7196 *Macromolecules* **1997,** *30,* 7196−7201

Thiophene-Based π-Conjugated Emitting Polymers: Synthesis and Photophysical Properties of Poly[2-(dodecyloxy)-5-methyl-*m*-phenyleneethynylene] and Poly[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenyleneoligothienylene]s

Bong Soo Kang, Dong Hyun Kim, Soo Min Lim, Jineun Kim, Moo-Lyong Seo, Ki-Min Bark, and Sung Chul Shin*

Department of Chemistry, Research Institute of Natural Science, Gyeongsang National University, Chinju, 660-701, Korea

Keepyung Nahm

Department of Chemistry, Yeungnam University, Kyongsan, 712-749, Korea

Received June 27, 1997; Revised Manuscript Received September 10, 1997[⊗]

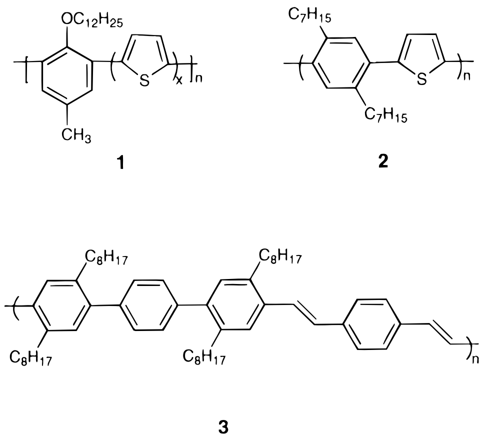
ABSTRACT: A series of copolymers, poly[2-(dodecyloxy)-5-methyl-*m*-phenyleneethynylene] and poly[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenyleneoligothienylene]s, in which ethynylene units are inserted into both of the meta positions of every phenylene for the elimination of the steric hindrance around the meta linkages, was synthesized by a Heck type coupling reaction. The resulting polymers were characterized by infrared and nuclear magnetic resonance spectroscopy and by elemental analysis and gel permeation chromatography. Their optical spectra show that the absorption and emission maxima regularly shift to lower energy with increasing number of the thiophene units between the consecutive *m*-phenylene linkages. It is confirmed that the role of the *m*-phenylene as an interrupting block does not come from the steric hindrance around the linkage but from the intrinsic property, e.g., the MO of the *m*-phenylene moiety. The quantum yields of their emissions gradually decrease with a decrease in concentration of the ethynylated *m*-phenylene units on the polymer backbone and the Stockes shifts increase. Both of the trends indicate that a nonradiative decay of the excited states increases with an increase in the possible configurations of thiophene rings within the repeating active block.

Introduction

Electronic and optical properties of π-conjugated polymers originated from their delocalized π-electron systems have been the subjects of a number of recent papers in the field of molecular electronics.[1−3] The modification of the substitution and/or the backbone of π-conjugated polymers endows them with unique physical properties and new functions.

The alternative substitution of donor and acceptor substituents on the adjacent thiophene units of polythienylenes results in the formation of multiple potential energy wells, by which charges formed during doping process are confined along the conjugated chains. As a result, the instantaneous recombination of polarons to energetically more favorable bipolarons can be retarded, which allows us to observe the various charged states, such as polarons, π-dimers, and bipolarons successively characterized during the electrochemical doping of these materials.[4,5] The carbon−carbon triple bonds of poly(aryleneethynylene)s, in which aromatic rings alternate with triple bonds, make the conjugated backbone more rigid and thus greatly improve their solution quantum yields compared to other families of π-conjugated polymers.[6,7] The conjugated polymers in which π-excessive heterocycles alternate with π-deficient aromatic rings possess charge-transferred structures, showing a large third-order nonlinear optical susceptibility.[8−10] The insertion of steric hindrance by alkyl substitutions on the regularly defined positions of the polyarene backbone results in large torsional angles around the linkages connecting the ring units and thus prevents formation of the extensive copolanar conjugation, the length of which adjusts the $\pi-\pi^*$ band gap (energy difference between HOMO and LUMO). This approach has been successfully applied to the color tuning of polyarene-based light-emitting diodes.[11,12]

Chart 1



The π-conjugation by resonance in oligo- and poly(*m*-phenylene)s does not exist between adjacent phenylene rings. Therefore, these polymers show wide band gaps and are essentially semiconductors.[13−15] Recently, we synthesized a series of poly(*m*-phenyleneoligothienylene)s (**1**), as shown in Chart 1. Their optoelectronic data demonstrate that the *m*-phenylene units inserted into the regularly defined positions of the thienylene backbone act as interrupting blocks with a broad band gap and thus can control the wavelength of the emitting chromophores with a narrow energy gap, accordingly providing a nice way to tune the wavelength of the

