.[5] The progress of studies on the structure–property relationship of polythiophenes contributes to further improvement in applicability to functional materials. Some conjugated polymers adopt chirally ordered secondary structures such as a helix, because of their stiff main chain stabilizing the conformation.[6] We have reported that a series of optically active poly(*m*-phenyleneethynylene-aryleneethynylene)s bearing amide groups form folded helical structures, which are stabilized by π-stacking, amphiphilicity, and intramolecular hydrogen bonding between the amide groups at the side chains.[3] In the course of our study on poly(*m*-phenyleneethynylene-aryleneethynylene)s forming chirally regulated structures, we designed novel optically active polythiophene derivatives bearing amide groups. Herein, we wish to report the synthesis of poly(thiophenyleneethynylene-phenyleneethynylene)s using an amino acid as a chiral source, and examination of the secondary structures of the obtained polymers.

The Sonogashira–Hagihara coupling polymerization of 2,5-dibromothiophene monomers **1a**–**1d** with *p*- and *m*-diethynylbenzenes **2p** and **2m** was performed in DMF/Et$_3$N = 2/3 at 80 °C for 0.5–24 h to obtain the corresponding polymers, poly(**1a**-**2p**)–poly(**1d**-**2m**), with moderate molecular weights (M_n = 3700–19000) in 8–89% yields (Scheme 1 and Table 1). The polymerization stopped in every case when the reaction mixture became heterogeneous.[7] All polymers, except poly(**1a**-**2m**) and poly(**1b**-**2m**), were completely soluble in CHCl$_3$ and DMF.



Scheme 1. Synthesis of L-alanine-based poly(thiophenyleneethynylene-phenyleneethynylene)s.

Table 1. Sonogashira–Hagihara coupling polymerization of **1a**–**1d** with **2p** and **2m**[a]

Monomers	Time/h	Yield[b]/%	M_n[c]	M_w/M_n[c]
1a + **2p**	0.5	10	8600	2.1
1a + **2m**	0.5	79	19000[d]	4.5[d]
1b + **2p**	1.0	14	3700	1.4
1b + **2m**	0.5	73	5700[d]	1.8[d]
1c + **2p**	24	51	11000	1.7
1c + **2m**	0.5	89	7500	2.0
1d + **2p**	3.0	8	4600	1.3
1d + **2m**	0.5	71	4800	2.7

[a]Conditions: [**1a**–**1d**]$_0$ = [**2p**]$_0$ = [**2m**]$_0$ = 100 mM, [Pd(PPh$_3$)$_2$Cl$_2$] = [PPh$_3$] = [CuI] = 5 mM, DMF/Et$_3$N = 2/3 (v/v), 80 °C. [b]Insoluble part in Et$_2$O. [c]Estimated by SEC measured in DMF, polystyrene calibration. [d]Data of DMF soluble part.

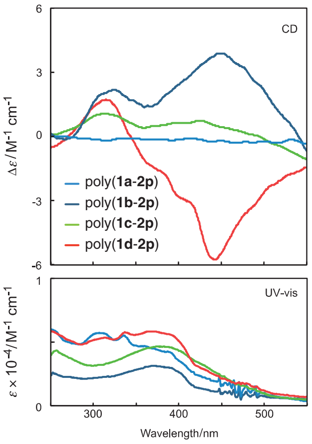


Figure 1. CD and UV–vis spectra of poly(**1a**-**2p**)–poly(**1d**-**2p**) measured in CHCl$_3$ (c = 0.04 mM) at 20 °C.

Figure 1 shows the CD and UV–vis spectra of poly(**1a**-**2p**)–poly(**1d**-**2p**) measured in CHCl$_3$ at 20 °C. The extension of conjugation from the monomers to polymers was confirmed by the red shift of UV–vis absorption (Table S1). Poly(**1a**-**2p**) bearing amide-ester side chains exhibited no CD signal, while poly(**1b**-**2p**)–poly(**1d**-**2p**) bearing amide-amide side chains exhibited CD signals around 450 nm, assignable to chirally regulated conjugated main chains. Poly(**1b**-**2p**)–poly(**1d**-**2p**) also exhibited CD signals around 320 nm, assignable to the transition of less conjugated chromophores, presumably thio-

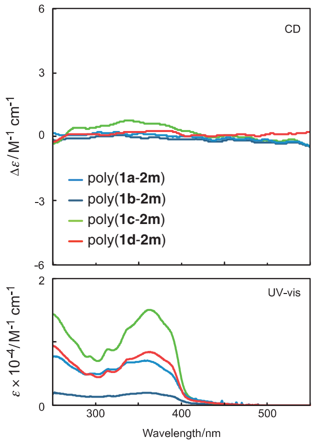


Figure 2. CD and UV–vis spectra of poly(**1a-2m**)–poly(**1d-2m**) measured in $CHCl_3$ ($c = 0.04$ mM) at 20 °C.

