Synthesis and Characterization of Diblock Copolymers Containing Oligothiophenes with Defined Regiospecificity and Molecular Weights

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ABSTRACT: A series of regiospecific, alkyl-substituted oligothiophenes were synthesized and their structure/property relationships were studied. The formylation of the oligothiophenes introduced an aldehyde functionality into one of the terminals which can be used to couple with living anionic polystyrene species to generate diblock copolymers. Three diblock copolymers were synthesized by coupling the oligothiophene aldehyde with living polystyrenes of different chain lengths. These copolymers were stable at temperature up to 380 °C and have similar glass transition temperatures to the corresponding polystyrene homopolymers.

Introduction

Diblock copolymers are fascinating materials exhibiting various phase behaviors.[1] They can self-assemble into multiphase domain structures on a nanometer scale due to the repulsive energetic interaction between the incompatible blocks. This unique self-assembling property offers the potential to achieve one-, two-, or three-dimensional confinements of the functional materials, such as conducting materials. Conjugated polymers are well-known to possess interesting electrical and optical properties, such as high electric conductivity upon doping, high third-order optical nonlinearity, and electroluminescent properties.[2−4] The incorporation of conjugated polymer chains into diblock polymers creates the potential for a new form of self-assembled, nanosized electroactive materials. These materials offer the opportunity to study quantum confinement effects, tunneling effects in carrier transport, and the phase transition phenomenon.[5−7] Recently, we initiated a research project to prepare such diblock copolymers with one π-conjugated block. We designed a two-stage approach to synthesize these diblock copolymers. The first stage involves the synthesis of the conjugated block with proper functionality which will be used in the second stage for coupling with a living polymer species. Numerous conjugated polymers are known and their physical properties have been studied to different depths.[2−4] For this study, we have chosen polythiophene (PT) as the target conjugated block because it possesses interesting physical properties and can be synthesized through a stepwise approach. In this paper, we report the synthesis of regiospecific oligothiophenes with defined molecular weights and terminal aldehyde functionality and the synthesis of the diblock copolymers.

Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from Na^+/benzophenone ketyl. 1,3-Dichlorobenzene was purified by distillation. Cyclohexane was purified according to ref 8. Styrene was vacuum distilled and dried over calcium hydride. Before use, the purified styrene was further treated with three freeze−thaw cycles to remove oxygen. All of the other chemicals were purchased from the Aldrich Chemical Co. and used without further purification unless otherwise noted.

Synthesis. 3-Hexylthiophene (**1**) was prepared following literature procedures.[9] The oligo(3-hexylthiopheneyl bromide)s were synthesized by the regiospecific bromination of the oligo(3-hexylthiophene)s with NBS in 50/50 (v/v) solution of chloroform/acetic acid according to ref 10.

Compound 2. The crude product was purified by fractional distillation under vacuum (76%, yield): bp 101−102 °C/(1.1 mmHg); ^{1}H NMR ($CDCl_3$, ppm) δ 7.12 (d, J = 5.6 Hz, 1 H), 6.74 (d, J = 5.6 Hz, 1 H), 2.54 (t, 2 H), 1.56 (quintet, 2 H), 130 (m, 6 H), 0.88 (t, 3 H).

Compound 4. The crude product was purified with flash chromatography on silica gel (using hexane) with a yield of 82%: ^{1}H NMR ($CDCl_3$, ppm) δ 7.16 (d, J = 5.2 Hz, 1 H), 6.91 (d, J = 5.2 Hz, 1 H), 6.78 (s, 1 H), 2.70 (t, 2 H), 2.60 (t, 2 H), 1.60 (m, 4 H), 1.31 (m, 12 H), 0.88 (m, 6 H).

Compound 6. The crude product was purified with flash chromatography on silica gel (using hexane) with a yield of 77%: ^{1}H NMR ($CDCl_3$, ppm) δ 7.10 (d, J = 5.1 Hz, 1 H), 6.88 (s, 2 H), 6.87 (d, J = 5.1 Hz, 1 H), 6.77 (s, 1 H), 2.75 (quintet, 4 H), 2.69 (t, 2 H), 2.55 (t, 2 H), 1.63 (m, 8 H), 1.31 (m, 24 H), 0.89 (m, 12 H). Anal. Calcd for $C_{40}H_{57}BrS_4$: C, 64.40; H, 7.70. Found: C, 64.65; H, 7.80.