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

S0024-9297(97)00946-7 CCC: $14.00

emitting polymers.[16] There would be two origins that *m*-phenylene unit can play a role in, in an interrupting block. One is the large torsional angle due to steric hindrances around its linkages connecting adjacent thienyl units. The other is the intrinsic property of molecular orbitals (MO) of the *m*-phenylene units owing to probable existence of orthogonal degenerated or nearly degenerated frontier molecular orbitals (FMO). However, it is not clear which origin is reasonable. It is known that the conjugation of polythiophene is fully interrupted at a torsional angle beyond 40°.[17,18] The AM1 calculation showed that the steric hindrance induced torsional angle is 27.5° at the anti-conformation of the phenyl alkoxy group and the thienyl sulfur atom of **1**; this is not so significant as to interrupt the effective conjugation. Nevertheless, this still remains ambiguous, since for structurally analogous polymers such as **2** and **3** it has been demonstrated that the $\pi-\pi^*$ band gap of polyarenes is controlled by a torsional angle from steric hindrance around linkages connecting adjacent aromatic rings.[19−21]

In order to clarify this ambiguity concerned with the role of the *m*-phenylene bridge at an experimental level, we decided to synthesize a series of polymers such as poly[*m*-phenyleneethynylene] and poly[*m*-bis(ethynyl)-phenyleneoligothienylene]s, in which ethynylene spaces rule out the possible interruption of conjugation by the steric hindrance around the *m*-phenylene units, and to investigate their optoelectronic properties. Herein, the results are reported.

Experimental Section

Measurements. NMR spectra were collected at 400 (^{1}H) and 100.6 (^{13}C) MHz on Bruker AM-400 spectrometer using chloroform-*d* as solvent and tetramethylsilane as an internal standard. IR spectra (KBr disk) were recorded on a Hitachi 270−50 spectrophotometer. Mass spectra were collected on Kratos Analytical Profile HV-3 spectrometer. UV/visible spectra were recorded in chloroform and *n*-hexane solutions on an SLM Amonco 3000 Array spectrophotometer. Fluorescence spectra were obtained in chloroform and *n*-hexane solutions on a Perkin-Elmer LS-50 spectrofluorometer. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario EL. The GPC measurements were performed on a Waters 150-c GPC system equipped with μ Styragel, 10^2−10^5 Å. Tetrahydrofuran (THF) and a standard polystyrene were used as an eluent and a reference for calibration, respectively.

Materials. Reagent-grade toluene was distilled under nitrogen from sodium benzophenone ketyl, and other solvents were used as received (p.a. grade). All of the other chemicals were purchased from the Aldrich Chemical Co. and were used as received. 2,6-Diiodo-1-(dodecyloxy)-4-methylbenzene,[22] 2,5-diiodothiophene, 2,5′-diiodobithiophene, and 2,5′′′-diiodoterthiophene[23] were prepared according to the known procedures, respectively.

Monomer Synthesis. 1-(Dodecyloxy)-2-(3-hydroxy-3-methylbutynyl)-6-iodo-4-methylbenzene (4). To a mixture of 1-dodecyl-2,6-diiodo-4-methylbenzene (21.1 g, 40 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.33 g, 1 mol %), and CuI (0.23 g, 3 mol %) in degassed diisopropylamine (200 mL) was added 2-methyl-3-butyn-2-ol (3.36 g, 40 mmol). The reaction mixture was refluxed with stirring for 5 h under nitrogen atmosphere. After confirmation of the disappearance of the starting diiodobenzene by TLC, the mixture was filtered and evaporated under reduced pressure. Distilled water was poured onto the residue, and the product was extracted with CH_2Cl_2. The extract was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a silical gel column using mixed eluent of *n*-hexane−ethyl acetate (10:1) to give 13.4 g (69% yield) of **4** as colorless liquid. ^{1}H NMR: δ 0.88 (t, J = 8.0 Hz, 3H, CH_3), 1.26−1.87 (m, 20H, $(CH_2)_{10}$), 2.20 (s, 3H, PhCH_3), 4.02 (t, J = 6.4 Hz, 2H, OCH_2), 7.13 (d, 1H, J = 1.6 Hz, phenyl H), 7.52 (d, 1H, J = 1.6 Hz, phenyl H) ppm. ^{13}C NMR: δ 14.1, 20.0, 22.7, 26.2, 29.4, 29.6, 29.7, 30.3, 31.4, 31.5, 31.9, 65.5, 74.1, 78.1, 91.9, 98.4, 116.8, 134.2, 134.8, 139.9, 157.5 ppm. IR: 3420 cm^{-1}. MS: *m/z* 484 (M^+). Anal. Calcd for $C_{24}H_{37}O_2I$: C, 59.50; H, 7.70. Found: C, 59.87; H, 7.74.

