Solvatochromic Properties of 2,7-Carbazole-Based Conjugated Polymers

Jimmy Bouchard,[†] Michel Belletête,[‡] Gilles Durocher,[‡] and Mario Leclerc*,[†]

Canada Research Chair in Electroactive and Photoactive Polymers, Centre de recherche en sciences et ingénierie des macromolécules, Département de Chimie, Université Laval, Quebec City, Quebec, Canada G1K 7P4, and Département de Chimie, Université de Montréal, Montréal, Quebec, Canada H3C 3J7

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ABSTRACT: The solvatochromic properties of poly(*N*-alkyl-2,7-carbazolediyl)s, poly(*N*-alkyl-2,7-carbazolediyl-*alt*-2,5-thiophene)s, poly(*N*-alkyl-2,7-carbazolediyl-*alt*-2,5-furan)s, and poly(*N*-octyl-2,7-carbazoleneethynylene) have been investigated experimentally and theoretically. All polymers have revealed solvatochromic effects, which have been interpreted in terms of the formation of H- and/or J-aggregates. It was observed that the optical properties of the polymers are strongly dependent on the rotational barriers between the subunits present in the polymers. For instance, poly(*N*-alkyl-2,7-carbazolediyl)s, which possess a relatively high barrier to rotation between adjacent carbazole units, shows a very weak H-band and an intense J-band. On the other hand, poly(*N*-alkyl-2,7-carbazolediyl-*alt*-2,5-thiophene)s and poly(*N*-alkyl-2,7-carbazolediyl-*alt*-2,5-furan)s, which can reach planarity upon aggregation (low values of torsional barriers), exhibit more intense H-bands. It was also observed that the presence of branched alkyl chains on the nitrogen atom of the carbazole units does not significantly affect the optical properties of the polymers.

Introduction

π-Conjugated polymers are interesting materials for a large range of electrical, optical, and electrooptical applications.[1] Indeed, conjugated polymers have attracted the attention of many research groups because they combine the electrical and optical properties of inorganic materials and ease of processing of polymeric materials. The development of such electroactive and photoactive materials has been sustained by the judicious utilization of a variety of synthetic tools to prepare highly pure and well-defined polymers with optimized physical properties. Among these properties, chromic (thermochromic, solvatochromic, ionochromic, photochomic, affinity chromic, etc.) effects have allowed the development of smart materials and sensors.[2]

As a first approximation, these optical effects have been related to a conformational transition of the conjugated backbone driven by a delicate balance between intrachain steric hindrance and attractive interchain (or intrachain through chain folding) interactions.[3] This conformational transition of the conjugated backbone is accompanied by a modification of the effective conjugation length, which induces optical shifts in the UV−vis absorption spectra of the conjugated polymers. However, interchain electronic interactions (excitons, $\pi-\pi$ interactions, etc.) may also contribute to the chromic effect. While planarization of the polymer backbone always leads to a red shift, the optical changes caused by aggregation depend on the details of the molecular packing.[4]

Along these lines, we report here the synthesis and characterization of various 2,7-carbazole-based conjugated polymers, namely, poly(*N*-octyl-2,7-carbazolediyl) (POC), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl) (PEHC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thiophene) (POCT), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl-*alt*-2,5-thiophene) (PEHCT), poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-furan) (POCF), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl-*alt*-2,5-furan) (PEHCF), poly(*N*-octyl-3,6-dimethyl-2,7-carbazolediyl-*alt*-2,5-furan) (P36DMCF), and poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE) (see Chart 1). In particular, their solvatochromic effects have been investigated in correlation with ab initio quantum chemical calculations performed on various dimer model compounds. This joint theoretical and experimental approach should shed some light on the structure−property relationships involved in 2,7-carbazole-based conjugated polymers and, hopefully, to a rational design of conjugated polymeric materials with optimized optical and electrooptical properties.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 or on a Varian AS400 apparatus in deuterated solvent solutions at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with a HPLC pump using a Waters 515 differential refractometer. The calibration curve was made with a series of monodispersed polystyrene standards in THF (HPLC grade, Aldrich). UV−vis absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) or on a Varian Cary 500 UV−vis spectrophotometer using 1 cm path length quartz cells. The concentrations of the polymers were about $(1-5) \times 10^{-5}$ M (repeat unit).

Theoretical Calculations. Ab initio calculations were performed on a Pentium III (900 Mz) personal computer with 256 Mb RAM using the Gaussian 98W program, version 5.2.[5] The conformational analysis of all the model compounds was done by changing the torsional angle θ by 15° steps. The geometries were optimized at the HF level with the 6-31G* basis set. The Berny analytical gradient method was used for the optimizations. The requested HF convergence on the density matrix was 10^{-8}, and the threshold values for the maximum force and the maximum displacement were 0.000 45 and 0.0018 au, respectively. To obtain the final torsional angles of the conformers in each minimum, calculations of these

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[†] Université Laval.

[‡] Université de Montréal.

* To whom correspondence should be addressed: Tel 1-418-656-3452, FAX 1-418-656-7916, e-mail mario.leclerc@chm.ulaval.ca.

