Macromolecules **2004,** *37,* 8951−8958

Synthesis and Characterization of Poly(triarylamine)s Containing Isothianaphthene Moieties

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Received March 1, 2004; Revised Manuscript Received September 14, 2004

ABSTRACT: We report the synthesis, characterization, and properties of a new class of hole−transport dyes, poly(dithienylisothianaphthene phenyldiamine)s (poly-DTITNPDs). These polymers are characterized by the presence of a low band gap isothianaphthene (ITN) and triarylamine units in the main chain. A modified Ullmann polycondensation reaction using a phase-transfer catalyst was utilized to prepare these polymers. The optical, thermal, and electrochemical properties were studied and compared to those of poly(triphenyldiamine ether) without having an ITN group and poly(dithienylisothianaphthene) without having triarylamine groups in the main chain. The new polymers, reported here, exhibit improved thermal stability and higher glass-transition temperatures. The incorporation of ITN group into the main chain of a polytriarylamine causes an appreciable lowering of the band gap energy up to 1.6 eV. This results in light-harvesting hole−transport dyes having less mismatch with the solar spectrum. Moreover, these polymers exhibit reversible redox behavior and possess HOMO values of about −4.7 eV and LUMO values of about −2.9 eV.

Introduction

Organic semiconductor technology utilizing low molecular weight compounds as well as conjugated polymers belonging to the classes of triarylamines and thiophenes are widely studied for potential applications in solar cells,[1] organic light emitting diodes,[2] field effect transistors,[3] etc.

In the case of triarylamines, the HOMO energy value can be varied considerably in the range from −5 to −5.5 eV by chemical modification to suit the hole injection from electrodes.[4] In the case of thiophenes, the band gap energy or wavelength of maximum absorption (λ_{max}) can be varied over a wide range in the visible region up to 600 nm, mainly by variation of the LUMO energy value.[2a,5] Moreover, modification of the thiophene ring into benzo[*c*]thiophene results in a new class of compounds generally called isothianaphthenes, which are well known for their low band gap energy values of about 1 eV.[6] However, isothianaphthene monomers are relatively unstable and poly(isothianaphthene) is insoluble.

At present the most widely used polymeric materials for light absorption in polymer solar cells are substituted poly(*p*-phenylene vinylene)s and polythiophenes. These polymers exhibit an optical band gap (E_g) of about 2 eV and there is a considerable mismatch between λ_{max} and irradiance of solar emission (below 2 eV). Hence, the design and development of low band gap polymers with E_g below 2 eV shall decrease this mismatch of the absorption spectrum of the cell with the solar spectrum, resulting in enhanced photon harvesting. In this respect, low band gap polymers containing only a dithienylisothianaphthene moiety with solubilizing substituents[7,8] as well as copolymers of benzothiadiazole monomers and hole conducting 9,9-dialkyl fluorine[9] or *N*-alkylpyrroles[10] have been reported recently as novel light-harvesting dyes for application in solar cells.

For obtaining efficient low molecular weight light-harvesting dyes, we successfully incorporated an isothianaphthene moiety and triarylamine units into oligomers by Pd-catalyzed amination of 1,3-bis(5-bromothiophen-2-yl)isothianaphthene.[11] This allowed us to combine the efficient hole−transport property of the triarylamines and the low band gap nature of the isothianaphthene unit into one molecule, generating a new class of low molecular weight isothianaphthene phenyldiamines (ITNPD) with $E_g < 1.8$ eV for the first time, and they find application in vapor-deposited solar cells. To extend this concept to film-forming polymers soluble in usual solvents such as $CHCl_3$, toluene, etc., a suitable synthetic strategy should be developed for incorporating ITN and diarylamines in a polymer main chain. We earlier demonstrated that poly(triarylamine ether)s with and without solubilizing spacers are efficient photoconductive polymers which can be used in electro-optical applications such as photorefractive holography,[12] polymeric LEDs,[13] and solar cells.[14] The motivation behind this work is to develop new polymeric hole-conducting dyes combining the positive aspects of ITN and triarylamine moieties.

In this paper we report the synthesis and characterization of a series of a new class of polymers, poly(dithienylisothianaphthene phenyldiamine)s (poly-DTITNPDs), which carry ITN and triarylamine moieties in the main chain. Our approach was to improve the hole injection/transport properties of ITN-containing polymers by introducing triarylamine units into the main chain. Moreover, the poly(triarylamine)s which do not absorb in the visible region ($E_g \approx 3$ eV) become suitable as light-harvesting hole−transport dyes via introduction of an ITN group.[11] Thus, this facilitates the preparation of hole-transporting polymers with a band gap lower than 2 eV, which is essential for application in solar cells, as the solar spectrum has maximum flux below 2 eV. The optical, thermal, and electrochemical properties of this new class of polymeric materials are also reported here. For comparison of optical and electrochemical properties, two polymers, (1) poly(triphenyldiamine

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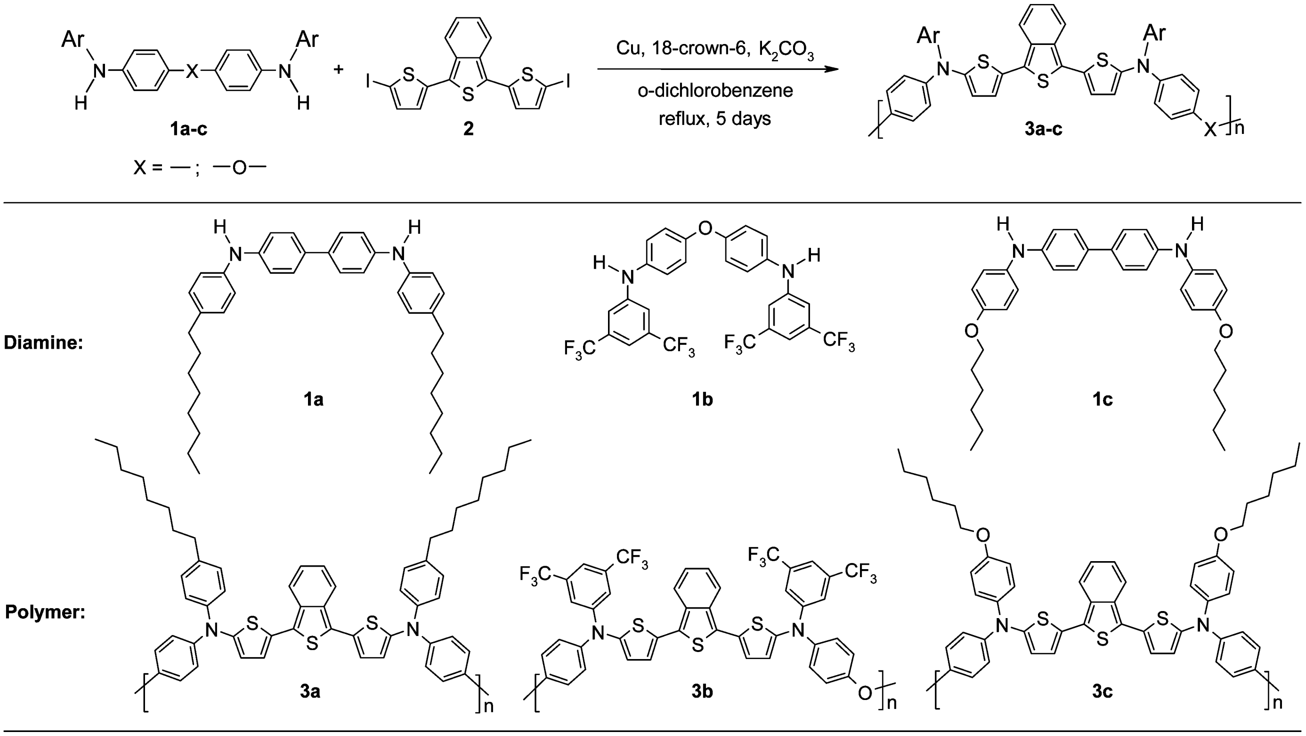
10.1021/ma0495947 CCC: $27.50