1-(Dodecyloxy)-2-ethynyl-6-iodo-4-methylbenzene (5). To a solution of **4** (4.84 g, 10 mmol) in a mixed solvent of degassed toluene−methanol (1:1) (50 mL) was added KOH (2.80 g, 50 mmol). The mixture was refluxed under nitrogen atmosphere for 24 h. After confirmation of the disappearance of starting **4** by TLC, the solvent was evaporated under reduced pressure. Distilled water was poured to the residue and extracted with CH_2Cl_2. The extract was washed with saturated NH_4Cl and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel column (*n*-hexane) to give 3.62 g (85% yield) of **5** as colorless liquid. ^{1}H NMR: δ 0.88 (t, J = 7.2 Hz, 3H, CH_3), 1.26−1.88 (m, 20H, $(CH_2)_{10}$), 2.22 (s, 3H, PhCH_3), 3.24 (s, 1H, acetylenic H), 4.05 (t, J = 4.8 Hz, 2H, OCH_2), 7.25 (d, 1H, J = 1.6 Hz, phenyl H), 7.57 (d, 1H, J = 1.6 Hz, phenyl H) ppm. ^{13}C NMR: δ 14.8, 20.6, 23.4, 26.7, 30.1, 30.2, 30.29, 30.33, 30.4, 30.9, 32.6, 74.8, 80.3, 82.3, 92.7, 116.8, 135.5, 141.2, 159.0 ppm. IR: 3300 cm^{-1}. MS: *m/z* 426 (M^+). Anal. Calcd for $C_{21}H_{31}OI$: C, 59.15; H, 7.33. Found: C, 59.38; H, 7.29.

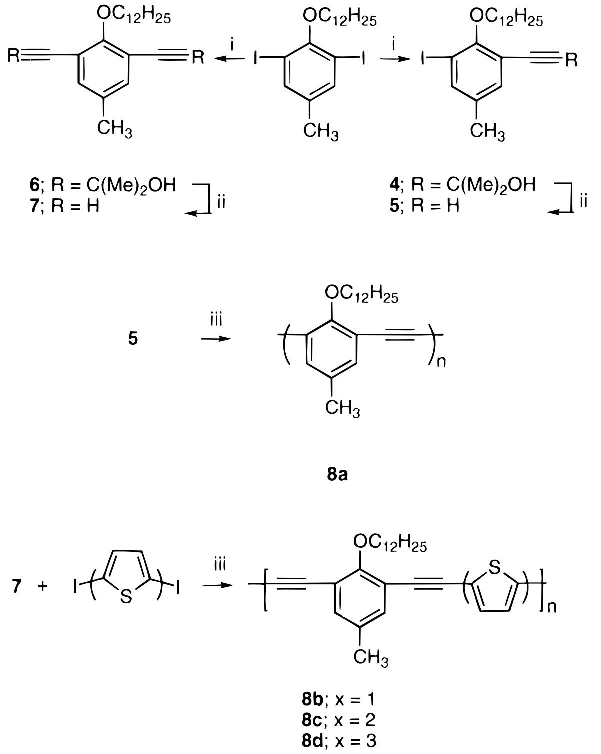
1-(Dodecyloxy)-4-methyl-2,6-bis(3-hydroxy-3-methylbutynyl)benzene (6). The same procedure used with **4** was performed from 1-(dodecyloxy)-2,6-diiodo-4-methylbenzene (21.1 g, 40 mmol) and 2-methyl-3-butyn-2-ol (7.40 g, 88 mmol), affording 8.83 g (68%) of **6** as colorless liquid. ^{1}H NMR: δ 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.25 - 1.84 (m, 20H, $(CH_2)_{10}$), 2.37 (s, 3H, PhCH_3), 2.60 (s, 2H, OH), 4.11 (t, J = 6.4 Hz, 2H, OCH_2), 7.12 (s, 2H, phenyl H) ppm. ^{13}C NMR: δ 14.8, 20.9, 23.3, 26.9, 30.0, 30.3, 31.1, 32.0, 32.6, 66.2, 75.14, 78.9, 98.5, 117.5, 133.4, 134.6, 159.6 ppm. IR: 3420 cm^{-1}. MS: *m/z* 440 (M^+). Anal. Calcd for $C_{29}H_{44}O_3$: C, 79.04; H, 10.06. Found: C, 78.90; H, 9.81.

1-(Dodecyloxy)-2,6-bis(ethynyl)-4-methylbenzene (7). The same procedure used with **5** was performed from **6** (4.41g, 10 mmol) and KOH (2.81 g, 50 mmol), affording 2.40 g (74%) of **7** as colorless liquid. ^{1}H NMR: δ 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.26−1.83 (m, 20H, $(CH_2)_{10}$), 2.23 (s, 3H, PhCH_3), 3.21 (s, 2H, acetylenic H), 4.16 (t, J = 6.4 Hz, 2H, OCH_2), 7.25 (s, 2H, phenyl H) ppm. ^{13}C NMR: δ 14.8, 20.9, 23.4, 26.6, 30.0, 30.2, 30.3, 30.4, 30.9, 32.6, 75.2, 80.4, 81.9, 117.1, 133.4, 135.9, 161.1 ppm. IR: 3300 cm^{-1}. MS: *m/z* 324 (M^+). Anal. Calcd for $C_{23}H_{32}O$: C, 85.13; H, 9.94. Found: C, 85.97; H, 9.97.