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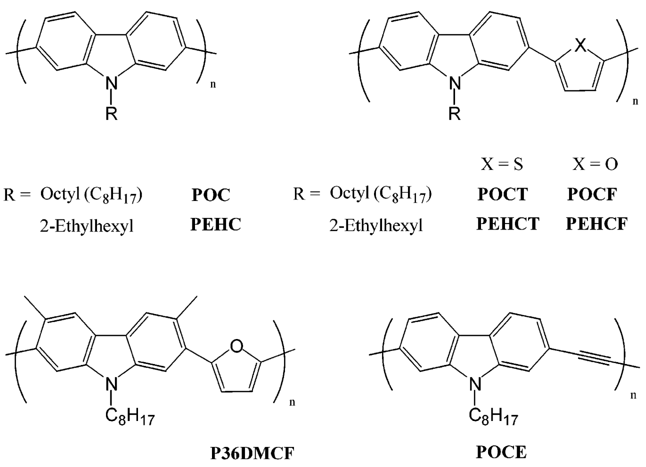
Chart 1. Polymers Synthesized



geometries were performed without constraint on the dihedral angle.

Materials. All starting organic and inorganic compounds were purchased from Aldrich Co. or Alfa Aesar Co. and used without further purification. All solvents used in the reactions were freshly distilled under an inert atmosphere.

Syntheses of 2,7-dimethoxycarbazole,[6] *N*-octyl-2,7-bis(trifluoromethanesulfonyl)carbazole,[6] *N*-(2′-ethylhexyl)-2,7-bis(trifluoromethanesulfonyl)carbazole,[6] 2,5-bis(trimethylstannyl)thiophene,[7] 2,5-bis(trimethylstannyl)furan,[7] and $Pd(PPh_3)_4$[8] have been already reported in the literature.

3,6-Dibromo-2,7-dimethoxycarbazole (1). In a 2 L flask, 10.00 g (44.00 mmol) of 2,7-dimethoxycarbazole[6] were added to a stirred solution of 500 mL of $CHCl_3$ and 500 mL of glacial acetic acid. The solution was cooled at 0 °C, and 16.06 g (90.23 mmol, Aldrich Co.) of *N*-bromosuccinimide (NBS) was added to the stirred mixture in the absence of light. The reaction temperature was increased to room temperature and stirred for 12 h. The precipitate was filtered through a Büchner funnel, rinsed with 20−30 mL of distilled water, and dried under reduced pressure to provide 14.36 g of the title product as a white solid; mp 258 °C (decomposition) (yield = 85%).

^{1}H NMR (400 MHz, dimethyl-d_6 sulfoxide, ppm): 11.23 (s, 1H); 8.24 (s, 2H); 7.07 (s, 2H); 3.86 (s, 6H).

^{13}C NMR (100 MHz, dimethyl-d_6 sulfoxide, ppm): 153.89; 140.84; 124.38; 117.11; 102.86; 95.53; 56.90.

HRMS: Calculated for $C_{14}H_{11}NO_2Br_2$: 382.9156. Found: 382.9160.

***N*-Octyl-3,6-dibromo-2,7-dimethoxycarbazole (2).** A 250 mL flame-dried flask was charged with 17.77 g (46.10 mmol) of 3,6-dibromo-2,7-dimethoxycarbazole (**1**), 17.82 g (92.30 mmol, Aldrich Co.) of 1-bromooctane, 3.69 g of sodium hydroxide (reagent grade), 470 mg (1.40 mmol) of tetrabutylammonium hydrogen sulfate (TBAH), and 87 mL of anhydrous acetone. The resulting stirring mixture was refluxed under argon for 24 h and then poured into distilled water. The aqueous layer was extracted three times with chloroform. The combined organic fractions were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude residue is added to approximately 500 mL of methanol, and the resulting mixture was cooled to −78 °C. The precipitate was filtered off, rinsed with cold methanol, and then dried under reduced pressure to provide 21.85 g of the title product as a white fluffy solid; mp 116−118 °C (yield = 95%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.05 (s, 2H); 6.80 (s, 2H); 4.18 (t, 2H, J = 7.3 Hz); 4.00 (s, 6H); 1.83 (m, 2H); 1.29 (m, 10H); 0.86 (t, 3H, J = 6.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 156.33; 139.98; 120.96; 118.29; 116.03; 91.01; 55.88; 43.20; 32.06; 29.62; 29.41; 29.05; 27.50; 22.84; 16.85; 14.30.

HRMS: Calculated for $C_{22}H_{27}NO_2Br_2$: 495.0408. Found: 495.0401.

***N*-Octyl-3,6-dimethyl-2,7-dimethoxycarbazole (3).** A 500 mL flame-dried flask was charged with 10.00 g (20.1 mmol) of *N*-octyl-3,6-dibromo-2,7-dimethoxycarbazole (**2**) in 200 mL of freshly distilled THF. The resulting mixture was cooled at −78 °C, and 16.90 mL (42.20 mmol, Aldrich Co.) of *n*-BuLi was added dropwise over 0.5 h under an argon atmosphere. The solution was stirred at this temperature for a period of 0.5 h, and 2.63 mL (42.20 mmol, Aldrich Co.) of iodomethane was added slowly to the mixture. The reaction temperature was then slowly increased at 0 °C and stirred for 20 min. The solution was quenched at 0 °C with a saturated aqueous solution of ammonium chloride, and the aqueous layer was extracted three times with diethyl ether. The combined organic fractions were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, 10% ethyl acetate in hexanes as eluent) to provide 6.50 g of the title product as a white solid. This product was recrystallized in methanol; mp 62−64 °C (yield = 88%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.70 (d, 2H, J = 0.8 Hz); 6.77 (s, 2H); 4.20 (t, 2H, J = 7.1 Hz); 3.95 (s, 6H); 2.37 (d, 6H, J = 0.7 Hz); 1.85 (m, 2H); 1.31 (m, 10H); 0.87 (t, 3H, J = 6.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 156.33; 139.98; 120.96; 118.29; 116.03; 91.01; 55.88; 43.20; 32.05; 29.62; 29.41; 29.05; 27.49; 22.84; 16.85; 14.30.