Scheme 1. Polycondensation of 1,3-Bis(5-iodo-2-thienyl)isothianaphthene (2) and Secondary Amines (1a−c) via Modified Ullmann Procedure in Absolute *o*-Dichlorobenzene Using Excess Cu in Combination with 18-Crown-6 as a Phase-Transfer Catalyst and K_2CO_3 as Base at 180 °C



ether) (poly-TPDE)[14] without an ITN group 6 and (2) poly(dithienylisothianaphthene) (poly-DTITN) without triarylamine groups in the main chain 7, were also synthesized and studied. In this way the effect of ITN and triarylamine groups in poly(DTITN)s on properties can be better understood.

Results and Discussion

First attempts to synthesize main-chain polymeric triarylamines by an Ullmann reaction from bis(secondary amine)s and diiodides resulted in oligomeric mixtures and insoluble products.[15] A modified Ullmann procedure[16] with 18-crown-6 as the phase-transfer catalyst was adopted by us for the synthesis of soluble and film-forming triarylamine polymers with appreciably high molecular weights.[12] On the other hand, Hartwig et al. reported oligomeric and polymeric triarylamines by Pd-catalyzed polymerization of bis(secondary amine)s and dibromides.[17] Two basic problems in using the Pd-catalyzed reaction for the synthesis of polymers were (1) hydrodehalogenation of aryl halide, limiting the formation of high molecular weight polymers, and (2) the concurring cyclization reactions leading to cyclic oligomers, which limits the molecular weight of the polymers.[17a] These difficulties could be only partially overcome by a suitable selection of phosphine ligands and using "oligomeric monomers" with meta- and para-linkages.[17b]

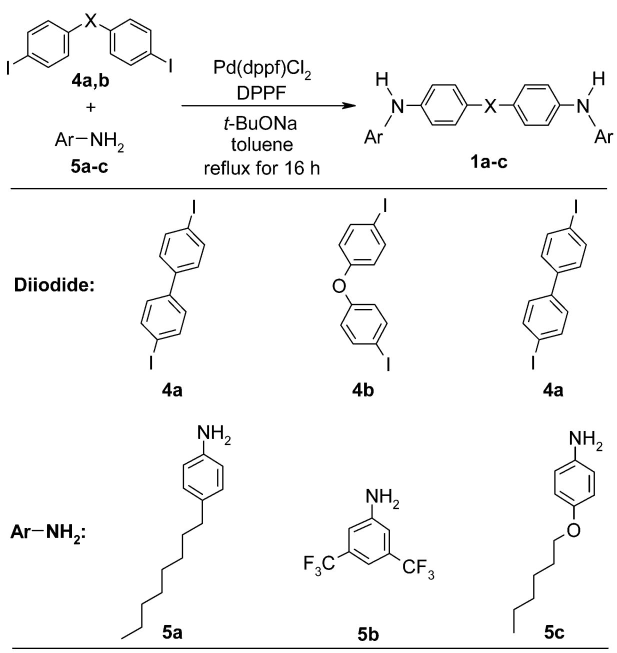
Therefore, we chose the modified Ullmann procedure for preparation of the target polymers. The synthetic route was selected in such a way as to obtain relatively high molecular weight poly[bis(diarylaminothienyl)isothianaphthene]s (**3a**−**c**) in good yields (see Scheme 1).

The polycondensation reactions of 1,3-bis(5-iodo-2-thienyl)isothianaphthene (**2**) and different secondary amines (**1a**−**c**) were carried out in absolute *o*-dichlorobenzene using excess Cu in combination with 18-crown−6 as a phase-transfer catalyst and K_2CO_3 as a base. Polymers **3a**−**c** were obtained as dark-brown solids. All the polymers possess solubility in common organic solvents, such as $CHCl_3$, THF, toluene, and xylene. Compounds **3a** and **3c** formed thin and stable amorphous films of high optical clarity by solution casting on glass substrates. The trifluoromethyl groups in polymer **3b** were selected with an aim to obtain hydrophobic material with a selective wetting property on substrates. Accordingly, we found that this polymer formed amorphous films only on hydrophobic substrates.

The starting diiodo compound, 1,3-bis(5-iodo-2-thienyl)isothianaphthene, **2,** was prepared by the iodination of 1,3-di(2-thienyl)isothianaphthene with *N*-iodosuccinimide in DMF at −55 °C by a similar procedure as that for its dibromo analogue, 1,3-bis(5-bromo-2-thienyl)-isothianaphthene, which was obtained by a three-step synthesis as reported earlier.[11]

The bis(secondary)amines (**1a**−**c**) were synthesized via Pd-catalyzed C−N coupling between anilines (**4a**−**c**) and diiodides (**5a,b**) by refluxing them with Pd(dppf)-Cl_2 in combination with DPPF and *t*-BuONa as a base in toluene for 16 h as shown in Scheme 2. The Pd-catalyzed amination of aryl halides was intensively and independently investigated by Buchwald[18] and Hartwig,[17] and an optimized procedure from the literature was adopted here.[19] For obtaining bis(secondary)amines in good yields, an excess amount of aniline was used which avoided formation of doubly substituted side products. In this way, the target monomers **1a**, **1b,** and **1c** were obtained in relatively good yields of 46%, 60%, and 79%, respectively. The final purification of **1a** and **1c** was carried out by washing with concentrated HCl and reprecipitation from concentrated THF solution into methanol. Monomer **1b** was purified by column chromatography with cyclohexane/ethyl acetate (5:1) as eluent.

