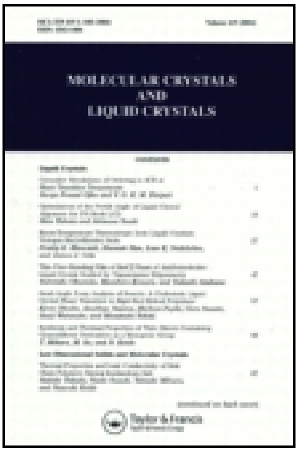

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Yoshio Aso, Yuko Obara, Takashi Okai, Shoji Nishiguchi & Tetsuo Otsubo (2002): Synthesis and Properties of Coil-Shaped 2,3-Thienylene-Ethynylene Oligomers, Molecular Crystals and Liquid Crystals, 376:1, 153-158

To link to this article: http://dx.doi.org/10.1080/713738413

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 153-158
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1058-725X/02 $12.00 + .00

Synthesis and Properties of Coil-Shaped 2,3-Thienylene-Ethynylene Oligomers

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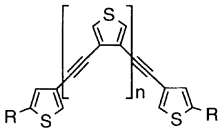
A series of 2,3-thienylene-ethynylene oligomers have been synthesized by repeated application of the Pd-catalyzed coupling reaction of terminal alkynes and thienyl iodides as the key building steps. The analytical GPC molecular weights, much deflated relative to the actual molecular weights, strongly suggest a coil shape for the conformation of the oligomers in solution. Their electronic absorption and emission spectral features are discussed.

Keywords oligomers; thienylene-ethynylenes; electronic absorptions and emissions

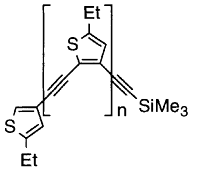
INTRODUCTION

Recently, well-defined conjugated oligomers have attracted much attention not only as useful alternatives to polymer systems but also as novel advanced materials.[1] The "para-linked" extension of aromatics and heteroaromatics gives rise to rigid rod systems, which are currently interesting as nanoscale molecular wires. On the other hand, the "ortho" or "meta" linkage of the aromatic rings leads to flexible helical systems,[2] which also enrich still very young nanoscale molecule-based material chemistry. Recently, we have reported the series of 3,4-

thienylene-ethynylene oligomers **1** up to the nonamer,[3] and the X-ray crystallographic and spectroscopic analyses revealed that they take a totally helical conformation both in the solid state and in solution. However, the poor solubility of these oligomers prevented further detailed investigation. We now report the synthesis and properties of a series of 2,3-thienylene-ethynylene oligomers **2**. Their improved solubility due to structural unsymmetrization and introduction of ethyl groups has enabled us to develop the much extended oligomers up to the 16-mer.



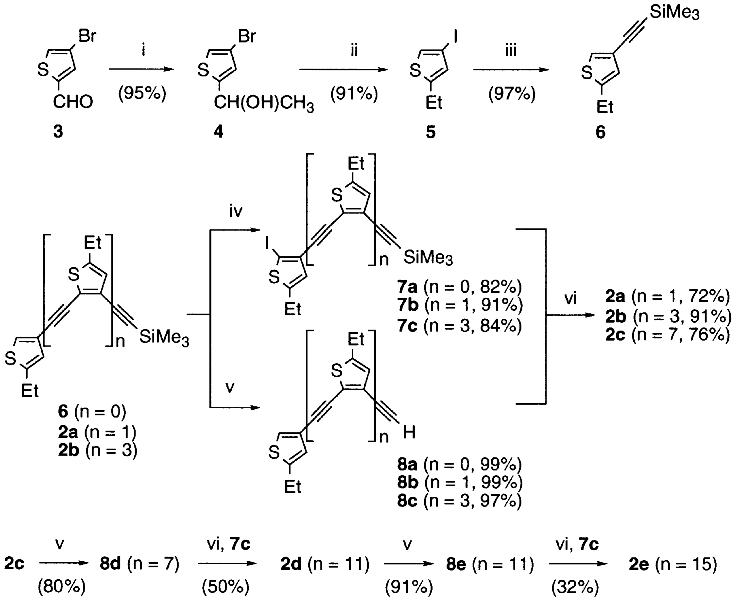
1a: n = 1, R = H
1b: n = 3, R = H
1c: n = 5, R = H
1d: n = 5, R = (CH$_2$)$_8$CH$_3$
1e: n = 7, R = (CH$_2$)$_8$CH$_3$