HRMS: Calculated for $C_{24}H_{33}NO_2$: 367.2511. Found: 367.2501.

***N*-Octyl-3,6-dimethyl-2,7-dihydroxycarbazole (4).** In a 250 mL flask 5.00 g (13.60 mmol) of *N*-octyl-3,6-dimethyl-2,7-dimethoxycarbazole (**3**) was mixed with 31.40 g (272 mmol, Alfa Aesar Co.) of pyridine hydrochloride. The mixture was stirred and heated at 200−220 °C for 5 h. Ethyl acetate was added to the cooled mixture; the organic layer obtained was washed several times with distilled water and dried over magnesium sulfate, and the solvent was removed under reduced pressure to afford 3.82 g of the title product as a pale yellow solid; mp 154−155 °C (yield = 83%).

^{1}H NMR (400 MHz, acetone-d_6, ppm): 8.00 (s, 2H); 7.61 (m, 2H); 6.82 (s, 2H); 4.08 (t, 2H, J = 7.1 Hz); 2.30 (d, 6H, J = 0.5 Hz); 1.75 (m, 2H); 1.21 (m, 10H); 0.82 (t, 3H, J = 6.9 Hz).

^{13}C NMR (100 MHz, acetone-d_6, ppm): 153.52; 140.44; 120.64; 116.29; 116.00; 94.81; 42.76; 31.85; 29.45; 29.33; 28.73; 27.22; 22.59; 16.00; 13.67.

HRMS: Calculated for $C_{22}H_{29}NO_2$: 339.2198. Found: 339.2190.

***N*-Octyl-3,6-dimethyl-2,7-bis(trifluoromethanesulfonyl)carbazole (5).** In a flame-dried 50 mL flask, under an inert atmosphere 3.50 g (10.30 mmol) of *N*-octyl-3,6-dimethyl-2,7-dihydroxycarbazole (**4**) 1.26 g (10.30 mmol, Aldrich Co.) and (dimethylamino)pyridine (DMAP) were mixed with 25.78 mL of anhydrous pyridine. The mixture was cooled at 0 °C, and 5.20 mL (30.90 mmol, Aldrich Co.) of trifluoromethanesulfonic anhydride was added dropwise. The mixture was stirred at 0 °C for 1 h and at room temperature for 24 h. The excess of trifluoromethanesulfonic anhydride was destroyed with slow addition of 30 mL of distilled water. The mixture was extracted three times with 30 mL of diethyl ether. The combined organic fractions were washed successively with five 50 mL portions of distilled water, five 50 mL portions of aqueous $CuSO_4$ (0.1 M), three 50 mL portions of brine, and again with a 50 mL portion of distilled water. The mixture was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column of silica gel with 5% ethyl acetate in hexanes as eluent. Evaporation of the solvent led to a pale yellow oil which crystallized upon standing to provide 5.00 g of pale yellow solid; mp 49−50 °C (yield = 88%).

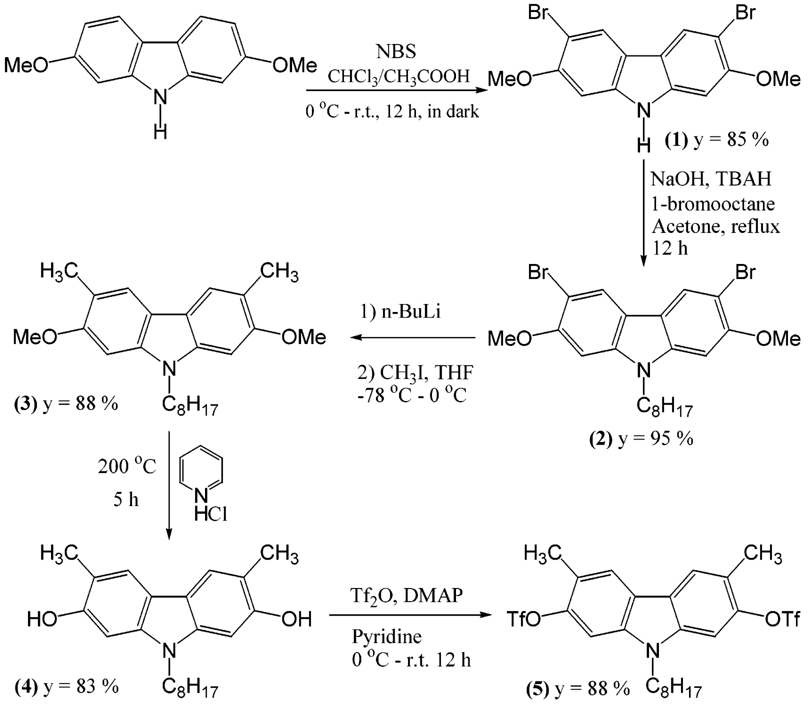
^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.91 (m, 2H); 7.26 (s, 2H); 4.20 (t, 2H, J = 7.1 Hz); 2.52 (s, 6H); 1.82 (m, 2H); 1.26 (m, 10H); 0.85 (t, 3H, J = 6.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 147.30; 140.15; 123.71; 123.15; 121.76; 121.66; 120.52; 117.34; 114.15; 102.36; 43.89; 31.87; 29.42; 29.24; 28.92; 27.39; 22.77; 16.79; 14.21.

HRMS: Calculated for $C_{24}H_{27}F_6NO_6S_2F_6$: 603.1184. Found: 603.1177.