Polymer synthesis. Poly(2-(dodecyloxy)-5-methyl-*m*-phenyleneethynylene) (8a). Monomer **5** (4.26 g, 10 mmol), Pd(dppf)Cl_2·CH_2Cl_2(0.16 g, 2 mol %) and CuI (0.11 g, 6 mol %) were combined in Et_3N (10 mL) and toluene (50 mL). The mixture was refluxed for 48 h under nitrogen atmosphere. The reaction mixture was poured into methanol. The precipitated material was centrifuged and dried under vacuum, giving 2.60 g of polymer **8a**. The crude polymer was dissolved in dichloromethane and filtered through a short path column of silica gel to remove traces of catalyst. The resulting solution was concentrated and precipitated in methanol. The sticky yellow solids were collected by centrifugation and dried under vacuum. ^{1}H NMR: δ 0.86 (t, 3H, CH_3), 1.20−1.91 (m, 20H, $(CH_2)_{10}$), 2.31 (s, 3H, PhCH_3), 4.31 (t, 2H, OCH_2), 7.29 (s, 2H, phenyl H) ppm. IR: 2210 cm^{-1}. Anal. Calcd for $C_{21}H_{30}O$: C, 84.50; H, 10.13. Found: C, 83.80; H, 9.80.

Poly[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenyleneethienylene] (8b). Monomer **7** (3.24 g, 10 mmol), 2,5-diiodothiophene, Pd(dppf)Cl_2·CH_2Cl_2(0.16 g, 2 mol %) and CuI (0.11 g, 6 mol %) were combined in Et_3N (10 mL) and toluene (50 mL). The mixture was refluxed for 48 h under nitrogen atmosphere. The reaction mixture was poured into methanol. The precipitated material was centrifuged and dried under vacuum, giving 1.61 g of polymer **8b**. The crude polymer was dissolved in dichloromethane and filtered through a short path column of silica gel to remove traces of catalyst. The resulting solution was concentrated and precipitated in methanol. The

Scheme 1. Syntheses of Monomers and Polymers[a]



[a] Reagents and conditions: (i) 2-methyl-3-butyn-2-ol, Pd(dppf)Cl_2·CH_2Cl_2−CuI, diisopropylamine, reflux, 5 h; (ii) KOH, toluene−methanol, reflux, 24 h; (iii) Pd(dppf)Cl_2·CH_2Cl_2−CuI, diisopropylamine, reflux, 48 h.

light brown solids were collected by centrifugation and dried under vacuum. ^1H NMR: δ 0.85 (br, 3H, CH_3), 1.20−1.89 (br. m, 20H, $(CH_2)_{10}$), 2.29 (br, 3H, $PhCH_3$), 4.24 (br, 2H, OCH_2), 7.12−7.31 (br. m, 4H, Ar H) ppm. IR: 2200 cm^{-1}. Anal. Calcd for $C_{27}H_{32}OS$: C, 80.15; H, 7.97. Found: C, 78.82; H, 8.04.

Poly[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenylenebithienylene)] (8c). The same procedure as that used for **8b** was performed with **7** (3.24 g, 10 mmol) and 2,5″-diiodobithienylene (4.18 g, 10 mmol), affording 3.78 g of **8c** as brown solids. ^1H NMR: δ 0.85 (br, 3H, CH_3), 1.21−1.88 (br m, 20H, $(CH_2)_{10}$), 2.29 (br, 3H, $PhCH_3$), 4.24 (br, 2H, OCH_2), 6.94−7.54 (br m, 6H, Ar H) ppm. IR: 2200 cm^{-1}. Anal. Calcd for $C_{31}H_{34}OS2$: C, 76.49; H, 7.04; S, 13.17. Found: C, 75.93; H, 6.95; S, 11.41.

Poly[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenyleneterthienylene] (8d). The same procedure as that used for **8b** was performed with **7** (3.24 g, 10 mmol) and 2,5‴-diiodoterthienylene (5.00 g, 10 mmol), affording 3.85 g of **8d** as brown solids. ^1H NMR δ 0.85 (t, 3H, CH_3), 1.21−1.90 (m, 20H, $(CH_2)_{10}$), 2.28/2.29 (s/s, 3H, $PhCH_3$), 4.24 (br, 2H, OCH_2), 7.00−7.28 (m, 6H, Phenyl H) ppm. IR: 2200 cm^{-1}. Anal. Calcd for $C_{35}H_{36}OS_3$: C, 73.90; H, 6.38; S, 16.90. Found: C, 74.06; H, 6.81; S, 16.26.

