Macromolecules **1998,** *31,* 9116−9120

Synthesis of Polymers with Isolated Thiophene-Based Chromophores

Elliad R. Silcoff and Tuvia Sheradsky*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received May 22, 1998; Revised Manuscript Received October 1, 1998

ABSTRACT: The polymers presented in this paper are designed for the intended use in light-emitting diodes. The synthesis of a new series of macromolecules containing isolated oligothiophene, oligothienylene vinylene, or bithiazole conjugated units bridged by aliphatic units is presented along with optical characterization by UV−vis absorption and fluorescence spectra in solution. These polymers gave very similar optical traits to their corresponding subunits while possessing the physical characteristics of a macromolecule.

Introduction

Electroluminescent polymers are presently becoming a viable alternative to inorganic filaments in micro-optoelectronic devices such as light-emitting diodes (LEDs).[1−3] Polymers such as poly(1,4-phenylene vinylene) (PPV), polyphenylene (PPP), and polythiophene (PT) are now in regular use. However, these have certain drawbacks, mainly low quantum yields[4] which result from the high level of freedom of the excited-state polaron species in its returning to the ground state. These possess numerous modes of decay other than photon emission, such as thermal decay and inter band crossing.[5] Another clear drawback in such polymers is a very broad bandwidth due to the relatively undefined chromophore unit. These problems do not exist or are less prevalent in monomers and short oligomers.

Consequently, to improve performance, small conjugated luminescent units can be connected by a saturated unit with no activity in the desired optical range, to form macromolecules.[6−8] This will curb the freedom of movement of the singlet exciton[5] and, thus, will overcome the problem of the low quantum yield. This effect will be amplified by the fact that the chromophore is "diluted" with the nonsaturated segment, decreasing the effect of aggregates. Furthermore, it can be reasonably assumed that the optical traits of the resulting copolymer will be similar to those of the conjugated monomer. As a result, these traits can be tuned by changing the conjugated unit used. This procedure has been put into practice previously most notably by Hadziioannou and co-workers in the synthesis of oligothiophene dibutyl silane copolymers.[8]

To further test this suggestion, we have now synthesized new, precisely structured polymers with alternating conjugated and nonconjugated units (Figure 1). These polymers provide an attractive and promising approach to the preparation of a series of different light-emitting devices. The light-emitting units can consist of either subsections of existing conjugated polymers (PT, PTV, etc.) or of any number of organic luminescent molecules known in the literature, including dyes and pigments, derivatized to make their polymerization possible. In this paper the syntheses of three series of such polymers are presented, those based on the oligothiophene, the oligothienylene vinylene, and the bithiazole unit.[9]

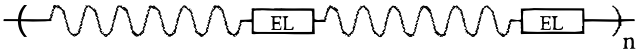

Figure 1. The general layout of polymers with isolated conjugated units.

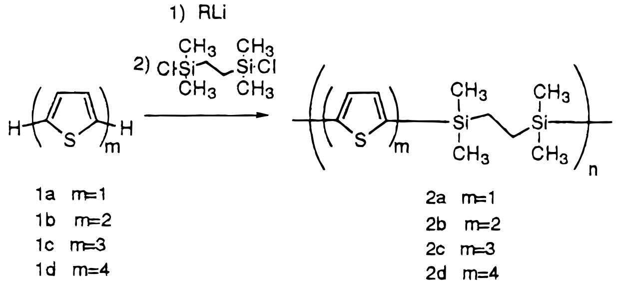

Figure 2. Synthesis of oligothienylene alkylsilyl polymers.

Results and Discussion

Polythiophene, usually synthesized by electrochemical polymerization of thiophene or by organometallic coupling,[9] has long been one of the leading conjugated polymers in the field of electro-optics. The ease of its synthesis and processing along with the relatively good electro-optical characteristics has made it a favorite, second only to polyphenylene vinylene (PPV), in the preparation of LEDs. Therefore, its subunits, thiophene and its oligomers, are good candidates for use in this research endeavor.

