Electrical and Thermoelectric Properties of Poly(2,7-Carbazole) Derivatives

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A series of alternating poly(2,7-carbazole) derivatives have been synthesized. The evaluation of their thermoelectric properties in doped films revealed high electrical conductivity (up to 500 S/cm) and a relatively high Seebeck coefficient (up to 70 μV/K). The best compromise between these two thermoelectric parameters led to a maximum value of 19 μW m^{-1} K^{-2} as the power factor. As observed from X-ray analyses, it has been observed that the high electrical conductivity was obtained with structured polymers. Good air stability was also observed with these thermoelectric polymers.

Introduction

Thermoelectric phenomena may be considered as a promising source of energy. Until recently, most investigations for thermoelectric materials focused on inorganic compounds. Several classes of compounds have been investigated (for instance, skutterudites,[1] half-Heusler alloys,[2] clathrates,[3] and pentatellurides[4]). Moreover, bismuth telluride has already been commercially available as one of the raw materials for a Peltier cooler.[5] However, these inorganic thermoelectric materials involve some issues such as toxicity, a shortage of natural resources, and complicated manufacturing processes. In parallel, organic-based electronic materials have received much attention. They have been extensively studied in many applications such as sensors,[6,7] field-effect transistors,[8,9] solar cells,[10,11] and thermoelectric power generators.[12,13] These semiconductor materials show many advantages over traditional inorganic semiconductors: for instance, through simple modifications of their molecular structure, it is easy to tune their chemical and physical proprieties in a fairly large range, providing great material flexibility to meet the requirements of the targeted applications. Many conjugated polymers, such as polyacetylenes, polyanilines, polypyrroles, polythiophenes, polyphenylenevinylenes, poly(3,6-carbazole)s, and poly(2,7-carbazole)s have been already studied. Unfortunately, not much attention has been paid to these organic semiconductors as thermoelectric materials, because their reported thermoelectric properties[13−18] were always inferior to those of inorganic materials. Typically, this is attributed to the low electrical conductivity that is generally obtained with these polymers.

To be useful in various devices, thermoelectric materials must have a figure of merit (thermoelectric efficiency, represented by the term ZT, that is >1, where

$$\mathrm{ZT} = \frac{S^2 \sigma T}{\kappa}$$

where S is the Seebeck coefficient, σ and κ are the respective electrical and thermal conductivities, and T is the temperature.[19] However, in the absence of precise data on the thermal conductivity of conjugated polymers, here, we will examine the performances of the polymers with the thermoelectric power factor (PF). It is given by the following equation:

$$\mathrm{PF} = S^2 \sigma$$

This factor is generally used to compare thermoelectric performances of materials that have similar thermal conductivities. Following these rules, here, we report the synthesis

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and characterization of new thermoelectric poly(2,7-carbazole) derivatives. It will be shown, for the first time, that this class of processable conjugated polymers can combine high electrical conductivities with good Seebeck coefficients. Finally, we will also investigate the air stability of these parameters.

Experimental Section

Instrumentation. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian AS400 apparatus in an appropriated deuterated solvent solution at a temperature of 298 K. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with a Viscotek high-temperature gel permeation chromatography (GPC) system (Model 350 HTGPC) and two Polymers Laboratories PolyPore columns (300 × 7.5 mm, Model PL1113-6500) using a refraction index (RI) detector at 135 °C in 1,2,4-trichlorobenzene (HPLC grade, Mallinckrodt). The calibration curve was constructed using a series of monodispersed polystyrene standards (Shodex). Ultraviolet−visible (UV−Vis) absorption spectra were taken using a Varian Model Cary 500 UV−Vis−NIR and Hewlett-Packard Model HP8542a spectrophotometer. Solution UV−Vis spectra were recorded at 135 °C using 1-cm quartz cells. X-ray diffraction (XRD) spectra were obtained from a X-ray diffractometer (Siemens/Bruker), using graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). The instrument consists of a Kristalloflex Model 760 generator, a three-circle goniometer, and a Hi-Star area detector, and it is equipped with GADDS software. The operation power was defined by an accelerating voltage of 20 kV and an accelerating current of 20 mA, and the collimator had a diameter of 0.8 mm.

