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Electrochemical, Conductive, and Magnetic Properties of 2,7-Carbazole-Based Conjugated Polymers

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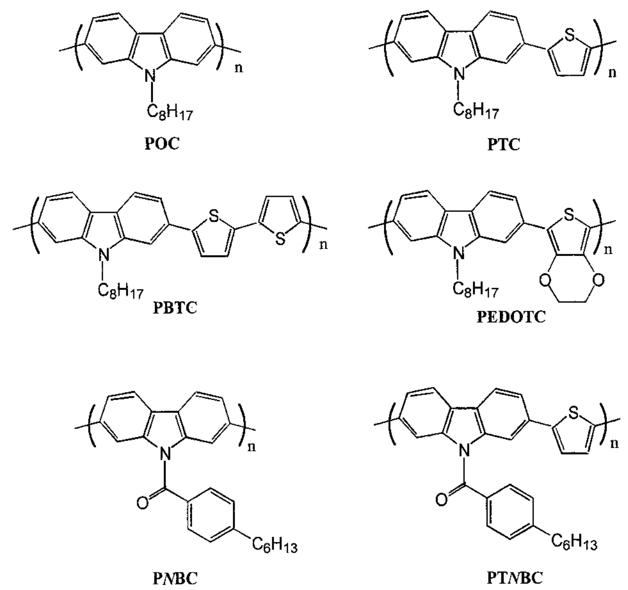
ABSTRACT: Novel poly(2,7-carbazole)s (i.e., poly(*N*-octyl-2,7-carbazolediyl) and poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl)) and their alternating thiophene, bithiophene, and 3,4-ethylenedioxy-2,5-thienylene copolymers have been investigated by cyclic voltammetry, UV−vis spectroelectrochemistry, electrochemical quartz crystal microbalance, in-situ electron spin resonance, and in-situ conductivity techniques. All polymer films undergo reversible oxidation and partially reversible reduction processes. In poly(*N*-octyl-2,7-carbazolediyl), two isoelectronic oxidation processes produce radical cations and dications with charge localization at the carbazole subunits. The presence of a strong electron-withdrawing substituent onto the nitrogen atom in the homopolymer leads to an increase by 3 orders of magnitude of the conductivity (i.e., 1×10^{-2} S/cm). Similarly, in alternating copolymers, the oxidative charge is more delocalized over the polyconjugated backbone with in-situ conductivities in the range of 4×10^{-2}−4×10^{-3} S/cm.

Introduction

Organic (both low molecular weight compounds and polymers) conjugated materials have recently received much attention due to their potential applications in light-emitting diodes, field effect transistors, charge storage devices, photodiodes, sensors, etc.[1] These organic electroactive and photoactive materials are usually based on thiophene, pyrrole, phenylene, fluorene, or carbazole moieties. In the case of carbazole-based conjugated oligomers and polymers, all previous studies were devoted to 3,6-linked N-substituted carbazole units.[2−10] Indeed, the most reactive sites for coupling are the 3- and 6-positions.[2] Despite a relatively short effective conjugation length (dimeric units), studies on poly(N-substituted-3,6-carbazole)s have revealed interesting electrochemical,[2−4] electrochromic,[5,6] electrical,[7] light-emitting,[8,9] and photorefractive[10] properties.

However, as reported for many other conjugated polymers,[1] the synthesis of well-defined and highly conjugated poly(N-substituted-2,7-carbazole)s should lead to optimized electrical and optical properties and should shed some light on the structure−property relationships in this class of materials. Interestingly, we recently reported the first syntheses of highly conjugated 2,7-carbazole-based polymers.[11] The synthetic strategy is based on a prefunctionalization at the 2,7-positions followed by a ring closure reaction. The resulting polymers have shown interesting luminescent properties which could be useful in electrooptical (light-emitting) devices. Along these lines, we would like to report here an extensive characterization of the electrochemical properties of these polymers (shown in Chart 1). In particular, it could be useful to characterize their redox and transport properties to get a rational optimization of any devices based on these novel polymeric materials.

Chart 1



Experimental Section

Chemicals and Reagents. All starting organic compounds were purchased from Aldrich Co. and used without further purification. All solvents used in the reactions were freshly distilled under argon. Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C.

Syntheses of 2,7-dichlorocarbazole (**1**),[11] *N*-octyl-2,7-dichlorocarbazole (**2**),[11] *N*-octyl-2,7-diiodocarbazole (**3**),[11] 2,7-dimethoxycarbazole (**4**),[12] 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**),[13] phenyl 4-hexylbenzoate (**6**),[14] 2,5-dibromo-3,4-ethylenedioxythiophene (**7**),[15] 2,5-bis(trimethylstannyl)thiophene (**8**),[16] 5,5′-bis(trimethylstannyl)thiophene (**9**),[16] $PdCl_2(dppf)$,[17] and $Pd(PPh_3)_4$[18] have been already reported in the literature.