Thiophene (**1a**), 2,2′-bithiophene (**1b**), 2,2′:5′,2″-terthiophene (**1c**), and 2,2′:5′,2″:5″,2‴-quaterthiophene (**1d**), prepared by procedures reported in the literature[10,11] on the basis of the nickel complex catalyzed Grignard reactions, were used as PT subunits. These were converted to the dilithio derivatives by the action of 2 equiv of butyllithium in THF under an inert atmosphere and subsequently polymerized by reaction with the nonconjugated spacer molecule 1,2-bis(chlorodimethylsilyl)ethane (Figure 2). This spacer was chosen because of the high reactivity of the silicon−chloride bond, with the hope of keeping reaction yields high, even at higher molecular weights. The polymers were all of relatively low molecular weight ($M_n = 5000-10000$) with very low dispersities. All polymers showed better solubility than the monomers and showed no signs of decomposition at 300 °C.

The UV−vis and fluorescence spectra of the polymers (see Table 1) were measured and compared to those of

10.1021/ma9808171 CCC: $15.00

Table 1. Polymerization and Optical Results for (2) (Polymerization for 18 h at room temperature)

polymer	yield[a] (%)	M_w	M_n[12]	MWD	color	λ(abs) (nm)	λ(em) (nm)
2a	56	8.7×10^3	8.8×10^3	1.003	colorless	257[b]	386[a]
2b	49	8.0×10^3	8.0×10^3	1.003	tan	308[b]	460[a]
2c	38	8.4×10^3	8.3×10^3	1.006	yellow	350[b]	525[a]
2d	27	8.9×10^3	8.8×10^3	1.010	orange	391[c]	535[b]

[a] Isolated yield. [b] 10^{-6} M solution in chloroform. [c] 10^{-6} M solution in THF.

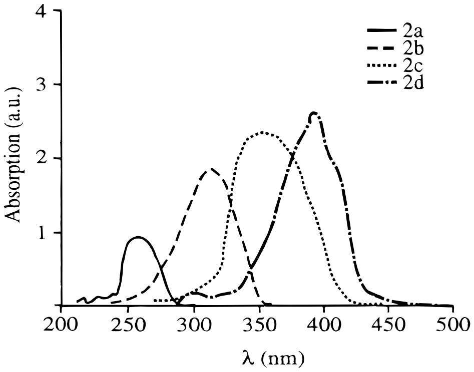

Figure 3. The absorption spectra of polymers (2a–d).

the corresponding oligomers. In all cases they were identical within experimental error. There was a sequential change with the increase in both wavelength and intensity becoming smaller as a function of the increase in the number of linked thiophenes (*m*) (Figure 3). The bandwidths in these cases were less broad, about 70 nm at half the signal height as compared to over 170 nm for PT.[13] These polymers proved inert to typical doping media such as sulfuric acid and perchloric acid.[14,15]

Poly(thienylene vinylene) (PTV) is generally very similar in many of its properties to its better-known derivative PPV; however, its electro-optical characteristics differ in that PTV is not considered electroluminescent, only giving off light at the high potential of $3.881 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1}$ at room temperature.[16] This is assumed to be due to the easy migration of excitons to quench sites.[17] In the corresponding oligomers migration would be limited and it is expected that these decay modes would be averted. Furthermore, the higher chemical reactivity of the thiophene ring (as compared to that of the benzene ring) would facilitate the synthesis of the copolymers.

The subsections of PTV, *E*-1,2-di-2-thienylethylene (**3a**), *E*,*E*-2,5-bis[2-(2-thienyl)ethenyl] thiophene (**3b**), and *E*,*E*,*E*-2,2′-(1,2-ethendiyl)bis[5-[2-(2-thienyl)ethenyl]thiophene (**3c**) were all synthesized according to the literature,[18,19] using the McMurry coupling[20] for molecules containing an even number of thiophenes and the Wittig reaction[21] for molecules containing an odd number of thiophenes. All double bonds were the *E*-configuration as was evident from the NMR spectra.