Thermogravimetric measurements (TGA) were performed with a Mettler−Toledo Model TGA SDTA 851e apparatus at a heating rate of 20 °C/min under a nitrogen atmosphere. The temperature of degradation (T_d) corresponds to a 5% weight loss. Differential scanning calorimetry (DSC) analysis was performed on a Mettler Toledo DSC823e instrument, calibrated with ultrapure indium. DSC curves were registered at a scanning rate of 10 °C/min, under a nitrogen flow on heating and cooling after initial isothermal treatment at 300 °C.

Cyclic voltammograms (CVs) were recorded on a Solartron Model 1287 potentiostat, using platinum electrodes at a scan rate of 50 mV/s and a Ag/Ag$^+$ reference electrode (0.10 M of $AgNO_3$ in acetonitrile) in an anhydrous and argon saturated solution of 0.1 M of tetrabutyl ammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile. Tetrabutyl ammonium tetrafluoroborate (98%, Aldrich) was recrystallized three times in a 50:50 mixture of methanol/water and dried at 100 °C under reduced pressure, as reported in the literature.[20] Under these conditions, the oxidation potential ($E_{ox}^{1/2}$) of ferrocene was 0.11 V versus Ag/Ag$^+$, whereas the $E_{ox}^{1/2}$ of ferrocene was 0.41 V versus SCE. For UV−Vis−NIR spectroelectrochemical analyses, the working electrode (ITO), counter electrode (Pt), and Ag/Ag$^+$ reference electrode were immersed in a solution of 0.1 M Bu_4NBF_4 in acetonitrile using a sealed 2-cm quartz cells. Oxidation spectra were done at constant potential using a Solartron potentiostat (Model 1287) and recorded on a Varian Model Cary 500 UV−Vis−NIR spectrophotometer (1800 nm/min). Under these conditions, the $E_{ox}^{1/2}$ value for ferrocene was 0.19 V versus Ag/Ag$^+$.

Thermoelectric measurements were obtained using a homemade apparatus that consisted of two copper blocks separated by a distance of 5−15 mm. The film was sandwiched between copper plates. These copper plates were covered with gold sheets (Aldrich, 99+% pure) to make good contacts. The copper blocks were cooled or heated using Peltier devices (maximum current of 3 A). The difference in temperature between the two copper blocks can be controlled. Thermocouples (Type K) were placed as close as possible to the polymer film. The thermocouples were electrically isolated using heat-conducting tape (Gap Band, VO Ultra Soft, from The Bergquist Company) and covered by Scotch 27 glass cloth electrical tape, from 3M, for heat isolation. All the measurements were performed in an air atmosphere. Voltage and resistance measurements were done using a Keithley Model 2000 multimeter, and a digital thermometer (Multilogger, Model HH 506 RA) was used to measure the temperature difference between the two copper blocks. The conductivity was determined by measuring the resistivity of the doped films on the thermoelectrical measurement device, using the gold plates as contacts (two probes were measured). All measurements were monitored using homemade software program, realized with Laboratory View software.

Materials. All starting organic compounds were purchased from Aldrich, Alfa Aesar, or TCI America and used without further purification. All reactions were conducted under an argon atmosphere, unless mentioned otherwise. 5,5′-Dibromo-2,2′-bithiophene[21] (**1**), 1,4-bis(5-bromothiophen-2-yl)benzene[22] (**2**), 4,7-di(2′-bromothien-5′-yl)-2,1,3-benzothiadiazole[23] (**3**), and 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole[24] (**4**), and poly[*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5′-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole][24] (**PCDTBT**) have been already reported in the literature. Other polymers have been synthesized following procedures described below.

Synthesis. *General Polymerization Procedure.* In a 50-mL flame-dried flask, 657.6 mg (1.000 mmol) of 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanyl-carbazole[24] (**4**), 1.000 mmol of bis(bromothiophene)arene (**1** or **2**), 4.6 mg (0.0050 mmol) of tris(dibenzylideneacetone)dipalladium and 6.1 mg (0.020 mmol) of tri(*o*-tolyl)phosphine were dissolved in 10.0 mL of degassed

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Scheme 1. Structure and Synthesis of the Carbazole-Based Copolymers

