

Synthesis and Thermoelectric Properties of Polycarbazole, Polyindolocarbazole, and Polydiindolocarbazole Derivatives

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Received January 8, 2007. Revised Manuscript Received February 6, 2007

In a quest for thermoelectric polymeric materials novel polycarbazole and polyindolocarbazole derivatives were synthesized. Alkyl side chains on the carbazole cycle and different side chains (alkyl or benzoyl) on the nitrogen atom of the backbone unit were introduced. Optical, electrochemical, electrical, and thermoelectric properties were investigated on these polymers and on two poly(diindolocarbazole)s. Band structure calculations were used to predict which polymers might be promising as thermoelectric materials. The best combination of Seebeck coefficient and conductivity (power factor) was around 10^{-7} W m⁻¹ K⁻² with copolymers comprising thiophene units alternating with carbazole or indolocarbazole. This family of polymers possesses good Seebeck coefficients, but there is still a need to improve the electrical conductivity, to produce useful thermoelectric materials.

Introduction

Conjugated polymers such as polyacetylenes, polyanilines, polypyrroles, polythiophenes, polyphenylenevinyls, polyfluorenes, poly(3,6-carbazole)s, and poly(2,7-carbazole)s show interesting optical and electrical properties^{1–13} and have been extensively studied in many applications such as sensors, light-emitting diodes, transistors, and photovoltaic cells.^{1–8} The incorporation of flexible side chains in the structures of such different conjugated polymers is now a common way of improving processability by increasing

solubility or fusibility. More recently, ladder type oligomers and polymers derived from diindolocarbazoles and indolocarbazoles have attracted attention because of their very rigid backbone which leads to good packing, high charge mobility, and high thermal stability.^{14–16}

Our main objective is to study conjugated polymers for their potential use as thermoelectric materials for power generation. Efficient thermoelectric materials need to have a high figure of merit, $ZT = S^2\sigma T/\kappa$, where S stands for the Seebeck coefficient, σ and κ are the electrical and thermal conductivities, and T is the temperature.¹⁷ $S^2\sigma$ is also known as the power factor. Polymers inherently possess a low thermal conductivity, which gives them a significant advantage over conventional thermoelectric materials.

In the literature, thermoelectric data have been reported previously^{17,18} for polyacetylenes, polyanilines, polypyrroles, and polythiophenes. The best conjugated polymer up to now is still polyacetylene, with a high figure of merit ZT (0.6–6) due to its good electrical conductivity and high Seebeck coefficient. However, it has poor stability in the doped state even in an inert atmosphere. The other polymers show better stability in the doped state, but lower Seebeck coefficient

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and conductivity, which limits the figure of merit to less than 10^{-2} . There is a need to find other stable polymers in the doped state which have the characteristics for a high ZT.

Our approach for the design of new promising materials combines band structure calculations and experimental measurements. Good thermoelectric materials should have a flat band near the Fermi level for high Seebeck coefficient and a dispersive band for high electrical conductivity.^{19,20} Generally, conductivity decreases as the Seebeck coefficient increases. On the basis of previous theoretical band structure calculations on some polycarbazole derivatives, we wish to maintain a high Seebeck coefficient while improving the electrical conductivity.

An interesting characteristic of the polycarbazoles (PC) and polyindolocarbazoles (PIC) is their doping behavior. In fact, it was found that the nitrogen atom is oxidized prior to the backbone.²¹ This is interesting because the charge is then very localized, and this should result in a large Seebeck coefficient. However, this can present a problem due to charge-carrier pinning, which adversely affects the conductivity. The objective is to strike a balance in the level of oxidation of the polymer such that a certain degree of localization is maintained while still allowing mobility of the charges for the polymer to be conductive. We have previously studied²² poly(*N*-octyl-3,6-dihexyl-2,7-carbazole-nevinylene) (PCVH), containing flexible side chains on the carbazole cycle. Unfortunately, although the Seebeck coefficient of PCVH was reasonably high, there was a lack of stability for this polymer in the doped state and the conductivity was too low (about 5×10^{-3} S/cm). Following from these results we have tried to synthesize polymers containing more stable conjugated units than vinylenes. Thus in the first stages of this study we used pyrrole or bis-3,4-(ethylenedioxy)thiophene (bi-EDOT) units as comonomers, which are relatively stable units in the doped state at room temperature and are generally good conductors.²³ Another objective was to keep the solubility of the 2,7-polycarbazole polymers high by introducing side chains at the para positions to the nitrogen atom (3,6-positions) of the carbazole unit, as we had previously accomplished with PCVH.

Following this work, the relatively high conductivity of derivatives of polyindolocarbazoles and polydiindolocarbazoles^{15,16} led us to investigate these as potential thermoelectric materials. Furthermore, the conductivity increase obtained using *N*-benzoyl side chains on 2,7-polycarbazole²¹ inspired us to synthesize more new materials: *N*-substituted polyindolocarbazoles and polycarbazoles. The project was also devoted to the improvement of the solubility of the polyindolocarbazoles produced.

In this paper we report the synthesis of novel polycarbazoles and polyindolocarbazoles and compare their thermo-

electric properties. We report theoretical and experimental results of derivatives and alternating copolymers of polycarbazoles, polyindolocarbazoles, and polydiindolocarbazoles.

Experimental Section

The details of the synthesis of the different compounds can be found in the Supporting Information.

Polymer Characterization. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with an HPLC pump using a Waters UV-visible detector. The calibration curve was made with a series of monodispersed polystyrene standards in tetrahydrofuran (THF), *N*-methyl-2-pyrrolidone (NMP), or chloroform (HPLC grade, Aldrich) depending on the eluent used for the experiment.

UV-visible absorption spectra were recorded using a Varian Cary 500 spectrophotometer, using 1-cm path length quartz cells or quartz (or glass) plates (solid state). The optical band gap (E_g) was determined at the onset of the absorption peak for the neutral polymers in the solid state. Oxidation of the thin films was done by dipping the plate into a doping solution of 0.01 to 0.1 M of ferric chloride in acetonitrile for 1–5 min.

For UV-vis-near-IR (NIR) spectroelectrochemical analyses, the working electrode (indium tin oxide, ITO, coated on glass, 10 Ω /square, Thin Film Devices), the counter electrode (Pt) and the Ag/Ag⁺ reference electrode (0.1 M AgNO₃, 0.1 M NBu₄BF₄, 0.34 V vs saturated calomel electrode, SCE) were immersed in a solution of 0.1 M Bu₄NBF₄ in MeCN in 2-cm quartz cells which were subsequently sealed. Absorption spectra were recorded (scanning at 1000 nm/min) while applying a constant potential using a Solartron potentiostat (model 1287).

Thermogravimetric analysis (TGA) was carried out with a TGA/SDTA851e (Mettler Toledo). The heating rate was 10 °C/min under a nitrogen atmosphere. At the temperature of degradation the corresponding weight loss was 5%.

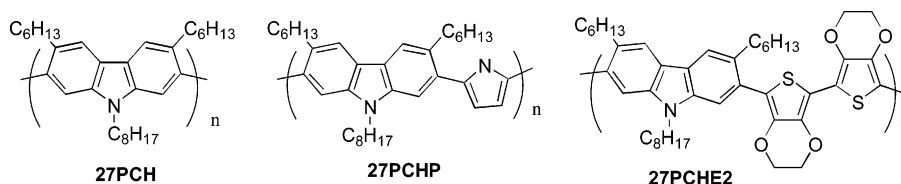
Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC 7, calibrated with ultrapure indium. The glass transition temperatures (T_g) were obtained after erasing the thermal history by first heating to 280–300 °C. The results are from the second heating scans at 20 °C/min between 25 and 350 °C.