2a: n = 1
2b: n = 3
2c: n = 7
2d: n = 11
2e: n = 15

RESULTS AND DISCUSSION

A series of oligo(2,3-thienylene-ethynylene)s **2** was synthesized in good yields by repeated application of the Pd-catalyzed coupling reaction of terminal alkynes and thienyl iodides (Sonogashira reaction) as key building steps as shown in Scheme 1. The starting monomer **6** was prepared form 4-bromo-2-formylthiophene **3**[4] by the three-step conversion. The monomer **6** was then used in the following two pathways, iodination to form **7a** and desilylation to **8a**. The two products were coupled together under the Sonogashira conditions to give the dimer **2a**. Iteration of this reaction sequence afforded the tetramer **2b** and then the octamer **2c**. When this reaction sequence was applied to the synthesis of the 16-mer **2e**, however, it turned out that the Sonogashira reaction afforded a considerable amount of a diacetylene by-product due to the oxidative homo-coupling of **8d**, and it was removable from **2e** neither by preparative GPC nor by column chromatography because of both molecular similarity. Alternatively, the 12-mer **2d** was prepared by the coupling of ethynyl-octamer **8d** with iodo-tetramer **7c**, and finally the 16-mer **2e** was similarly obtained from ethynyl-12-mer **8e** and **7c**.[5]



SCHEME 1 Reagents and conditions: i) MeMgI, ether, rt; ii) TMSCl, NaI, CH_3CN–hexane, rt; iii) TMS–C≡C–H, $Pd(PPh_3)_4$, CuI, Et_3N, 75 °C; iv) 1) LDA, ether, –78 °C then 0 °C, 2) I_2, –78 °C then rt; v) K_2CO_3, MeOH–CH_2Cl_2, rt; vi) $Pd(PPh_3)_4$, CuI, Et_3N, 75 °C.

It has been already stated that, on measurement with GPC using randomly shaped polystyrene standards, the molecular weights of the rod-type molecules such as oligo(2,5-thienylene-ethynylene)s[6] and oligo(paraphenylene-ethynylene)s[7] are much inflated relative to the actual. On the other hand, not only the previously reported helical oligo(3,4-thienylene-ethynylene)s **1** but also the present oligo(2,3-thienylene-ethynylene)s **2** show much deflated molecular weights as shown in Figure 1. This result strongly suggests that the oligomers **2** adopt a coil-shaped conformation like **1**, as illustrated in Figure 2 by a

MM2-optimized molecular model of **2e**, which attains a height of 1.9 nm.

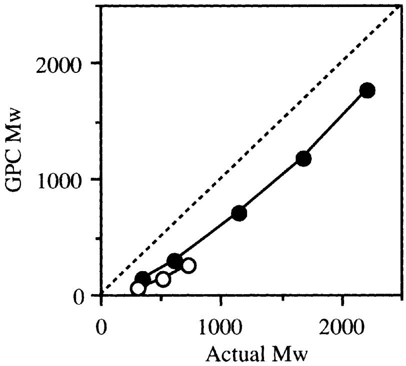


FIGURE 1 Relationship of molecular weights determined by GPC versus the actual molecular weights of **1a–c** (○) and **2** (●).

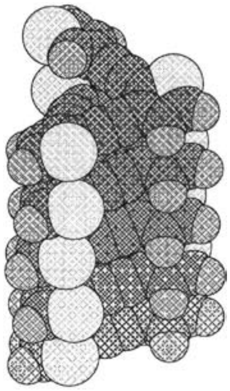


FIGURE 2 A molecular model of coil-shaped **2e**.

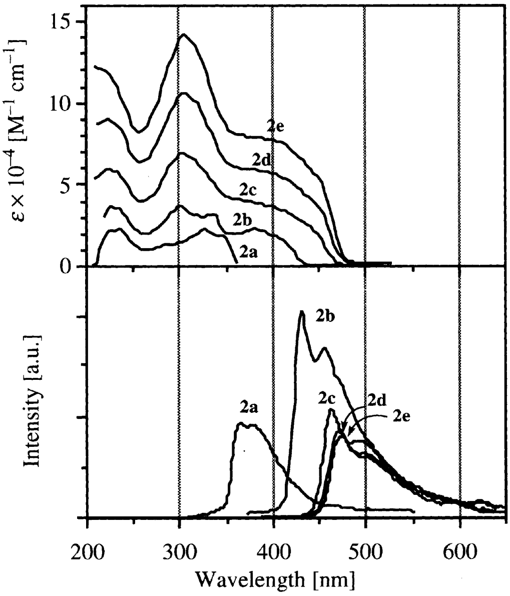


FIGURE 3 Electronic absorption (upper) and emission spectra (lower) of oligo(2,3-thienylene-ethynylene)s in THF.