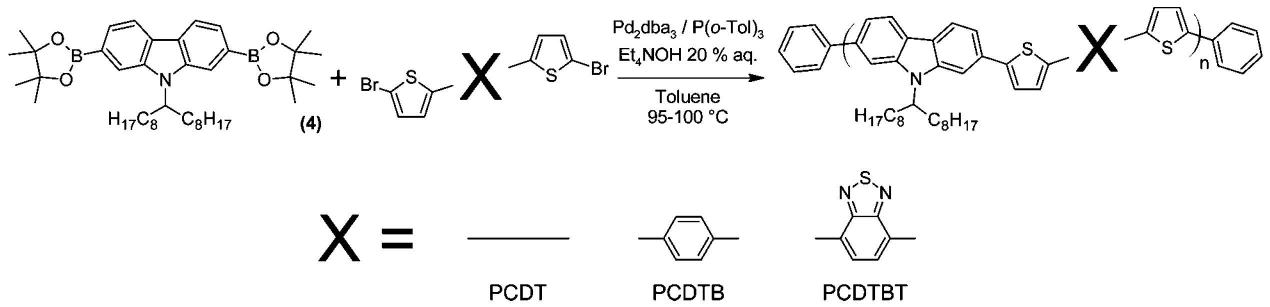

Table 1. Number-Average Molecular Weight (M_n), Polydispersity Index (PDI), and Thermal, Electrochemical, and Optical Properties of Polycarbazole Derivatives

polymer	M_n (kDa)	PDI	T_g (°C)	T_m (°C)	ΔH (J/g)	T_d (°C)	E_{ox}^{onset} (V vs SCE)[a]	E_{red}^{onset} (V vs SCE)[a]	E_g^{elec} (eV)	E_g^{opt} (eV)[b]
PCDT	25	1.7	90	230	0.97	450	0.76	−1.61	2.37	2.34
PCDTB	29	1.9	107			425	0.76	−1.69	2.45	2.41
PCDTBT	33	1.9	130	270	0.38	470	0.75	−1.10	1.85	1.88

[a] Measured with a cast film in a CH_3CN solution of 0.1 M Bu_4NBF_4. SCE = standard calomel electrode. [b] Measurements performed on spin-coated films from the onset of the absorption band.

toluene and 3.4 mL of 20% (w/w) aqueous tetraethyl ammonium hydroxide. The reaction mixture was vigorously stirred at 90−95 °C. After 72 h, bromobenzene (11 μL, 0.10 mmol) was added to the reaction then one hour later, phenylboronic acid (12 mg, 0.10 mmol) was added and the reaction refluxed overnight to complete the end-capping reaction. The polymer was purified by precipitation in methanol/water (10:1), filtered through 0.45 μm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, and chloroform. The chloroform fraction (550−600 mL) was reduced to 40−50 mL under reduced pressure, precipitated in methanol/water (10:1, 500 mL), and filtered through a 0.45-μm nylon filter, and the resulting polymer is finally air-dried overnight.

*Poly[*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5-(2,2′-bithiophene)] (PCDT).* Following the general polymerization procedure, 324.1 mg of compound **1** was reacted to afford the title polymer as an orange powder (0.402 g, yield = 71%). ^{1}H NMR (400 MHz, ODCB-d_4, 130 °C, ppm): δ 7.96 (d, J = 7.1 Hz, 2H); 7.84 (br, 2H); 7.44 (d, J = 6.6 Hz, 2H); 7.24 (br, 2H); 4.67 (br, 1H); 2.36 (br, 2H); 2.01 (m, 2H); 1.37−1.15 (br, 8H); 1.15−0.98 (br, 16H); 0.71 (t, J = 5.9 Hz, 6H). (One aromatic peak is missing, hidden by the solvent peaks.)

*Poly[*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5′-(2,2′-(1,4-phenylene)dithiophene)] (PCDTB).* Following the general polymerization procedure, 400.2 mg of compound **2** was reacted to afford the title polymer as a brown powder (0.478 g, yield = 74%). ^{1}H NMR (400 MHz, ODCB-d_4, 130 °C, ppm): δ 7.97 (d, J = 7.4 Hz, 2H); 7.85 (br, 2H); 7.54 (s, 4H); 7.48 (d, J = 6.2 Hz, 2H); 7.31 (br, 2H); 7.20 (br, 2H); 4.71 (br, 1H); 2.40 (br, 2H); 2.04 (m, 2H); 1.39−1.15 (br, 8H); 1.15−0.99 (br, 16H); 0.71 (br, 6H).