Oligo(3-hexylthiophene)s: Compound 3. *n*-Butyllithium (16.8 mL, 2.5 M solution in hexanes, 42 mmol) was added dropwise to a solution of compound **1** (7.06 g, 42 mmol) and tetramethylethylenediamine (TMEDA) (4.87 g, 42 mmol) in THF (35 mL) at room temperature through a syringe under a nitrogen atmosphere. The solution was refluxed for 1 h and then cooled to room temperature. It was stirred for an additional hour and then transferred to a solution of anhydrous zinc chloride (6.27 g, 46 mmol) in THF (10 mL) via a double-tipped needle. The resulting mixture was refluxed for 1 h. and allowed to cool to room temperature for an additional hour. The mixture was transferred dropwise to a solution containing compound **2** (9.38 g, 38 mmol) and $Pd(PPh_3)_4$ (0.44 g, 0.38 mmol) in THF (8 mL). The resulting solution was stirred under reflux for 20 h. An aqueous HCl solution (10%, 20 mL) was added to the mixture after it was cooled to room temperature and the aqueous layer was extracted with ether three times. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (silica gel, hexane) to give 12.1 g of yellow liquid (88% yield): ^{1}H NMR ($CDCl_3$, ppm) δ 7.14 (d, J = 5.2 Hz, 1 H), 6.93 (s, 1 H), 6.91 (d, J = 5.2 Hz, 1 H), 6.88 (s, 1 H), 2.74 (t, 2 H), 2.60 (t, 2 H), 1.62 (m, 4 H), 1.31 (m, 12 H), 0.89 (m, 6 H).

Compound 5 was obtained from compounds **3** and **4** in 87% yield, following a procedure similar to that described for compound **3**. ^{1}H NMR ($CDCl_3$, ppm) δ 7.10 (d, 1 H), 6.92 (s, 1

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H), 6.90 (s, 1 H), 6.88 (m, 2 H), 6.84 (s, 1 H), 2.74 (m, 6 H), 2.59 (t, 2 H), 1.63 (m, 8 H), 1.31 (m, 24 H), 0.88 (m, 12 H).

Compound 8. A solution of compound **2** (4.45 g, 18 mmol) and $NiCl_2$(dppp) (98 mg, 0.18 mmol) in ether (10 mL) was added dropwise to an ethereal solution of phenyl magnesium bromide (20 mmol). After refluxing for 24 h, the mixture was hydrolyzed with 1 M aqueous HCl. The aqueous layer was extracted with ether three times. The combined organic layers were dried over $MgSO_4$. After the solvent was evaporated, the residue was purified by flash chromatography (silica gel, hexane) to give 3.73 g of yellow liquid (85% yield): ^{1}H NMR ($CDCl_3$, ppm) δ 7.37 (d, 2 H), 7.34 (dd, 2 H), 7.26 (t, 1 H), 7.16 (d, J = 5.1 Hz, 1 H), 6.92 (d, J = 5.1 Hz, 1 H), 2.62 (t, 2 H), 1.58 (quintet, 2 H), 1.24 (m, 6 H), 0.85 (t, 3 H). Anal. Calcd for $C_{16}H_{20}S$: C, 78.63; H, 8.25. Found: C, 78.50; H, 8.30.

Compound 13 was synthesized from compounds **8** and **2** in 82% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.40 (d, 2 H), 7.35 (dd, 2 H), 7.25 (t, 1 H), 7.10 (d, J = 5.1 Hz, 1 H), 6.93 (s, 1 H), 6.88 (d, J = 5.1 Hz, 1 H), 2.76 (t, 2 H), 2.63 (t, 2 H), 1.62 (m, 4 H), 1.30 (m, 12 H), 0.86 (m, 6 H). Anal. Calcd for $C_{26}H_{34}S_2$: C, 76.04; H, 8.35. Found: C, 76.08; H, 8.30.

Compound 9 was obtained from compounds **8** and **4** in 67% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.10 (d, J = 5.2 Hz, 1 H), 6.96 (s, 1 H), 6.89 (s, 1 H), 6.87 (d, J = 5.2 Hz, 1 H), 2.76 (t, 4 H), 2.64 (t, 2 H), 1.64 (m, 6 H), 1.31 (m, 18 H), 0.88 (m, 9 H). Anal. Calcd for $C_{36}H_{48}S_3$: C, 74.94; H, 8.39. Found: C, 75.03; H, 8.46.

Compound 14 was obtained from compounds **13** and **4** in 55% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.10 (d, 1 H), 6.97 (s, 1 H), 6.91 (s, 1 H), 6.88 (m, 2 H), 2.76 (m, 6 H), 2.64 (t, 2 H), 1.66 (m, 8 H), 1.32 (m, 24 H), 0.86 (m, 12 H). Anal. Calcd for $C_{46}H_{62}S_4$: C, 74.34; H, 8.41. Found: C, 74.26; H, 8.48.