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Poly(*N*-octyl-2,7-carbazolediyl) (POC) and poly(*N*-(2-ethylhexyl)-2,7-carbazolediyl-*alt*-2,2′-(5,5′-bithienylene)) (PBTC) were prepared from already published procedures.[11] In the case of poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thienylene) (PTC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-3,4-ethylenedioxy-2,5-thienylene) (PEDOTC), poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl) (P*N*BC), and poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl-*alt*-2,5-thienylene) (PT*N*BC), slightly different synthetic procedures were utilized and are given in the Supporting Information.

Electrochemical Apparatus and Procedures. Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. Polymer films (typically $10-20 \times 10^{-6}$ g cm^{-2}) were cast on electrodes from chloroform solution (0.1 wt %). The working electrode for cyclic voltammetry was a glassy carbon minidisk electrode (0.2 cm^2). For electronic spectroscopy a 0.8 × 2.5 cm indium−tin oxide (ITO) sheet (ca. 80% transmittance, ca. 20 ohm sq^{-1} resistance, from Balzers, Liechtenstein) was used.

In-situ spectroelectrochemical spectra were obtained from a Perkin-Elmer Lambda 15 spectrometer. In-situ ESR spectra were taken on a Bruker ER 100D following the procedure previously described.[20] Absolute spin calibration was performed with $VOSO_4{\cdot}5H_2O$ crystals, *g*-value calibration with thin films of DPPH ($g = 2.0037$).

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were cast. The oscillator circuit was homemade, and the frequency counter was a Hewlett-Packard model 5316B.

The apparatus and procedures used for the in-situ conductivity experiments were previously described in detail.[20] The electrode for conductivity measurements was a microband array platinum electrode (5 μm bandwidth, 100 nm thick) with interband spacing of 5 μm. The deposit was thick enough to ensure minimum resistance, under which condition the conductivity σ is given by $\sigma = k/(R - R_0)$, where R is the measured resistance, R_0 the lead resistance (was 100 ohm), and k the cell constant (0.2 cm^{-1}).

Results and Discussion

Synthesis. The syntheses of poly(*N*-octyl-2,7-carbazolediyl) (POC) and poly(*N*-(2-ethylhexyl)-2,7-carbazolediyl-*alt*-2,2′-(5,5′-bithienylene)) (PBTC) were carried out following recently reported procedures.[11] PBTC has a branched 2-ethylhexyl side chain to get some solubility. However, for the preparation of poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl) (P*N*BC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thienylene) (PTC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-3,4-ethylenedioxy-2,5-thienylene) (PEDOTC), and poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl-*alt*-2,5-thienylene) (PT*N*BC), slightly different synthetic procedures were utilized (see Scheme 1). In contrast to previously published methodologies,[12] the biphenyl unit **10** was obtained using a Suzuki coupling between 4-methoxyphenylboronic acid and 4-bromo-3-nitroanisole in standard conditions. Then, a Cadogan ring closure reaction was carried out in hot triethyl phosphite to give 2,7-dimethoxycarbazole (**4**).[12] This compound was alkylated using finely powdered NaOH, phase transfer agent, and primary alkyl bromide in anhydrous acetone. For amidation of compound **4**, neat NaH and 4-phenylhexyl benzoate in anhydrous THF were used. From compounds **11** and **16**, a standard deprotection reaction using BBr_3 in methylene chloride was achieved to give 2,7-dihydroxycarbazoles, in relatively good yields. Finally, monomers **12** and **17** were treated with DMAP and trifluoromethanesulfonic anhydride in cold pyridine to give monomers that can undergo Stille or Suzuki polycondensation reaction. When necessary, boronic esters can be introduced at the 2,7-positions (compound **14**). In all cases, these polymerization reactions gave polymers with number-average molecular weights around 5 kDa and polydispersity indexes of 1.5. These values were determined by size exclusion chromatography (SEC) in THF using monodisperse polystyrene as standards and, as such, must therefore be taken with caution. The resulting polymers are soluble in chloroform, and thin polymer films can be cast onto various substrates and electrodes for further investigation.