Thermoelectric Film Preparation. The polymer films (PCDT, PCDTB, and PCDTBT) characterized in this study were cast from chloroform solutions on a specially designed Teflon plate. Polyaniline (PANI) films were cast using the same Teflon plate from *m*-cresol solution and dried under vacuum. The oxidation of new polymer films was done at different concentrations of $FeCl_3$ solutions in acetonitrile (distilled over CaH_2); the doping time has been varied to obtain different doping levels. To compare the thermoelectric properties of the polymers in this study, we have also reported the results of the polyaniline (PANI) doped with (±)-10-camphorsulfonic acid (CSA) prepared according to a procedure previously reported by Cao et al.[25]

Results and Discussion

Synthesis of the Polymers. Three poly(2,7-carbazole) derivatives were synthesized according to Scheme 1. The same polymerization reaction as already reported for the PCDTBT[24] was chosen to obtain the two new copolymers. Indeed, 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole[24] (**4**) and the desired comonomers (**1**−**3**) were copolymerized through Suzuki coupling reaction[26] to produce the desired polymers (PCDT, PCDTB, and PCDTBT) with high molecular weights (see Table 1). PCDT was also previously prepared from Stille coupling.[27] This new procedure using Suzuki coupling polymerization produces a polymer with a higher molecular weight.

Characterization of the Polymers. The resulting polymers show good thermal stability (T_d) and high glass-transition temperature (T_g) values (see Table 1). The polymers are soluble in chloroform, chlorobenzene (CB), 1,2-dichlorobenzene (ODCB), and 1,2,4-trichlorobenzene (TCB). Although clear solutions were obtained in those solvents, SEC data suggest the presence of aggregation in these solutions at room temperature. For that reason, solution UV−Vis spectra were recorded at 135 °C to eliminate any polymer aggregation (see the Supporting Information). The solid-state UV−Vis spectra of polymers show a bathochro-

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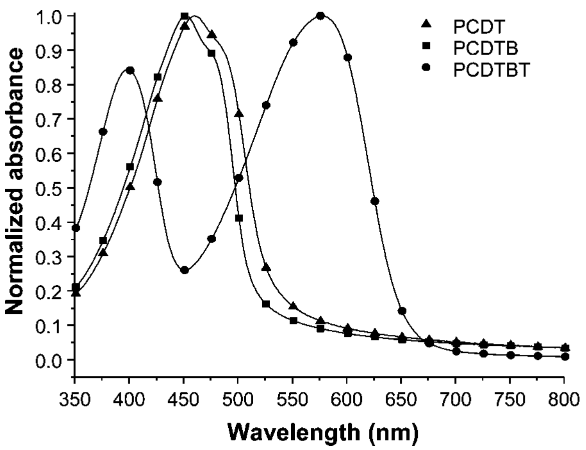

Figure 1. Solid-state UV−vis absorption spectra for PCDT, PCDTB, and PCDTBT.

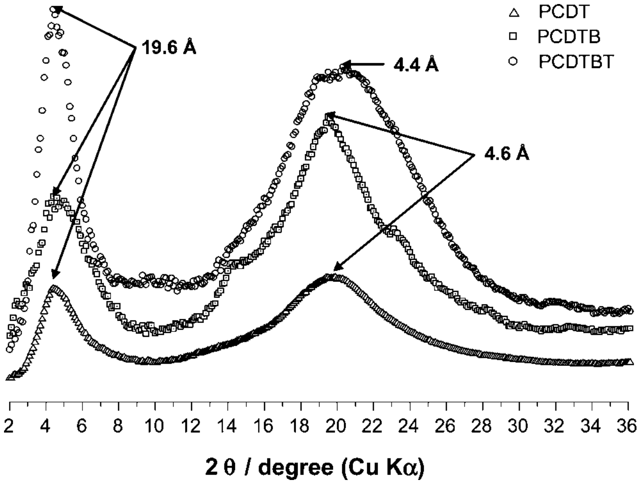

Figure 2. X-ray diffraction (XRD) graphs of PCDT, PCDTB, and PCDTBT films.