Compound 11 was obtained from compounds **8** and **6** in 90% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.10 (d, 1 H), 6.97 (s, 1 H), 6.92 (s, 1 H), 6.91 (s, 1 H), 6.88 (m, 2 H), 2.78 (m, 8 H), 2.64 (t, 2 H), 1.68 (m, 10 H), 1.32 (m, 30 H), 0.89 (m, 15 H). Anal. Calcd for $C_{56}H_{76}S_5$: C, 73.95; H, 8.42. Found: C, 74.14; H, 8.43.

Compound 15 was obtained from compounds **14** and **4** in 42% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.10 (d, 1 H), 6.97 (s, 1 H), 6.92 (m, 3 H), 6.89 (m, 2 H), 2.78 (m, 10 H), 2.64 (t, 2 H), 1.68 (m, 12 H), 1.32 (m, 36 H), 0.89 (m, 18 H); Anal. Calcd for $C_{66}H_{90}S_6$: C, 73.69; H, 8.43. Found: C, 73.61; H, 8.43.

Compound 10 was obtained from compounds **9** and **6** in 20% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.37 (dd, 2 H), 7.28 (t, 1 H), 7.11 (d, 1 H), 6.98 (s, 1 H), 6.92 (m, 4 H), 6.89 (m, 2 H), 2.77 (m, 12 H), 2.64 (t, 2 H), 1.69 (m, 14 H), 1.33 (br, 42 H), 0.90 (m, 21 H); Anal. Calcd for $C_{76}H_{104}S_7$: C, 73.49; H, 8.44. Found: C, 73.56; H, 8.48.

Compound 16 was obtained from compounds **14** and **6** in 23% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.10 (d, 1 H), 6.98 (s, 1 H), 6.92 (m, 5 H), 6.89 (m, 2 H), 2.78 (m, 14 H), 2.64 (t, 2 H), 1.69 (m, 16 H), 1.33 (br, 48 H), 0.90 (m, 24 H); Anal. Calcd for $C_{86}H_{118}S_8$: C, 73.34; H, 8.45. Found: C, 73.21; H, 8.42.

Compound 12 was obtained from compounds **11** and **6** in 30% yield, following a procedure similar to that described for compound **3**: ^{1}H NMR ($CDCl_3$, ppm) δ 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.10 (d, 1 H), 6.98 (s, 1 H), 6.92 (m, 6 H), 6.88 (m, 2 H), 2.78(m, 16 H), 2.64 (t, 2 H), 1.69 (m, 18 H), 1.33 (br, 54 H), 0.90 (m, 27 H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.12, 22.67, 28.73, 29.20, 29.29, 29.47, 30.51, 30.63, 30.93, 31.71, 123.49, 127.30, 128.08, 128.48, 128.67, 128.89, 129.16, 130.04, 130.41, 130.49, 130.82, 133.43, 133.61, 133.69, 133.97, 134.08, 134.37, 137.73, 138.96, 139.52, 139.76. Anal. Calcd for $C_{96}H_{132}S_9$: C, 73.23; H, 8.45. Found: C, 73.30; H, 8.43.

Preparation of Oligothiophene Aldehydes. Compound 17. *n*-Butyllithium (4 mmol, 1.6 mL, 2.5 M in hexanes) was added dropwise to a solution of compound **8** (0.98 g, 4 mmol) and TMEDA (0.6 mL, 4 mmol) in THF (4 mL) at room temperature. The mixture was stirred at room temperature for 1 h and refluxed for an additional 30 min. DMF (4.6 mL, 60 mmol) was then added to the mixture after it was cooled to room temperature. The resulting solution was stirred at 80 °C for 3 h and was then poured into water. The aqueous layer was extracted with ether three times. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (silica gel, hexane/ethyl acetate (100/3)) to give 0.95 g of yellow liquid (88%, yield): ^{1}H NMR ($CDCl_3$, ppm) δ 9.79 (s, 1 H), 7.60 (s, 1 H), 7.39 (m, 5 H), 2.64 (t, 2 H), 1.60 (quintet, 2 H), 1.25 (m, 6 H), 0.85 (t, 3 H).