Results and Discussion

Monomer Synthesis. The synthetic strategy is shown in Scheme 1. Palladium(II) catalyzed cross-coupling of aryl halide and terminal acetylene, known as the Heck reaction,[24] was employed as the pivotal reaction for the synthesis of *m*-ethynylated benzene, a key building block of polymerization. Thus, 1-(dodecyloxy)-2-ethynyl-6-iodo-4-methylbenzene (**5**), in which alkoxy and alkyl groups are grafted for the purpose of improvement of solubility, was obtained in 59% overall yield by cross-coupling of 1-(dodecyloxy)-2,6-diiodo-4-methylbenzene (**4**) with 2-methyl-3-butyn-2-ol in the presence of a dichloromethane complex of [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) [Pd(dppf)Cl_2·CH_2Cl_2] and CuI in diisopropylamine, followed by hydrolysis in the mixed solvent of aqueous KOH−toluene. 1-(Dodecyloxy)-2,6-bis(ethynyl)-4-methylbenzene (**7**) was obtained in 74% yield by a procedure similar to **5**. In place of diiodobenzene **4**, the employment of dibromoenzene led mainly to the production of the monoethynylated benzene **5** and the desired diethynylated benzene **7** was obtained only in low yield (<10%), due to the lower reactivity of the bromide than the corresponding iodide at the sterically congested ortho-position of the alkoxy substitution. It is known that the reaction of terminal alkynes with aryl iodides is more effective than that with aryl bromides.[25]

Table 1. Properties of Polymer 8a−d

polymer	yield (%)	M_n	M_w/M_n
8a	87	8399	3.82
8b	81	3563	2.35
8c	78	8362	3.29
8d	68	4662	5.95

Synthesis and Characterization of Polymers. Poly(2-(dodecyloxy)-5-methyl-*m*-phenyleneethynylene) (**8a**) was synthesized by refluxing the monomer **9** in the mixed solvent toluene−triethylamine in the presence of pd(dppf)Cl_2·CH_2Cl_2 and CuI. Poly[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenyleneoligothienylene)]s (**8b**−**d**) were synthesized by cross-coupling of **7** with 2,5-diiodothiophene, 2,5′-diiodobithiophene and 2,5″-diiodoterthiophene, under conditions similar to those used for the synthesis of **8a**, respectively. Polymers **8a**−**d** were purified by repetitive precipitation using THF and MeOH. **8a**−**d** are sticky yellow to brown solids. All four polymers are soluble in $CHCl_3$ and THF, and insoluble in polar solvents. The synthesis and some properties of **8a**−**d** are shown in Scheme 1 and Table 1. The molecular weights of **8a**−**d** were determined to be M_n = 3563−8399 by GPC, relative to polystyrene standards. The molecular weight distributions for the polymers **8a**−**c** were monomodal and that for **8d** was trimodal. The observed dispersity in **8a**−**d** varied from 2.35 to 5.95.

Attempts to obtain **8b**−**d**, in the presence of conventional catalysts for the Heck reaction such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, or $Pd(MeCN)_2Cl_2$, resulted in the production of low molecular weight oligomers ($<M_n = 2000$). The variation of solvent, reaction temperature, and base was also unfruitful. Although the Heck coupling was previously shown to have a great potential in polymerization,[26−28] the production of low-molecular weight polymers has been often observed in the construction of conjugated polymers by the cross-coupling of terminal acetylenes.[29] The low efficiency of this reaction in present study can be attributed to the low reactivity of the electron-rich diiodooligothienylene in the oxidative addition to a Pd(0) species generated *in situ* from the Pd(II) catalyst. It is known that the oxidative addition of aryl halides to Pd(0) is generally disfavored when electron donors reside on aromatic rings.[30]

After some effort, we found that the best condition to achieve **8a**−**d** with reasonable molecular weights was to use Pd(dppf)$_2Cl_2$·CH_2Cl_2 and CuI as the catalysts.

In IR spectra of **8a**−**d** the C−H stretching vibrations of the terminal acetylene of monomers **5** and **7** at about 3300 cm^{-1} disappear and the characteristic stretching vibrations of the C−C triple bond appear near 2200 cm^{-1}. Figure 1 shows a representative 400 MHz ^1H NMR spectrum of **8b** in order to illustrate the degree of perfection achieved. All the aromatic resonances are