***N*-Octyl-bis[(trimethylsilyl)ethynyl]carbazole (6).** In a flame-dried 50 mL flask, under an inert atmosphere, *N*-octyl-2,7-bis(trifluoromethanesulfonyl)carbazole[6] (2.00 g, 3.48 mmol),

Scheme 1. Synthesis of *N*-Octyl-3,6-dimethyl-2,7-bis(trifluoromethanesulfonyl)carbazole (5)



bis(triphenylphosphine)palladium dichloride (120 mg, 0.17 mmol, Aldrich Co.), and copper iodide (32 mg, 0.17 mmol, Aldrich Co.) were mixed with 20.8 mL of freshly distillated piperidine. Trimethyl acetylene (1.08 mL, 7.65 mmol, Aldrich Co.) was slowly added to the mixture at room temperature. The reaction temperature was then slowly increased, and the mixture was refluxed for 1 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel with 2.5% diethyl ether in hexanes as eluent). Evaporation of the solvent led to a pale yellow oil which crystallized upon standing to provide 1.20 g of pale yellow solid; mp 87−88 °C (yield = 73%).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.95 (d, 2H, $J = 8.0$ Hz); 7.52 (s, 2H); 7.35 (d, 2H, $J = 8.0$ Hz); 4.22 (t, 2H, $J = 7.3$ Hz); 1.85 (m, 2H); 1.32 (m, 10H); 0.90 (t, 3H, $J = 6.6$ Hz), 0.34 (s, 18H).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): 140.56; 123.28; 122.69; 120.37; 112.40; 106.51; 93.84; 43.17; 31.84; 29.36; 29.20; 28.93; 27.20; 22.64; 14.11; 0.13.

HRMS: Calculated for $C_{30}H_{41}NSi_2$: 471.2777. Found: 471.2770.

***N*-Octyl-2,7-diethynylcarbazole (7).** 45 mL of methanol and 2.33 mL (20% w/w) of aqueous potassium hydroxide were added at room temperature to a stirred solution of *N*-octyl-bis[(trimethylsilyl)ethynyl]carbazole (**6**) (1.20 g, 2.54 mmol, in 47 mL of THF). The mixture was left at room temperature overnight. It was then poured into water (20 mL) and extracted three times with diethyl ether. The combined organic extracts were dried over anhydrous magnesium sulfate and then filtrated. The solvent was removed, and the residue was purified by column chromatography (silica gel, 2.5% diethyl ether in hexanes as eluent) to provide 700 mg of the title product as a pale yellow solid; mp 62−64 °C (yield = 85%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.00 (dd, 2H, $J = 8.0$ and 0.7 Hz); 7.55 (s, 2H); 7.37 (dd, 2H, $J = 8.0$ and 1.3 Hz); 4.24 (t, 2H, $J = 7.4$ Hz); 3.17 (s, 2H); 1.85 (m, 2H); 1.28 (m, 10H); 0.87 (t, 3H, $J = 6.9$ Hz).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): 140.72; 123.43; 123.03; 120.75; 119.54; 112.95; 85.09; 43.45; 32.01; 29.55; 29.39; 29.12; 27.44; 22.83; 14.31.

HRMS: Calculated for $C_{24}H_{25}N$: 327.1987. Found: 327.1981.

Polymerization. Poly(*N*-octyl-2,7-carbazolediyl) (POC) and poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl) (PEHC) were synthesized via Yamamoto coupling reaction using *N*-alkyl-2,7-ditrifluoromethanesulfonylcarbazole, Ni(0) as catalyst, and cyclooctadiene (COD) as ligand following already published procedures.[9,10] Poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thiophene) (POCT), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl-*alt*-2,5-thiophene) (PEHCT), poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-furan) (POCF), poly(*N*-(2′-ethylhexyl)-2,7-carbazolediyl-*alt*-2,5-furan) (PEHCF), and poly(*N*-octyl-3,6-dimethyl-2,7-carbazolediyl-*alt*-2,5-furan) (P36DMCF) were prepared via palladium-catalyzed Stille couplings between ditrifluoromethanesulfonylaryl and distannylaryl comonomers following already published procedures (yields = 15−25% soluble fractions only).[6,7,12] Poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE) was prepared by palladium-catalyzed cross-coupling condensation, known as the Heck reaction[12,13] following this procedure: *N*-octyl-2,7-diethynylcarbazole (**7**) (250 mg, 0.76 mmol), *N*-octyl-2,7-bis(trifluoromethanesulfonyl)carbazole[6] (439 mg, 0.76 mmol), tetrakis(triphenylphosphine)palladium [($Pd(PPh_3)_4$]][8] (44 mg), and cuprous iodide (7 mg) were combined in 30.54 mL of degassed toluene and 15.27 mL of degassed triethylamine. The reaction mixture was stirred under reflux for 48 h in an argon atmosphere. The solvent was removed under reduced pressure, and the residue was dissolved in 6 mL of chloroform. This solution was poured into 60 mL of cold methanol (0 °C), and the precipitated polymer was collected by filtration. The crude polymer was washed in a Soxhlet apparatus with methanol for 72 h. To remove catalyst residues, the polymer was passed through a short column of silica gel using chloroform as eluent. After the evaporation of the solvent, the polymer was dried under reduced pressure to afford 83 mg (33%) of POCE as an orange solid.

Results and Discussion

Synthesis and Characterization. Most 2,7-carbazole-based conjugated homopolymers and copolymers were prepared from well-established synthetic procedures. In particular, homopolymers were prepared from Yamamoto coupling reaction using *N*-alkyl-2,7-ditrifluoromethanesulfonylcarbazoles as the monomers.[9,10] Various copolymers were prepared from the Stille coupling reaction between ditrifluoromethanesulfonylaryl and distannylaryl comonomers.[6,7,12] However, the synthesis of both P36DMCF and POCE did need new synthetic strategies (see Schemes 1 and 2).