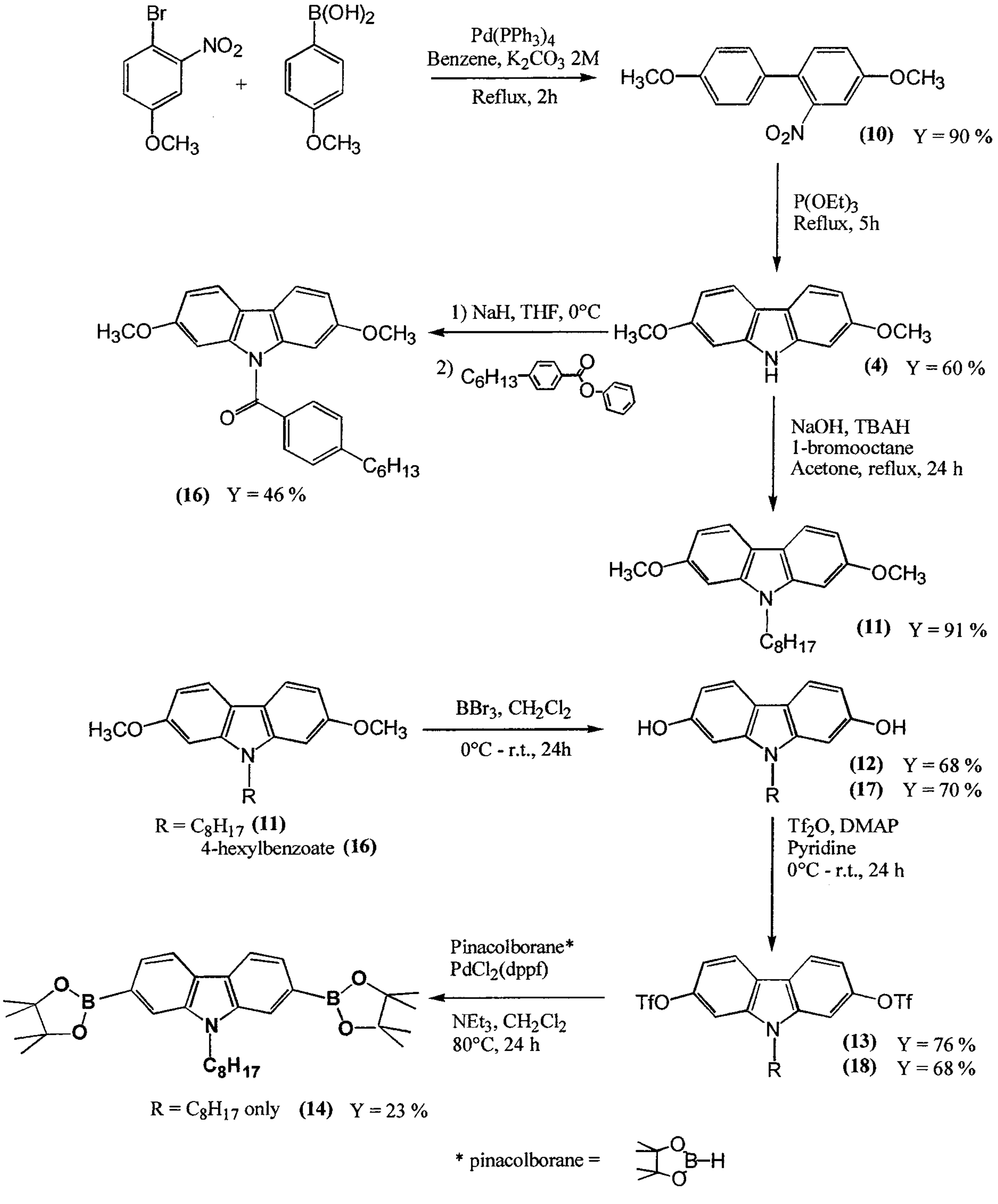
Electrochemical Characterization. The cyclic voltammogram (CV) in acetonitrile + 0.1 M Bu_4NClO_4 of all the polymer films (Figure 1) displays reversible oxidative processes at redox potentials $E°$ summarized in Table 1. All these polymers can also be reduced with partial reversibility (at a scan rate of 0.1 V s^{-1}) at $E°$ values also given in Table 1. The limited reversibility can be attributed to a dissolution of the oligomeric carbanions as indicated the mass losses recorded by electrochemical quartz crystal microbalance (EQCM) measurements. The difference of reduction and oxidation redox potentials $\Delta E°$ for all the polymers is close to the optical energy gaps E_g, which are also given in Table 1. Homopolymer POC displays two reversible oxidative processes at $E° = 0.45$ and 0.74 V (Figure 2) only after an activating CV cycle brought up to 0.9−1.0 V. The reversible charge stored in the overall response appears to be equally divided into the two redox processes. The width of the redox processes measured at half-height (ca. 0.2 V) is low when compared to other polymers (see below), which suggests for the present case the occurrence of charge localization.