Monomers **3** were polymerized, as in the previous section, first by dilithiation followed by the reaction with the previously presented spacer, 1,2-bis(chlorodimethylsilyl)ethane (Figure 4). Once again, the polymers were of relatively low molecular weight ($M_n = 7000-8000$), with low dispersities. They showed good thermal stability with only a mild weight loss after 1 h at ~300 °C. All the above-mentioned macromolecules were soluble in most organic solvents. These solutions exhibited, upon illumination, an emission of light in the visible range with λ_{max} ranging from 386 to 535 nm (see Table 2).

As in the case of the oligothiophene polymers, a sequential change in the wavelength and the intensity of the UV–vis spectra was observed (Figure 5). Although this change was not pseudoasymptotic as in the previous series, that behavior was previously observed in larger oligomers.[19,22]

Combining the structural features of the monomers in the two polymer series described above gives molecules of the type oligo(oligothienylene) vinylene. Of these the most simple example is that of the substance (**5**), *E*-1,2-bis(2,2′-bithiophene-5-yl)ethylene,[23] which is a combination of 2,2′-bithiophene (**1b**) and *E*-1,2-di-2-thienylethylene (**3a**). This monomer was prepared in a manner similar to monomers based on thienylene vinylene, by the functionalization of bithiophene using the Vilsmeier reaction, followed by coupling by the McMurry reaction with titanium(IV) chloride and zinc. The product gave a very strong fluorescence spectra with a maximum at ~540 nm.

However, in this case the dilithio derivative was unreactive, probably because of charge delocalization in the molecule. As a result, an indirect method in which the McMurry generation of the double bond served as the polymerization step was undertaken. Bithiophene was first reacted with 1 equiv paraformaldehyde to give 5-(hydroxymethyl)-2,2′-bithiophene (**6**).[24,25] Subsequently, two molecules of the sodium salt of (**6**) were joined by reaction with the highly reactive 1,2-bis[3-(bromomethyl)phenyl]ethane[26] to give the adduct (**7**). After dicarbonylation via the Vilsmeier reaction, the aldehyde groups were joined via a McMurry polymerization to give the polymer (**9**). This method of polymerization gave considerably higher molecular weights, but a much less uniform dispersity. Once again the final optical characteristics were similar to the corresponding monomeric conjugated units characteristics.

Unlike the first two series of polymers which can be classified as polymers containing subsections of known conjugated polymers, polymers containing the bithiazole group can be categorized as polymers made from coloring agents or dyes. The bithiazole group is a well-known coloring agent[27,28] with a strong light absorbance in the range of ~350 nm and strong photoluminescence. Recently, the bithiazole has been polymerized and has shown itself to be a good redox polymer.[29]

Preliminary reaserch as to the effect of the spacer in conjugated–nonconjuaged AB copolymers suggests that the effect of the spacer unit is minimal.[30,31] However, these have been done on PPV-based systems. Thiophene and thiophene-like systems have yet to be examined. To check whether the aliphatic spacer would, in some way, have an effect on the optical traits of thienyl polymers, we have synthesized this series of three polymers in which the bithiazole units were connected by different spacers.

Because of the ease of its synthesis,[33] the specific bithiazole group used was 4,4′-dimethyl-2,2′-bithiazole. A mixture of chloroacetone and dithiooxamide was refluxed in ethanol for several hours, yielding the

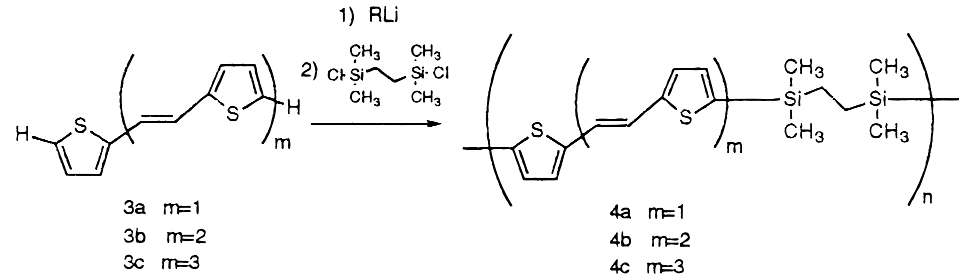

Figure 4. Synthesis of thiophenyl oligothienylene vinylene alkylsilyl polymers.