Electrochemical Apparatus and Procedures. Experiments were carried out at 25 °C under nitrogen in three-electrode electrochemical cells. The counter electrode was platinum; the reference electrode was Ag/Ag⁺ 0.1 M in 0.1 M tetrabutylammonium perchlorate Bu₄NClO₄ in acetonitrile (CH₃CN). The potential of the reference electrode was 0.34 V versus SCE. The polymer films were cast onto electrodes from a polymer solution in chloroform, chlorobenzene (CB), THF, or NMP (evaporation at 80–90 °C for NMP). For the in situ conductivity measurements, the polymers were dissolved in CB or chloroform and cast, and cyclic voltammograms (CVs) were run at 0.1 V/s. The apparatus and procedures used for the in situ conductivity experiments were previously described in detail.^{24,25} The electrode for conductivity measurements was typically a two-band platinum electrode (0.3 cm \times 0.01 cm for each band) with interband spacing of 20 μ m. In case of conductivities lower than 10^{-2} S cm⁻¹, the electrode was a microband array platinum electrode (5 μ m bandwidth, 100 nm thick) with interband spacing of 5 μ m. The deposit was thick enough to ensure minimum resistance, under which condition the conductivity

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Scheme 1. Poly[(3,6-diethyl)2,7-carbazole] Derivatives



σ is given by $\sigma = k/(R - R_0)$, where R is the measured resistance, R_0 is the lead resistance, and k is the cell constant.

The monomer CV characterization was performed in dichloromethane containing 0.1 M Bu_4NClO_4 .

Two-Probe Conductivity and Thermoelectric Measurements.

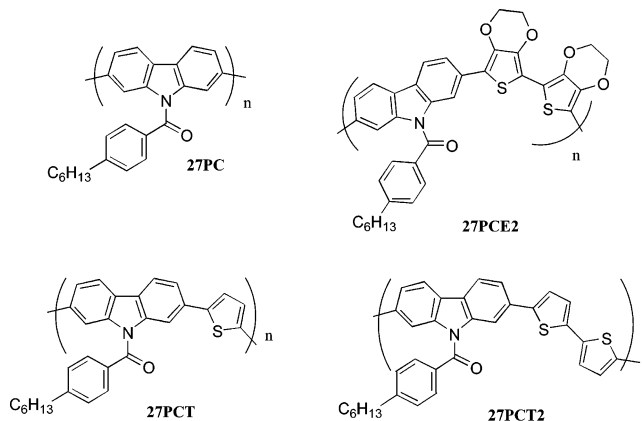
The doping solution was usually made of ferric chloride (or exceptionally ferric tosylate) in dry acetonitrile, and the powdered polymer was stirred under an argon atmosphere in this doping solution. The doping time varied from 30 min to 4 h, and the dopant concentration varied from 0.01 to 0.1 M. Each polymer was doped using one to four different doping conditions. The doped material was filtered, rinsed with acetonitrile, and dried in a desiccator under vacuum at room temperature for 30 min to 2 h. The material was then pressed into a pellet and cut as a rectangle of typically 6 mm \times 8 mm (sometimes larger) and a thickness of about 0.3 mm. Thermoelectric data were obtained using a homemade apparatus consisting of two blocks of copper, and the free-standing doped polymer sample was placed across these copper blocks, separated by a distance of 5–10 mm. The sample was sandwiched on each side between copper plates. The copper was covered with thin gold plates (Aldrich, 99+% pure). On one side the copper block was cooled using a Peltier device (max 3A), and the other side was kept at room temperature. The difference in temperature between the two copper blocks was typically 3 to 6 °C. 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 (The Bergquist Company)) and covered by Scotch 27 glass cloth electrical tape (3M) for heat isolation. The measurements were done in a nitrogen bag, keeping the relative humidity below 10%. Voltage and resistance measurements were done using a Keithley 2000 multimeter, and a digital thermometer (Omega model HH-22) was used to measure the temperature difference between the two copper blocks.

Conductivity was also determined by measuring the resistivity of the doped films in air at room temperature on the thermoelectric measurement device, using the gold plates as contacts (two-probe measurement).

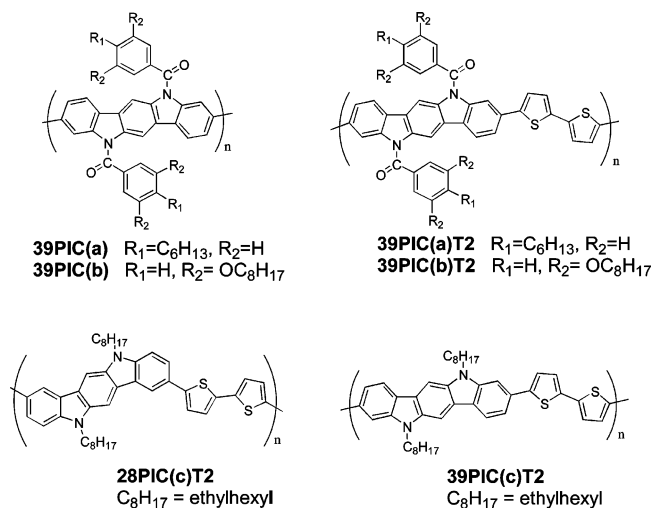
Band Structure Calculations. The pseudopotential plane wave method using the VASP program^{26,27} was employed to perform the band structure calculations, as described previously in detail.^{19,20,22} In this work the ultra-soft pseudopotential²⁸ was used, and the electron–electron interaction was treated by a generalized gradient approximation (GGA).²⁹ Alkyl side chains were replaced in the calculations by hydrogen atoms, to make the calculations feasible within practical time frames.

Results and Discussion

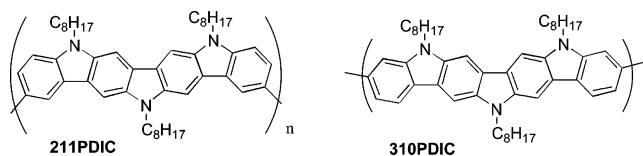
Polymers Studied. All homopolymers and alternating copolymers studied in this work are presented in Schemes 1–4. Four distinct classes of polymers were synthesized, involving one ring, two fused-rings, or three fused-rings of

Scheme 2. Poly(2,7-*N*-hexylbenzoyl)carbazole Derivatives

Scheme 3. Polyindolocarbazole Derivatives



Scheme 4. Polydiindolocarbazole Derivatives



carbazole: (a) The 3,6-diethylsubstituted polycarbazoles (27PCHs) coupled in the 2,7-positions of the carbazole moiety are novel polymers presented in Scheme 1. (b) The 2,7-polycarbazole series (27PCs, Scheme 2) are substituted with a hexylbenzoyl moiety on the nitrogen atom and do not have any substituent at the 3,6-positions. Synthesis, optical, electrochemical, and conducting properties of 27PC and 27PCT were previously reported,²¹ and these polymers are used for comparisons with the two novel 27PCs in Scheme 2. (c) The polyindolocarbazole series (PICs, Scheme 3) is separated into three groups, depending on the substituent on the nitrogen atom; the first one where the benzoyl group is substituted with a *n*-hexyl side chain, 39PIC(a), the second

