Polymerization of 3,4-Difluoropyrrole: Electrochemical and Physicochemical Behavior of Poly(Difluoropyrrole)

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The electrochemical polymerization of 3,4-difluoropyrrole (DFP) has been examined by cyclic voltammetry (CV) as a function of scan rate and solvent. The polymerization is facile in dichloroethane, leading to a stable electroactive film. In contrast, the corresponding polymerization in acetonitrile occurs only with difficulty. Poly(3,4-difluoropyrrole) (PDFP) exhibits a high redox potential (+0.90 V vs Ag/AgCl), a particularly high doping level (ca. 55%), and a rather good conductivity (up to 0.1 S·cm^{-1}), in comparison to other polyhalopyrroles. Meanwhile, the lifetime of the DFP radical cation, as determined by fast scan CV experiments, is about 1 ms. This lifetime is substantially longer than that of other pyrrole derivatives under identical experimental conditions. Theoretical calculations are in agreement with experiment in showing that the DFP radical cation is a powerful oxidant in comparison to pyrrole radical cation. However, these computational studies indicate that the net charge and spin distributions are similar for the cation radicals of DFP and pyrrole itself. To interpret these results, we propose that the introduction of fluorine substituents could be responsible for a lower polarizability of the cation radical, leading to a higher activation barrier for dimerization of DFP in comparison to pyrrole and other halopyrroles.

1. Introduction

One of the major challenges in the field of conducting polymers is to prepare materials possessing both good electrical conductivity and the highest possible redox potential, especially for applications in accumulators.[1] Incorporation of halogens is a highly successful approach to stabilizing organic compounds against oxidation. In principle, this approach could also be successful with organic conductors. In the past, Audebert and Bidan prepared poly(3,4-dihalopyrroles), with iodine, bromine, or chlorine as the halogen.[2−4] These poly(halopyrroles) were found to display high redox potentials, occasionally also high doping levels, especially in the case of poly(diiodopyrrole).

Poly(3,4-difluoropyrrole) is a particularly attractive target due to the strong electron-withdrawing power of the fluorine atom. Until recently, the monomer was somewhat difficult to obtain; its first synthesis is recent and not straightforward.[5] An improved preparative method[6] now allows us to dispose of appreciable quantities of 3,4-difluoropyrrole (DFP). Therefore, the electropolymerization of this monomer is now open to investigation. Films of poly(3,4-difluoropyrrole) (PDFP) are readily deposited on platinum or carbon electrodes, and the resulting polymer is found to be electroactive. In addition, the electropolymerization of difluoropyrrole shows that the cation radical of this compound is surprisingly stable, given its very high potential of formation.

2. Experimental Section

3,4-Difluoropyrrole was prepared according to a recently described procedure.[6] This compound is a stable, white crystalline powder, in contrast to all other halopyrroles, which decompose with formation of a polymer[4] (dibromopyrroles are especially unstable). All electrochemical experiments were made in a three compartment cell with a platinum or glassy carbon working electrode, platinum counter electrode, and a silver/silver chloride reference electrode (the redox couple of ferrocene was checked at +0.425 V vs this reference). The electrolyte was either acetonitrile (SDS, HPLC Grade) with

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[1] For a recent overview on conducting polymers, see: *Handbook of organic conductive molecules and polymers*; Nalwa, H. S., Ed.; John Wiley and Sons: New York, 1997.

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tetraethylammonium perchlorate added, or dichloroethane with tetrabutylammonium (TBA) perchlorate added, or dichloromethane (SDS, HPLC Grade) with (TBA)PF_6 added, as stated in the text. The electrolyte salts (Fluka, puriss.) were used as received in all but the electropolymerization experiments, which were performed under argon atmosphere in a glovebox. For the electropolymerization works, the solvents were distilled from P_2O_5 and the electrolytes were stored over P_2O_5.

The electropolymerization and subsequent study of the polymer films were performed using an EG&G PAR273 potentiostat, interfaced to a PC. The study of the electrochemical behavior of DFP was performed using a fast homemade potentiostat,[7] equipped with an ohmic drop compensation system, and connected to a Tacussel pilot and a Nicolet digital oscilloscope, with a 1 mm diameter glassy carbon electrode. When larger amounts of polymer were necessary, a 6 cm^2 platinum foil was used as a working electrode.