Scheme 2. Synthesis of *N*-Octyl-2,7-bis(ethynyl)carbazole (7)

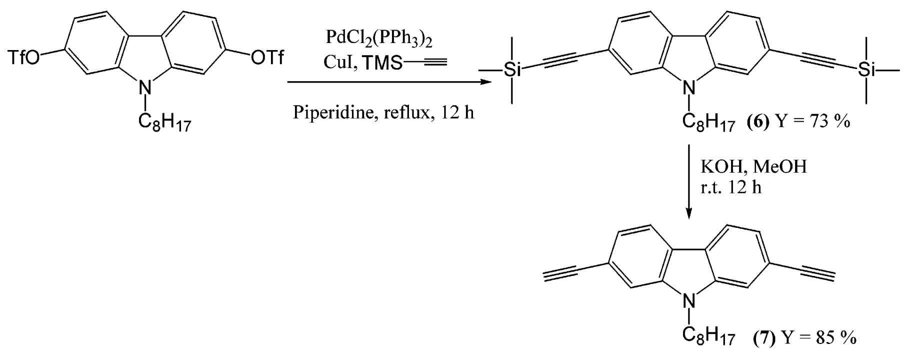


Table 1. Polymerization Yields and Molecular Weights of the Polymers

polymer	yield (%)[a]	M_n	M_w/M_n
POC	52	5300	1.8
PEHC	77	3700	1.7
POCT	20	2100	1.7
PEHCT	15	1800	1.4
POCF	22	2900	1.2
PEHCF	21	3400	1.5
P36DMCF	24	3700	1.2
POCE	33	2700	2.0

[a] Soluble fractions.

Scheme 1 presents the synthesis of the tetrasubstituted monomer **5** in five steps. First, 2,7-dimethoxycarbazole[6] is brominated at positions 3 and 6 by the action of NBS in a mixture of $CHCl_3/CH_3COOH$. It is important to keep the reaction mixture in the dark to avoid multiple undesirable bromination reactions. Compound **1** is simply recovered by filtration without further purification. Compound **2** was obtained by a standard N-alkylation with 1-bromooctane.[6] A double lithiation of compound **2** was achieved from *n*-BuLi at −78 °C. It is important to add *n*-BuLi slowly to avoid transmetalation reactions. Compound **3** was finally obtained in a good yield (88%) by reaction of iodomethane. Compound **4** was obtained by deprotection at the positions 2 and 7 of the methoxy groups by using pyridine hydrochloride at 200 °C.[13] Finally, compound **4** was treated with DMAP and trifluoromethanesulfonic anhydride in cold pyridine to give monomer **5**, which can undergo the Stille polycondensation reaction.

As shown in Scheme 2, compound **7** was prepared in two steps from *N*-octyl-2,7-bis(trifluoromethanesulfonyl)carbazole[6] via a palladium-catalyzed cross-coupling reaction and the subsequent cleavage of the trimethylsilyl protecting group in basic conditions. This monomer is then copolymerized with *N*-octyl-2,7-bis(trifluoromethanesulfonyl)carbazole[6] via a Heck reaction to afford the desired conjugated polymer (POCE).

In all cases, polymerization reactions (Yamamoto, Stille, Heck) gave polymers with soluble fractions exhibiting number-average molecular weights around 3 kDa and polydispersity indexes of 1.5 (see Table 1). These relatively modest molecular weights can be tentatively explained by a low degree of substitution, flexible side chains being required to obtain both soluble and high molecular weight conjugated polymers. All resulting polymers are soluble in choroform or THF and can be precipitated by adding methanol. If necessary, thin polymer films can be easily cast onto various substrates.

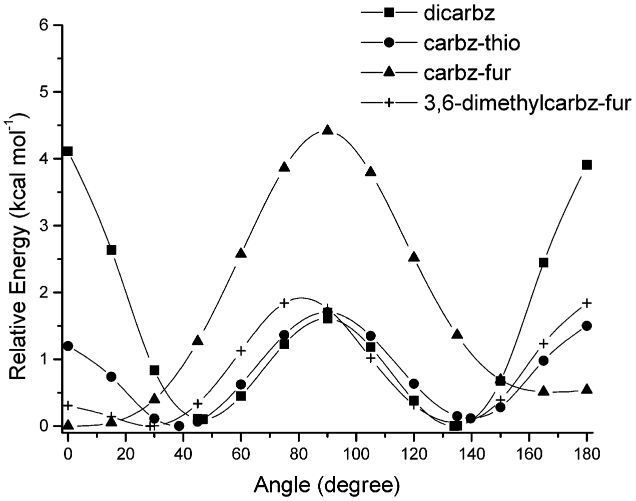


Figure 1. Ground-state energy surfaces of various dimer model compounds.

Solvatochromic Properties. Recently, the thermochromic and solvatochromic properties of a series of polythiophenes, polyphenylenes, and polyfluorenes have been investigated experimentally and theoretically.[3] A correlation between the observed optical properties of the conjugated polymers and the rotational energy barrier between adjacent moieties (based on ab initio calculations performed on dimer model compounds) has been established.[3e] For instance, poly[1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene] and poly[1,4-(2,5-dioctylphenylene)-2,5-furan] having a rather flexible backbone with an energy barrier against planarity smaller than 1.3 kcal mol^{-1} have revealed interesting chromic effects. On the other hand, it was observed that polymers having rotational barrier close to zero (e.g., poly[1,4-(2,5-dioctylphenylene)-2,5-thiophene] can maintain a highly conjugated (coplanar or nearly coplanar) conformation, even at high temperatures, resulting in the absence of significant chromic effects. Finally, if the steric interactions are too strong, as observed with poly[1,4-(2,5-dioctylphenylene)-2,5-thiophene] (energy barrier = 5 kcal mol^{-1}), no coplanar conformation can be adopted upon cooling or aggregation, avoiding any significant optical changes in the absorption spectrum of this polymer. It is thus believed that theoretical calculations could help in the rational design of chromic polymers. However, these calculations have some limitations since excitonic coupling can also induce strong chromic effects.