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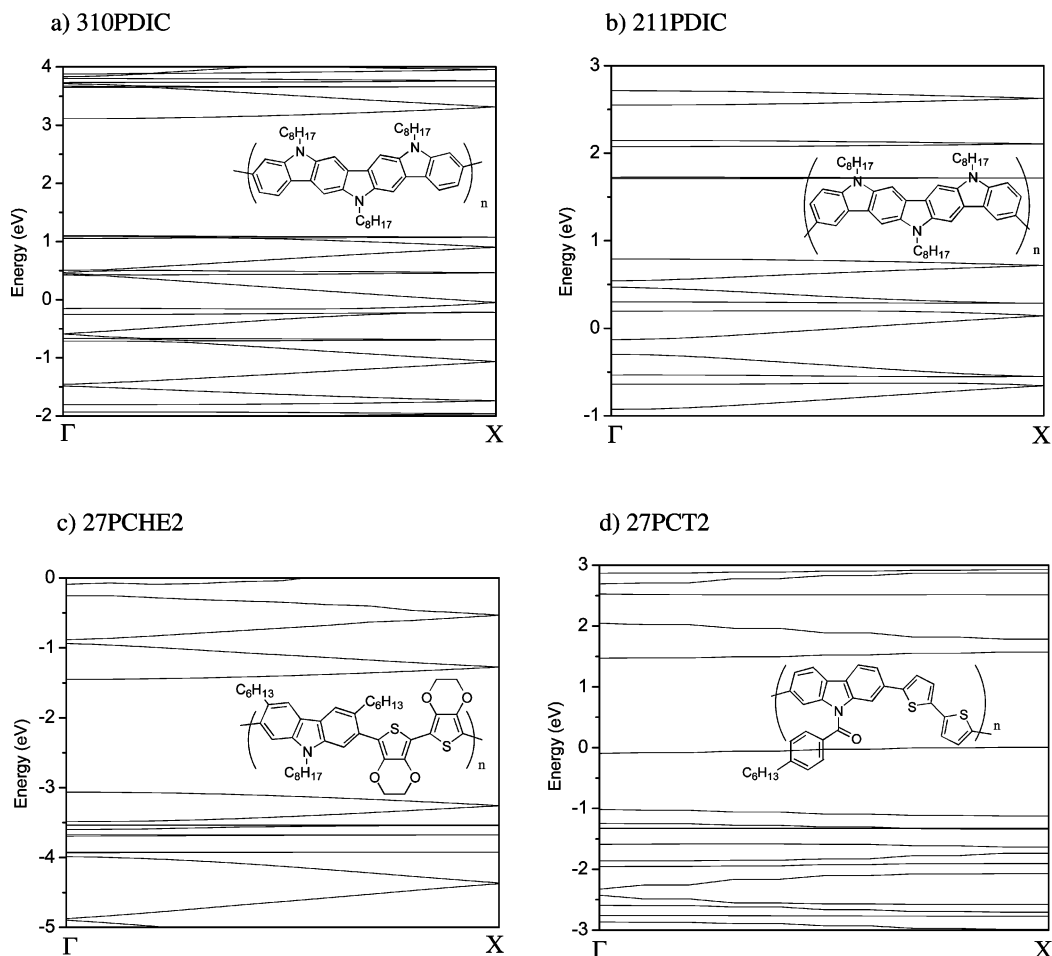


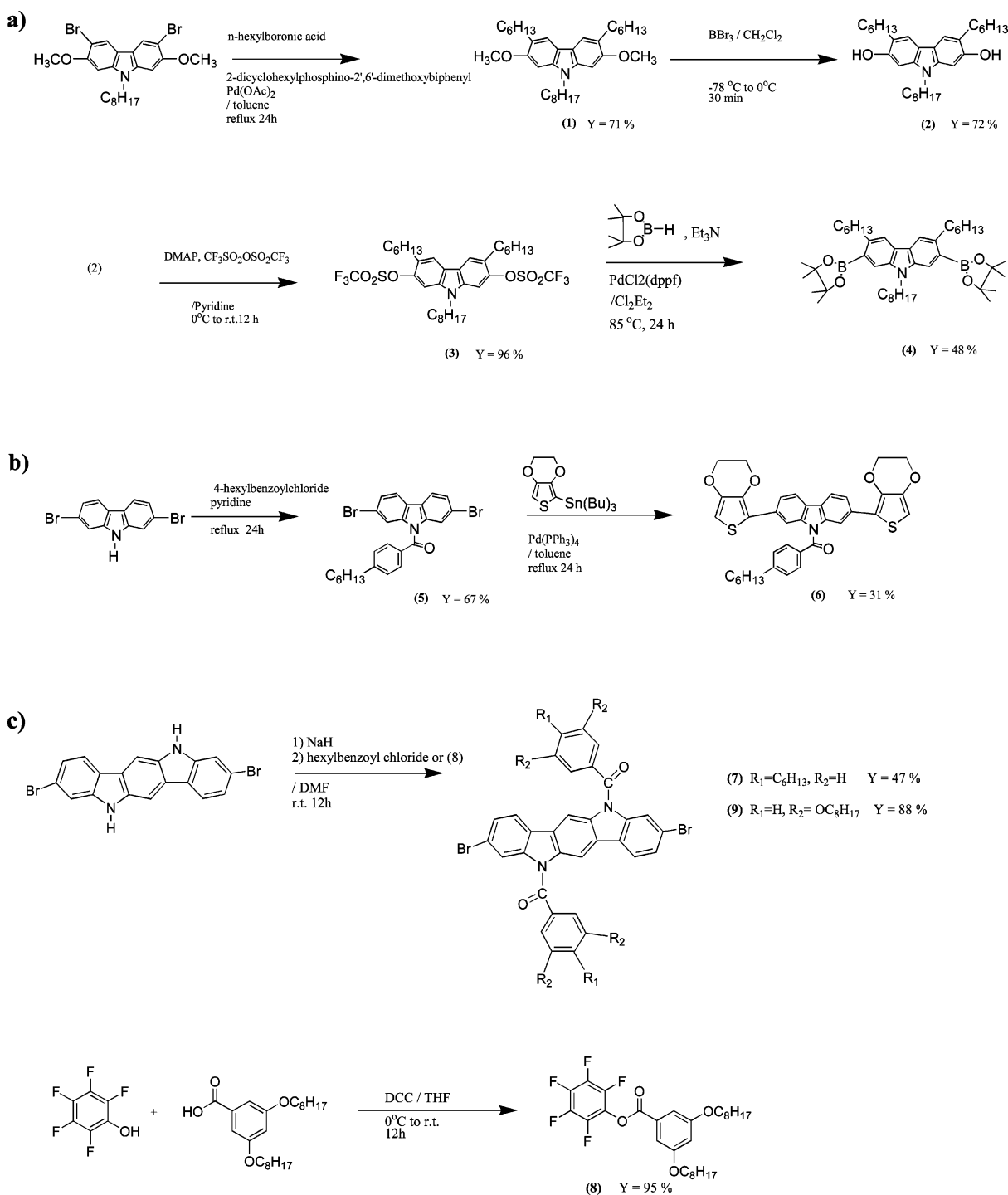
Figure 1. Band structure calculations for (a) 310PDIC, (b) 211PDIC, (c) 27PCHE2, and (d) 27PCT2.

one where the benzoyl group is substituted with two octyloxy side chains, 39PIC(b), and the third one, where two other copolymers of polyindolocarbazoles are bearing 2-ethylhexyl substituents, 28PIC(c)T2 and 39PIC(c)T2. For the polyindolocarbazoles, the 3,9-coupling (positions meta to the nitrogen atom) is analogous to the 2,7-coupling in polycarbazoles, whereas the 2,8-coupling (positions para to the nitrogen atom), such as in 28PIC(c)T2, it is analogous to the 3,6-coupling in polycarbazoles. The PIC(a)s and PIC(b) are novel polymers containing a benzoyl moiety. (d) Finally, the last family studied, polydiindolocarbazoles (PDICs), is presented in Scheme 4. The four last polymers (the PIC(c)-T2s, and PDICs) have been the subject of previous publications,^{15,16} and for these polymers, we will focus on the conducting and thermoelectric properties.