IR spectrum was recorded on a Bruker IFS 25 spectrometer. UV−vis spectroelectrochemistry was performed using a homemade cell: the working electrode was made of a thin transparent platinum layer (about 10 nm thick) sputtered on a glass substrate; this electrode was then sealed in the homemade glass cell, perpendicularly to the probe beam. Platinum wire and silver/silver chloride were used respectively as counter and reference electrodes and located on the cell sides in order not to disturb the beam. The area of the coated polymer was about 1 cm^2, and the charge passed during electrosynthesis was 75 mC. A double beam UVIKON 923 (Bio-Tek Kontron) spectrophotometer was used for the spectra acquisition: a spectrum was recorded every 200 mV; after that the film was equilibrated in the given redox state for about 1 min.

In situ conductivity measurements were performed on a film synthesized under argon atmosphere (glovebox) in dichloromethane. The device comprises a five platinum microelectrode array connected to a voltage supply and current detector. The microelectrodes (90 μm diameter, 5 μm spacing) were coated potentiostatically with a synthetic charge of 20 mC, for a total covered area of 2.5 mm^2. This corresponds to a film thickness of about 2 μm, according to Diaz et al..[8] A box of calibrated resistances was used as a standard for resistance measurements. Ex situ measurements were performed on a pressed pellet of oxidized polymer (0.3 mm thick), using a four-probe apparatus, with linearly separated contacts distant of 1 mm each.

Density functional and solvation calculations were performed using the Gaussian 98 package.[9] Gas-phase geometries and electronic energies were calculated by full optimization of the conformations using the B3LYP[10] density functional, with the 6-31G* basis set,[11] starting from preliminary optimizations at the HF/6-31G* level. Solvation free energies were calculated on the gas-phase optimized conformations, according to the SCRF (self-consistent reaction field) method,[12] using the polarizable conductor calculation model (Cosmo) and the B3LYP density functional.

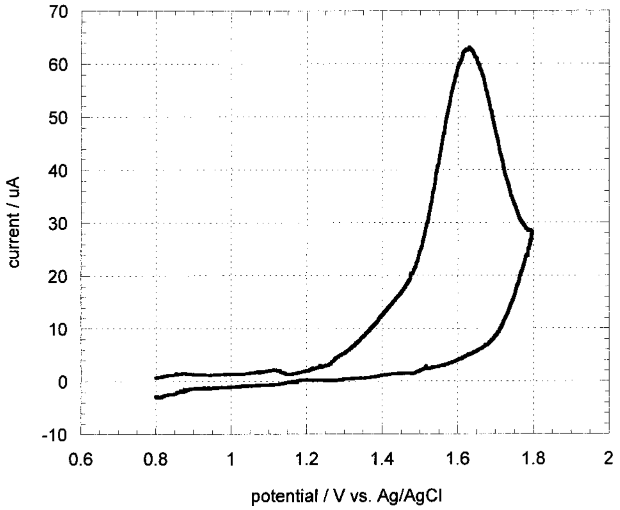

Figure 1. Cyclic voltammogram of 3,4-difluoropyrrole 5 mmol/L in acetonitrile + tetraethylammonium perchlorate (0.1 M), at 100 mV/s.

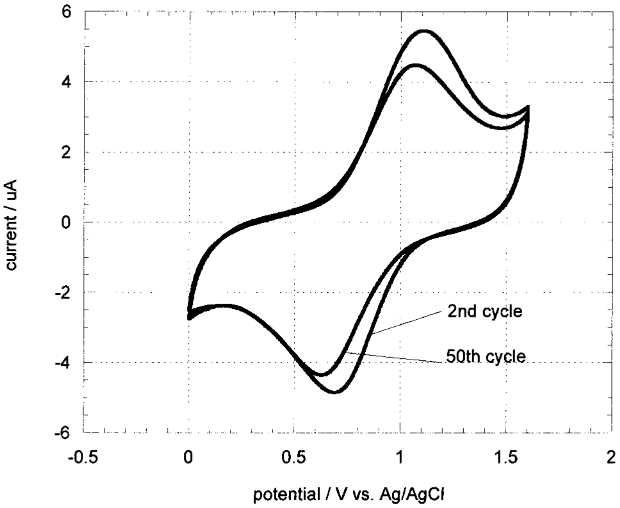

Figure 2. Cycling at 100 mV/s of poly(difluoropyrrole) in dichloroethane + tetrabutylammonium perchlorate (0.1 M). Comparison between 2nd and 50th cycles.