Table 2. Polymerization and Optical Results for (4)

polymer	yield[a] (%)	M_w	M_n[12]	MWD	color	λ(abs)[c] (nm)	λ(em)[c] (nm)
4a	73	8.0×10^3	7.8×10^3	1.019	yellow	340	420
4b	60	7.9×10^{3}[b]			orange	405	480
4c	74	7.1×10^3	7.1×10^3	1.008	red	456	520

[a] Isolated yield. [b] By NMR end-group analysis. [c] Optical data from a filtered 10^{-6} M solution in chloroform.

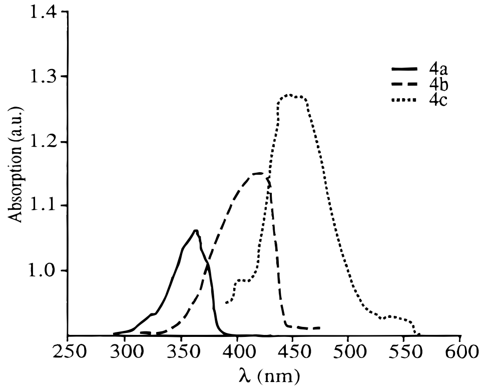

Figure 5. The absortion spectra of polymers (4a–c).

bithiazole system in one step. The bithiazole was then polymerized in a similar manner as before, with butyllithium followed by the addition of a chlorosilane-containing spacer. In this case, two such spacers were used, the standard 1,2-bis(chlorodimethylsilyl)ethane used in the previous two cases and dichlorodimethysilane. The nickel-catalyzed reaction of the di-Grignard reagent of 1,6-dibromohexane with the dibromo derivative of the bithiazole (Figure 8) was used to prepare the third polymer of the series.

All three polymers had similar, yet not identical, UV–vis and fluorescence spectra (see Table 3) with a mild blue shift of approximately 13 nm in the absorption of the polymer with the shorter spacer (**11b**). This can be attributed to the crowding in the area of the spacer chromophore boundary. This may likely cause a small deformation of the practically planar bithiazole group, accounting for the higher energy absorbance. The other two polymers with the greater conformational freedom showed nearly identical spectra. This supports the data showing that the effect of the spacers on the total optical characteristics is virtually negligible.

These new series of polymers, based on the preliminary results, show a good likelihood of being functional for use in LEDs in the future. They gave satisfactory films both on glass and indium tin oxide (ITO). Therefore, they should give positive solid-state photo-optic and electro-optic results. As a result, making a series of LEDs with different wavelengths and electrical conductivity should be feasible. These experiments are now in progress.

Experimental Section

Instrumentation. NMR spectra were measured on either a Bruker DRX-400 or AMX-300 spectrometer. Melting points were determined using a Phillips Mel-TempII apparatus. UV–vis spectra were measured on a Kontron UVIKON 860 spectrophotometer. Fluorescence was measured on a Kontron SFM25 fluorimeter. Molecular weights of the polymers were estimated on a gel permeation chromatography (GPC) system consisting of a Spectra Physics P1000 pump, an Applied Bioscience 759A UV detector relative to polystyrene standards (Polyscience) with molecular weights of 4000, 5570, 9100, and 22000. Elemental analysis was performed by the Microanalysis Laboratory, the Hebrew University of Jerusalem.

Materials. All reagents were purchased from Aldrich Chemical and were used as received. Solvents were purchased from Frutarom. THF was distilled from sodium and benzophenone. Hexane was dried with sodium. Column chromatography was conducted with silica gel, 200–400 mesh (Merck). TLC, analysis was conducted on silica gel 60 plates with a F_{254} indicator (Merck). *Bi*, *ter*, and *quater*thiophene (**1a**, **1b**, and **1c**),[11] *E*-1,2-di-2-thienylethylene, *E*,*E*-2,5-bis[2-(2-thienyl)ethenyl]thiophene, and *E*,*E*,*E*-2,2′-(1,2-ethendiyl)bis[5-[2-(2-thienyl)ethenyl]thiophene (**3a**, **3b**, and **3c**),[19] *E*-1,2-bis(2,2′-bithiophene-5-yl)ethylene (**5**),[19] 5-(hydroxymethyl)-2,2′-bithiophene (**6**),[24,25] 4,4′-dimethyl-2,2′-bithiazole,[32] and 5,5′-dibromo-4,4′-dimethyl-2,2′-bithiazole (**10**)[33] were prepared according to the literature. All polymers were identified by proton NMR and IR measurements and in all cases the results were as expected.