Band Structure Calculations. Selection of the polymers was guided by previous conductivity results^{15,16,21} and the band structure calculations. The calculations were performed to understand the importance of chemical structure in the thermoelectric behavior. As stated earlier, a good thermoelectric material should possess flat bands and dispersive bands close to the Fermi level.^{19,20} The band structures of 2,7-coupled polycarbazoles (27PC series) were compared to 3,6-coupled polycarbazoles (36PC series, Supporting Information), and the conclusion was that we generally see more dispersive bands for the 27PC series, which would suggest a higher conductivity for 2,7-coupled polymers compared to 3,6-coupled polymers. We have in fact synthesized these

3,6-coupled derivatives (unpublished results), and the results corroborate the lower conductivity which strongly affects the thermoelectric behavior. Among the polymers studied, the band structures for two different classes ((i) one ring and (ii) three fused rings) are compared in Figure 1. In Figure 1a, for 310PDIC, the flat band condition near the Fermi level is shown to be fulfilled. By comparing parts a and c of Figure 1, we can see that 310PDIC shows both flat bands and dispersive bands near the Fermi level, whereas the bands for 27PCHE2 are more dispersive. This would suggest that thermoelectric behavior should be better for 310PDIC than for 27PCHE2. 211PDIC (Figure 1b) has a calculated band structure similar to that of 27PCHE2. 27PCT2 (Figure 1d) shows less dispersive bands than 27PCHE2, indicating a possibly lower electrical conductivity, which could also result in a lower Seebeck coefficient. These indications are, however, only qualitative. Starting with this information, the polymers in Schemes 1–4 were investigated experimentally.

Synthesis and Characterization. The synthesis of the monomers and polymers are given in detail in the Supporting Information, and the syntheses of some novel monomers are presented in Scheme 5. The introduction of different flexible side chains was meant to improve the solubility, whereas the benzoyl substituents were introduced to try to enhance the conductivity. For the 39PIC(b) series, the benzoyl substituents were obtained using perfluorophenyl 3,5-bis-(octyloxy)benzoate (**8**) instead of the corresponding acyl derivative used for 27PC and 39PIC(a) series. Compound **8**

Scheme 5. Synthesis of Novel Monomers^a

^a (a) 3,6-Hexyl substituents on the carbazole unit, for 27PCH derivatives; (b) *N*-hexylbenzoyl substituent, for the 27PC derivatives; (c) *N*-benzoyl Substituents for 3,9-indolocarbazoles.

was synthesized with good yield (95%) and could be easily purified. Polymerizations were performed by Stille, Yamamoto, Suzuki–Miyaura, or oxidative coupling with ferric chloride. In general, for the polyindolocarbazoles bearing hexylbenzoyl side chains (39PIC(a)), the polymers start to precipitate soon after the polymerization process took place. Polymerizations (especially Yamamoto coupling reaction) for polyindolocarbazoles were done in very dilute solutions. Even though it is possible to obtain a very thin film on a substrate by casting the polymer from THF, chloroform

(CHCl₃), or NMP, none of these polymers form thick free-standing films.

Physical and thermal properties of the different polymers synthesized are presented in Table 1. The variety of molecular weights obtained is probably due to a lack of solubility in some cases as well as to the different polymerization methods used. We have not tried to optimize the solvent or the concentration for the polymerizations. For the 27PCH series, relatively modest molecular weights can be obtained for 27PCH and 27PCHE, possibly due to the

Table 1. Structural and Thermal Properties of the Polymers Synthesized^a

polymer	M_w^b (g/mol)	PI	T_g (°C)	T_d (°C)
27PCH	10 200 ^c	1.6	n.d.	415
27PCHP	83 400 ^c	1.6	n.d.	450
27PCHE2	22 500 ^c	1.9	n.d.	385
27PC ^(R15)	64 100 ^d	1.9	n.d.	n.d.
27PCT	55 500 ^d	2.4	109	367
27PCT2	58 800 ^d	2.3	131	341
27PCE2	36 600 ^c	1.7	245	385
39PIC(a)	5 500 ^e	1.6		435
39PIC(a)T2	2 500 ^e	1.1		370
39PIC(b)	64 900 ^d	2.5		368
39PIC(b)T2	32 700 ^d	2.5		400

^a PI, polydispersity index; n.d.: not determined; blank, not visible on the scans performed. ^b Soluble part of the polymer. ^c In THF. ^d In CHCl₃. ^e In NMP.

reasons mentioned above. 27PCH is freely soluble in chloroform and THF. 27PCHE2 is fairly soluble too, but 27PCHP is less soluble once the *N*-*tert*-butoxycarbonyl (BOC) protecting group (present during polymerization) is removed.

For the relatively insoluble polymers, 39PIC(a)s and 39PIC(a)T2s, gel permeation chromatography (GPC) measurements were inadequate because only the lowest molecular weight fraction was analyzed, even when the solvent was NMP instead of THF. Moreover, because polystyrene calibration standards were used, the GPC analysis overestimates the molecular weight of these rigid-rod polymers due to the different behavior of the flexible coils in solution.³⁰ There also seemed to be aggregation of the polymers, and retention on the columns was shown by very broad peaks at higher molecular weights. For these polymers, the polymerization's success was proven by UV–visible absorption spectroscopy (Supporting Information) where the spectra of the polymers are red-shifted compared to the monomers and are represented by a broader spectrum. The 39PIC(b)s are more soluble than the 39PIC(a)s and easier to characterize, 39PIC(b)s having molecular weights of 32.7 kD and 64.9 kD, and a polydispersity index (PI) of 2.5. 39PIC(b)T2 is freely soluble in THF and chloroform, and even though 39PIC(b) is much less soluble, GPC characterization is possible using very dilute solutions to overcome possible aggregation.

DSC measurements reveal a glass transition temperature (T_g) above 100 °C for the hexylbenzoyl substituted polycarbazoles (27PCT, 27PCT2) and up to 245 °C for the 27PCE2 derivative. No clear melting is observed by DSC measurements (on the second scan, after erasing thermal history). The polyindolocarbazole derivatives do not show any clear transition by DSC. TGA demonstrated excellent thermal stability: a 5% weight loss can be observed from 340 °C to 450 °C depending on the polymer. As expected, the polymers containing thiophene units are generally less stable at high temperatures (in the range 340–400 °C).

Optical Properties. UV–visible absorption spectra of the 27PCs are presented in Figure 3. The solid-state spectra are generally broader than in solution. The spectra and their maximum wavelength of absorption in the solid are closely

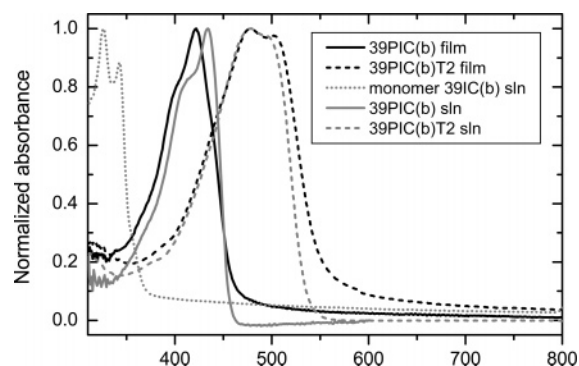


Figure 2. UV–visible absorption spectra of the 39PIC(b) derivatives in solution in THF (gray) and in solid state (black). (Films cast from THF or CHCl₃.)