The other homopolymer P*N*BC is also oxidized in two reversible oxidative processes. In this case, the electron-withdrawing substituent shifts the potentials to more positive values than for POC and the processes are scarcely resolved. The oxidative CV of the thienylene and bithienylene copolymers PTC and PBTC display a single reversible process. The subunits of PTC and PBTC, carbazole and thiophene or bithiophene, are electron donors with a significant difference in ionization potential. The oxidation peak potential of the individual molecules is 0.80 vs Ag/Ag$^+$ for *N*-ethylcarbazole;[7] for thiophene and bithiophene the values are 1.73 and 0.97 V.[21] Therefore, the first oxidation process of PTC may be assumed to involve the carbazole unit, though the intervention of the thiophene moieties cannot be ruled out. In the case of PBTC, the difference is negligible so that complete delocalization is possible.

3,4-Ethylenedioxy-2,5-thienylene (EDOT) copolymer (PEDOTC) displays two almost completely fused reversible oxidative processes at $E° = 0.20$ and 0.50 V. The electron-rich EDOT comonomer shifts the oxidative potential to values more negative than for PTC. The oxidation peak potential of EDOT is 1.04 V vs Ag/Ag$^+$,[7] i.e., close to that of bithiophene and therefore of carbazole. Thus, the oxidation process may be assumed to be equally distributed along the polyconjugated chain.

Electrochemical Quartz Crystal Microbalance (EQCM) Analyses. EQCM analyses of the polymer films have shown that during the first oxidative CV a considerable amount of mass is lost. This is due to the labile attachment of some polymer to the electrode. The reversible charge stored in the polymer deposit which

Scheme 1



is stable to repeated CV cycling has been correlated with its dry mass. It must be mentioned that, given the capacitive tail of the oxidation CV, the charges were evaluated at switching potentials selected to cover the maximum possible amount of charge without damaging the polymer. In practice, a switching potential of 0.8 V was used for all the polymers except P*N*BC, which could stand a voltage of 1.1 V without overoxidation. These results, given as electrons per repeat unit, are summarized in Table 2.

In the case of POC, the ratio of the reversible charge involved in the whole redox process to the stable dry mass corresponds to 0.2 electrons per repeat unit. This rather low value is obtained with samples of different thicknesses (20–200 × 10^{-6} g cm^{-2}) which allows to rule out the possibility that the scarce oxidation level is due to segregation of some bulk polymer from the conductive pathways. EQCM correlation of the dry mass and the reversible oxidative charge of PTC, PBTC, P*N*BC, and PT*N*BC indicates that ca. 0.5 electrons per repeat unit are exchanged in these polymers. This value, which is much higher than for POC, is in the range normally found in aromatic polymers and points out to the formation of one bipolaron per four repeat units. In the case of PEDOTC, 1.2 electrons per repeat unit are exchanged. This comparatively high value agrees with the presence of the EDOT moiety, which lowers the redox potential and allows a higher charge.[7]

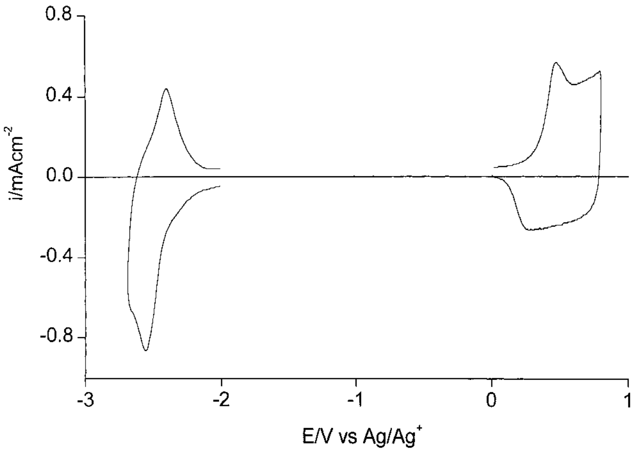


Figure 1. Cyclic voltammetry of PTC in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Reversible charge: 1.4 mC cm^{-2}.

Table 1. Oxidation and Reduction Redox Potentials $E°$, Electrochemical Energy Gap $\Delta E°$ (= $E°_{ox} - E°_{red}$), Maximum Absorption λ_p, and Optical Energy Gap E_g for Polymer Films

polymer	$E°_{ox}$/V	$E°_{red}$/V	$\Delta E°$/V	λ_p/nm[a]	E_g/eV
POC	0.45; 0.74	−2.68	3.13	380	3.27
P*N*BC	0.65; 0.95	−2.35	3.00	370	3.35
PT*N*BC	0.53	−2.35	2.88	460	2.70
PTC	0.37	−2.50	2.87	418	2.97
PBTC	0.43	−2.40	2.83	423	2.93
PEDOTC	0.20; 0.50	−2.54	2.74	434	2.86

[a] In $CHCl_3$ solution.