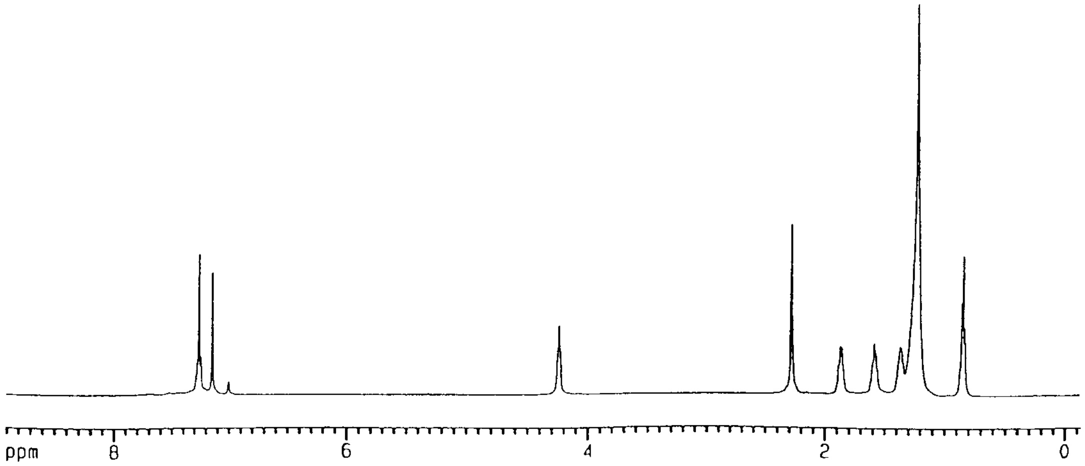


Figure 1. Representative ^{1}H-NMR spectrum of **8a** in deuteriochloroform.

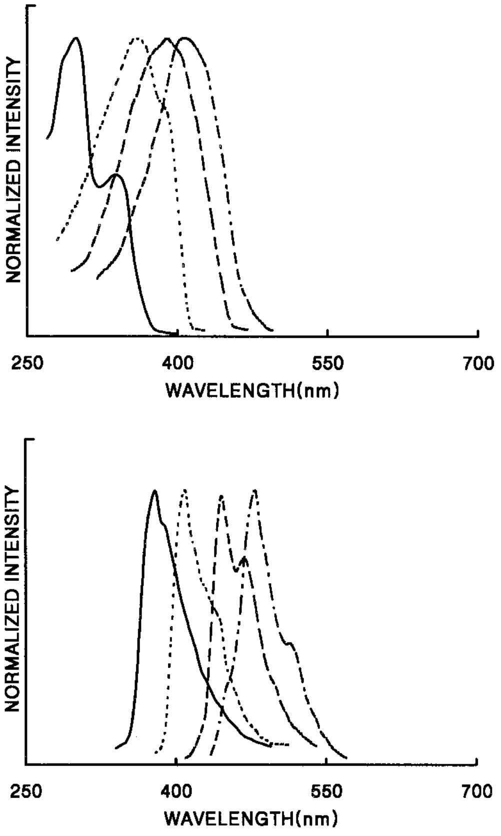


Figure 2. Absorption spectra (top) and emission spectra (bottom) of **8a** (solid line), **8b** (dotted line), **8c** (dashed line), and **8d** (dot–dashed line) in chloroform at 295 K. Intensities were normalized in order to optimally fit the graphs.

between 6.92 and 7.31 ppm. Resonances for methyl on the phenylene ring and alkoxy α-methylene appeared at 2.24–2.30 and 4.18–4.24 ppm, respectively. In the ^{13}C NMR spectrum of **8a**–**d**, exact assignment of each resonance is difficult due to the interference of carbon resonances originating from end groups (not described here).

Optical Properties of Polymers. The absorption and emission spectra of **8a**–**d** obtained for diluted and deoxygenated $CHCl_3$ solutions are shown in Figure 2. The absorption spectrum of **8a** shows a couple of peaks and that of **8b** shows a broad main peak and a shoulder at the low-energy (long wavelength) side. Those of **8c** and **8d** show a broad main peak for each. All the emission spectra given here were obtained under excitation at the wavelength of the main absorption band, which shows vibrational fine structures. Similar fine structures have also been observed for other thiophene polymers and ascribed to a greater rigidification of the polymers in their first relaxed excited state than in the ground state.[16] The absorption maxima progressively shift from 337 nm for **8a**, to 365 nm for **8b** to 388 nm for **8c**, and to 407 nm for **8d**. The emission maxima also shift from 378 nm for **8a** to 410 m for **8b**, to 451 nm for **8c**, and to 485 nm for **8d**.

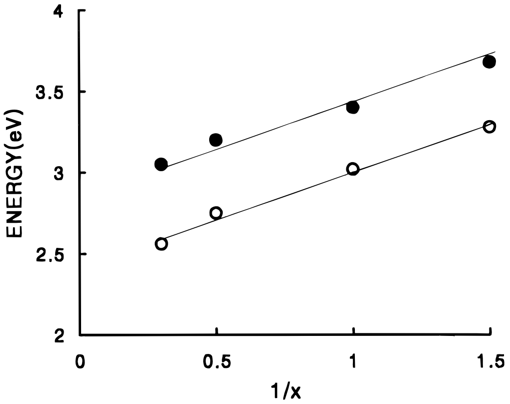


Figure 3. Variation of absorption and emission maximum energies of **8a**–**8d** in chloroform solution as a function of the inverse number of thiophene rings (1/*x*) between consecutive *m*-phenylene bridges: (●) absorption; (○) emission.