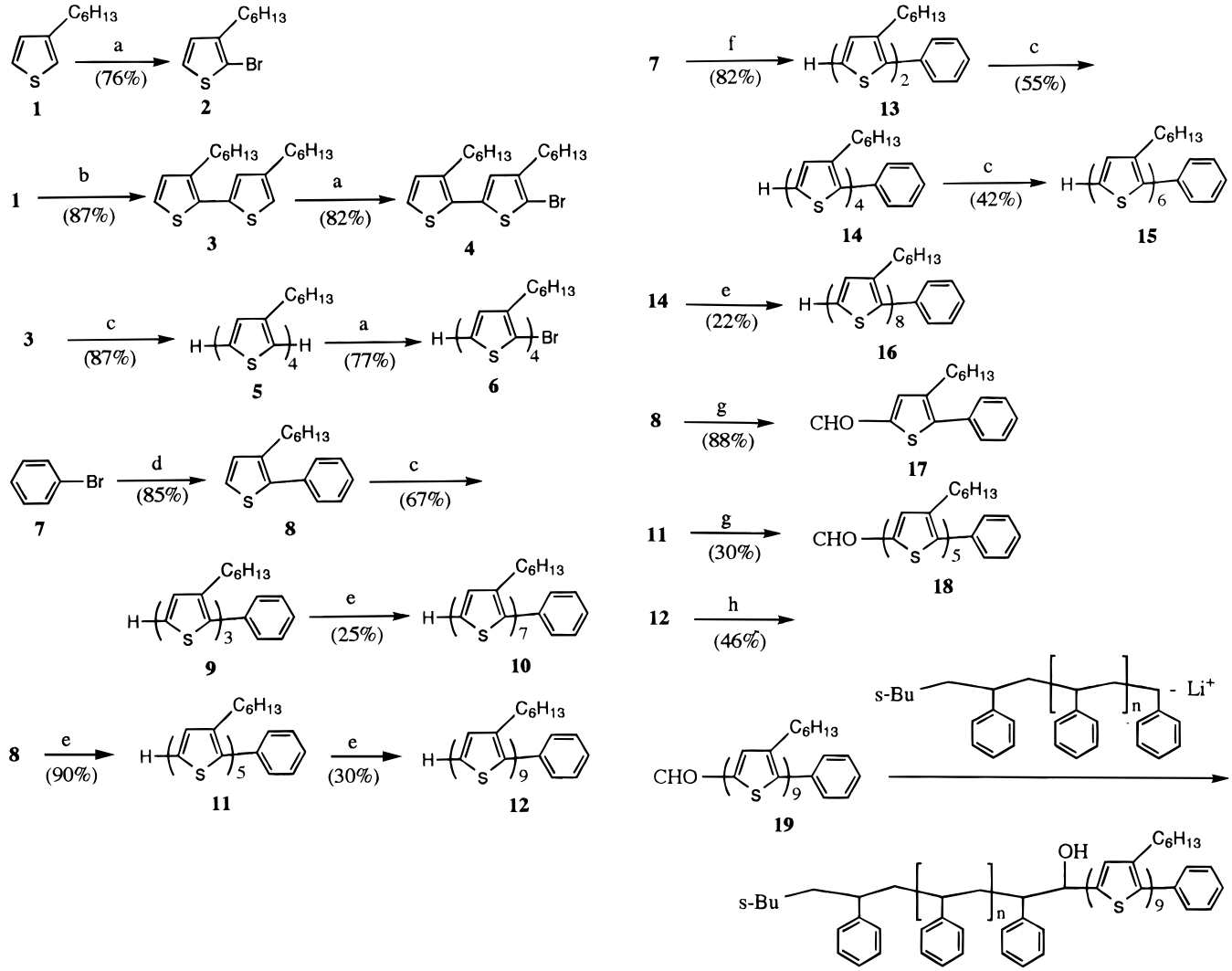
Compound 18 was obtained from compound **11** in 30% yield, following a procedure similar to that described for compound **17**: ^{1}H NMR ($CDCl_3$, ppm) δ 9.75 (s, 1 H), 7.53 (s, 1 H), 7.41 (d, 2 H), 7.37 (dd, 2 H), 7.29 (t, 1 H), 7.07 (s, 1 H), 6.98 (s, 1 H), 6.95 (s, 1 H), 6.93 (s, 1 H), 2.78 (m, 8 H), 2.64 (t, 2 H), 1.68 (m, 10 H), 1.33 (m, 30 H), 0.90 (m, 15 H).