Theoretical HF/6-31G* ab initio calculations performed on isolated dimer and trimer model compounds are shown in Figures 1 and 2, respectively. According

Table 2. Relative Energies (in kcal mol^{-1}) and Torsional Angles (θ) Obtained by ab Initio Calculations Performed at the HF/6-31G* Level

molecule	syn	syn–gauche	perpendicular	anti–gauche	anti
di(*N*-ethylcarbazole)	4.11	0.1 (46.8°)	1.61	0.0 (134.0°)	3.91
N-ethylcarbazole–thiophene	1.20	0.0 (38.5°)	1.70	0.12 (139.7°)	1.50
N-ethylcarbazole–furan	0.0		4.41	0.51 (165.0°)	0.54
3,6-dimethyl-*N*-ethylcarbazole–furan	0.31	0.0 (28.5°)	1.76	0.050 (134.5°)	1.84
N-ethylcarbazole–ethynyl	0.0		1.52×10^{-4}		0.0
N-ethylcarbazole–ethynyl–*N*-ethylcarbazole	0.0		0.54		0.059

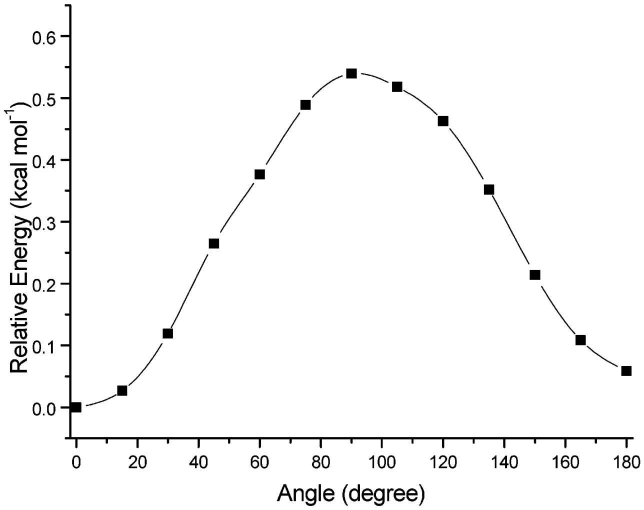


Figure 2. Ground-state energy surfaces of carbazole–ethynylene–carbazole model compound.

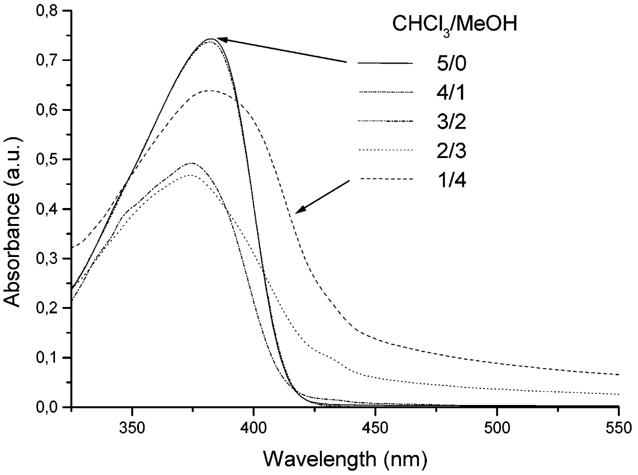


Figure 3. Solvent-dependent (v/v) UV–vis absorption spectra of poly(*N*-octyl-2,7-carbazolediyl) (POC).

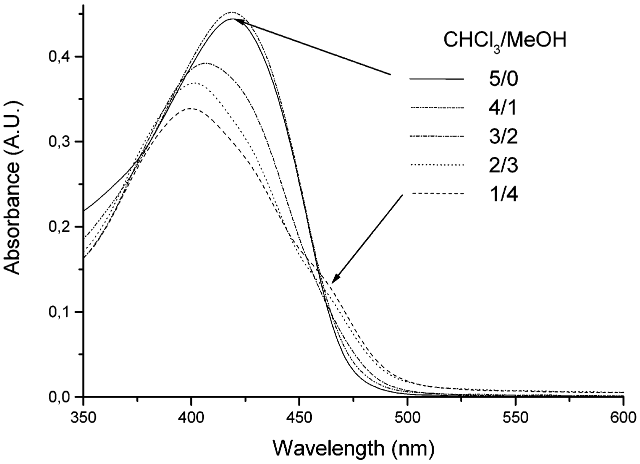


Figure 4. Solvent-dependent (v/v) UV–vis absorption spectra of poly(*N*-octyl-2,7-carb-azolediyl-*alt*-2,5-thienylene) (POCT).

to the above statements, it seems that only carbazole–thiophene copolymers (POCT and PEHCT) and poly(3,6-dimethyl-2,7-carbazolediyl-*alt*-2,5-furan) (P36DMCF) should exhibit chromic features because their more stable conformation is not planar and their barrier against planarity is relatively small (see Table 2). In contrast, carbazole–furan copolymers (POCF and PEHCF) and poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE) should keep highly conjugated coplanar (or nearly coplanar) conformational structures in good or poor solvents with negligible chromic effects. At the other extreme, poly(*N*-alkyl-2,7-carbazolediyl)s (POC and PEHC) should keep nonplanar conformation and should therefore exhibit weak chromic effects. It is important here to remind the reader that all these theoretical calculations completely neglect any interchain electronic interactions.