Figure 3 shows the variation of the absorption and emission maximum energies as a function of the inverse number of thiophene rings (1/*x*) between consecutive *m*-phenylene linkages. The data exhibit the same good linearity as those of poly(*m*-phenyleneoligothienylene)s previously reported by us and the other related polymeric systems.[16,31,32]

The variation of the torsional energy and C_{phenyl}–$C_{thienyl}$ bond length with rotation between the two *m*-thiophene rings of the model structure **9** was investigated, employing a semiemprical PM3 method.[33] While one thienyl ring **A** was conjugated and fixed planar to the phenylene ring, the other **B** was rotated from 0° to 180°. Values obtained from 180 to 360° (syn/syn) are not exhibited, since they are not important for the present argument. The selected data were summarized in Table 2. The maximum barrier for rotation is *ca.* 4.5 kcal mol^{-1} at 180° torsional angle. Even though structure **9** has some strain in rotation between two rings, the barrier is low enough for free rotation over the range 0–180°; the rotation should not be sterically restricted. In addition,

Table 2. Torsional Energies and Bond Lengths for the C_{phenyl}–$C_{thienyl}$ Linkage Rotation of the Model Structure 9

torsional angle (deg)	bond length (Å)	energy (relative, kcal mol^{-1})
free[a]	1.459	0.0
0[b]	1.459	2.40
90[c]	1.460	0.25
180[d]	1.463	4.50

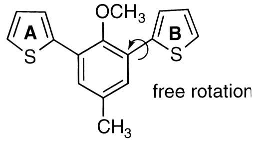
[a] At the most stable conformer. [b] Thienyl sulfur/phenyl oxygen/thienyl sulfur = anti/anti conformation. [c] Orthogonal of phenyl ring to thienyl **B**. [d] Anti/syn.

Table 3. Quantum Yields and Stockes Shifts of 8a–b in Solution[a]

polymer	Stockes shifts (eV)	Φ_s[b] chloroform	*n*-hexane
8a	0.40	0.28	0.39
8b	0.38	0.18	0.33
8c	0.45	0.09	0.11
8d	0.49	0.02	0.09

[a] All experiments were performed in degassed solutions. [b] Emission quantum yield were obtained using quinine sulfate as reference. The wavelength of the absorption maximum was chosen for the excitation.

if there is conjugation between the ring **A** and **B**, the rotation must accompany the substantial change of the $C_{phenyl-}C_{thienyl}$ bond length. However, the bond length is nearly constant throughout the rotation.



9

Together with our previous results,[16] the data obtained from present studies clearly confirm that the role of the *m*-phenylene as an interrupting block does not come from a steric hindrance around its linkage but mainly from the intrinsic property, e.g., MO, of the moiety itself. MO studies of the *m*-phenylene inserted onto present polymers will be another subject for further research and will be investigated in our laboratory. *m*-Conjugated phenylenes are popularly applied, as ferromagnetic coupling units, to the field of organic molecule based ferromagnetism, a characteristic of which is attributed to the existence of a pair of degenerated, orthogonal FMOs.[34,35]

The Stockes shifts and the quantum yields are listed in Table 3. The Stockes shifts between the maxima of absorption and emission are comparatively small and in the range 0.38–0.49 eV. The shifts roughly increase on going from **8a** to **8d**. The quantum yields of emission from chloroform solutions of the polymers were calculated by using measured values of integrated emission. The quantum yield of a sample in solution, Φ_s, may be related by the following equation:

$$\Phi_s = (A_r/A_s)(F_s/F_r)$$

A_s and A_r are the respective absorbances of the sample and the reference solutions at the excitation wavelength, F_r and F_s are the corresponding relative integrated emission intensities. The quantum yields are ranged from 0.28 (for **8a**) to 0.02 (for **8d**) in chloroform and from 0.39 to 0.09 in *n*-hexane, indicating them to be higher in *n*-hexane than in chloroform. It is known that organic fluorophores show generally higher quantum yields in nonpolar solvents than those in polar media.[36] The quantum yields gradually decrease on going from **8a** to **8d**. Together with above variation of Stockes shifts, this indicates that nonradiative decay of the excited states increases with a decrease in concentration of the ethynylated *m*-phenylene units (an increase of possible configurations of thiophene rings) within the repeating active block, the trend of which may be in agreement with the previously asserted contribution of triple bonds to backbone rigidification of the π-conjugated polymers.[6] The solution quantum yield of the polymers generally increases with the degree of rigidification of its backbone and the Stockes shift decreases.