Scheme 2. Synthesis of Bis(secondary amine)s 1a−c by Pd-Catalyzed Coupling of Diiodides 4a,b and Anilines 5a−c in the Presence of Pd(dppf)Cl$_2$, DPPF, and *t*-BuONa as Base in Toluene at 110 °C



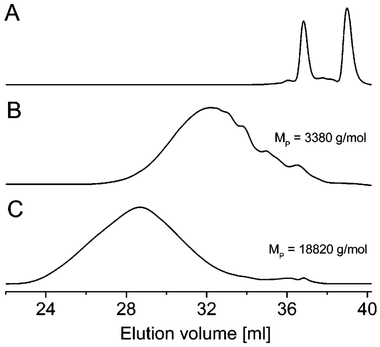


Figure 1. Monitoring of the polycondensation of **1c** and **2** via modified Ullmann procedure using SEC. SEC eluogram (A) of starting monomers **1a** and **2**, (B) precipitated product after 3 days reaction time, (C) precipitated polymer after 5 days reaction time.

Table 1. SEC Data of Polymers 3a−c Determined Using UV WAT 486 Detector (relative to polystyrene standards) with THF Containing 0.25 wt % of *tert*-Butyl Ammonium Bromide as Eluent

polymer	M_n (g/mol)	M_w (g/mol)	M_p (g/mol)	PDI
3a	10.480	127.520	146.580	12.1
3b	5.980	47.540	45.280	7.9
3c	7.240	28.990	18.820	4.0
6	4.240	12.010	8.040	2.8
7	9.160	26.390	11.240	2.9

The polymers were fully characterized by spectroscopic methods, such as FTIR, ^{1}H NMR, etc. (see Experimental Section). In polymers **3a**−**c** the strong IR absorptions at 3405−3419 cm^{-1} due to N−H stretching in compounds **1a**−**c** and 1189 cm^{-1} due to C−I stretching in compound **2** disappeared completely and the characteristic C−N stretching of amine at 1250−1314 cm^{-1} and characteristic C−H stretching of thiophene 742−746 cm^{-1} were observed in the products. Additionally, polymers **3a**−**c** exhibited characteristic aromatic absorptions at 3029−3064 cm^{-1} (C−H stretching) and 1492−1496, 1603−1617 cm^{-1} (C−C stretching) as well as characteristic aliphatic absorptions at 2851−2858, 2924−2928 cm^{-1} (C−H stretching). All the proton signals in the ^{1}H NMR spectra for monomers and polymers could be assigned accordingly. The end-group (iodine) analysis of these polymers exhibits only a negligible weight percent of iodine in the range of 0.02−0.03 wt %, indicating a high degree of polymerization.

With each polycondensation the progress of reaction was monitored by size exclusion chromatography (SEC). The SEC elution curves for the reaction between **1c** and **2** resulting in polymer **3c** are shown in Figure 1. Curve A represents the monomers, curve B represents the product obtained after 3 days of reaction, and curve C represents the polymer obtained after 5 days of reaction. It can be clearly seen that the discrete oligomers up to the pentamer stage formed in 2−3 days get converted into high molecular weight polymers with prolonged time of polymerization. Similar results were obtained for the polycondensations of **1a** and **1b** with **2,** resulting in appreciably high molecular weights of **3a** and **3b**.

The SEC data for all the polymers with polystyrene as standard and THF containing 0.25 wt % of *tert*-butylammonium bromide as eluent is given in Table 1. Polymers **3a**, **3b**, and **3c** exhibit number-average molecular weights (M_n) of 10 480, 5980, and 7240 g/mol, respectively. As expected for polycondensation, the polydispersity varies over a wide range between 4 and 12 depending on the reactivity and concentration of monomers. The weight-average molecular weights (M_w) for **3a**, **3b**, and **3c** are 127 520, 47 540, and 28 990 g/mol, respectively. The highest molecular weight (M_w) was obtained for polymer **3a** carrying octyl groups, and the lowest molecular weight was observed for polymer **3c** with hexyloxy groups, in agreement with the degree of solubility due to the corresponding side groups. To study the effect of the concentration of monomers on the polycondensation reaction, polymer **3a** was also prepared under more dilute reaction conditions (0.09 M instead 0.15 M). The resulting polymer has a lower molecular weight of M_n = 7730 g/mol, M_w = 23 180 g/mol, and a narrow molecular weight distribution of 3. The low polydispersity can be explained as due to efficient removal of the oligomers by repeated reprecipitation. In general, the SEC data obtained against polystyrene standards have to be taken as relative values. A comparison of end-group iodine analysis and SEC values shows that the molecular weights obtained by SEC are smaller than the values obtained from end-group analysis. End-group iodine analysis of polymers **3a, 3b**, and **3c** shows iodine contents of 0.031, 0.028, and 0.018 wt %, respectively; the corresponding average molecular weights were 409 677, 453 570, and 705 555 g/mol.

For comparison purposes, two reference polymers, (1) poly(triphenyldiamine ether) (poly-TPDE) without an ITN group and (2) poly(dithienylisothianaphthene) (poly-DTITN) without triarylamine groups in the main chain, were also synthesized and studied (see Figure 2). This allowed us to understand the effect of ITN and triarylamine groups in **3a**−**c** on electrochemical and optical properties. The poly-TPDE (**6**) was also synthesized by the Ullmann reaction as reported earlier.[14] Poly-DTITN was obtained by oxidative polymerization of 1,3-bis(3-hexyl-2-thienyl)benzo[*c*]thiophene using anhydrous FeCl$_3$ in CHCl$_3$ by a general procedure known in the literature.[20] Monomer 1,3-bis(3-hexyl-2-thienyl)benzo[*c*]thiophene was synthesized using 2-magnesiumbromo-3-

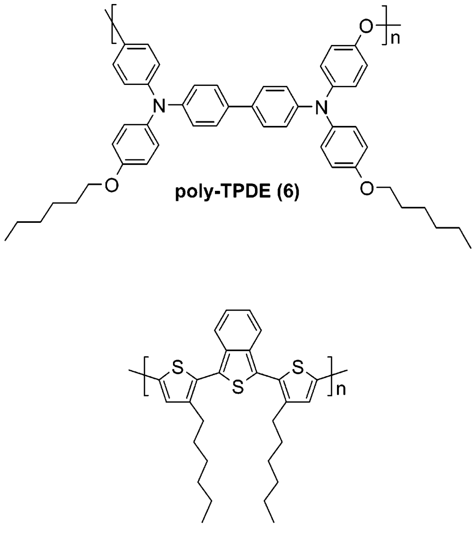


Figure 2. Chemical structures of the polymers used for comparative studies, poly(triphenyldiamine ether) (**poly-TPDE 6**) without having an ITN group and poly(dithienylisothianaphthene) (**poly-DTITN 7**) without having triarylamine groups in the main chain.