According to the last prediction, POC should not show significant chromic effects related to conformational changes. However, one can see in Figure 3 that the absorption band of POC is red-shifted as the content of methanol is increased. One explanation for this solvatochromic behavior could involve intermolecular interactions giving rise to an excitonic coupling effect.[14] Thus, the band intensity around 425 nm would involve head-to-tail molecular arrangements (J-aggregates). However, one can see a small increase in intensity around 325 nm upon the addition of methanol, which could arise from weak parallel geometrical arrangements (H-aggregates). Recently, similar optical features were reported for POC in the solid state (thin film).[15] Further experiments carried out with PEHC did reveal similar optical changes (figures not shown), suggesting that the nature of the side chains on the nitrogen atoms does not significantly modify the geometrical arrangements. These spectral features can be correlated with the theoretical data described above. Indeed, postulating that POC should remain twisted upon aggregation due to relatively high rotational energy barriers between adjacent units, parallel geometrical arrangements (giving rise to H-aggregates) are not favored for this polymer. Thus, mainly J-aggregates could be formed for POC upon addition of methanol.

Studies on poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thiophene) (POCT) revealed interesting optical features when the quality of the solvent decreases (see Figure 4). Indeed, the maximum of the absorption band is blue-shifted by about 25 nm upon aggregation together with the appearance of weak red-shifted band around 460 nm. According to our theoretical calculations, these results cannot be explained in terms of conformational changes, which should give rise to a red shift of the absorption band upon addition of the poor solvent (small rotational energy barrier). On the other hand, these chromic effects can be interpreted in terms of an

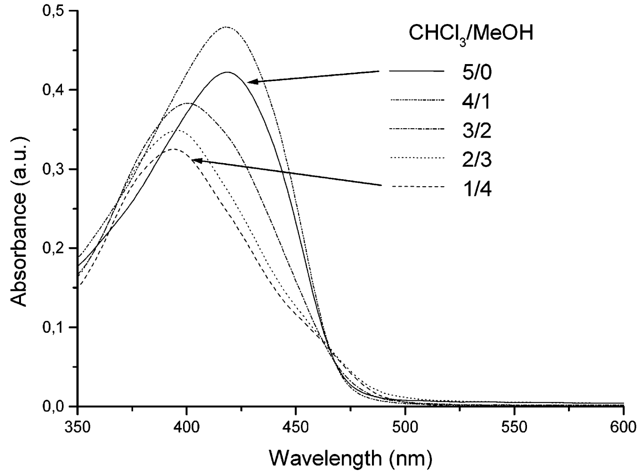


Figure 5. Solvent-dependent (v/v) UV−vis absorption spectra of poly(*N*-2-ethylhexyl-2,7-carbazolediyl-*alt*-2,5-thienylene) (PEHCT**)**.

excitonic coupling. However, in this case, the absorption band due to H-aggregates is much more allowed than the one originating from the J-aggregates, causing an overall blue shift of the absorption band upon aggregation. Again, these results can be correlated to our theoretical calculations. Indeed, the rotational barrier between carbazole and thiophene rings is much lower than that between two carbazole units (see Table 2). Thus, POCT should become planar upon aggregation, giving rise to stronger parallel interactions (H-aggregates). A similar behavior has been observed for poly(*N*-2-ethylhexyl-2,7-carbazole-*alt*-2,5-thiophene) (PEHCT) (Figure 5). Again, this strongly suggests that the presence of the side chains on the nitrogen atom does not significantly modify the geometrical arrangements of these thiophene−carbazole polymers. Recently, excitonic effects were also observed for some oligothiophenes like terthiophene,[16] quaterthiophene,[17] and 3,3‴-dimethyl-2,2′:5′:2″:5″,2‴-quaterthiophene.[17] Strong excitonic effects are known to drastically decrease the photoluminescence quantum yield (which was observed experimentally) but could lead to greater mobility in related oligomeric or polymeric transistors.[4]

The replacement of the sulfur atom of the thiophene ring by an oxygen atom (i.e., furan unit) should decrease the steric hindrance[3d] and, as a result, should lead to coplanar (or nearly coplanar) structures in both good or poor solvents. Accordingly, the rotational barrier between carbazole and furane rings is calculated to be zero. Thus, no chromic effects caused by conformational changes is predicted for POCF. However, Figure 6 shows a net increase of the absorbance near 350 nm as the quality of the solvent decreases, which could be related to excitonic effects (H-aggregates). Similar effects were observed with PEHCF (figure not shown), showing that the presence of the side chains on the nitrogen atom does not affect the conformation of this polymer. To further check the effect of the side chains on the optical properties, Figure 7 reports the solvatochromic behavior of P36DMCF. Upon aggregation, the absorption maximum of this polymer is red-shifted by about 10 nm, whereas a new band appears around 475 nm. On the basis of the theoretical calculations performed on the corresponding dimer compound (see Figure 1), planarization should occur upon aggregation, which could explain the red shift of the main absorption band. On the other hand, the presence of the band at 475 nm could be explained by the formation of J-aggregates. However, comparisons with absorption spectra obtained for POC and POCF suggest that the formation of H-aggregates is not favored for P36DMCF. This is probably related to the presence of methyl groups at the 3,6-positions, which should preclude the formation of parallel aggregates.