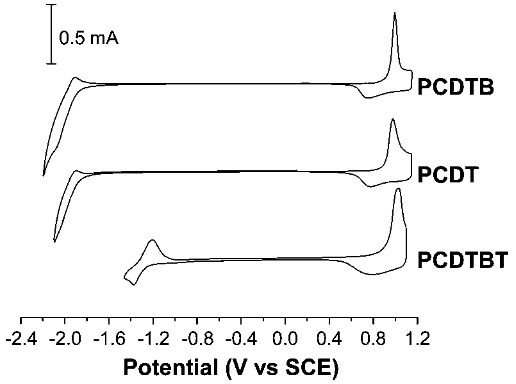

Figure 3. Cyclic voltammogram (second scan) of polymer films cast on platinum wire in Bu$_4$NBF$_4$/acetonitrile at 50 mV/s.

mic shift (ca. 30−40 nm), compared to the solution spectra at 135 °C in TCB. In addition, the absorption spectra of spin-coated PCDT and PCDTB thin films exhibit a vibronic splitting (see Figure 1). Those two observations from the solution to the solid-state spectrum comparison suggest higher structural organization in the solid state for the three polymers. Moreover, because of the donor−acceptor nature[28−32] of the PCDTBT, the absorption maximum is red-shifted by ~115−125 nm, with respect to PCDT and PCDTB. In the solid state, these polymers are not highly fluorescent.

Analyses from differential scanning calorimetry (DSC) reveal one melting process for both the PCDT and PCDTBT, at 230 and 270 °C, respectively, which indicated the presence of some order in the solid state. Furthermore, XRD analyses on these polymer films also support this assumption (see Figure 2). X-ray data suggest a lamellar packing for these polymers.[33,34] For all polymers (PCDT, PCDTB, and PCDT-BT), the peak at ~4.5° corresponds to a layering distance of $d = 19.6$ Å between sheets of each one of polymer chains that are packed in the plane, perpendicular to their longitudinal axes.[33,35] The second broader peak, near 20.5° for PCDTBT and near 19.5° for both PCDTB and PCDT, corresponds to a d-spacing of 4.4 and 4.6 Å, respectively, and could be attributed to the distance between the polymer chains within the layered planes.[33] Typically, the relatively small distance d that is observed with PCDTBT might be related to favorable dipole−dipole and $\pi-\pi$ interactions induced by the benzothiadiazole unit.[36,37]

The electrochemical properties of these polymers were investigated using cyclic voltammetry (see Figure 3). The oxidation and the reduction potential onset were defined as the position where the current starts to differ from the baseline. With this definition, the electrochemical and optical band gap values are in good agreement (Table 1). This choice has been further confirmed by spectroelectrochemical experiments (Figure 4). Those experiments reveal that the oxidation process starts at 0.75 ± 0.05 V vs SCE for the PCDTBT and PCDT and at 0.85 ± 0.05 V vs SCE for the PCDTB.

Upon oxidation, the copolymer spectroelectrochemical plots (see Figure 4) can be described by the Fesser, Bishop, and Campbell (FBC) model.[38,39] A polaron state is clearly evident with two new absorption bands at ω_1 (>1600 nm for the three polymers) and ω_2 (630 nm for PCDT, 600 nm for PCDTB, and 760 nm for PCDTBT). The complete oxidation to the bipolaron state is not reached in the first oxidation process, because the elimination of the ω_2 transition in the UV−Vis spectra is not observed. Further oxidation at higher potential leads to irreversible oxidation process and polymer degradation. Furthermore, according to the recorded oxidation potential, the neutral polymers should show a good

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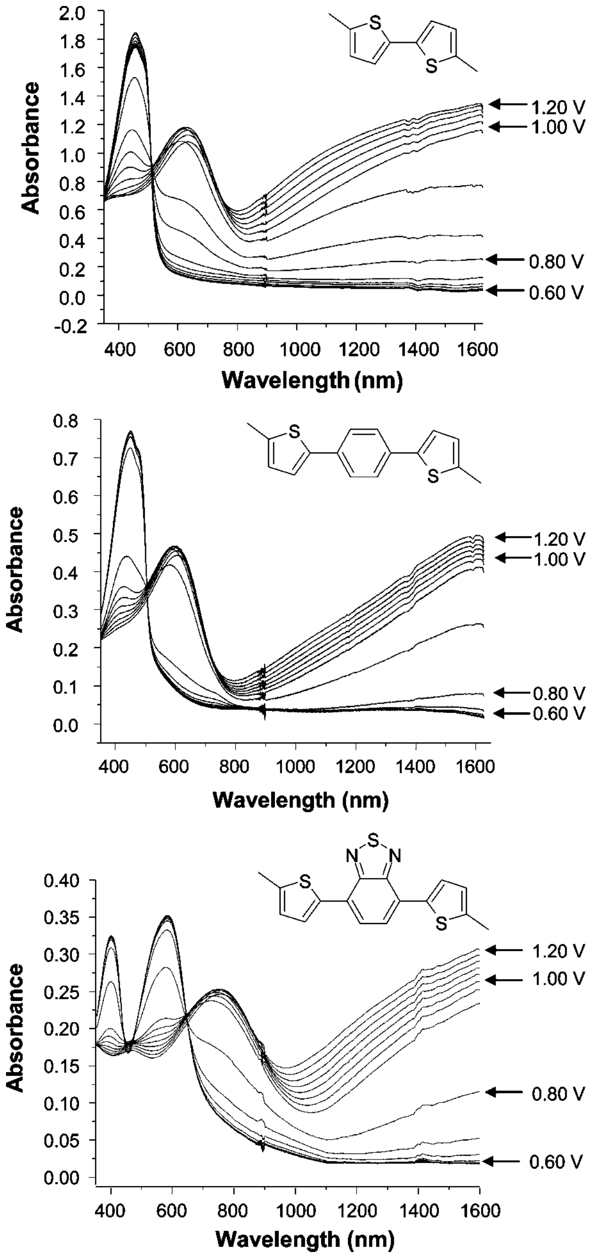