Table 2. Optical and Thermal Properties of the Polymers 3a−c, 6, and 7[a]

	UV−vis absorption, E_g^{opt} (eV) (edge (nm))		thermal properties	
polymer	in $CHCl_3$	in film	T_g (°C)	$T_{-5\%}$ (°C)
3a	1.77 (700)	1.67 (741)	132	381
3b	1.81 (685)	1.56 (794)	108	393
3c	1.90 (653)	1.64 (755)	130	385
6	3.17 (391)	3.12 (398)	105	405
7	2.18 (570)	2.03 (612)	90	315

[a] E_g^{opt} = optical band gap. T_g = glass-transition temperature. $T_{-5\%}$ = onset temperature at 5% weight loss.

hexylthiophene as a Grignard reagent via a modified procedure to that reported in the literature.[21]

The different methods of polymerization of thiophene monomers were reviewed recently by R. D. McCullough.[22] One of the simplest methods is polymerization of the monomer with $FeCl_3$, which is generally known to give irregular poly(3-alkylthiophenes). However, poly-DTITN (**7**), synthesized by the $FeCl_3$ oxidative polymerization, can have only regioregular structure due to the symmetrical nature of dithienylisothianaphthene used here. One of the major problems in oxidative polymerization with $FeCl_3$ is the high Fe content in the resulting polymer, which is detrimental to electronic materials, because the Fe impurity level in a polymer affects the performance of electrooptical devices. This problem was overcome here by developing an improved purification procedure to reduce Fe content in polymer **7**. The Fe content in polymer **7** was reduced to 0.013 wt % by repeated washing with HCl, aqueous ammonia, and finally KSCN solution (see Experimental Section). Polymers **6** and **7** were also characterized by spectroscopic methods such as FTIR, NMR, etc. (see Experimental Section). The SEC data for both polymers **6** and **7** are also given in Table 1.

The optical properties of **3a**−**c**, **6,** and **7** were studied by measuring UV−vis spectra both in solution ($CHCl_3$) and in thin films prepared by spin coating from $CHCl_3$ (**3a**−**c**, **6**) and chlorobenzene (**7**) solutions, and the various spectra in film are compared in Figure 3.

Figure 3A compares the UV−vis spectra of polymers **3a**−**c** in thin films, and Figure 3B shows the spectra of **3a** as an example compared to those of polymers **6** and **7**. The absorption band edges obtained from solution and film are also given in Table 2. All three polymers **3a**−**c** show similar absorption spectra with two vibronic bands. However, polymer **3a** has the highest absorption coefficient compared to polymers **3b** and **3c**. Polymers **3a, 3b**, and **3c** absorb up to 750 nm, and they have E_g values (as calculated from absorption edge) of 1.67, 1.56, and 1.64 eV, respectively. On the other hand, polymers **6** and **7** exhibit E_g values of 3.12 and 2.03 eV, respectively. Thus, incorporation of the ITN group results in a red shift of 170 nm in **3a** compared to that of polymer **6**. Introduction of an ITN group in polymers **3a**−**c**, leading to a shifting of the absorption band edge to longer wavelengths, is in agreement with our results on low molecular weight DTITN diamines.[11] Polymers **3a**−**c** show a red shift of about 70 nm compared to polymer **7**, which carries an ITN group in the main chain. This result can be explained as follows. The steric hindrance due to the two hexyl substituents in polymer **7** causes a stronger torsion around the inter-ring bonds, which leads to lower conjugation. In addition, incorporation of the triaryldiamine unit into polymers **3a**−**c** leads to longer conjugation, as already shown in our work[11] for the case of low molecular weight DTITNPDs.

The thermal properties of polymers **3a**−**c**, **6,** and **7** were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. TGA curves of polymers **3a**−**c** and **7** obtained at a heating rate of 10 K·min^{-1} under nitrogen atmosphere are shown in Figure 4. The onset temperatures for the polymers for 5% weight loss ($T_{-5\%}$) are also given in Table 2. It can be clearly seen that polymers **3a**−**c**

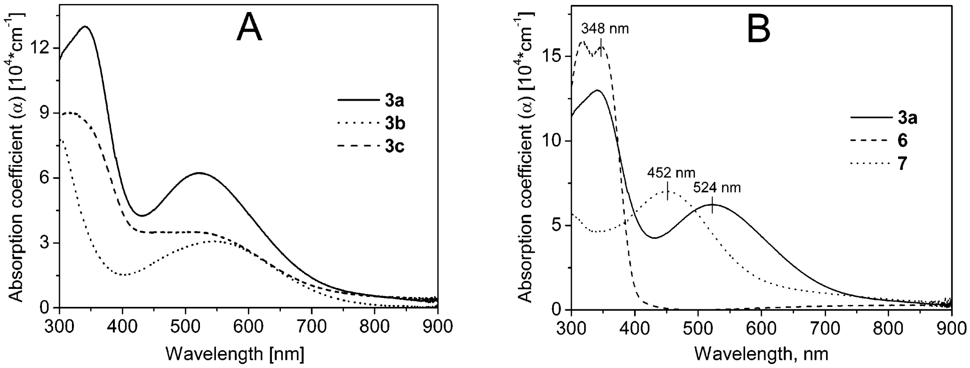


Figure 3. UV−vis spectra of polymers. (A) Poly-DTITNPDs **3a**−**c** in film, and (B) comparison of UV−vis spectra of poly-DTITNPDs **3a**, poly-TPDE **6** without any ITN group, and poly-DTITN 7 without triarylamine groups in film.