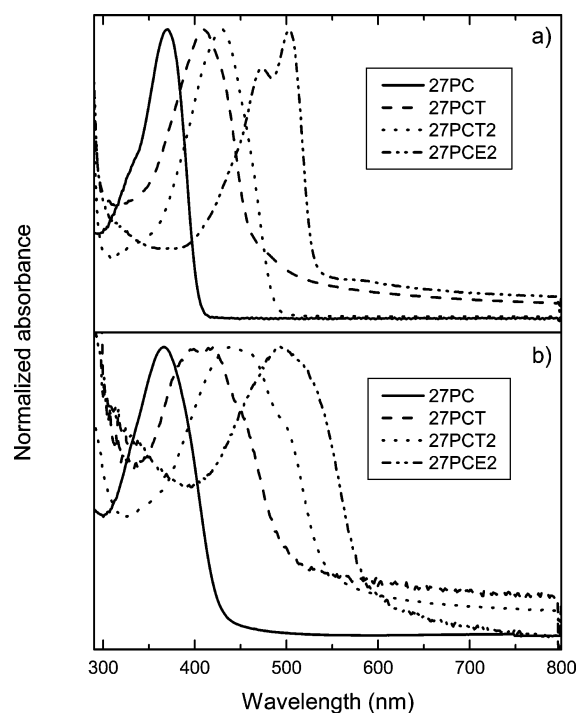


Figure 3. UV–visible absorption spectra for the 2,7-coupled polycarbazole derivatives (a) in THF and (b) in the solid state.

related to the spectra in solution, indicating very rigid systems with similar conformations in both cases. The increasing wavelengths of the absorption maxima indicate that the polymers are more conjugated as more thiophene units are added to the structure. When two units of 3,4-ethylenedioxythiophene (EDOT) are present, the increased absorption wavelength can be explained by the higher highest occupied molecular orbital (HOMO) energy levels³¹ compared to the bithiophene unit. The optical characteristics (and molecular weight) of 27PCT are similar to the polymer first synthesized (previously called PTNBC in the literature).²¹ UV–visible absorption spectra of the 39PIC(a) series are presented in Supporting Information. 39PIC(b) (Figure 2) is slightly more conjugated in solution (2–12 nm red-shift) compared to the solid-state. This could be explained by some reorganization and better packing in the solvent. This phenomenon was also observed for 27PC and 27PCT.

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Table 2. Electrochemical, Electrical, and Thermoelectric Properties of the Polymers^a

polymer	E°_{ox} (mV; vs Ag/Ag ⁺)	σ (in situ; S/cm)	[FeCl ₃] (mol/L)	T (h)	s (ex situ; S/cm \pm 10%)	S ($\mu\text{V/K} \pm 5\%$)	PF (W/(K ² m) \pm 20%)
27PCH	0.80						
27PCHP	0.50; 0.72	1×10^{-3}					
27PCHE2	0.45; 0.75	4×10^{-3}	0.01	1.75	4.5×10^{-3}	55	1.4×10^{-9}
27PC	0.65; 0.95 ²¹	1×10^{-2} ²¹	0.1	2	1.2×10^{-2}	61	4.6×10^{-9}
27PCT	0.68	5×10^{-2}	0.05	2	2.9×10^{-2}	64	1.2×10^{-8}
27PCT2	0.55	0.1	0.05	2	0.29	71	1.5×10^{-7}
27PCE2	0.35; 0.78	0.2	0.01	0.5	0.16	62	6.2×10^{-8}
39PIC(a)	0.45						
39PIC(a)T2	0.60	4×10^{-2}	0.05	2	0.12	53	3.4×10^{-8}
39PIC(b)	irrev.						
39PIC(b)T2	0.40	0.2	0.05	2	1.9×10^{-2}	7.3	1.0×10^{-10}
28PIC(c)T2	0.15; 0.40 ¹⁶	0.7 ¹⁶	0.05	2	0.21	4.9	5.0×10^{-10}
39PIC(c)T2	0.30; 0.63 ¹⁶	0.1 ¹⁶	0.05	2	0.29	65	1.2×10^{-7}
211PDIC	0.08; 0.64; 0.89 ¹⁵	0.04 (0.5) ¹⁵	0.007	0.5	3.0×10^{-3}	127	4.8×10^{-9}
310PDIC	0.09; 0.71; 0.89 ¹⁵	0.01 (0.04) ¹⁵	0.007	0.8	2.7×10^{-4}	290	2.3×10^{-9}

^a irrev., irreversible; T , doping time; σ (in situ), conductivity obtained from electrochemistry; σ (ex situ), conductivity from chemically oxidized polymers by two-probe measurement; S , Seebeck coefficient; PF, power factor.

The optical band gap (E_g , obtained from the onset of the UV–visible absorption spectra) is the lowest for 27PCE2 (2.11 eV) and 27PCT2 (2.28 eV). For the indolocarbazole series, the lowest band gaps are observed with 39PIC(b)T2 (2.25 eV) and 39PIC(a)T2 (2.27 eV). Larger band gap polymers such as 27PCH and 27PCHP showed absorption maxima at 317 and 373 nm respectively in the solid state, while 27PCHE2 was at 388 nm.

Electrochemistry. The redox oxidation (E°) potentials of the polymers studied are presented in Table 2. The polymers show similar behavior in NBu_4BF_4 or NBu_4ClO_4 electrolytes. The subunits of 27PCHE2, carbazole and 2,2'-bi-EDOT, are electron donors with a significant difference in ionization potential. The repeat units of the copolymers can be compared as a first approximation to the relevant monomers (cooperative conjugation lowers the whole redox potential). The oxidation peak potentials of the individual molecules are 0.95 V³² and 0.53 V³² versus Ag/Ag⁺ respectively, so that the first oxidation process of the polymer may be assumed to involve the 2,2'-bi-EDOT moiety. The subsequent process is likely to involve the carbazole unit.^{33,34} The subunits of 27PCHP, carbazole and pyrrole, are electron donors with quite close ionization potentials. The oxidation peak potential of pyrrole is in fact 0.97 V³⁵ versus Ag/Ag⁺. In this case the location of oxidation is not evident. The polymer starts to degrade at the second oxidation process near 0.75 V versus Ag/Ag⁺.

Homopolymer 27PC presents two oxidative processes. Compared to the N-alkylated polymer, the oxidation potentials of N-benzoyl substituted polymers²¹ are shifted to more positive values as a result of the electron-withdrawing side chain on the nitrogen atom. The individual oxidation potentials for thiophene and bithiophene units are 1.73 and 0.97 V, respectively.³⁵ Only one oxidation process is observed with copolymers containing one or two thiophene

units, making it difficult to determine the location of the oxidation processes from the two subunits. Two thiophene units shift the oxidation potential to lower values, as expected for a more conjugated system and with perhaps better delocalization. For 27PCE2, two oxidation processes are observed, the first one probably due to the 2,2'-bi-EDOT moiety, and the second one may involve the carbazole unit.