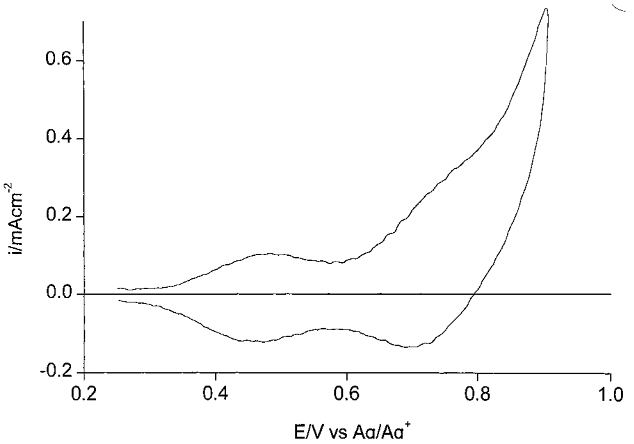


Figure 2. Cyclic voltammetry of POC in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Reversible oxidation charge: 0.5 mC cm^{-2}.

Table 2. EQCM Maximum Doping Level x, EQCM Mass Uptake upon Oxidation $F\Delta m/Q$, Maximum Absorption λ_p, and Conductivity σ for Oxidized Polymer Films

polymer	x[a]	$F\Delta mQ^{-1}$/g mol^{-1}	λ_p/nm	σ/S cm^{-1}
POC	0.2[b]	140	770	1×10^{-5}
P*N*BC	0.5[c]	90	470	1×10^{-2}
PT*N*BC	0.7[b]	150	590	4×10^{-2}
PTC	0.5[b]	170	555	1×10^{-2}
PBTC	0.5[b]	200	540	4×10^{-3}
PEDOTC	1.2[b]	70	595	2×10^{-2}

[a] Electrons per repeat unit. [b] Measured at a switching potential of 0.8 V. [c] Measured at a switching potential of 1.1 V.

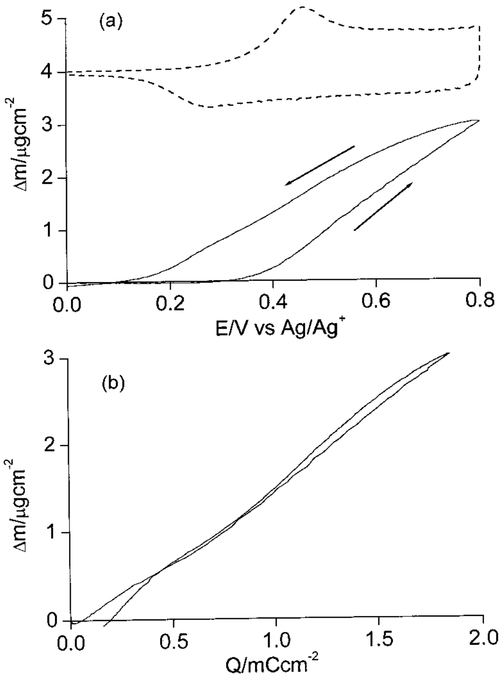


Figure 3. In-situ EQCM vs (a) potential and (b) charge of PTC in acetonitrile + 0.1 M Bu_4NClO_4. Dry mass: 13 μg cm^{-2}. Dashed curve: CV for comparison.

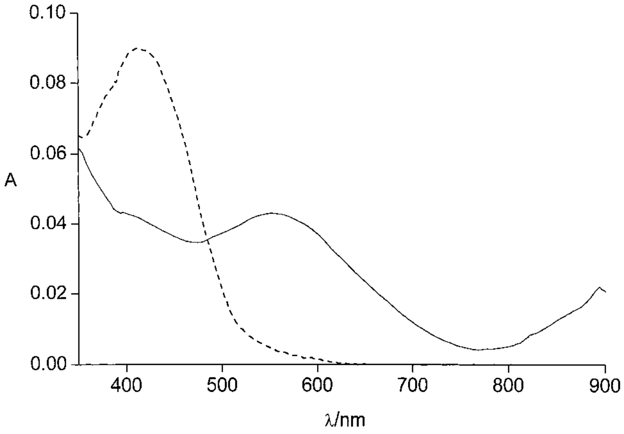


Figure 4. In-situ spectroelectrochemistry of PTC in acetonitrile + 0.1 M Bu_4NClO_4 (- - -) before and (—) after oxidation.

In-situ EQCM shows for all the polymers a mass increase during oxidation (Figure 3a). The mass change is linear with redox charge (Figure 3b), and the values of the slopes $F\Delta m/Q$ for the various polymers are given in Table 2. For POC and PT*N*BC films, the slope corresponds to the reversible uptake of one perchlorate anion and one solvent molecule, i.e., with some polymer swelling. For PTC and PBTC the slopes indicate the reversible uptake of one perchlorate anion and 2−3 solvent molecules, i.e., an increased polymer swelling. For PEDOTC and P*N*BC, the slopes indicate the reversible uptake of one perchlorate anion with only a minor solvent exchange.