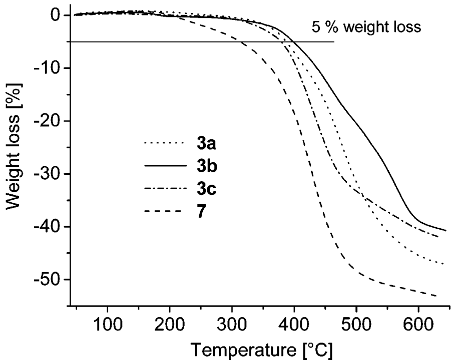


Figure 4. Thermogravimetric analysis of poly-DTITNPDs **3a**−**c** and poly-DTITN **7** at 10 K·min^{-1} under N_2 atmosphere.

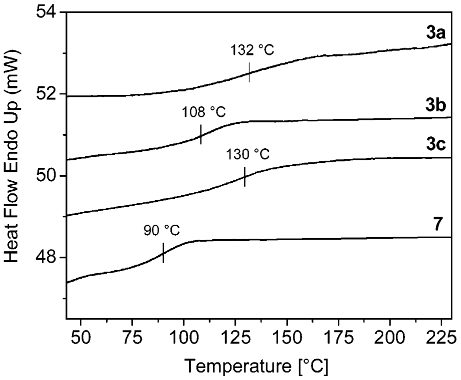


Figure 5. Determination of the glass-transition temperature (T_g) from second heating curves of poly-DTITNPDs **3a**−**c** and poly-DTITN **7** using differential scanning calorimetry (DSC) measurements (heating rate 10 K min^{-1}).

and **6** having triarylamine groups in the main chain are more thermostable than polymer **7**. The $T_{-5\%}$ data for **3a**, **3b,** and **3c** are 381, 393, and 385 °C, respectively. Thus, introduction of triarylamine groups increases the thermal stability of polymers **3a**−**c** by about 70 °C compared to poly-DTITN, **7**, which shows onset by 315 °C.

The second heating curves obtained from DSC for polymers **3a**−**c** and **7** are shown in Figure 5. Polymers **3a**−**c** exhibit a glass-transition temperature (T_g) in the range of 108−130 °C depending on the substituents. In comparison with polymers **6** and **7**, this is an improvement of about 30 °C, which gives an indication about the rigidity of the DTITN unit in combination with triarylamine units in polymers **3a**−**c**. As is the case with thermal stability, T_g is also improved in polymers **3a**−**c** due to incorporation of ITN and triarylamine groups into the polymer main chain. The low T_g value in polymer **7** can be attributed to the higher weight percentage of the side groups compared to the DTITN part as well as to the high torsion arising from the steric effect. No melting and no crystallization behavior on further heating and cooling cycles between 40 and 230 °C at 10 K·min^{-1} were observed for these polymers.

Electrochemical Properties. The electrochemical stability and reversibility of the redox processes of polymers **3a**−**c**, **6,** and **7** were studied using cyclic voltammetry (CV). The measurements were carried out using a glassy carbon electrode in a solution of carefully dried THF containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) at room temperature. The potentials were measured against $Ag/AgNO_3$ as the reference electrode, and each measurement was calibrated as usual with the standard ferrocene/ferrocenium (Fc) redox system.[23] The HOMO and LUMO energy values of the compounds were determined from the first oxidation and first reduction potentials (E_{ox1} and E_{red1}), respectively, taking a value of −4.8 eV as the HOMO energy level for Fc with respect to zero vacuum level as described by Daub et al. in the literature.[24] The cyclic voltammograms of polymers **3a**, for example, and **7**, for comparison, measured at a scan rate of 50 mV·s^{-1}, are given in Figure 6.

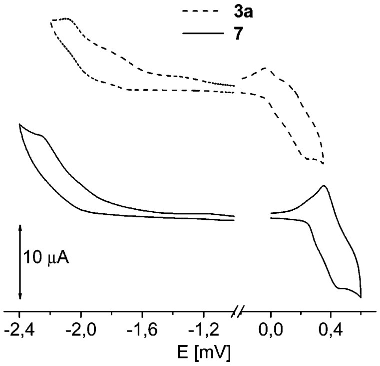


Figure 6. Cyclic voltammograms of poly-DTITNPDs **3a** and poly-DTITN **7** (in THF containing 0.1 M tetrabutylammonium hexafluorophosphate vs $Ag/AgNO_3$ at a 50 mV/s scan rate).

Table 3. Electrochemical Properties of the Polymers 3a−c, 6, and 7 Obtained from Cyclic Voltammetry Measured in THF vs $Ag/AgNO_3$ as Reference Electrode and Calibrated vs Ferrocene (Fc)[a]

polymer	E_{OX1} vs Fc (V)	HOMO (eV)	E_{RED1} vs Fc (V)	LUMO (eV)	band gap (eV)
3a	−0.13	−4.67	−1.88	−2.92	1.75
3b	−0.10	−4.70	−1.88	−2.92	1.78
3c	0	−4.80	−1.85	−2.95	1.85
6	0.22	−5.02	*b*	*b*	*b*
7	0.15	−4.96	−2.12	−2.68	2.28

[a] HOMO/LUMO values are relative to vacuum level. [b] No reduction observed up to −2.5 V vs Fc.

The polymers are electrochemically stable, and the same redox potentials were observed for repeated cycles of redox processes. They show completely reversible oxidation and reduction steps after measuring three cycles for the entire scan rate of 50−150 mV·s^{-1}. Polymers **3a**, **3b,** and **3c** show a similar oxidation behavior with E_{ox1} = −0.13, −0.10, and 0 V and reduction behavior with E_{red1} = −1.88,−1.88, and −1.85 V, respectively. E_{ox1} of 0.15 V and E_{red1} of −2.12 V was observed for polymer **7**. The corresponding HOMO and LUMO values for all of the polymers determined from the first oxidation and reduction potentials with respect to ferrocene/ferrocenium (Fc) as internal standard are presented in Table 3. Polymers **3a**−**c** have similar HOMO values of about −4.7 eV, and polymers **6** and **7** have similar HOMO values of about −5.0 eV. Polymers **3a**−**c** have similar LUMO values of about −2.9 eV, and polymer **7** has a LUMO value of −2.7 eV. The electrochemical band gap (E_g^{ec}) values, given in Table 3, were calculated as the difference between the HOMO and LUMO levels of the polymers. These values are in close agreement with the optical band gap (E_g^{opt}) values obtained from absorption band edges measured in solution (see Table 2). Moreover, polymers **3a**−**c** possess lower band gap energy values than polymer **7**, and this lowering was achieved through an improvement of both HOMO and LUMO values. These low band gap polymers should be suitable as efficient light-harvesting dyes with improved matching of absorption to the solar spectrum.