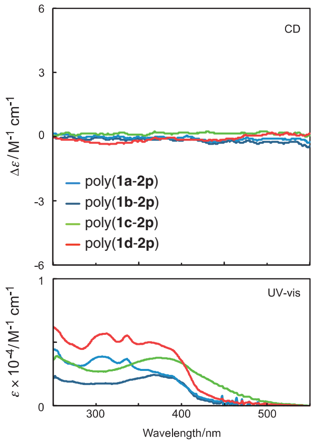


Figure 3. CD and UV–vis spectra of poly(**1a-2p**), poly(**1b-2p**), poly(**1c-2p**), and poly(**1d-2p**) measured in $CHCl_3$ at 20 °C after filtration using a membrane filter with a pore size of 0.50 µm.

phene moieties bearing chiral substituents.[8] It is considered that the terminal amide moieties play an important role in the formation of chirally ordered structures. On the other hand, poly(**1a-2m**)–poly(**1d-2m**) exhibited no CD signal in $CHCl_3$, as shown in Figure 2. The *p*-phenylene linkage is effective for inducing chirally ordered secondary structures, while the *m*-phenylene linkage is not. The band edges of the *m*-linked polymers were ca. 100 nm shorter than the *p*-linked polymers, indicating the shorter conjugation length of the *m*-polymers than the *p*-polymers.

Figure 3 shows the CD and UV–vis spectra of $CHCl_3$ solutions of poly(**1a-2p**)–poly(**1d-2p**) measured after filtration using a membrane filter (pore size: 0.50 µm). The CD signals of poly(**1b-2p**)–poly(**1d-2p**) completely disappeared after filtration. Since the solutions still exhibited UV–vis absorption signals, it is assumed that the CD signals of poly(**1b-2p**) and poly(**1d-2p**) observed in Figure 1 do not come from a unimolecular secondary structure, such as a helix, but from aggregates. This assumption agrees with the fact that the *p*-phenylene-linked polymers showed CD signals while the *m*-phenylene-linked polymers did not. Compared with the *m*-linked polymers, the *p*-linked polymers possibly adopt a more extended conformation, leading to the formation of aggregates. The amide-amide side chains of poly(**1b-2p**)–poly(**1d-2p**) seem to stabilize the aggregated structures by forming intermolecular hydrogen bonds together with π-stacking between the conjugated main chains.

The CD and UV–vis spectra of poly(**1a-2p**)–poly(**1d-2p**) and poly(**1a-2m**)–poly(**1d-2m**) were also measured in $CHCl_3/Et_2O = 1/9$ (v/v) (Figures S1 and S2), wherein Et_2O is a poor solvent for the polymers, and in $CHCl_3/DMF = 1/9$ (v/v) (Figures S3 and S4), wherein DMF is a good solvent. No remarkable difference was observed between the spectroscopic patterns in $CHCl_3$, $CHCl_3/Et_2O$, and $CHCl_3/DMF$ mixed solvents. It is common that the addition of poor solvents to polymer solutions induces aggregation, and that DMF disturbs the formation of hydrogen bonds between polymer molecules. It is proved that the aggregation-induced CD patterns of the present polymers are only slightly affected by the solvents. Judging from the difference of signs of the CD signals around 450 nm between the polymers [poly(**1b-2p**) ($R = C_3H_7$): +, poly(**1c-2p**) ($R = C_6H_{13}$): +, poly(**1d-2p**) ($R = C_{12}H_{25}$): −], the way of van der Waals interaction between the alkyl groups at the side chains is of key importance for the chirality of the aggregates. The presence of alkyl group interactions may be the reason for the negligibly small solvent effect on aggregation. Namely, once the polymers form aggregates, the external alkyl groups possibly shield the internal amide groups from solvent molecules, resulting in the small solvent effect mentioned above.

In summary, we have demonstrated the synthesis of novel optically active poly(thiophenyleneethynylene-phenyleneethynylene)s bearing amide-amide/amide-ester side chains with *p*-/*m*-phenylene linkages. It was revealed that *p*-phenylene-linked poly(**1b-2p**)–poly(**1d-2p**) formed chirally regulated aggregated structures, presumably stabilized by intermolecular hydrogen bonding between amide-amide side chains together with π-stacking between the conjugated main chains. Further investigation regarding the effect of alkyl chain length on the sense of chirality is now ongoing.

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Supporting Information is available electronically on J-STAGE.

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7 The chiroptical properties of the polymers definitely depend on the molecular weights, but it is commonly difficult to control the molecular weights of the polymers obtained by step-growth polymerization including the Sonogashira–Hagihara coupling polymerization. In the present study, extension of polymerization time resulted in the formation of a large amount of solvent-insoluble polymers. In the case of poly(**1c**-**2p**), shortening of polymerization time resulted in the formation of a CD-silent polymer.

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