Spectroelectrochemical Characterization. Spectroelectrochemical analyses of the polymers, with the exception of POC, have revealed that, upon oxidation, the yellow films turn to bluish (Figure 4) with a maximum absorption at values given in Table 2. These spectral changes are reversible in these polymers, but not in POC. The spectroelectrochemical response of POC is in fact quite peculiar. This polymer, which in the neutral state displays its absorption maximum at 380 nm, shows a chromatic shift from colorless to blue (770

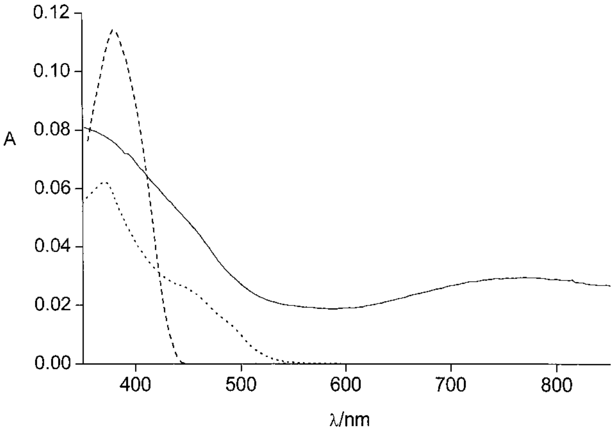
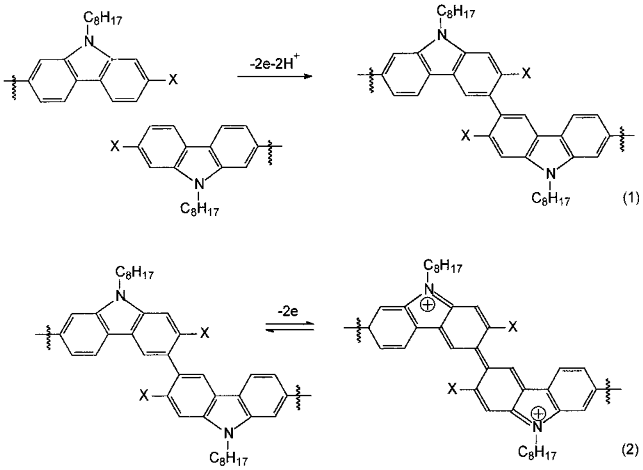


Figure 5. In-situ spectroelectrochemistry of POC in acetonitrile + 0.1 M Bu_4NClO_4 (- - -) before and (—) after oxidation and (• • •) backward reduction.

Scheme 2



nm) upon full oxidation (Figure 5). Backward reduction of the polymer after oxidation causes the appearance of new bands (as shoulders) at 450 and 490 nm (Figure 5).

An overall examination of the electrochemistry of POC has revealed that with this polymer (and not with the others) an irreversible process takes place in the course of the first oxidation procedure. As reported above, oxidation and backward reduction gives an orange color to the colorless pristine polymer. Moreover, it has been observed that this treatment renders this polymer insoluble. On the contrary, FTIR analysis does not show dramatic changes in the spectrum. On the basis of these experimental data, it is suggested that the formed radical cations, quite reactive to coupling due to strong localization of the unpaired electron at the terminal 3−3′-positions, couple to longer chains in a solid-state polymerization process as shown in eq 1 of Scheme 2. This suggestion is also based on the fact that the oxidation of the nitrogen atom would interrupt the delocalization of the electrons along the backbone and would therefore mainly occur at the end groups. In this regard, GPC measurements on the soluble fraction of pristine POC indicate a degree of polymerization of about 15,[11] which would mean about two end groups per 15 repeat units. Thus, the observed cyclic voltammogram is suggested to be that of the 3,3′-dicarbazole units produced by coupling of the oligomeric terminals (eq 2 of Scheme 2). In agreement with this suggestion, (i) the stored charge in the first redox process is 0.1 electron per unit in approximate agreement with the 0.13 value calculated from the GPC results and (ii) the redox potentials are the same of 9,9′-diethyl-3,3′-dicarbazole, which is the only species produced by anodic coupling of carbazole.[6] Following these arguments, results reported here and in the following sections for POC are in fact those of 3,3′-coupled 2,7-oligomeric sequences.