Figure 4. Absorption spectroelectrochemical plots for PCDT, PCDTB, and PCDTBT between 0.2 and 1.2 V vs SCE, with a step of 0.05 V.

air stability, the oxidation potential (Table 1) being clearly lower than the air oxidation threshold at 0.57 V vs SCE.[40]

Electrical and Thermoelectric Properties of the Polymers. Several studies have been already performed to demonstrate that structural parameters can influence the charge transport properties and the electrical conductivity in conjugated polymers. For instance, orientation and solid-state organization of the polymers may play a crucial role.[27,41] Previously, we showed, through X-ray analyses, that a structured state can be obtained by the introduction of secondary alkyl sidechain on the carbazole unit and packing units such as benzene and benzothiadiazole moieties. These strong interchain interactions should facilitate the transport of the charge carriers through the polymeric structure.[42,43]

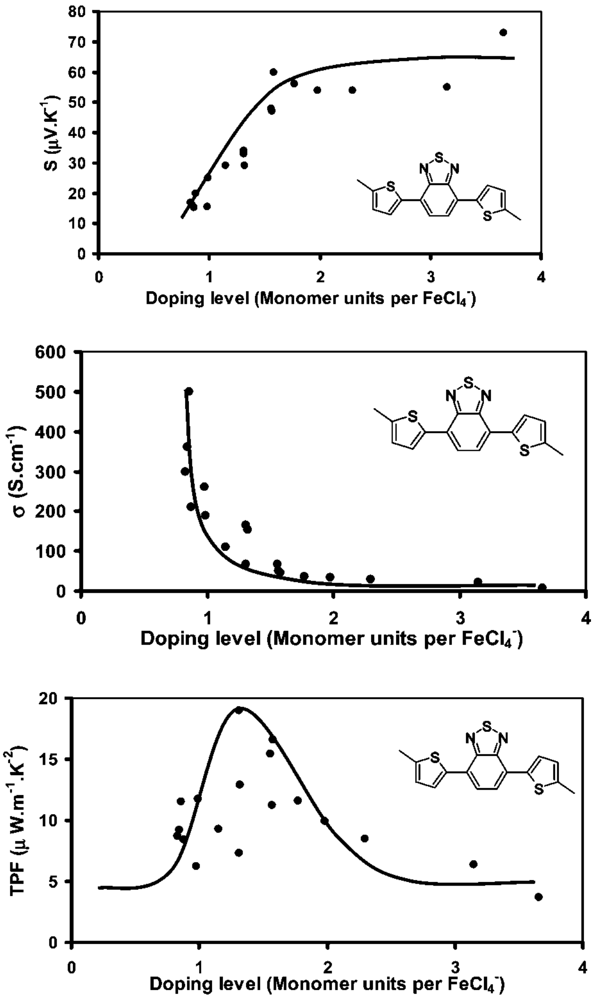

Figure 5. Seebeck coefficient, electrical conductivity, and power factor for FeCl$_3$-doped PCDTBT films as a function of the doping level. Curves are drawn as guide lines for the eye.