39PIC(a) homopolymer shows a reversible oxidation, but 39PIC(b) homopolymer shows only a non-reversible oxidation peak around 1.1–1.2 V. 39PIC(a)T2 shows a higher oxidation potential compared to 39PIC(a). 39PIC(a)T2 should be more conjugated than the homopolymer and have a lower oxidation potential, but because the films were cast from the soluble fractions, the low molecular weight fraction (which generally is less conjugated) of the soluble part of 39PIC(a)T2 could affect its oxidation potential. The oxidation peak potentials (vs Ag/Ag⁺) of the individual molecules are 0.97 V (bithiophene), whereas indolocarbazole (IC) is oxidized at 0.55 V.³⁶ 39IC(a) (dibromine monomer) is oxidized near 0.60 V versus Ag/Ag⁺ in dichloromethane. This time, the N-benzoyl substituents do not cause a clear positive shift of the oxidation potential in the N-benzoyl substituted polyindolocarbazoles compared to the N-alkyl substituted compounds (PIC(c)). Because 39PIC(a)T2 and 39PIC(b)T2 show only one oxidation peak before degradation, it is difficult to distinguish where the oxidation occurs first. The oxidation of the 39IC(b) (dibromine monomer) displays non-reversible peaks around 1.4 V versus Ag/Ag⁺, showing the same trend as in the homopolymer.

Chemical Oxidation and Spectroelectrochemistry. Figure 4 represents the UV–visible–NIR absorption spectra of some oxidized polymers. Upon oxidation with ferric chloride, the polymers become black, and new absorption bands appear in the visible–NIR range. The intensity of the initial absorption band decreases drastically for 27PCT2, 39PIC(c)T2, and 27PCHE2, as usually observed for doped polymers. Upon doping, new polaronic bands appear, the initial absorbance band is shifted in most cases to higher energies, and its intensity is decreased. The two absorption bands are

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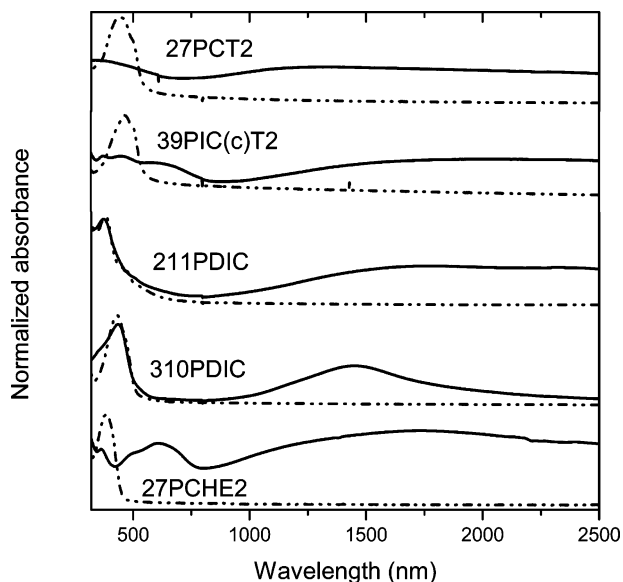


Figure 4. UV-visible-NIR absorption spectra for various polymers in the solid state on quartz. Dashed line, undoped; black line, same film doped with ferric chloride.

related to the formation of polarons (radical cations) and bipolarons (bications).

For 211PDIC and 310PDIC, the intense band related to the π - π^* transition does not seem to decrease significantly upon doping. This has been previously attributed to the fact that low intensity absorption bands (slightly red-shifted from the π - π^* transition), related to the electronic transitions of the nitrogen atoms, are the ones affected during the doping process.¹⁵ Moreover, these polymers have two oxidation states. By comparison with the spectro-electrochemical spectra previously registered for these two polymers,¹⁵ the spectra in Figure 4 seem to represent the neutral polarons created upon doping, which correspond to the first oxidation state obtained by chemical doping with ferric chloride. With a stronger chemical oxidant (nitrosonium tetrafluoroborate, NOBF₄), for 310PDIC, the doping was slightly increased (hypsochromic shift to 1340 nm, not shown). For 211PDIC, the second oxidation state is 10 times more conducting (0.5 S/cm).¹⁵ Attaining this oxidation state would be very difficult, requiring a strong oxidant that would not degrade the polymer. Also, stability problems may occur (see below).

Figure 5 corresponds to the spectro-electrochemistry data for 27PCT2. The UV-visible-NIR spectra on an ITO substrate were recorded along with the electrochemical oxidation of the polymer. Because ITO is less conducting than platinum, the voltage necessary to oxidize the polymer is slightly higher than the one found on platinum. The appearance of polaronic and bipolaronic bands can be observed, and a hypsochromic shift is also noted as the oxidation is increased.³⁷ As depicted in Figure 4, ferric chloride can oxidize this polymer, giving rise to new absorption bands around 600 and 1400 nm, similar to those observed in Figure 5 at high oxidation potential. However, as stated above, for other polymers with higher oxidation potentials, it is possible that ferric chloride does not oxidize the polymer to a sufficiently high level, so that the

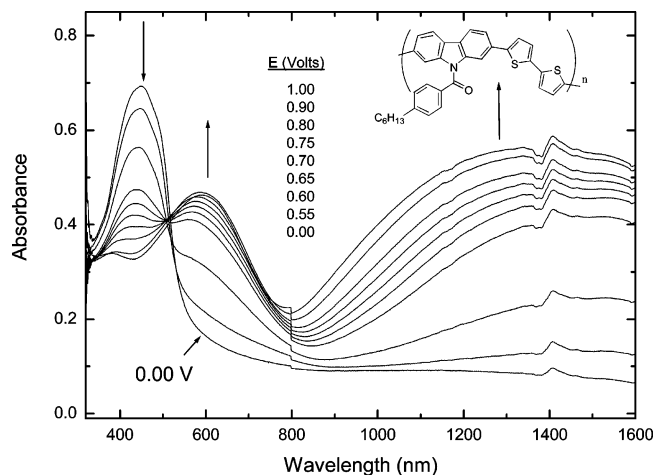


Figure 5. UV-visible-NIR absorption spectra of 27PCT2 film on ITO, as a function of the electrochemical oxidation in 0.1 M NBuBF₄/CH₃CN. The arrows indicate the evolutions of the peaks as the potential is increased.

conductivity obtained is lower compared to the maximum observed by in situ conductivity. UV-visible-NIR spectra obtained using ferric tosylate as a dopant were comparable to those obtained with ferric chloride as a dopant for the few polymers tested (for example, 27PCHE2).

Conductivity. Table 2 shows the results for conductivity measurements performed by an electrochemical technique (in situ conductivity) and from chemical oxidation with FeCl₃. The in situ conductivity represents the highest conductivity obtained for the polymer as a film on an electrode, while the ex situ conductivity in this table is linked to the thermoelectric data that will be discussed in the next section. In the case of the carbazole homopolymer²¹ (27PC), it has been shown previously that the benzoyl moiety helps to increase the conductivity by a factor of 10³ compared to an N-alkyl substituted polymer. In the present study, the 27PC copolymers are in fact more conductive than the 27PCH copolymers by a factor of 100.

Figure 6 represents the in situ conductivity (bottom) of three polymers, along with their respective CVs (top), namely, 27PCHE2, 27PCT2, and 39PIC(b)T2. 27PCHE2 is not very conductive (4×10^{-3} S/cm), and although its conductivity increases at higher potentials it then decreases due to degradation. The low conductivity is probably due to the steric decoplanarization by the hexyl substituents at the 3,6-positions. In fact, the poly(*N*-octyl-2,7-carbazolediyl-*alt*-3,4-ethylenedioxy-2,5-thienylene) (PEDOTC)²¹ derivative, which contained only one EDOT comonomer unit but no substituent on the carbazole cycle, was even more conductive (2×10^{-2} S/cm). Semiempirical calculations (unpublished results) have shown a significant torsion angle between 60° and 115° in 27PCHE2 compared to PEDOTC²¹ which prefers a planar conformation.