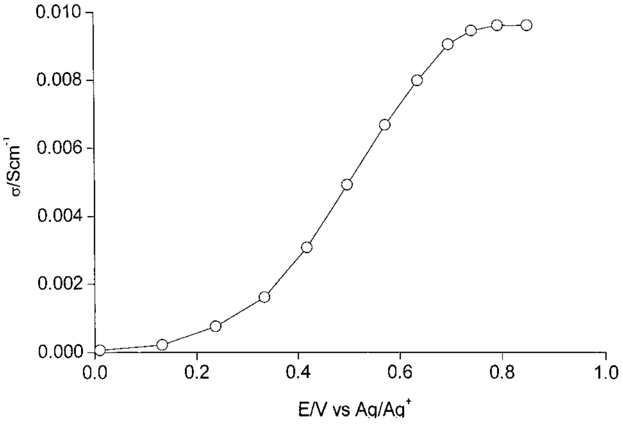


Figure 6. Electrical conductivity vs potential of PTC in acetonitrile + 0.1 M Bu_4NClO_4.

In-Situ Electrical Conductivity. In-situ electrical conductivity measurements of all the investigated polymers show that oxidation causes the transition from a low-conductivity to a conductive state as generally found in conjugated polymers.[1] The conductivity of the polymers (with the exception of POC) as a function of the applied potential displays a sigmoidal shape (Figure 6). The limiting conductivities (see Table 1) are around 10^{-2} S cm^{-1} with a limited span (ca. 1 order of magnitude) within the series. Indeed, the slightly lower electrical conductivity of oxidized PBTC could be related to the presence of branched substituents which were necessary to allow the solubilization of the resulting polymer.

The conductivity of POC is much lower. At a potential close to the second redox potential the conductivity may be evaluated as 1×10^{-5} S cm^{-1}, at most. For this reason and because of the background currents at the highly positive potentials, it could not be accurately measured as a function of the applied potential. Thus, though the relationship with potential could have given a better proof of the redox conduction of the material, the low value does in fact agree with highly localized charge carriers. It is worth noting that poorly conjugated poly(*N*-alkyl-3,6-carbazolediyl) films exhibit conductivities up to 10^{-3} S/cm upon electrochemical oxidation[7b] (values up to 1−5 S/cm have been reported for chemically doped materials[7a]), indicating that oxidation of the nitrogen atoms and conjugation through 3,6 couplings can be a relatively good pathway for electrical conduction in this class of materials. Interestingly, the introduction of an electron-withdrawing substituent on the 2,7-linked carbazole backbone has led to a significant increase (by 3 orders of magnitude when compared to *N*-alkyl derivatives) of the electrical conductivity.

In-Situ Electron Spin Resonance (ESR) Measurements. For all polymers, in-situ ESR measurements during the oxidation processes show the appearance of a 2×10^{-4} T wide signal with *g* values given in Table 3. With the exception of POC, the *g* value (ca. 2.003) is close to that of polythiophene and poly(*p*-

Table 3. ESR *g* Value and Maximum Spin Concentration (*s*) for Oxidized Polymer Films

polymer	*g*	*s*[a]	polymer	*g*	*s*[a]
POC	2.0043	0.1	PTC	2.0028	0.02
P*N*BC	2.0028	0.1	PBTC	2.0028	0.02
PT*N*BC	2.0028	0.05	PEDOTC	2.0031	0.06

[a] Spins per repeat unit.

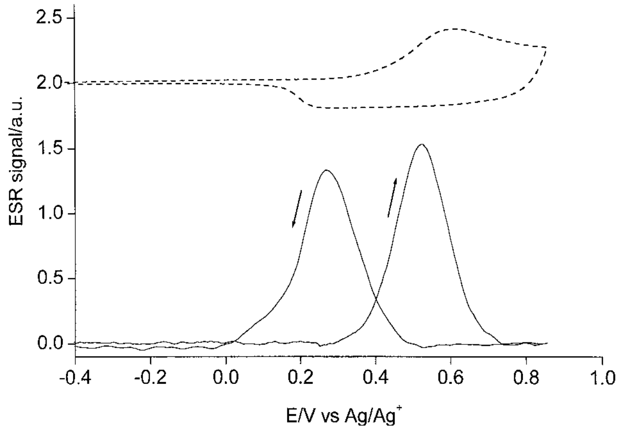


Figure 7. Intensity of the ESR signal vs potential of PBTC in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

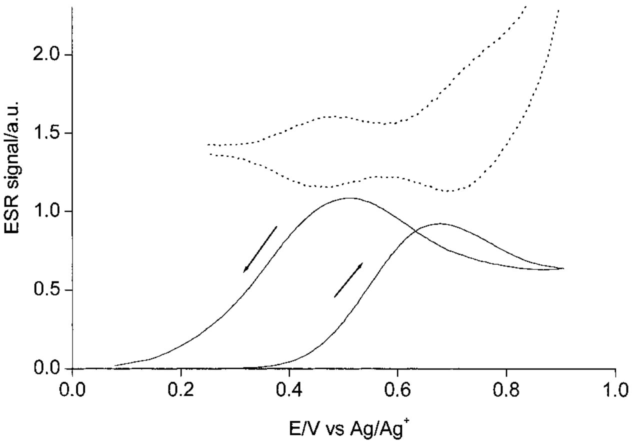


Figure 8. Intensity of the ESR signal vs potential of POC in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve: CV for comparison.