However, thermoelectric materials must combine both high electrical conductivities and high Seebeck coefficients. Unfortunately, the Seebeck coefficient usually decreases when the electrical conductivity is very high. As a typical example, Figure 5 shows the results obtained with PCDTBT films. With PCDTB and PCDT films, we noted lower values of thermoelectric parameters but similar behaviors. Figure 5 shows the experimental data of the Seebeck coefficient (S), electric conductivity (σ), and power factor (PF) obtained with PCDTBT for different doping levels with FeCl$_3$. In our calculations, we assume that all dopant molecules are FeCl$_4^-$ species. The selection of FeCl$_3$ as a doping agent was guided by previous thermoelectric results obtained with other carbazole-based polymers.[13,44]

Positive values of the Seebeck coefficient S are obtained for all doped films, indicating that the charge carriers are holes.[44]

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Table 2. Maximum Conductivity, Optimized Conductivity (σ), Maximum Seebeck Coefficient, Seebeck Coefficient (S), and Thermoelecrical Power Factor (PF) of PCDTBT-, PCDTB-, PCDT-, and PANI-Doped Films

	Maximum Data		Optimized Data		
doped film	σ (S/cm)	S (μV/K)	σ (S/cm)	S (μV/K)	PF (μW m^{-1} K^{-2})
PANI	160	6	160	5	0.4
PCDT	65	77	23	53	6.5
PCDTB	130	40	87	40	14
PCDTBT	500	70	160	34	19

The best Seebeck coefficient ($S \approx 70\ \mu$V/K) was obtained with PCDTBT for low doping levels with $FeCl_4^-$ species. PCDTBT films showed a Seebeck coefficient that was ~1 order of magnitude higher than that for polyaniline.[45] The second parameter evaluated was the dependence of the electrical conductivity upon the doping level of PCDTBT films. The best electrical conductivity (500 S/cm) was obtained at high doping levels; this electrical conductivity is 2−3 times higher than that obtained with polyaniline and is very similar to the best electrical conductivity that could be obtained with stretched poly(phenylene vinylene) derivatives.[18,46,47] Clearly, this electrical conductivity level is the highest among those reported for carbazole-based polymers.[13,44]

Figure 5 exhibits also the doping dependence of the power factor PF. Because the power factor is proportional to the square of the Seebeck coefficient, the high Seebeck coefficient of PCDTBT films did result in a power factor that was ~40 times higher than that of polyaniline.[48] The best balance between the electrical conductivity and Seebeck coefficient led to a power factor of 19 mW m^{-1} K^{-2} for PCDTBT at intermediate doping levels.

For comparison purposes, the maximum and optimized data of all these thermoelectric parameters obtained with PCDT, PCDTB, and PCDTBT films are summarized in Table 2. PANI films doped with (±)-10-camphorsulfonic acid (CSA), which is known to be a good thermoelectric polymer, was evaluated with our experimental setup and also was used for comparison.[25]

Stability Studies of Thermoelectric Parameters. Among all parameters, the stability of the conducting polymers is an important issue for thermoelectric devices. Some polymers, such as iodine-doped polyacetylene, can show electric conductivities up to 60 000 S/cm[49] but limited stability, even in an inert environment. We have tested the stability of doped PCDTBT films (with $FeCl_3$) by following their thermoelectric parameters under different conditions. Figure 6 shows these parameters as a function of time after doping, in air (including a normal level of moisture).

As it can be observed, after an initial decrease within the first few hours, the electrical conductivity of PCDTBT reaches a plateau at ~120 S/cm. This is partly due to its relatively low oxidation potential. In parallel, the Seebeck coefficient S shows a small increase, which ensures a relatively stable power factor of PF ≈ 17−18 μW m^{-1} K^{-2}. These data are among the best values reported up to now without physical treatment (annealing or stretching)[18,48] and more importantly, it is the first time that good and relatively stable thermoelectric properties can be observed in this class of conjugated polymers. Based on these results, poly(2,7-carbazole) derivatives now seem to exhibit promising