Compound 19. Phosphorus oxychloride (0.35 mL, 0.38 mmol) was added dropwise to DMF (1.2 mL, 1.52 mmol) at 0 °C. The solution was stirred at 0 °C for 1 h and at 25 °C for an additional hour. About $^1/_{10}$ of the above solution was then transferred to a solution of compound **12** (0.61 g, 0.38 mmol) in *o*-dichlorobenzene (6 mL). The resulting mixture was stirred at 90 °C for 12 h. The reaction solution was poured into an ice/water mixture, which was then neutralized with a saturated sodium acetate solution and extracted with chloroform three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (silica gel, hexane/benzene (1/1)) to give 0.28 g of red solid (46% yield): ^{1}H NMR ($CDCl_3$, ppm) δ 9.75 (s, 1 H), 7.52 (s, 1 H), 7.41 (d, 2 H), 7.36 (dd, 2 H), 7.28 (t, 1 H), 7.07 (s, 1 H), 6.98 (s, 1 H), 6.93 (m, 7 H), 2.78 (m, 16 H), 2.64 (t, 2 H), 1.69 (br, 18 H), 1.33 (br, 54 H), 0.90 (br, 27 H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.09, 22.63, 28.70, 29.15, 29.24, 29.43, 30.20, 30.48, 30.55, 30.90, 31.66, 127.31, 128.10, 128.50, 128.69, 129.06, 129.15, 130.42, 130.53, 130.70, 130.80, 131.19, 132.41, 132.90, 133.37, 133.52, 133.91, 134.34, 137.72, 139.04, 139.55, 139.73, 139.81, 139.90, 140.05, 140.14, 140.23, 182.40. Anal. Calcd for $C_{97}H_{132}OS_9$: C, 72.70; H, 8.30. Found: C, 72.61; H, 8.34.

Preparation of Diblock Copolymers. A typical procedure for the synthesis of copolymers is described as follows: The polystyrene segment was prepared by anionic living polymerization in moisture and oxygen-free cyclohexane, according to the method of ref 8. The diblock copolymers were then obtained by injecting about 0.8 equiv of the living polystyrene solution into the oligothiophene aldehyde **19** in dry and deoxygenated THF. At the same time, an aliquot of the polystyrene solution was terminated with methanol for use in comparison to the diblock copolymer. After 30 min of reaction, the diblock copolymer solution was precipitated into a 5-fold excess of methanol. Further purification of the product was achieved by precipitation into hexane to remove unreacted aldehyde. The polymer was then dissolved in $CHCl_3$ and precipitated into methanol again to give a yellow to orange powder depending on the composition of the copolymer.

Characterization. The ^{1}H NMR spectra were collected on a UC 500 MHz spectrometer. The ^{13}C NMR spectra were obtained using a GE QE 300 MHz spectrometer. The FTIR spectra were recorded on a Nicolet 20 SXB FTIR spectrometer. A Shimadzu UV−2401PC UV-Vis recording spectrophotometer and a Shimadzu RF-5301PC spectrofluorophotometer were used to record the absorption and emission spectra. The cyclic voltammetry was measured on an EG&G Princeton Applied Research potentiostat interfaced to a personal computer. The experiment was carried out in THF (5 mL) with tetrabutylammonium tetrafluoroborate (0.15 g) as the supporting electrolyte under a nitrogen atmosphere. The gel permeation chromatography (GPC) measurements were performed on a Waters RI system equipped with an UV detector, a differential

Scheme 1[a] Synthesis of the Oligothiophenes and Diblock Copolymers



[a] Reagents: (a) NBS, $CHCl_3/CH_3COOH$ (50/50); (b) *n*-BuLi, TMEDA; $ZnCl_2$; **2**, $Pd(PPh_3)_4$; (c) *n*-BuLi, TMEDA; $ZnCl_2$; **4**, $Pd(PPh_3)_4$; (d) Mg; **2**, $Ni(dppp)Cl_2$; (e) *n*-BuLi, TMEDA; $ZnCl_2$; **6**, $Pd(PPh_3)_4$; (f) Mg; **4**, $Ni(dppp)Cl_2$; (g) *n*-Buli, TMEDA; DMF; H_2O; (h) $POCl_3$, DMF; H_2O.

refractometer detector, and Ultrastyragel linear columns at 35 °C using THF (HPLC grade, Aldrich) as the eluent. The molecular weight and molecular weight distribution were calculated based on monodispersed styrene standards. Thermal analyses [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)] were done using the DSC-10 and TGA-50 systems of TA Instruments with a heating rate of 10 °C/min under a nitrogen atmosphere.