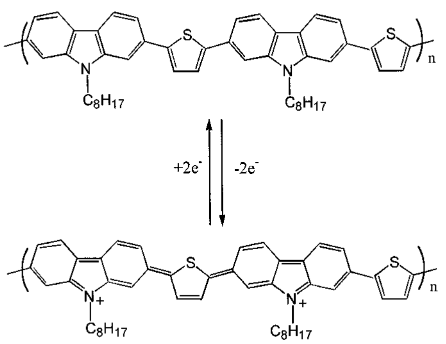
phenylene).[22,23] The signal reaches its maximum at a potential close to the *E*° value and then disappears (Figure 7). The maximum spin concentration corresponds to 0.02−0.06 spins per repeat unit, i.e., close to the low values normally encountered in polythiophenes and attributed to π-dimerization of radical cations.

In-situ ESR analyses of POC during the oxidation process show a very strong signal at $g = 2.0043$. The signal reaches its maximum at a potential intermediate between the two *E*° values (Figure 8) and then starts to decrease. The maximum spin concentration corresponds to one spin per injected electron. These results indicate the production of free monomeric radicals at the first redox process and their disappearance as dications at the second. The previously suggested production of a localized free radical is therefore confirmed. A particular consideration is deserved to the fact that the *g* value is unusually high compared with that of polythiophene (2.0025) and poly(*p*-phenylene) (2.0029). In fact, *g* values are related to the participation to the carbon, sulfur, and oxygen atoms according to the equation

$$\Delta g = g - g_e \propto \lambda / E_g$$

where g_e is the free electron *g* value (2.0023), λ is the spin−orbit coupling parameter (29 cm^{-1} for C_{2p}, 382 cm^{-1} for S_{3p}, 76 cm^{-1} for N_{2p}, 151 cm^{-1} for O_{2p}), and E_g is the band gap of the polymer.[24] As a consequence, the high *g* value must be attributed to a strong interaction with the nitrogen atom of the amine moiety. The radical cations would in fact be localized on the nitrogen atom (besides on the 3- and 6-positions) of the carbazole unit without conjugation with the poly(*p*-phenylene) backbone.

Scheme 3



Conclusions

Poly(*N*-octyl-2,7-carbazolediyl) (POC) shows an unpaired electron *g* value and electrical conductivity indicative of localized charge carriers. In contrast, the unpaired electron *g* values (ca. 2.003) and the conductivities (ca. 10^{-2} S cm^{-1}) are more or less the same for all carbazole−thiophene copolymers and poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl) (P*N*BC) which indicate a better delocalization of the charge carriers over the conjugated backbone. Despite this, the conductivities (4 × 10^{-2}−4 × 10^{-3} S cm^{-1}) are rather low when compared to those of polythiophenes.[1] The reason for such low conductivities in 2,7-carbazole-based polymers cannot be attributed to a twisting along the polyconjugated chain at the thienylene−phenylene ring junctions since the thiophene units should decrease the steric hindrance and possibly lead to coplanar structures.[25] Therefore, although delocalization of the charge carriers is better in some polymeric structures, it is believed that some charge carrier pinning is still possible onto the nitrogen atoms (see Scheme 3). Consequently, stronger electron-withdrawing substituents onto the nitrogen atom and/or the introduction of more easily oxidizable aromatic units along the conjugated backbone seem necessary for the design of future highly conducting polycarbazole derivatives. It could also be interesting, using similar synthetic strategies, to develop fully conjugated ladder polycarbazole derivatives. For instance, by introducing nitrogen bridges at the 3,6′-positions between 2,7′-linked carbazole units, it could be possible to obtain highly conducting and processable polymeric (or oligomeric) materials.

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Supporting Information Available: Synthetic procedures for poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thienylene) (PTC), poly(*N*-octyl-2,7-carbazolediyl-*alt*-3,4-ethylenedioxy-2,5-thienylene) (PEDOTC), poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl) (P*N*BC), and poly(*N*-(4-hexylbenzoyl)-2,7-carbazolediyl-*alt*-2,5-thienylene) (PT*N*BC). This material is available free of charge via the Internet at http://pubs.acs.org.

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