As for the polyindolocarbazole copolymers, 39PIC(b)T2, 28PIC(c)T2, and 39PIC(c)T2 show comparable or superior conductivities compared to the 27PCT2 (in situ conductivities 0.1–0.7 S/cm). For 39PIC(a)T2 (4×10^{-2} S/cm), the in situ conductivity of the soluble low molecular weight fraction (about three to four repetition units revealed by GPC measurements) may not be representative of the polymer, but ex situ conductivity (in which we use the bulk material)

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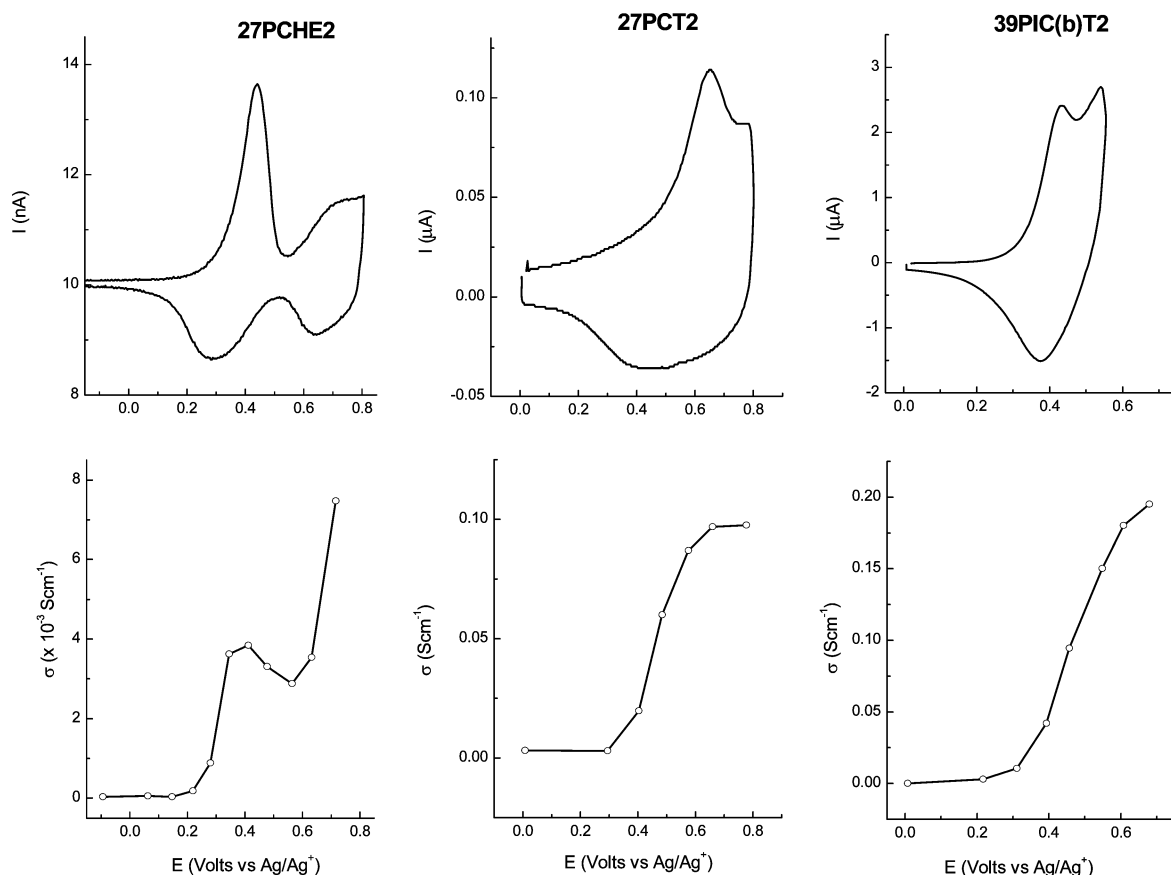


Figure 6. CVs (top) and in situ conductivity (bottom) of PCE2, 27PCT2, and 39PIC(b)T2 in acetonitrile with 0.1 M Bu₄NClO₄.

of the polymer revealed a conductivity up to 0.12 S/cm, which is also comparable to the other PICT2s. The homopolymer 39PIC(a) is not soluble enough to cast as a thick enough conducting film on the electrode, and thus the in situ conductivity measurement could not be performed. For 39PIC(b), measurements were not possible as a result of degradation. These results indicate that in the case of the copolymers, the benzoyl moiety does not seem to interfere with the conduction pathway in the bithiophene copolymer. Also, the addition of one fused ring does not seem to increase dramatically the conductivity, compared to 27PCT2 and 27PCE2.

Previous studies showed that for bithiophene copolymers (28PIC(c)T2 and 39PIC(c)T2),¹⁶ the in situ conductivity was higher (0.7 S/cm compared to 0.1 S/cm, Table 2) for the 2,8-coupled polyindolocarbazole. In this case, it was assumed that the nitrogen oxidation over this conjugation pathway was more favorable. We have synthesized the 2,8-coupled derivatives of the polyindolocarbazoles containing benzoyl substituents on the nitrogen atom, but we observed the opposite behavior. On the basis of in situ and ex situ conductivity measurements, 39PIC(a)T2 and 39PIC(b)T2 showed 0.12 and 0.20 S/cm, which was about 100 times superior to the conductivity of the 2,8-coupled derivatives (unpublished results). A possible explanation of this result is as follows: In the 2,8-coupled derivatives bearing N-benzoyl substituents, the electron pair on the nitrogen atom which is attracted by the benzoyl group could inhibit the nitrogen oxidation process. The oxidation process would then be attributed to the bithiophene unit or the *para*-phenylene

backbone. Because the conductivity is an important issue for thermoelectric behavior, the new 39PIC derivatives mentioned above became the main focus.

The three fused-ring homopolymers (211PDIC and 310PDIC) show also high in situ conductivities but only in their higher oxidation states (up to 0.5 S/cm for 211PDIC). We could assume that with bithiophene comonomers, the conductivity would be increased even further. The main interest in studying this polymer is its rigidity which tends to improve the stability of the doped materials.

Thermoelectricity. The relevant parameters for thermoelectric properties are also given in Table 2, and the relative errors represent an average of the uncertainties due to the instruments used, principally due to the measurement of the sample size for the ex situ conductivity and to the temperature for the Seebeck coefficient. The ex situ conductivity is obtained via a two-probe measurement, which indicates only the order of magnitude of the conductivity. Because none of the polymers synthesized in this work formed flexible free-standing films, thermoelectric characterization was performed using pressed pellets. Some pellets (39PCT2, for example) were extremely brittle, and others (39PIC(b)T2) were more flexible.

For thermoelectric purposes, the most interesting candidates are the polymers having a low oxidation potential, which generally results in enhanced stability in the doped state.^{38–40} It is important to note that the conductivities

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obtained by doping with FeCl_3 can also be limited by the oxidation potential of the polymers. However, it is more interesting to use a medium strength dopant such as ferric chloride or ferric tosylate, compared to nitrosonium salts (NOBF_4 or NOBF_6) where overoxidation and degradation often becomes a problem.