Conclusion

It can be concluded that the strategy of incorporating ITN and triarylamine groups into a polymer main chain was successfully realized. The resulting polymers constitute a new class of light-harvesting dyes with band gap energy values below 1.8 eV. The thermal stability and glass-transition temperatures were improved in these polymers compared to poly(triphenyldiamine ether) (poly-TPDE) without an ITN group and poly(dithienyl isothianaphthene) (poly-DTITN) without triarylamine groups. These polymers are promising candidates for use in solar cells because they form stable films with amorphous nature. Moreover, the absorption spectra of these polymers are red shifted by more than 150 nm, thus decreasing the mismatch with the solar spectrum. Application of these polymers in thin-layer plastic solar cells is under current research, and the results will be published later.

Experimental Section

Materials. Chloroform ($CHCl_3$) was purified by distillation over calcium hydride. Tetrahydrofuran (THF) and toluene were dried over sodium and distilled under argon. *o*-Dichlorobenzene was refluxed and distilled with calcium hydride. 1,3-Di-2-thienylbenyo[*c*]thiophene was prepared by a three-step synthetic method as reported earlier.[11] All other chemicals were purchased from Aldrich Chemical Co. and used as received.

Instrumentation. Size exclusion chromatography (SEC) measurements were performed on a Waters system with Waters 410 RI and Waters 440 UV detectors at room temperature by using THF containing 0.25 wt % of *tert*-butylammonium bromide as an eluent. The molecular weights and molecular weight distributions were calculated on the basis of monodispersed polystyrene standards. ^1H NMR (250 MHz) spectra were obtained on a Bruker AC250 spectrometer. Chemical shifts (δ) were reported in ppm downfield from tetramethylsilane (TMS). The UV−vis measurements were carried out on a Hitachi U-3000 spectrophotometer in $CHCl_3$ solutions and in thin films prepared by spin coating from $CHCl_3$ or chlorobenzene solutions. Fourier-transformed infrared spectra (FT-IR) were measured on a BioRad Digilab FTS-40 (FT-IR) using a potassium bromide (KBr) pellet for substances in the solid state and a sodium chloride (NaCl) pellet for substances in the liquid state (16 scans; resolution, 4 cm^{-1}). Cyclic voltammetry measurements were carried out using millimolar solutions of polymer in highly dried acetonitrile (Acn) or THF at room temperature. A glassy carbon disk electrode (0.2 cm^2) was used as a working electrode. A platinum wire was used as the counter electrode, and a silver wire in a solution of $AgNO_3$ was used as the reference electrode. Each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system. The HOMO and LUMO values were determined from the value of −4.8 eV for Fc with respect to vacuum level. Scan rates in the range of 50−500 $mV \cdot s^{-1}$ were used. Thermogravimetric analysis (TGA) of polymers was conducted on a thermoanalysis apparatus TGA/SDTA851^e from Mettler Toledo Co. at a heating rate of 10 $K \cdot min^{-1}$ under a nitrogen flow rate of 75 $cm^3 \cdot min^{-1}$ in the temperature range from 30 to 650 K. Differential scanning calorimetry (DSC) measurements were carried out using a Diamond DSC from Perkin-Elmer Co. The heating/cooling rate was 10 $K \cdot min^{-1}$ for all experiments. Melting point measurements were performed on Leitz Laborlux 12-Pol equipped with a Mettler FP 82 hot stage using a heating rate of 5 K/min. The Fe content in polymer **7** and end-group iodine amount for polymers **3a**−**c** were analyzed at the Mikroanalytisches Labor Pascher, An der Pulvermühle 1, 53424 Remagen, Germany.

1. Monomer Synthesis. *(a) Bis(secondary)amines (**1a**−**c**).* Syntheses of **1a**, **1b,** and **1c** were performed in dried toluene with 6 mol % Pd(dppf)Cl_2, 18 mol % DPPF, 4.5 equiv of *t*-BuONa, and 3 equiv of aniline per 0.25 M of diiodide at 125 °C for 16 h under Ar. After completion of the reaction, toluene was removed under reduced pressure. The reaction mixture was dissolved in THF and filtered through Al_2O_3 on a glass filter to remove polar impurities. The product was precipitated in methanol from concentrated THF solution (THF/methanol 20:200 mL). The precipitate was dissolved in CH_2Cl_2, washed with aqueous 32% HCl to remove aniline, followed by water, and dried over Na_2SO_4. After evaporation of CH_2Cl_2, the product was dissolved in THF and precipitated in methanol twice. White solid was collected.

*(i) N,N′-Di(4-octylphenyl)-4,4′-diaminobiphenyl (**1a**).* Molecular formula (MF) = $C_{40}H_{52}N_2$; mol weight (M_w) = 560.87 g/mol. Yield: 1.28 g (46%). ^1H NMR (C_6D_6), δ [ppm]: 7.46 (d, 4H), 7.05 (d, 4H), 6.97 (d, 8H), 5.07 (s, 2H), 2.55 (t, 4H), 1.62 (m, 4H), 1.27 (m, 20H), 0.91 (t, 6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3415, 3028, 2956, 2916, 2848, 1612, 1519, 1314, 816. MS [*m/z*]: 560 (M^+), 461 ($[C_8H_{17}-C_6H_4-NH-C_6H_4-C_6H_4-NH-C_6H_4=CH]^+$), 181 ($[C_6H_4-NH-C_6H_4=CH]^{2+}$).

*(ii) 4,4′-Oxybis[N-(2,4-di(trifluoromethyl)phenyl)]benzenamine (**1b**).* MF = $C_{28}H_{16}F_{12}N_2O$; M_w = 624.43 g/mol. Precipitation of product from THF into methanol, *n*-hexane, or petrolether (bp 60−80 °C) did not work. Final purification by column chromatography with cyclohexane/ethyl acetate (5:1) yielded 1.40 g (60%). ^1H NMR ($CDCl_3$), δ [ppm]: 7.26 (s, 12H), 7.12 (d, 4H), 7.06 (d, 4H), 5.88 (s, 2H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3405, 1618, 1497, 1378, 1274, 1168, 1139, 870. MS [*m/z*]: 624 (M^+), 320 ($[(CF_3)_2-C_6H_4-NH-C_6H_4-O]^+$). mp: 116.4 °C.