Conclusions

A series of thiophene-based copolymers, poly[2-(dodecyloxy)-5-methyl-*m*-phenyleneethynylene] and poly-[2-(dodecyloxy)-5-methyl-*m*-bis(ethynyl)phenyleneoligothienylene]s was synthesized by a Heck type coupling reaction. The absorption and emission maxima of the polymers regularly shift to lower energies with an increase in the number of the thiophene rings between consecutive *m*-phenylene linkages. These optical data demonstrate that the role of *m*-phenylene as an interrupting block does not come from a steric hindrance around its linkage but from the intrinsic property. MO studies of the *m*-phenylene inserted onto present thiophene-based polymers will be further investigated.

Acknowledgment. The authors are grateful to Professor K. Yang at Gyeongsang National University for helpful discussions. This work was supported by KOSEF, Korea, 1996 (Project No, 96-2-03-01-01-2) and in part by the Basic Science Research Institute program, Ministry of Education, Korea, 1995 (Project No, BSRI-96-3441).

References and Notes

(1) Aldissi, M. Ed. *Intrinsically Conduction Polymers: Emerging Technology;* Kluwer: Dordrecht, The Netherlands, 1993.
(2) Bredas, J. L., Chance, R. R., Eds. *Conjugated Polymeric Materials: Opportunity in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer: Dordrecht, The Netherlands, 1990.
(3) Skotheim, T. A. Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.
(4) Demanze, F.; Yassar, A.; Garnier, F. *Adv. Mater.* **1995**, *7*, 907.
(5) Demanze,F.; Yassar, A.; Garnier, F. *Macromolecules* **1996**, *29*, 4267.
(6) Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1955**, 1433.
(7) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157.
(8) Yamamoto, T.; Zhou, Z.-H.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.-L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389.
(9) Saito, H.; Ukai, S.; Iwatsuki, S.; Itoh, T.; Kubo, M. *Macromolecules* **1995**, *28*, 8363.
(10) Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Soc.* **1993**, 797.
(11) Gill, R. E.; Malliaras, G. G.; Wildeman, J.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*, 132.
(12) Andersson, M. R.; Berggren, M.; Inganäs, O.; Gustafsson, G.; Gustafsson-Carlberg, J. C.; Selse, D.; Hjertberg, T.; Wennerström, O. *Macromolecules* **1995**, *28*, 7525.
(13) Alexander Jr., R. L. *J. Org. Chem.* **1956**, *21*, 1464.
(14) Woods, G. F.; Artsdale, A. L. V.; Reed, F. T. *J. Am. Chem. Soc.* **1950**, *72*, 3221.
(15) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190.
(16) Kang, B. S.; Seo, M.-L.; Jun, Y. S.; Lee, C. K.; Shin, S. C. *Chem. Commun* **1996**, 1167.
(17) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(18) Brédas, J. L.; Street, G. B.; Thémans, B. J.; André, M. *J. Chem. Phys.* **1985**, *83*, 1323.

(19) Hilberer, A.; Brouwer, H.-J.; van der Scheer, B.-J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 4525.

(20) Fahlman, M.; Birgersson, J.; Kaeriyama, K.; Salaneck, W. R. *Synth. Met.* **1995**,*75*, 223.

(21) Birgerson, J.; aeriyama, K. K.; Barta, P.; Bröms, P.; Fahlman, M.; Granlund, T.; Salaneck, W. R. *Adv. Mater.* **1996**, *12*, 982.

(22) Burger, A.; Wilson, E. L.; Brindley, C. O.; Bernheim, F. *J. Am. Chem. Soc.* **1945**,*67*, 1416.

(23) SteinKopf, W.; Leitsmann, R.; Hofmann, K. H. *Liebigs Ann.* **1940**, *546*, 180.

(24) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1990.

(25) Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571.

(26) Heitz, W.; Brugging, W.; Freund, L.; Gailberger, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niessner, N.; Osan, F.; Schmidt, H.-W.; Wicker, M. *Makromol. Chem.* **1988**, *189*, 119.

(27) Weitzel, H.-P.; Mullen, K. *Makromol. Chem.* **1990**, *191*, 2837.

(28) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.

(29) Hilberer, A.; Brouwer, H.-J.; van der Scheer, B.-J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 4525.

(30) Tsuji, J. *Palladium Reagents and Catalyst. Innovations in Organic Synthesis*; John Wiley and Sons; New York, 1995; p 127.

(31) Yassar, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490.

(32) Janssen, R. A.; Smilowitz, L.; Saricifti, N. S.; Moses, D. *J. Chem. Phys.* **1994**, *101*, 1787.

(33) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(34) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(35) Nishide, H. *Adv. Mater.* **1995**, *7*, 937.

(36) Bark, K.-M.; Force, R. K. *Spectrochim. Acta* **1993**, *49A*, 1605.

MA9709462