Generally, the Seebeck coefficient decreases when the conductivity increases, and the power factor (σS^2) reaches a maximum, which is not necessarily at the highest conducting state. Different doping conditions for a few promising polymers (doping time and dopant) and results of conductivity, Seebeck coefficients, and power factors are presented in Supporting Information for a few polymers. A good balance between conductivity and Seebeck coefficient is required to obtain a maximum power factor. In the present study, a comparison of the conductivities and Seebeck coefficients by a family of polymers was done by doping at high enough concentration (0.01–0.1 M of FeCl_3) for 30 min to a few hours. We have already measured the power factor as a function of the doping level of polymers (poly-(3-decylthiophene), PDT, and PCVH),²² and we have found that the best conditions were obtained below the highest doping level for these two polymers. To do a screening of all the polymers synthesized, up to four different conditions were tested on each sample. The results are quite reproducible for a particular set of experimental conditions. One of the conditions used was at 0.05 M of FeCl_3 in acetonitrile for 2 h, which very often corresponded to a conductivity just below the maximum obtained by ex situ measurements. However, we obtained better results at lower doping concentration for the low oxidation potential polymers such as bi-EDOT derivatives. To fully optimize the samples for the highest power factor possible, more conditions (dopants, solvents, and doping time) would need to be tested, but this is not the objective of this study.

For the sake of clarity, in Table 2, only the best results in terms of the power factor obtained for the different doping conditions tested for each polymer are represented. The results represent the adequate doping level to achieve the highest power factor. This allowed us to select the candidates with the best thermoelectric properties among all the polymers produced. As a result of their low conductivities (in situ and ex situ), the thermoelectric measurements were not performed on 27PCHP and 27PCHE2. From Table 2, it is obvious that the best candidates are 27PCT2 and 39PIC-(c)T2, with power factors in the range of $10^{-7} \text{ W}/(\text{K}^2 \text{ m})$. At room temperature, assuming that the thermal conductivity is $0.1 \text{ W}/(\text{m K})$, this would correspond to $ZT = 3 \times 10^{-4}$. 27PCE2 and 39PIC(a)T2 displayed results similar to those of PCVH²² (on the order of $10^{-8} \text{ W}/(\text{K}^2 \text{ m})$). Even if its in situ conductivity is high, 39PIC(b)T2 is not selected as a good thermoelectric material due to its low Seebeck coefficient. Table 2 shows that in the same doping conditions, 39PIC(c)T2 has a higher power factor than 28PIC(c)T2, due to the higher conductivity and Seebeck coefficient.

The PDIC polymers show less interesting power factors, around $10^{-9} \text{ W}/(\text{K}^2 \text{ m})$. However, PDICs are homopolymers compared to the other two classes of copolymers, and their power factor is similar to the 27PC homopolymer. From these results, there does not seem to be any significant improvement of the power factor when increasing the number of fused rings, as long as the hexyl benzoyl side chain is present on the carbazole unit or the coupling pattern of the polyindolocarbazole is in the 3,9-positions. There would be a possibility to enhance the power factor of 211PDIC because its maximum of conductivity (from in situ measurements) could go up to $0.5 \text{ S}/\text{cm}$.¹⁵ However, as stated earlier, on the basis of the UV–visible–NIR spectra in the doped state (Figure 4), for 211PDIC and 310PDIC, the maximum conducting state is not reached when chemically doped with FeCl_3 . Ferric chloride has the power to oxidize only up to the first process (about 0.53 V vs SCE),⁴¹ and at that point the conductivity of the two polymers is very similar (in situ, around $10^{-2} \text{ S}/\text{cm}$).¹⁵ If the second oxidation state was reached, the conductivity of the 2,11-coupled polymer would increase by a factor of 10. Thus the maximum increase in power factor could be a factor of 10, but this increase would be mitigated to an unknown extent by an expected reduction in the Seebeck coefficient at the higher conductivity. The introduction of low oxidation potential and highly conductive moieties such as bithiophene units as comonomers would facilitate the doping process. Synthesis of such potentially more conducting copolymers of polydiindolocarbazoles are in progress.

The band structure calculations predicted promising thermoelectric materials such as 310PDIC, 211PDIC, 27PCHE, and 27PCT2. In our experimental study, the two PDICs are not at their maximum conductivity state, and the first three polymers seem to give essentially similar results (1.4×10^{-9} to $4.8 \times 10^{-9} \text{ W}/(\text{K}^2 \text{ m})$) at the adequate doping level for maximum power factor. 27PCT2 finally seems to perform better than 27PCHE ($1.5 \times 10^{-7} \text{ W}/(\text{K}^2 \text{ m})$), and this could be explained by the fact that, during the band structure calculations, the torsion angle of the 27PPCHE is not taken into account, which can affect strongly the thermoelectric behavior of the polymer.

Stability. Attempts to improve the power factor by annealing some doped samples (211PDIC, 310PDIC, and 27PCHE2) at 100 °C for 1–5 h did not result in significant increases. There was generally a small decrease of the conductivity (probably related to dedoping at this temperature) and an increase of the Seebeck coefficient which overall resulted in a decrease of the power factor. For one sample of 211PDIC, a weak increase of both properties was observed. Although no extensive study of the stability has been done in this work, the polymers studied are generally more stable in the doped state than the PCVH polymer previously studied.²² The high stability in the doped state has been observed for samples stored under nitrogen (no special precautions were taken, the samples being exposed to air for transport between measurements), for a period of 10 days to 3 months; for example, (a) for highly doped

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samples of 310PDIC, the conductivity and Seebeck coefficient were stable for 10 days, (b) after 3 months, the conductivity of 211PDIC decreased by a factor of 2 and the Seebeck coefficient decreased also (factor of 1.1–1.3), and (c) for 27PCT2, the Seebeck coefficient had not changed after 3 months.

Conclusions

The best candidates for thermoelectric materials found by this study are copolymers involving bithiophene and carbazole or indolocarbazole units, 27PCT2 and 39PIC(c)T2. These two polymers have linkages in the positions meta to the nitrogen atom. A power factor up to around 10^{-7} W/(K² m) can be obtained with pressed pellets. However, morphology and adequate doping level need to be taken into account to improve the power factor.

The incorporation of benzoyl substituents on the nitrogen atom increased the conductivity of 2,7-polycarbazoles but made no further improvement in the indolocarbazole copolymers. Preliminary results from experimental and band structure calculations on polydiindolocarbazoles show that the 2,11-coupled 211PDIC would be an interesting moiety for copolymers if the second conduction level could be reached. Synthesis of promising candidates such as 211PDIC copolymers is in progress.

The polymers synthesized seem to be relatively stable in the doped state. We have not, however, surpassed PDT,

which has a power factor of 1.35×10^{-6} W/(K² m)²² even though its Seebeck coefficient is very low. To obtain higher power factor, we still need to increase the conductivity without decreasing the relatively high Seebeck coefficient found in polycarbazoles, polyindolocarbazoles, and polydiindolocarbazoles. We are currently investigating the use of carbon nanotubes to increase the electrical conductivity of our materials.

Acknowledgment. The authors thank the Office of Naval Research for funding part of this research. I.L. thanks Prof. J.-F. Morin for supplying *N*-(*tert*-butoxycarbonyl)pyrrole and 27PC, Dr. S. Beaupré for 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene, and P. Harding-Lepage for semiempirical calculation of torsion angle. N.B. thanks the Georges-Elie-Amyot Foundation and NSERC for M.Sc. and Ph. D. scholarships. They also gratefully acknowledge Prof. T. Tritt (Clemson University) for an initial design of the thermoelectric measurement apparatus.

Supporting Information Available: Experimental details, UV–visible absorption spectra of 39PIC(a) derivatives, table of thermoelectric data as a function of different doping levels, and band structure calculations of 27PCT, 36PCT, 36PCT2, 27PC, and 36PC (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM070063H