Polymers (2). A solution of 10 mmol of the thiophene oligomer in 75 mL of dry THF was added to an ice-cooled solution of 12.5 mL of butyllithium (1.6 M in hexane, 20 mmol), 5 mL of *n*-hexane, and 10 mL of dry THF under a N_2 atmosphere. The ice bath was removed and the mixture was stirred for 30 min. A solution of 2.15 g (10 mmol) of 1,2-bis(chlorodimethylsilyl) ethane in 20 mL of dry THF was then added slowly and the solution was stirred overnight. The reaction was quenched with 50 mL of ice water and the product extracted in dichloromethane. The organic phase was dried with $MgSO_4$ and evaporated to give the crude polymer. Recrystallization from ethyl acetate–petroleum ether was performed to purify the polymers.

Polymers (4). A solution of 10 mmol of the thienyl oligothienylene vinylene in 40 mL of dry THF was added to an ice-cooled solution of 13.75 mL of butyllithium (1.6 M in hexane, 22 mmol), 10 mL of *n*-hexane, and 10 mL of dry THF under a N_2 atmosphere. The ice bath was removed and the mixture was stirred for 30 min. A solution of 2.15 g (10 mmol) of 1,2-bis(chlorodimethylsilyl)ethane in 20 mL of dry THF was added slowly and the solution stirred overnight. The reaction was quenched with 50 mL of ice water and the product extracted in ether. The organic phase was dried with $MgSO_4$