*(iii) Di(4-hexyloxyphenyl)-4,4′-diaminobiphenyl (**1c**).* MF = $C_{36}H_{44}N_2O_2$; M_w = 536.76 g/mol. Yield: 1.36 g (79%). ^1H NMR ($CDCl_3$), δ [ppm]: 7.37 (d, 4H), 7.04 (d, 4H), 6.95 (d, 4H), 6.86 (d, 4H), 5.50 (s, 2H), 3.92 (t, 4H), 1.76 (m, 4H), 1.45 (m, 4H), 1.32 (m, 4H), 0.89 (t, 6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3419, 3029, 2954, 2934, 2871, 1611, 1517, 1250, 817. MS [*m/z*]: 536 (M^+), 451 ($[M - C_6H_{13}]^+$), 367, ($[M - 2(C_6H_{13})]^{2+}$), 184 ($[C_6H_4-NH-C_6H_4-O]^{2+}$). mp: 177.3 °C.

*(b) 1,2-Bis(5-iodo-2-thienyl)isothianaphthene (**2**).* MF = $C_{16}H_8I_2S_3$; M_w = 550.24 g/mol. Under exclusion of light, a solution of *N*-iodosuccinimide (6.80 g; 30.22 mmol) in abs. DMF (200 mL) was added dropwise to a solution of 1,3-di-2-thienylbenzo[*c*]thiophene (4.4 g; 14.74 mmol) in abs. DMF (130 mL) at −55 °C. The resulting mixture was kept for 4 h at −55 °C, and then it was allowed to reach the room temperature overnight. The black precipitate formed was collected on a glass filter, washed with water, and dried in a vacuum. The mother liquor was diluted with water, extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4, and the solvent was removed to obtain the rest of the product. The black precipitate and this residue extract were combined, and final purification by column chromatography on silica gel with *n*-hexane/THF (20:1) yielded 4.28 g (52%) of red solid. The product was finally recrystallized in a *n*-hexane/$CHCl_3$ (10:1) mixture. Bright-fluorescent, dark-red needles were obtained. ^1H NMR (C_6D_6), δ [ppm]: 7.82 (m, 2H), 7.26 (d, 2H), 7.15 (m, 2H), 6.99 (d, 2H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 1529, 1189, 875, 777, 582. MS [*m/z*]: 550 (M^+, triplet), 423 ($[M - I]^+$). mp: 133.9 °C.

(c) 1,3-Bis(3-hexyl-2-thienyl)benzo[c]thiophene. 1,3-Bis(3-hexyl-2-thienyl)benzo[*c*]thiophene was synthesized by a three-step synthetic procedure.

(i) Step 1: 2-Bromo-3-hexylthiophene. MF = $C_{10}H_{15}BrS$; M_w = 247.20 g/mol. To a solution of 3-hexylthiophene in (3.1 g; 18.4 mmol) in $CHCl_3$ (15 mL) and acetic acid (15 mL) portions of *N*-bromosuccinimide (3.38 g; 19 mmol) were added at 0 °C over 30 min. After being stirred for an additional 30 min at 0 °C, the mixture was diluted with water and extracted with $CHCl_3$. The extracts were washed first with 2 M KOH followed by water and then dried over Na_2SO_4. The residue obtained after removal of solvent was purified by column chromatography on silica gel with cyclohexane/ethyl

acetate (20:1) as the eluent to give 2-bromo3-hexylthiophene (3.06 g; 67%). ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.15 (d, 1H), 6.78 (d, 1H), 2.54 (t, 2H), 1.55 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3107, 2956, 2926, 2856, 1467, 1409, 992, 830, 713, 635. MS [*m*/*z*]: 246 (doublet), 97 ($[C_4H_3S{=}CH]^+$).

(ii) Step 2: 1,2-Bis(3′-hexylthienoyl)benzene. MF = $C_{28}H_{34}O_2S_2$; M_w = 466.71 g/mol. 2-Bromo-3-hexylthiophene (5.0 g; 20.2 mmol) was slowly added to a refluxing mixture of iodine-activated magnesium (0.49 g; 20.2 mmol) in abs. THF (30 mL). After formation of the Grignard reagent (6 h reflux) it was slowly added to a flask containing a solution of 1,2-di(*S*-pyridinyl)benzenedithioate (3.40 g; 9.6 mmol) in abs. THF (150 mL) at 0 °C. The mixture was stirred for 30 min, and finally 10% HCl (15 mL) was added to hydrolyze the complex formed. The product was extracted with ether repeatedly, and the combined organic fractions were washed with 2 M NaOH solution and water until neutral and dried over Na_2SO_4. After evaporation of the solvent, a light-brown, honey-like product was obtained. Final purification by column chromatography with cyclohexane/ethyl acetate (3:1) yielded a yellowish viscous liquid (3.54 g; 74%). ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.62 (m, 2H), 7.55 (m, 2H), 7.40 (d, 2H), 6.96 (d, 2H), 2.78 (t, 4H), 1.52 (m, 4H), 1.22 (m, 12H), 0.83 (t, 6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3101, 3067, 3018, 2956, 2928, 2856, 1638, 1519, 1465, 1408, 1294, 1278, 1250, 912. MS [*m*/*z*]: 466 (M^+), 299 ($[C_6H_{13}{-}C_4H_2S{-}CO{-}C_6H_4{-}CO]^+$), 228 ($[O{\equiv}C{-}C_6H_4{-}CO{-}C_4H_3S{=}CH]^{2+}$), 215 ($[O{\equiv}C{-}C_6H_4{-}CO{-}C_4H_2S]^{2+}$), 97 ([C4H4S=CH]$^+$).

(iii) Step 3: 1,3-Bis(3-hexyl-2-thienyl)benzo[c]thiophene. MF = $C_{28}H_{34}S_3$; M_w = 466.78 g/mol. A mixture of 2,4-bis-(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, known as Lawesson reagent (2.0 g; 5 mmol), 1,2-bis(3′-hexylthienoyl)benzene (2.2 g; 4.7 mmol), and CH_2Cl_2 (150 mL) was refluxed for 30 min. After evaporation of CH_2Cl_2, ethanol (150 mL) was added and the mixture was refluxed for an additional 30 min. Finally, 500 mL of water was added, and the product was extracted with ether. The combined ether fractions were washed with copious amounts 10% NaOH and water and dried. Final purification was done by column chromatography (CH_2Cl_2, *n*-hexane 9:1) to obtain 1.78 g (81%) of a yellow oil. ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.56 (m, 2H), 7.36 (d, 2H), 7.08 (m, 2H), 7.04 (d, 2H), 2.64 (t, 4H), 1.57 (m, 4H), 1.19−1.24 (m, 12H), 0.78 (t, 6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3065, 2956, 2926, 2856, 1457, 747. MS [*m*/*z*]: 466 (M^+), 395 ($[C_6H_{13}{-}C_4H_2S{-}C_8H_4S{-}C_4H_2S{=}CH]^+$), 309 ($[C_6H_{13}{-}C_4H_2S{-}C_8H_4S]^+$), 227 ($[C_8H_4S{-}C_4H_2S{=}CH]^{2+}$).