Results and Discussion

Synthesis of Oligothiophenes and Diblock Copolymers. The chemistry of thiophene has been extensively studied.[11] Some of the peculiar reactions of 3-alkylthiophenes provide an opportunity to synthesize oligothiophenes according to a stepwise approach with controlled regiospecificity. Experimental results show that the reaction of 3-alkylthiophene with alkyllithium leads to the formation of 3-alkyl-5-lithiothiophene while the bromination of 3-alkylthiophene yields 2-bromo-3-alkylthiophene.[10,12] The synthetic approach of this work utilizes the orientational differences of the substituted thiophene in these two reactions (Scheme 1). Compounds **1**, **3**, and **5** can be preferentially lithiated at a less hindered 5 position and selectively brominated with NBS in the presence of acetic acid in chloroform at the 2-position. Oligothiophene bromides **2**, **4**, and **6** were used as the building blocks for the synthesis of various oligothiophenes. We used a phenyl group to cap one of the oligothiophene terminals to make sure the lithiation occurred exclusively at the 5-position. An interesting result is that as the thiophene repeating units increased, the efficiency of the lithiation process decreased. It seems that the reactivity of the terminal hydrogen of the oligothiophenes toward butyllithium decreases as the conjugation length increases. More experiments to elucidate the detailed mechanism are in progress.

The oligothiophenes were further functionalized with an aldehyde moiety at the thiophene end. Since butyllithium is not active enough to lithiate oligothiophene **12**, the Vilsmeier reaction was applied to synthesize oligothiophene aldehyde **19**. The obtained aldehydes thus provide the opportunity to prepare diblock copolymers through either living anionic polymerization or living metathesis polymerization. We attempted the living anionic polymerization of polystyrene and used the living polystyrene species to couple with oligothiophene aldehyde **19**. We used an excess amount of aldehyde to perform the coupling reaction. We did this to ensure that most of the living polystyrene species reacted since removal of the unreacted polystyrene from the reaction mixture is difficult. The excess oligothio-

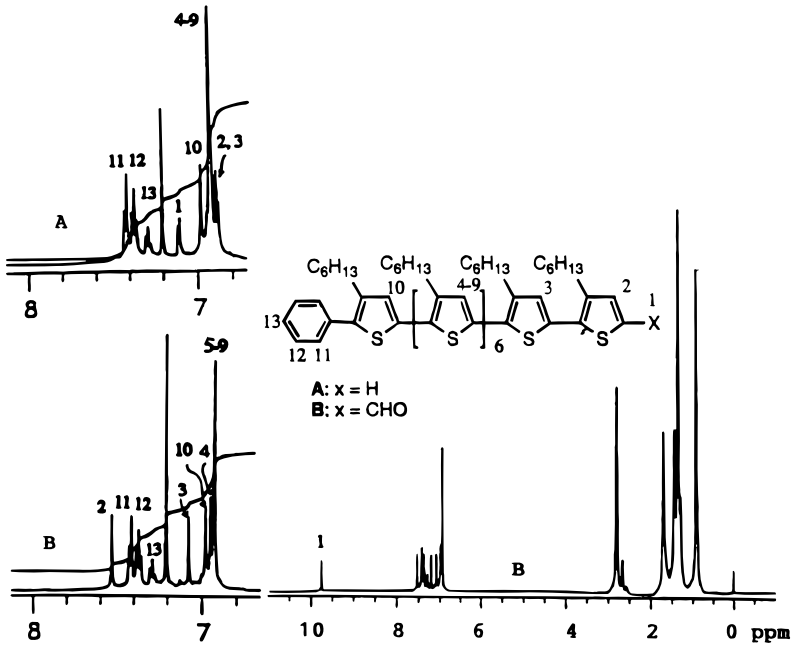


Figure 1. ^{1}H NMR spectra of compound **12** and its aldehyde derivative.

phene aldehyde was removed by selective precipitation of the copolymer into hexane. Three copolymers were obtained after coupling the polystyrenes of different chain lengths with aldehyde **19**. These copolymers are quite soluble in most organic solvents.

Structural Characterization. The structure of the oligothiophenes were characterized both spectroscopically and analytically. The combustion analysis results are consistent with all of the expected structures. The ^{13}C NMR spectra of these oligomers become more complicated as the number of repeating units increases. However, the ^{1}H NMR spectra are still assignable. For example, the overall integration ratio between the aliphatic protons and the aromatic protons is consistent with the composition of the different oligomers. A tentative assignment of the ^{1}H NMR spectra for compound **12** and its corresponding aldehyde derivative **19** is shown in Figure 1, where three of the chemical shifts appear at 7.28, 7.36, and 7.41 ppm due to the end-capping phenyl group. The terminal thiophene exhibits two doublets at 6.88 and 7.10 ppm for compound **12**. After formylation, the later peak disappears while the former peak shifts to 7.52 ppm and becomes a singlet peak. The chemical shift of the formyl proton appears at 9.75 ppm. All the chemical shifts in the aliphatic region are typical of hexyl groups.