3. Results and Discussion

3.1. Electropolymerization Process. Electrochemical polymerization of DFP is facile in non nucleophilic solvents such as dichloroethane. The polymerization was found to be more efficient on glassy carbon than on gold or platinum electrodes. The oxidation of DFP occurs around 1.6 V, compared to 1.2 V for pyrrole under similar conditions (Figure 1). Transient currents during electropolymerization are analogous to those previously observed for pyrrole or thiophene oxidation. The resulting black polymer film has a redox potential of +0.90 V. This film can be repetitively cycled in dichloroethane (Figure 2); 50 cycles lead only to a 10% decrease in electroactivity, which shows the rather good stability of the film. Peak currents vary linearly with the scan rate between 10 and 100 mV/s (Figure 3), as is expected for a species deposited on the electrode surface. Surprisingly, the redox potential of PDFP is lower than the one of poly(dichloropyrrole), showing probably that, despite the stronger inductive electron attracting power of the fluorine atoms, the mesomeric stabilization of the charge in the polymer is also much more important than in

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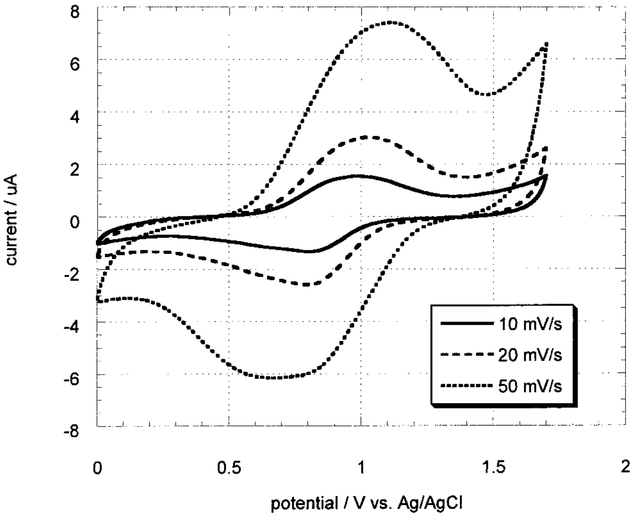

Figure 3. Influence of scan rate on the cyclic voltammogram of poly(difluoropyrrole) in dichloroethane + tetrabutylammonium perchlorate (0.1 M).

other poly(halopyrroles),[2-4] and thus has the highest influence. This is also in contrast with the DFP behavior, which has a redox potential higher than other halopyrroles; however, the difference is not as high as would have been expected on the basis of the σ^* Hammett scale for example. In addition, PDFP cyclic voltammograms display a much less important so-called capacitive current than other polypyrroles (or polythiophenes) usually do.

The electropolymerization of DFP shows a marked solvent dependence. At low scan rates (100 mV/s) and 5 mM concentrations of DFP in CH_3CN, cyclic voltammograms display a characteristic irreversible oxidation at a potential of about 1.63 V (Figure 1). However, at this concentration, polymer formation occurred with difficulty, in contrast to almost all other pyrrole derivatives, including functionalized pyrroles.[13-15] Even at higher concentrations ([DFP] > 20 mM) polymer formation remains sluggish in acetonitrile. Because of the large solvent dependence of the DFP electropolymerization kinetics, we embarked on more detailed experimental and theoretical studies on the initial electropolymerization reactions.

