

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 to 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.

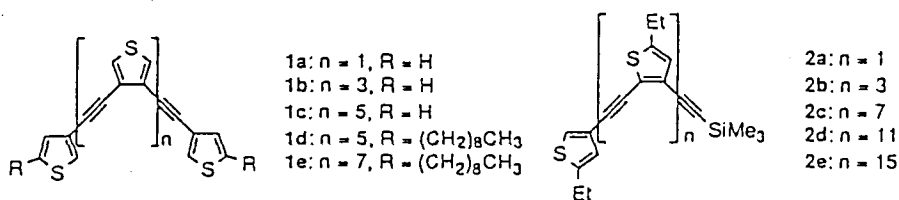
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INTRODUCTION

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-

Y. ASO et al.

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.

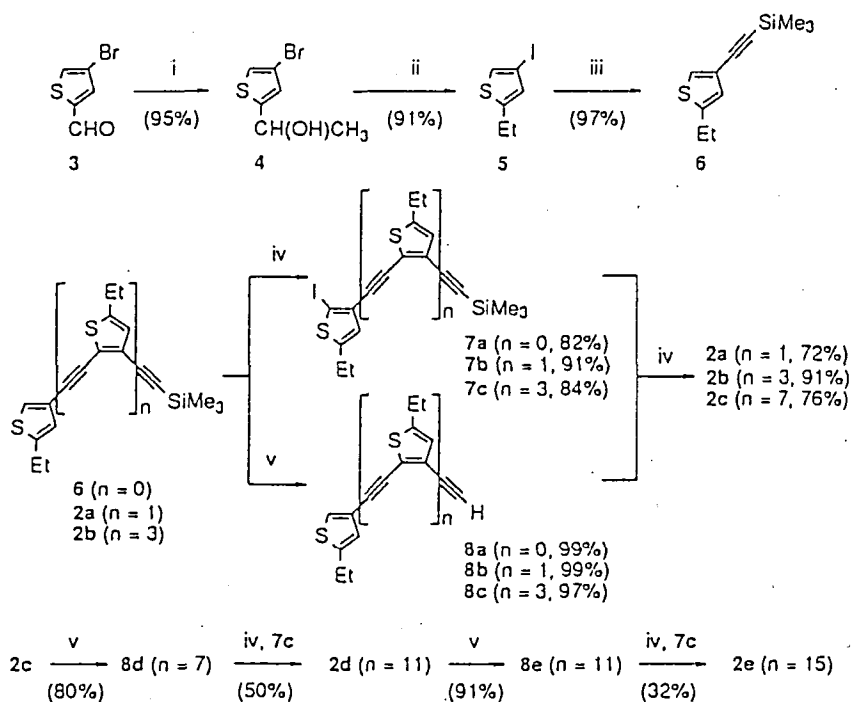


RESULTS AND DISCUSSION

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 from 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,

2,3-THIENYLENE-ETHYNYLENE OLIGOMERS

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, CH₃CN-hexane, rt; iii) TMS-C≡C-H, Pd(PPh₃)₄, CuI, Et₃N, 75 °C; iv) 1) LDA, ether, -78 °C then 0 °C, 2) I₂, -78 °C then rt; v) K₂CO₃, MeOH-CH₂Cl₂, rt; vi) Pd(Ph₃P)₄, CuI, Et₃N, 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

Y. ASO et al.

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

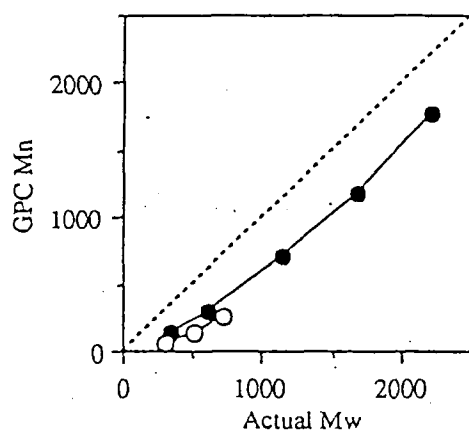


FIGURE 1 Relationship of molecular weights determined by GPC versus the actual molecular weights of 1a-c (○) and 2 (●).

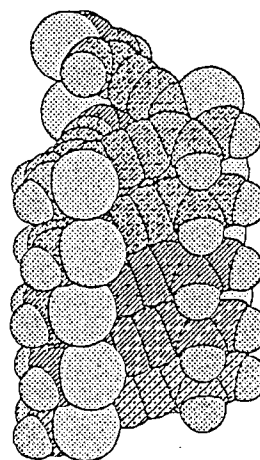


FIGURE 2 A molecular model of coil-shaped 2e.

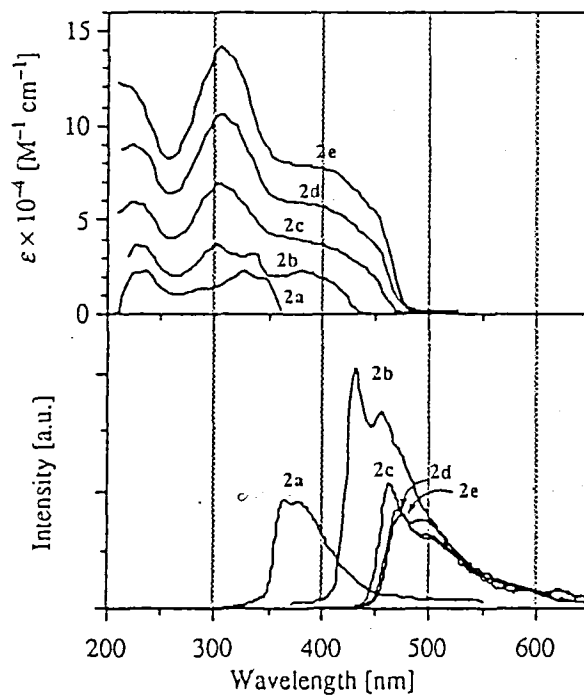


FIGURE 3 Electronic absorption (upper) and emission spectra (lower) of oligo(2,3-thienylene-ethynylene)s in THF.

2,3-THIENYLENE-ETHYNYLENE OLIGOMERS

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.

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Y. ASO et al.

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- [5] All new compounds were characterized by spectroscopic and elemental analyses, and the selected data are as follows: 5: a colorless oil; MS (DI) m/z 208 (M^+); ^1H 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^+); ^1H 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^+); ^1H 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 ($M^+ + 1$); ^1H 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^+); ^1H 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 form CH_2Cl_2 -MeOH; mp 214 °C (with decomp.); MS (MALDI-TOF) m/z 2221.8 (M^+ : calc. 2220.4); ^1H 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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