In the FTIR spectra of oligothiophene **12**, a very weak absorption band at 3106 cm^{-1} could be attributed to the terminal $=C-H_\alpha$ stretching, which disappears after compound **12** was converted into its aldehyde derivative. The strong C=O stretching band at 1667 cm^{-1} for aldehyde **19** also disappears after it was coupled with living polystyrenes.

UV/vis spectra of the oligothiophenes in chloroform exhibit trends well correlated with the number of repeating units of the oligothiophenes (Figure 2). As the number of repeating units increases, the maximum absorption wavelength also increases nonlinearly and reaches a plateau at approximately nine repeating units. Similar trends were observed for the maximum emission wavelength. The extinction coefficient increases linearly with the number of repeating units because the oscillator strength of the molecules increases in the same manner. Similar to the nonsubstituted oligothiophenes, the maximum absorption wavelength of this system can be correlated to a linear relationship with the reciprocal of the number of the thiophene units, 1/*n* (phenyl ring is not included), which is different from the results reported by Bäuerle et al.[13] This correlation exists even after including the results for the polymer (456 nm with about 154 repeating units).[14] However, the maximum emission wavelength deviates significantly from the linear relationship with 1/*n*.

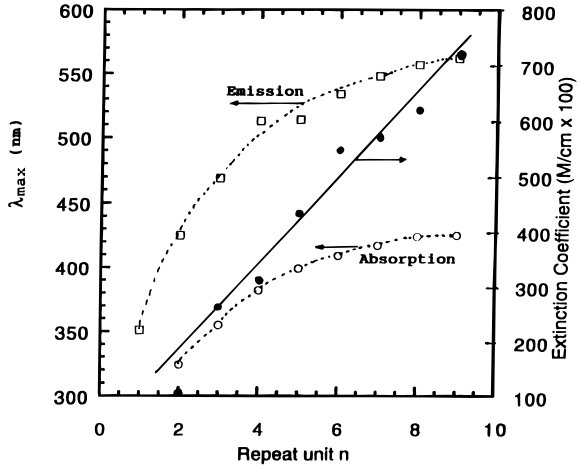


Figure 2. The absorption maxima, extinction coefficients, and the emission maxima of the oligothiophenes as a function of the number of repeating units.

The solid-state UV/vis spectra of the oligothiophene films showed the absorption maxima for the π-π^* transition of compounds **10**, **16**, and **12** at 436, 450, and 456 nm, respectively (Table 1). The red shifts of the absorption maxima in the solid state relative to those in the solution are about 20 nm. The solid-state absorption maxima of these compounds are much lower than those of the poly(3-hexylthiophenes) (526, 560, 610 nm;[14] 504 nm[15]), possibly due to the less effective π-stacking in these oligothiophenes.

The results of the UV/vis study of the diblock copolymers are shown in Figure 3. Polystyrene has an

Table 1. Physical Properties of the Oligothiophenes

compd	no. of thiophene	λ_{max},[a] nm	$\epsilon_{max} \times 10^{-4}$ [L mol^{-1}cm^{-1}]	λ_{max},[b] nm	E_{ox},[c] V
13	2	324	1.04	425	
9	3	355	2.65	454, 469	1.28
14	4	382	3.11	488, 513	1.16
11	5	399	4.35	514	1.21
15	6	409	5.47	534	1.12
10	7	417 (436)	5.67	548	1.15
16	8	424 (450)	6.20	557	1.11
12	9	425 (456)	7.16	562	1.15

[a] Absorption maxima in $CHCl_3$; numbers in parentheses are absorption maxima in the solid state. [b] Fluorescence maxima in $CHCl_3$. [c] Oxidation potential E_{ox} vs Pt.

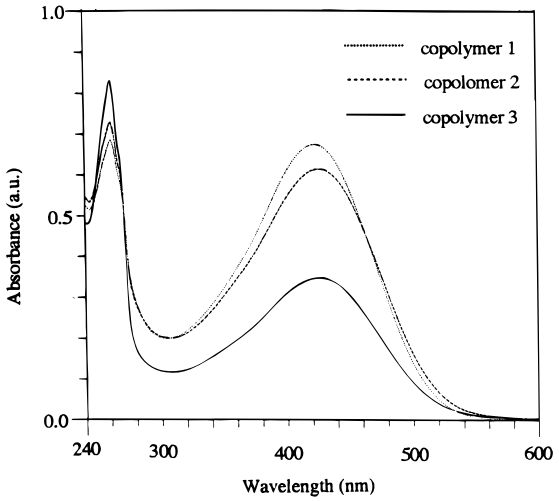


Figure 3. The absorption spectra of the copolymers.