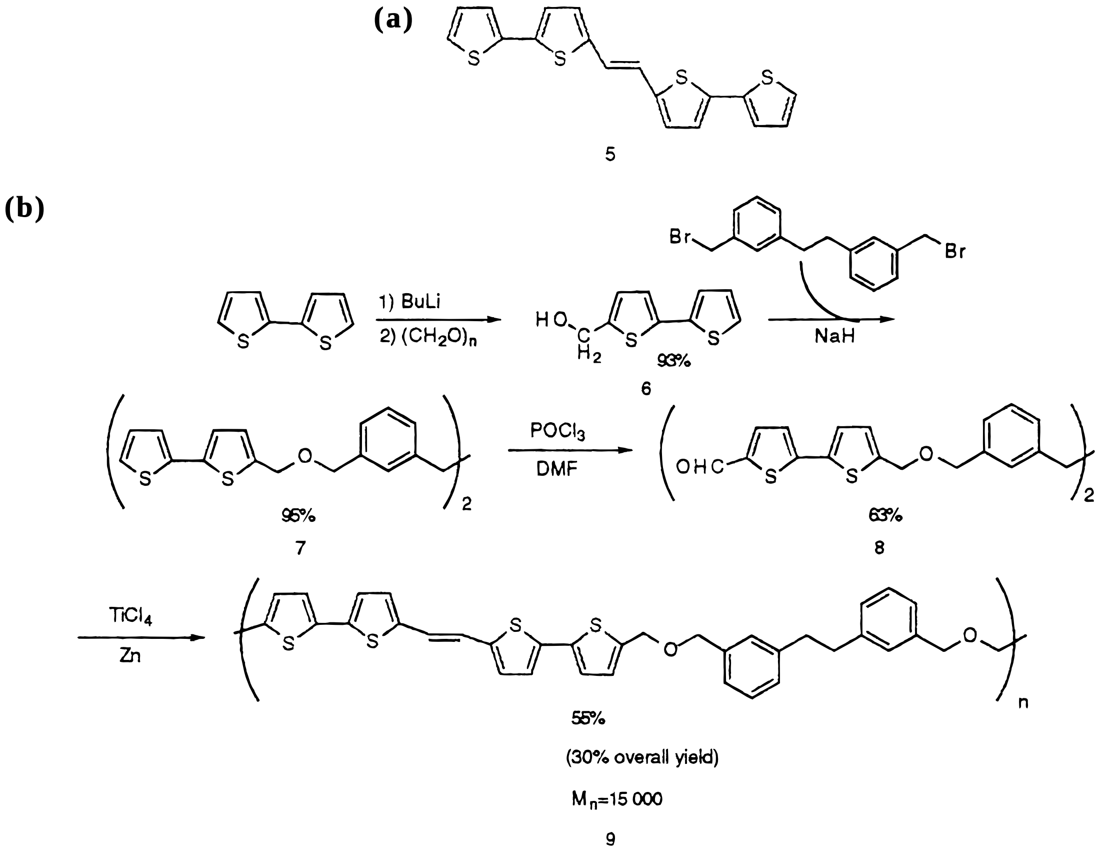

Figure 6. (a) The monomeric unit (5). (b) Synthesis of a bithiophenylene vinylene polymer (9).

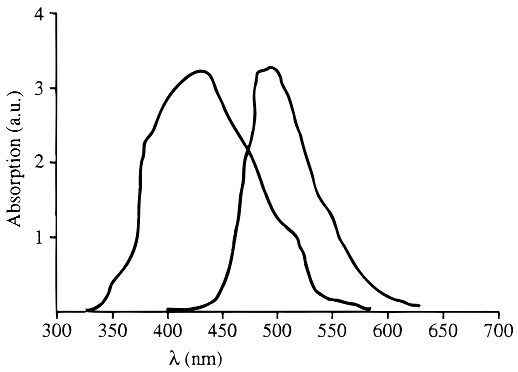

Figure 7. The absorption and emission spectra of polymer (9) (10^{-8} M in THF).

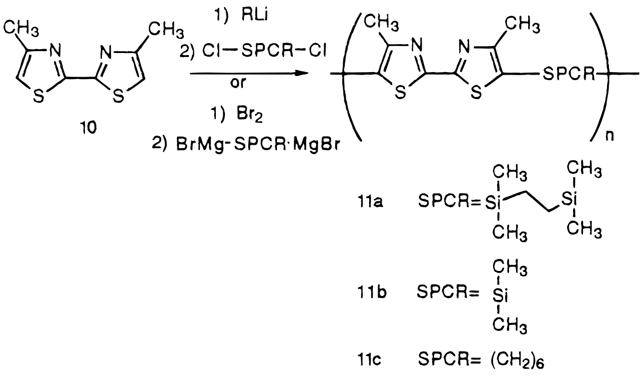

Figure 8. Synthesis of bithiazole-based polymers. (SPCR = aliphatic spacer).

and evaporated to give the crude polymer. Recrystallization from dichloromethane−petroleum ether was performed to purify the polymers.

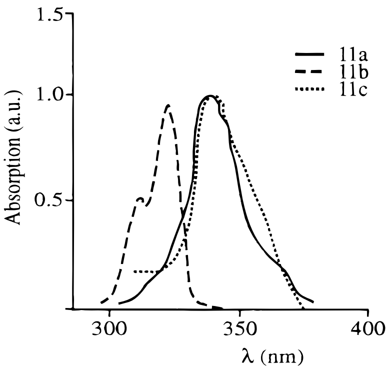

Figure 9. The absortion spectra of polymers (11a−c).

Table 3. Polymerization and Optical Results for (11)

polymer	yield[a] (%)	M_w	M_n[12]	MWD	λ(abs)[b] (nm)	λ(em)[b] (nm)
11a	43	6.8×10^3	6.8×10^3	1.003	340	450
11b	67	8.0×10^3	8.0×10^3	1.003	327	450
11c	20	8.4×10^3	8.3×10^3	1.006	342	450

[a] Isolated yield. [b] Optical data from a filtered 5×10^{-4} M solution in chloroform.