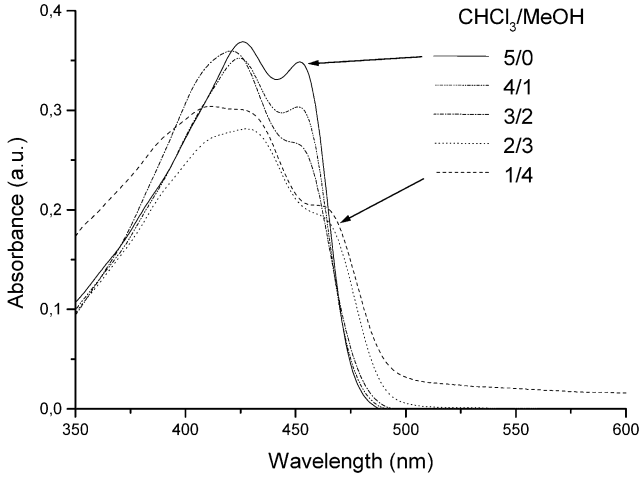


Figure 6. Solvent-dependent (v/v) UV−vis absorption spectra of poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-furan) (POCF).

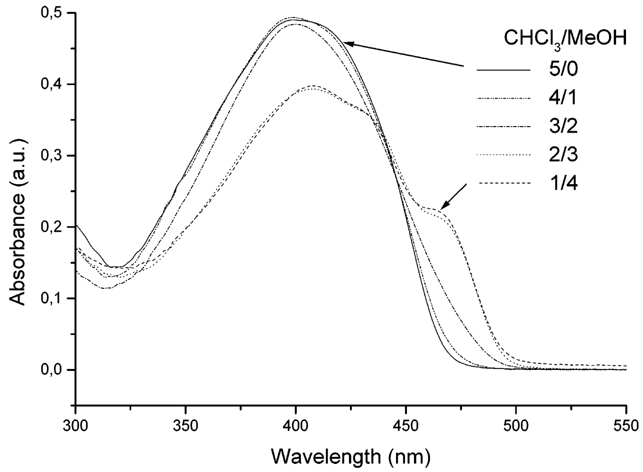


Figure 7. Solvent-dependent (v/v) UV−vis absorption spectra of poly(*N*-octyl-3,6-dimethyl-2,7-carbazolediyl-*alt*-2,5-furan) (P36DMCF).

Finally, the solvatochromic properties poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE) were investigated. Calculations on the dimer model compound (carbazole−ethynyl) revealed a totally flexible backbone with all twisting angles having more or less the same energy at room temperature. On the other hand, calculations on a trimer model compound (see Figure 2) show that a coplanar structure between two carbazole units is favored, with a very low rotational barrier against planarity (0.55 kcal mol^{-1}). Consequently, upon aggregation and neglecting any interchain electronic interactions, no significant red shift should be observed, and only a narrowing of the absorption spectrum could take place. As shown in Figure 8, this is obviously not the case. Indeed, a clear broadening of the absorption band is observed with appearances of a red-shifted tail around 450 nm and a blue-shifted tail near 300 nm. Following the arguments discussed above, one can conclude that significant excitonic effects are involved

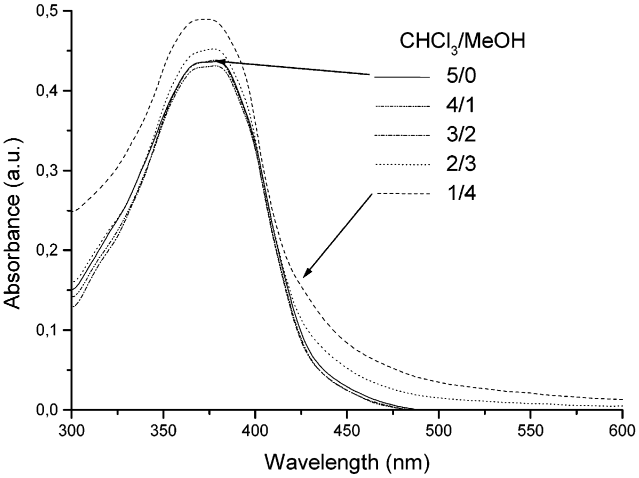


Figure 8. Solvent-dependent (v/v) UV−vis absorption spectra of poly(*N*-octyl-2,7-carbazoleneethynylene) (POCE).

for POCE upon aggregation. Along these lines, strong solvatochromic effects have also been reported for some poly(2,5-dialkyl-*p*-phenyleneethynylene)s[18] and poly(fluorenyleneethynylene)s.[19] According to our proposed model, these strong optical changes should be mainly related to interchain electronic interactions. However, this subject is still matter of debate, and careful experiments have been recently designed to shed some light on this issue.[20]

Conclusions

Upon aggregation, all the polycarbazoles investigated show optical changes, which seem mainly governed by excitonic effects. A clear dependence of this process upon the conformational changes adopted by the polymers is observed. POC, which should remained twisted with the addition of a poor solvent (i.e., methanol), exhibits a weak absorption band associated with H-aggregates and an intense band caused by J-aggregates. This gives rise to an overall red shift of the absorption band in chloroform/methanol mixtures. On the other hand, POCT, which can reach planarity through intermolecular interactions (small rotational barriers between subunits), shows a strong H-band, inducing blue shifts in the absorption spectra. Finally, polycarbazoles, which are already planar or nearly planar in a good solvent (POCF and POCE), also show H- and J- aggregates. The nature of the alkyl chains on the nitrogen atom does not significantly affect the optical properties of the polymers. On the other hand, the presence of methyl groups at the 3,6-positions of POCF inhibits the formation of H-aggregates precluding any significant parallel arrangements, giving rise to an overall red shift of the absorption band of P36DMCF.

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