Cyclic voltammograms on ultramicroelectrodes (Figure 4) demonstrate the reversible character of the electrochemical oxidation at high scan rate. The exact redox potential of the DFP/$DFP^{\bullet +}$ couple has been found to be 1.63 V. The dependence of the peak potentials on the logarithm of the scan rate at moderate to relatively high scan rates (20 mV/units slope, Figure 5a) indicates that the disappearance of the electrogenerated species corresponds to the coupling of two cation radicals[16] (the theoretical slope value is 19.6 mV/log units). [Such a variation may also occur in the case of a reversible substrate/cation radical coupling; however, the occurrence of this mechanism is rare, and moreover, it has never been observed in the case of heterocycles oxidation.] This is in accordance with previous reports on the electrochemical coupling of the cation radicals of pyrrole oligomers [observation made in acetonitrile (Audebert, P.; Hapiot, P. Personal communication)]. The concentration dependence (Figure 5b) has a −17 mV/decade slope, which is typical of a second-order process. These data support the arguments above and also exclude reversible cation radical/substrate coupling.[17]

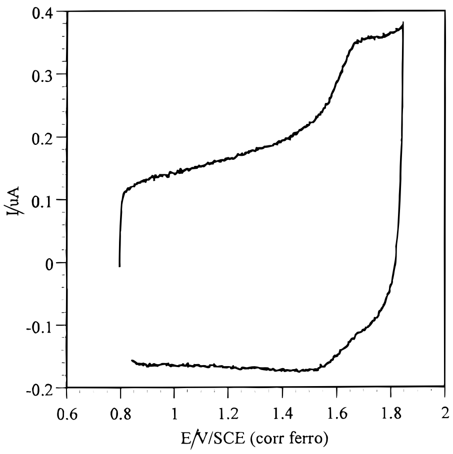

Figure 4. Example of high scan rate (8500 V/s) cyclic voltammogram of difluoropyrrole (1 mmol/L) in acetonitrile + tetrabutylammonium perchlorate (0.1 M) on ultramicroelectrode (10 μm diameter).

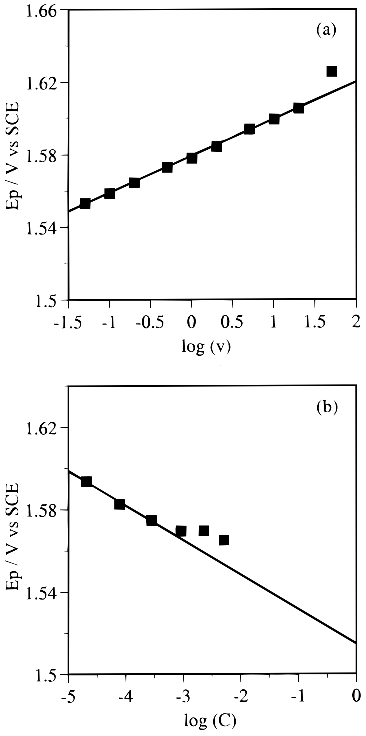

Figure 5. Variation of peak potential as a function of logarithm of scan rate (a) and difluoropyrrole concentration (b) (same conditions as in Figure 4).

These results allow us to estimate the lifetime of the cation radical of DFP. The value of the dimerization rate constant (2−4) × 10^{-8} $mol^{-1}\cdot L\cdot s^{-1}$ in acetonitrile, (4−8) × 10^{-8} $mol^{-1}\cdot L\cdot s^{-1}$ in dichloromethane) leads to a

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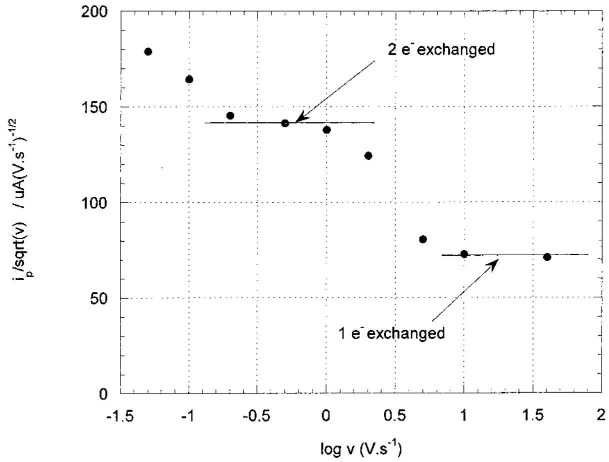