Compound (7). To a solution of 1.6 g (8.15 mmol) of 5-hydroxymethyl-2,2′-bithiophene in 40 mL of dry THF was added 0.41 g (10.2 mmol, 1.25 equiv) of a 60% NaH emulsion at 0 °C. To this was added a solution of 1.48 g (4.07 mmol) of 1,2-bis[3-(bromomethyl)phenyl]ethane in 30 mL of dry THF over 45 min. The mixture was stirred overnight and poured onto ice water. The organic matter was taken up into chloroform, rinsed with 10% NaOH and water, and evaporated to give the crude product. Recrystallization from ether−petroleum ether gave 1.4 g (2.22 mmol, 54%) of the pure product as a yellow solid. m.p. 212−4 °C. ^{1}H NMR (ppm): 4.4, s, 4H; 4.65, s, 4H; 4.8, s, 4H; 6.9−7.5, m, 18H. Elemental analysis for $C_{34}H_{30}O_2S_4$: calcd. C, 68.2; H, 5.05; S, 22.0. Found C, 68.5; H, 5.00; S, 21.5.

Compound (8). At 0 °C, 0.61 g (4 mmol, 0.45 mL) of phosphorusoxychloride and 5 mL of dry DMF were mixed for 30 min. To this mixture was added a solution of 1.4 g (2.22 mmol) of (**7**) in 10 mL of DMF and heated at 100 °C for 6 h. After being quenched with ice water, the product was isolated from the mixture by extraction with chloroform followed by repeated rinsings with sodium bicarbonate, brine, and several times with water. Evaporation gave the crude product as a thick oil (0.9 g, 1.37 mmol, 61%). ^{1}H NMR (ppm): 4.4, s, 4H; 4.6, s, 4H; 4.8, s, 4H; 7.0−7.4, m, 16H; 9.9, s, 1H. IR (C═O) 1640 cm^{-1}.

Polymer (9). A solution of 0.66 g (1 mmol) of (**8**) in 30 mL of dry THF under an N_2 atmosphere was cooled to −20 °C. Over 30 min 0.23 g (0.13 mL, 1.2 mmol) of $TiCl_4$ was added and the solution was stirred at this temperature for an additional 15 min. Zinc (0.39 g, 5 mmol) was added in portions over 30 min. The mixture was warmed to room temperature, stirred for 30 min, and then refluxed for 4 h. The reaction mixture was cooled and then quenched with 100 mL of a water/ice mixture. The slurry was filtered and the solid extracted with 50 mL of dichloromethane. The organic solution was filtered and worked up in the standard manner to give a brown solid. The solid was recrystallized in an ethanol:water 1:1 mixture to give 0.44 g of the polymer (**9**) as on orange solid. $M_n = 17 \times 10^3$, $M_w = 14 \times 10^3$, MWD = 1.22, isolated yield = 55%.

Polymers (11a) and (11b). A turbid solution of 1.96 g (10 mmol) of 4,4′-dimethyl-2,2′-bithiazole in 100 mL of dry THF was added to an ice-cooled solution of 13.75 mL (1.6 M in hexane, 22 mmol) of butyllithium, 5 mL of *n*-hexane, and 10 mL of dry THF under a N_2 atmosphere. The ice bath was removed and the mixture was stirred for 30 min. A solution of 2.15 g (10 mmol) of 1,2-bis(chlorodimethylsilyl)ethane or 1.57 g (1.47 mL, 10 mmol) of dimethyldichlorosilane in 20 mL of dry THF was added slowly and the solution was stirred overnight at 50 °C. The reaction was quenched with 50 mL of ice water and the product extracted with several portions of chloroform. The organic phase was dried with $MgSO_4$ and evaporated to give the crude polymer. Recrystallization from hot chloroform was performed to purify the polymers.

Polymer (11c). A mixture of 2.68 g (1.65 mL, 10 mmol) of 1,6-dibromohexane and 0.61 g (25 mmol) of Mg turnings in 50 mL of dry ether were refluxed until the Mg was mostly consumed. The resulting solution was added to a turbid solution of 1.96 g (10 mmol) of 5,5′-dibromo-4,4′-dimethyl-2,2′-bithiazole and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2) (0.2 g, ∼3.7 mol %) in 100 mL of dry THF under N_2 and was refluxed overnight. The reaction was quenched with 100 mL of ice water and the product extracted with several portions of chloroform. The organic phase was dried with $MgSO_4$ and evaporated to give the crude polymer. Recrystallization from hot chloroform was performed to purify the polymer.