Table 2. GPC and DSC Results of the Homopolymers and Copolymers

polymer	M_n[a]	P_d[b]	W_{ot}[c]	T_g, °C
homopolymer **1**	6300	1.12		91
copolymer **1**	9000	1.12	0.20	87
homopolymer **2**	8900	1.15		92
copolymer **2**	11600	1.16	0.15	91
homopolymer **3**	20600	1.14		101
copolymer **3**	23300	1.15	0.07	102

[a] Number average molecular weight based on polystyrene standards. [b] Polydispersity. [c] Weight fraction of oligothiophene block in diblock copolymers.

absorption maximum at 260 nm. Oligothiophene **12** exhibits absorption maxima at both 260 and 426 nm. The absorption spectrum of the copolymer consists of the mixture of these two components. As we expected, the increase in the weight fraction of the oligothiophene in the copolymer system leads to an increase in the intensity ratio of 426 nm:260 nm.

The molecular weights and polydispersities of the polystyrenes before and after coupling to the aldehyde were characterized using GPC (Table 2). The polydispersities of both polystyrenes and copolymers are slightly deviated from 1, ranging between 1.12 and 1.16 due to the lack of a high vacuum setup in our lab at present. The coupling reaction does not significantly broaden the polydispersity of the polystyrene.

Thermal and Physical Properties. Cyclic voltammetric studies for the oligothiophenes were performed at 5 °C (Pt as the reference electrode, Bu_4NBF_4 as the electrolyte). For each molecule, there exists an oxidation process. The general trend is that the oxidation potential decreases as the number of thiophene repeating units increases. For example, the E^0 values for compounds with $n = 3$, 5, 7, and 9 are 1.28, 1.21, 1.15, and 1.15 V and for those with $n = 4$, 6, and 8 are 1.16, 1.12, and 1.11 V, respectively (Table 1). However, due to the uncertainty associated with the experiment and the small difference in the oxidation potentials between the close neighbors, a clear-cut relationship between the repeating units and the oxidation potential was not observed and the above results should be viewed with caution.

The thermal properties of these copolymers were investigated by TGA and DSC measurements. TGA thermograms showed that the decomposition temperatures for all of the copolymers are above 380 °C, at which the polystyrene backbone starts to decompose. The DSC study indicated that the glass transition temperatures (T_g) of the copolymers increase as the chain becomes longer, similar to the corresponding polystyrene homopolymers (Table 2).

The microphase separation behavior of these block copolymers was examined by transmission electron microscopy (TEM). Ultrathin films were prepared by spin-coating a 2% solution of the copolymer in toluene onto silicon nitride substrates, which consisted of a 100 nm thick silicon nitride layer deposited on a silicon wafer. In some small areas the silicon was selectively etched away, providing TEM-transparent silicon nitride membranes. The films were annealed at different temperatures ranging from 100 to 150 °C and stained by different staining techniques. Unfortunately, no microphase morphology was observed in this system. From earlier theoretical work[16,17] it is known that the morphological features of diblock copolymer systems are dependent upon both the molecular weight and composition of the copolymers. Cohen's work[18] on the diblock copolymers of norbornene and 5-((trimethylsiloxy)-methyl)norbornene revealed that microphase separation cannot occur at relatively low molecular masses. We do not know the exact volume fractions in our diblock copolymer system because of a lack in the density of the oligothiophenes. However, judging from the weight fractions (Table 2), we can assume that they are relatively low. The low molecular weight and small volume fraction of the oligothiophene in the copolymer system could be the major factors which result in the absence of the microphase separation phenomenon. More detailed studies, including the synthesis of longer oligothiophenes and the development of different TEM sample preparations are still underway.

In summary, we have synthesized a series of oligothiophenes with defined regiospecificity and molecular weights that are useful in defining the structure/property relationships. The formylation of these oligothiophenes yields aldehydes which can be coupled with living anionic polystyrene species to form diblock copolymers having a conjugated block. Three of these copolymers were synthesized and characterized by NMR, UV/vis spectrophotometer, GPC, TGA, and DSC. TEM measurements showed no microphase separation behavior in this system, possibly due to the low molecular weight and small volume fraction of the oligothiophene in the copolymer system.

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