Electronic absorption and emission spectra of oligo(2,3-thienylene-ethynylene)s **2** are shown in Figure 3. Although these oligomers show similar absorption spectra except for **2a**, the longer wavelength broad weak absorption band is gradually red-shifted with extension of the chain length up to the 12-mer **2d**. The emission wavelengths also show a progressive red-shift with the chain length up to **2d**. These chain length dependencies are in marked contrast to those of the oligo(3,4-thienylene-ethynylene) series **1**, whose absorption and emission maxima are almost identical independent of their chain lengths. This is attributable to a better conjugation of the 2,3-thienylene substitution pattern than the 3,4-thienylene one. The fluorescence quantum yields of **2** increase from the dimer **2a** (ϕ_f 1.5%) to the tetramer **2b** (3.1%) and then gradually decrease (**2c**: 1.7%, **2d**: 1.4%, **2e**: 1.4%). Similar decreasing of fluorescence quantum yields with increasing chain length is also observed for the oligo(3,4-thienylene-ethynylene)s **1**. These results indicate possible fluorescence quenching due to the intramolecular π-stacking induced by the coil-shaped conformations of both oligomer systems.

In summary, we have succeeded in the synthesis of a series of thienylene-ethynylene oligomers **2** up to the 16-mer. The GPC molecular weight analyses and the electronic spectra strongly suggest that the molecules take a coil-shaped conformation. These conjugated coil-shaped molecules (molecular coil) would provide a building block for new nanoscale functional materials.

Acknowledgments. This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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[5] All new compounds were characterized by spectroscopic and elemental analyses, and the selected data are as follows: **6**: a colorless oil; MS (DI) *m/z* 208 (M^+); ^{1}H NMR(acetone-d_6) δ 0.20 (s, 9H), 1.27 (t, J = 7.6 Hz, 3H), 2.81 (dq, J = 0.96 and 7.6 Hz, 2H), 6.84 (dt, J = 1.44 and 0.96 Hz, 1H) 7.42 (d, J = 1.44 Hz, 1H). **2a**: a colorless oil; MS (DI) *m/z* 342 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H) 1.28 (t, J = 7.6 Hz, 3H), 1.31 (t, J = 7.6 Hz, 3H) 2.75 (dq, J = 0.96 and 7.6 Hz, 2H), 2.82 (dq, J = 0.96 and 7.6 Hz, 2H), 6.70 (t, J = 0.96 Hz, 1H), 6.86 (dt, J = 1.48 and 0.96 Hz, 1H), 7.28 (d, J = 1.48 Hz, 1H). **2b**: pale yellow fine needles from MeOH; mp 75–76 °C; MS (DI) *m/z* 610 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9H), 1.22–1.33 (m, 12H), 2.71 (dq, J = 0.96 and 7.60 Hz, 2H), 2.75–2.82 (m, 6H), 6.67 (t, J = 0.96 Hz, 1H), 6.77 (t, J = 0.96 Hz, 1H), 6.80 (t, J = 0.96 Hz, 1H), 6.84 (dt, J = 1.48 and 0.96 Hz, 1H), 7.26 (d, J = 1.48 Hz, 1H). **2c**: a yellow solid from CH_2Cl_2–MeOH; mp 110–112 °C; MS (FAB) *m/z* 1147 (M^+ + 1); ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9H), 1.21–1.29 (m, 24H), 2.67–2.80 (m, 16H), 6.65 (t, J = 0.98 Hz, 1H), 6.69 (t, J = 1.20 Hz, 1H), 6.70 (t, J = 1.10 Hz, 1H), 6.72 (t, J = 1.10 Hz, 1H), 6.75 (m, 2H), 6.77 (t, J = 0.98 Hz, 1H), 6.86 (dt, J = 1.48 and 0.96 Hz, 1H), 7.27 (d, J = 1.48 Hz, 1H). **2d**: a yellow solid from CH_2Cl_2–MeOH; mp 185–187 °C; MS (FAB) *m/z* 1684 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9H), 1.21–1.30 (m, 36H), 2.67–2.80 (m, 24H), 6.65 (t, J = 1.10 Hz, 1H), 6.69 (t, J = 1.00 Hz, 1H), 6.67–6.71 (m, 4H), 6.72 (t, J = 1.10 Hz, 1H), 6.73 (t, J = 1.10 Hz, 1H), 6.75 (t, J = 1.10 Hz, 1H), 6.76 (t, J = 1.10 Hz, 1H), 6.77 (t, J = 1.10 Hz, 1H), 6.86 (dt, J = 1.48 and 0.96 Hz, 1H), 7.26 (d, J = 1.48 Hz, 1H). **2e**: a yellow solid from CH_2Cl_2–MeOH; mp 214 °C (with decomp.); MS (MALDI-TOF) *m/z* 2221.8 (M^+: calc. 2220.4); ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9H), 1.21–1.25 (m, 48H), 2.67–2.80 (m, 32H), 6.65 (t, J = 1.00 Hz, 1H), 6.69 (t, J = 1.10 Hz, 1H), 6.70–6.73 (m, 10H), 6.75 (t, J = 1.00 Hz, 1H), 6.76 (t, J = 1.10 Hz, 1H), 6.77 (t, J = 1.10 Hz, 1H), 6.86 (dt, J = 1.48 and 0.96 Hz, 1H), 7.27 (d, J = 1.48 Hz, 1H).

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