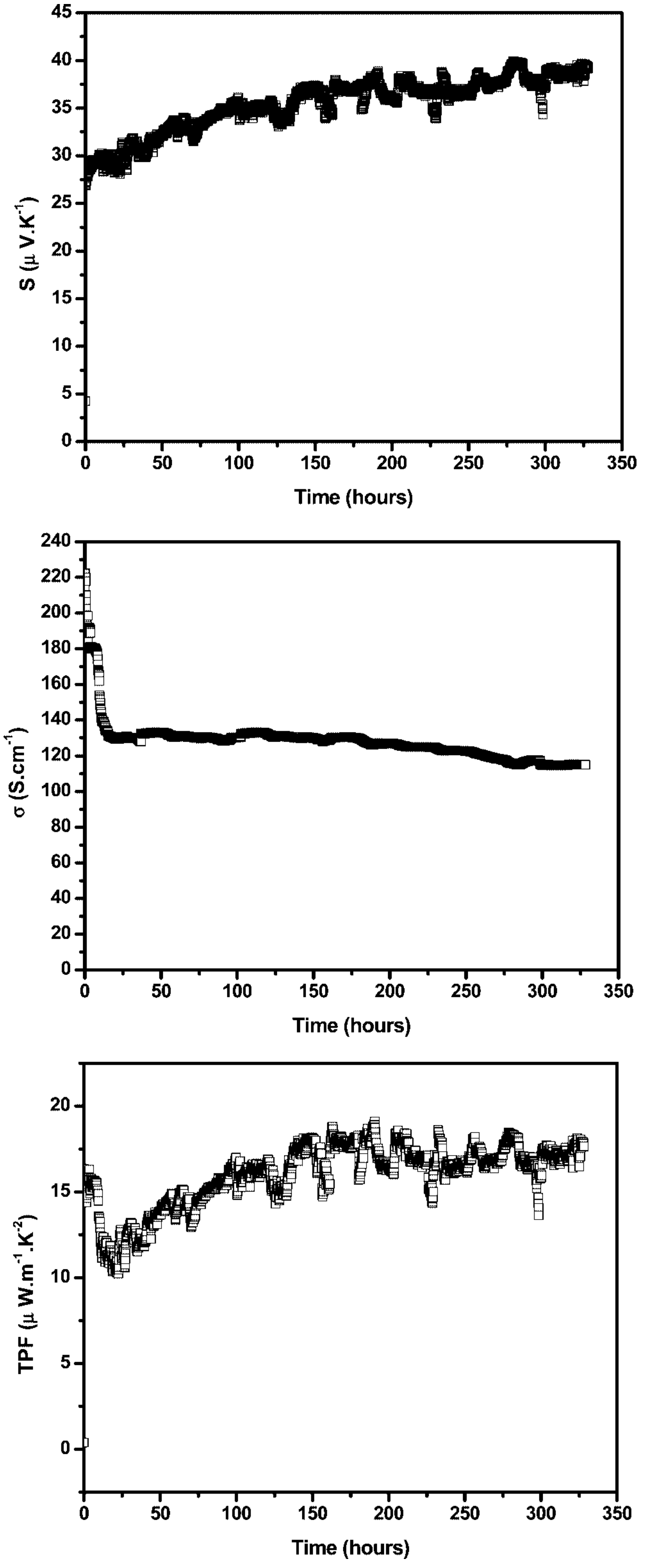

Figure 6. Stability study of thermoelectric parameters of doped PCDTBT films.

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parameters for the future development of polymeric thermoelectric devices.

Conclusions

X-ray analyses have shown that a structured morphology can be obtained by introducing a secondary alkyl sidechain on the carbazole unit and packing units such as benzene and benzothiadiazole unit along the conjugated backbone. Conductivity measurements indicate that, for identical processing parameters (the doped state), $FeCl_3$-doped PCDTBT films show the highest electrical conductivity, with values up to 500 S/cm. Maximum conductivity values of conductivity reached 130 S/cm for PCDTB and 65 S/cm for PCDT, respectively. All these conductivity values are the highest reported for carbazole-based polymers. Moreover, the Seebeck coefficients are relatively high with values up to 70 μV/K. The best balance between these parameters led to power factor (PF) values of 19, 14, and 6.5 $\mu W\ m^{-1}\ K^{-2}$ for PCDTBT, PCDTB, and PCDT, respectively. To the best of our knowledge, these data are among the highest thermoelectric parameters obtained with conjugated polymers that have been deposited without mechanical or thermal treatment. Moreover, these performances seem to be stable in air. However, to further increase the thermoelectric properties, it could be useful to evaluate the effects of some stretching or annealing. Other *N*-containing conjugated polymers will also be investigated, because it has been shown that this class of materials can lead to highly conducting materials.

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Supporting Information Available: Solution UV−visible absorption spectra of all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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