2. Polymer Synthesis. *(a) Poly[bis(diarylaminothienyl)-isothianaphthene]s (**3a**−**c**).* Poly[bis(diarylaminothienyl)isothianaphthene]s (**3a**−**c**) were prepared by the following general polycondensation procedure: 1,3-bis(5-iodo-2-thienyl)benzo-[*c*]thiophene 2 (0.15 M), bis(secondary)amine **(1a**, **1b,** or **1c)** (0.15 M), copper[0] (0.6 M), 18-crown-6 as a phase-transfer catalyst (0.03 M), and potassium carbonate (1.2 M) in anhydrous *o*-dichlorobenzene (7 mL) were mixed at room temperature and refluxed under nitrogen atmosphere for 5 days. The reaction mixture was diluted with THF, and inorganic salts were filtered off. After removing the solvent, the polymer was dissolved in $CHCl_3$, followed by refluxing this polymer solution with 25% aqueous ammonia for 30 min to dedope any in situ doping of the material, washed with water and methanol, and dried in a vacuum. Then the polymer was repeatedly precipitated into *n*-hexane from $CHCl_3$.

(i) Polymer 3a. Final purification was done by reprecipitation of the polymer in cyclohexane from $CHCl_3$ solution. After drying in high vacuum, 0.51 g of polymer was collected with a yield of 63%. ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.89, 7.34, 7.14, 6.80 (m, 24H), 2.53 (m, 4H), 1.55 (m, 4H), 1.24 (m, 20H), 0.84 (m, 6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3029, 2924, 2852, 1603, 1494, 1284, 1061, 815, 745. UV−Vis, λ_{max} [nm]: 497 ($CHCl_3$), 520 (film). End-group elemental analysis: 0.031 wt % of iodine.

(ii) Polymer 3b. Further purification was done by Soxhlet extraction with methanol. After drying in high vacuum, 0.47 g of polymer was collected with a yield of 43%.^{1}H NMR ($CDCl_3$), δ [ppm]: 7.97 (m, 2H), 7.43, 7.28, 7.13, 6.82 (m, 20H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3064, 2926, 2851, 1617, 1495, 1378, 1277, 1229, 1176, 1133, 875, 742, 682. UV−vis, λ_{max} [nm]: 526 ($CHCl_3$), 538 (film). End-group elemental analysis: 0.028 wt % of iodine.

(iii) Polymer 3c. Further purification was done by reprecipitation of the polymer from $CHCl_3$ in petrol ether (fraction with a bp 60−80 °C). After drying in high vacuum, 0.77 g of polymer was collected with a yield of 78%. ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.97, 7.34, 7.14, 6.82 (m, 24H), 3.88 (m, 4H), 1.71 (m, 4H), 1.31 (m, 12H), 0.87 (m, 6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3033, 2928, 2858, 1606, 1492, 1240, 820, 746. UV−vis, λ_{max} [nm]: 430−520 ($CHCl_3$), 440−540 (film). End-group elemental analysis: 0.018 wt % of iodine.

*(b) Poly[1,3-bis(3-hexyl-2-thienyl) benzo[c]thiophene] (**7**).* To a solution of 1,3-bis(3-hexyl-2-thienyl)benzo[*c*]thiophene (7.5 g; 16.2 mmol) in dried $CHCl_3$ (300 mL), powdered anhydrous $FeCl_3$ (10.54 g; 65 mmol) was added slowly during 6 h under Ar at room temperature. After stirring for an additional 18 h, the reaction mixture was poured into *n*-hexane as a bluish-black powder (17.3 g) was precipitated. Soxhlet extraction with methanol to remove Fe salts and unreacted monomer gave a brown solid (8.9 g of dedoped polymer). After further Soxhlet extraction with THF to dissolve the polymer left, 1.95 g (26%) of black residue insoluble in THF was obtained (0.25% of Fe content), which is also insoluble in common organic solvents such as $CHCl_3$, NMP, DMF, and DMAc. The THF solution of the polymer was added slowly to *n*-hexane under vigorous stirring to precipitate 1.7 g (23%) of high molecular weight polymer containing 0.43% of Fe. The THF/*n*-hexane mother liquor after evaporation of solvents gave a residue, which on GPC analysis was detected as oligomers (3.46 g; 46% yield). ^{1}H NMR ($CDCl_3$), δ [ppm]: 7.71, 7.55, 7.33, 7.11 (8H), 2.70 (4H), 1.65 (4H), 1.23 (12H), 0.81 (6H). FT-IR (KBr), $\tilde{\nu}$ [cm^{-1}]: 3060, 2952, 2924, 2854, 1641, 1453, 746. The polymer fraction was treated as follows using an improved purification procedure to reduce Fe content. The polymer was diluted with $CHCl_3$ followed by washing with 15 wt % HCl to remove possible Fe-containing compounds such as $FeCl_3$, $FeCl_2$, Fe_2O_3, $Fe(OH)_2$, and $Fe(OH)_3$, then water until neutral and dedoping of the organic material by refluxing the $CHCl_3$ solution repeatedly (3×) with aqueous 25% NH_3 for 30 min when the color of the material changed from deep blue to reddish-brown. The product was washed with aqueous KSCN solution to remove the rest of the Fe salts and after washing with water, drying over Na_2SO_4, and evaporation of $CHCl_3$, the pure polymer with a Fe content of only 0.013 wt % was obtained by precipitating it from THF solution into *n*-hexane.

Acknowledgment. We thank Mrs. Helga Wietasch and Dr. Haridas R. Karickal for synthesis of polymer **6**. We gratefully acknowledge Sonderforschungsbereich 481 (Project B4), German Research Council (DFG), for providing financial support for this research work.

Supporting Information Available: ^{1}H NMR data of the monomers and SEC plots for polymers **3a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0495947