Acknowledgment. We thank the late Professor J. Klein and Professor I. Willner for helpful discussions and Professor A. Domb and Doron Teomim for their help in the determination of the molecular weights. This research is funded by the Israeli Ministry of Sciences.

References and Notes

(1) Kraft, A.; Grimsdale, L.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402−428.
(2) Service, R. T. *Science* **1996**, *273*, 878−880.
(3) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93−116.
(4) Bradley, D. D. C. *Synth. Met.* **1993**, *54*, 401−415.
(5) Bradley, D. D. C.; Friend, R. H. *J. Phys.: Condens. Matter* **1989**, *1*, 3671−3678.
(6) Spangler, C. W.; Liu, P.-K.; Hall, T. J.; Polis, D. W.; Sapochak, L. S.; Dalton, L. R. *Polymer* **1992**, *33*, 3937−3941.
(7) Yoshino, K.; Hosoda, K.; Fujii, A.; Ishikawa, M. *Jpn. J. Appl. Phys.* **1997**, *36*, L368−L371.
(8) Garten, F.; Hilberer, A.; Cacialli, F.; van Dam, Y.; Schlatmann, B.; Friend, R. H.; Klapwijk, T. M.; Hadziioannou, G. *Adv. Mater.* **1997**, *9*, 127−131.
(9) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912.
(10) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347−3354.
(11) Donat-Bouillud, A.; Mazerolle, L.; Leclerc, M. *Synth. Met.* **1997**, *84*, 235−236.
(12) Molecular weights measured by GPC were within 5% of the weights found by NMR end-group analysis.
(13) Compared to poly(3-hexylthiophene). Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212−215.
(14) Kalaji, M.; Peter, L. M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 853−860.
(15) Imae, I.; Nawa, K.; Ohsedo, Y.; Noma, N.; Shirota, Y. *Macromolecules* **1997**, *30*, 380−386.
(16) Härtel, M.; Kossmehl, G.; Manecke, G.; Wille, W.; Wöhrle, D.; Zerpner, D. *Angew. Makromol. Chem.* **1973**, *29−30*, 307−347.
(17) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States 6*; Lim, E., Ed.; Academic Press: New York, 1992; p 87.
(18) Kossmehl, G.; Härtel, M.; Manecke, G. *Makromol. Chem.* **1970**, *131*, 15−36.
(19) Nakayama, J.; Fujimori, T. *Heterocycles* **1991**, *32*, 991−1002.
(20) Furstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442−2469.
(21) Maercker, A. *Org. Reac.* **1965**, *14*, 270−490.
(22) Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, *119*, 10774−10784.
(23) Nakayama, J.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1986**, *24*, 2639−2643.
(24) Schaap, A.; Brandsma, L.; Arens, J. F. *Recuil* **1965**, *84*, 1200−1202.
(25) Krishnaswami, N. R.; Siva Sai Kamana Kumar, Ch. *J. Chem. Res., Miniprint* **1991**, 1801−1803.
(26) Takahashi, S.; Mori, N. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2029−2032.
(27) Karrer, P.; Leiser, P.; Graf, W. *Helv. Chim. Acta* **1944**, *27*, 624−625.
(28) Karrer, P.; Sanz, M. C. *Helv. Chim. Acta* **1943**, *26*, 1778−1784.
(29) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Kubota, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1613−1614.
(30) Yang, Z.; Karasz, F. E.; Geise, H. J. *Macromolecules* **1993**, *26*, 6570−6575.
(31) Kim, H. K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M.; Cho, S.-W.; Park, J.-W. *Macromolecules* **1998**, *31*, 1114−1123.
(32) Longone, D. T.; Un, H. H. *J. Polym. Sci., Part A: Polym. Chem.* **1965**, *3*, 3117−3130.
(33) Audisio, G.; Catellani, M.; Destri, S.; Polli, B.; Traldi, P. *J. Heterocycl. Chem.* **1990**, *27*, 463−467.

MA9808171