Figure 6. Variation of peak current divided by the square root of the scan rate, as a function of the logarithm of the scan rate for difluoropyrrole in dichloroethane.

cation radical lifetime of about 1 ms, which is longer than that observed for pyrrole (20 μs),[17–18] and is comparable to that of 3,4-dimethylpyrrole.[17] The long lifetime is somewhat surprising, given that the small size of the fluorine substituents should not offer any significant steric barrier for the dimerization reaction. Similar studies with 3,4-diiodopyrrole indicate that the radical cation has a lifetime even shorter than that observed for pyrrole.[19] These results indicate that fluorine substitution provides an unusual degree of kinetic stabilization for pyrrolic cation radicals, despite the fact that such radicals are highly oxidizing.

The influence of the scan rate has also been analyzed in terms of peak current. The variation of the reduced peak currents with the scan rate is shown in Figure 6. One can see two stages with proportional ratios 2/1. Each of these stages can be clearly ascribed to respectively the one-electron oxidation, gradually changing toward the two-electron oxidation. The final change of slope in the slow scan rate region corresponds to the ($2 + \delta$) electron oxidation, the δ quantity accounting for the additional oxidation of the polymer formed on the electrode (doping level). Extrapolation of this part of the curve tends to indicate that PDFP exhibits a rather high doping level (>0.5).

3.2. Polymer Characterization. *Microanalysis and IR Spectroscopy.* Microanalysis data on PDFP show that the pyrrole ring C_4N is always retained in the polymer; however, the content of fluorine is always lower than 2 atoms/ring (between 1.5 and 1.8), showing that some defluorination occurs during electropolymerization. This should be due to the occurrence of the concurrent autopolymerization reaction, catalyzed by protons, which is known to occur with all halopyrroles (except diiodopyrrole), with HX loss (here $X = F$).[4] When polymerizing thick films, protons are produced in the vicinity of the electrode and induce the production of some autopolymer which mixes to the electrogenerated polymer. The most striking feature of PDFP is its remarkably high doping level: 55 ± 3%, in agreement with the previous electrochemical characterization. Despite the fact that other poly(halopyrroles) were found to have doping levels in the 40% range,[2] already much higher than polypyrrole itself, poly(difluoropyrrole) displays the highest value of the series. This demonstrates that a noticeable amount of charge is localized on the fluorine atoms and is consistent with the remarkable stabilization of the cation radical by fluorine substitution as discussed above.

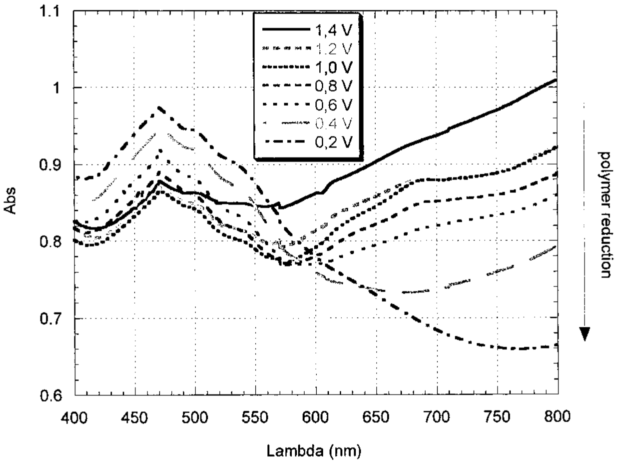

Figure 7. Spectroelectrochemistry of a thin film of PDFP in 0.1 M tetrabutylammonium perchlorate in dicholoroethane. Spectra were recorded under polarization of the film at the potentials indicated in the figure, starting from the full oxidized state.

The IR spectrum [supporting information available upon request from the author] of a pellet of oxidized PDFP mixed with KBr exhibits the vibration band characteristic of the N−H moieties at 3500 cm^{-1}, as well as the deformation bands associated with the C−F bonds (around 1100 cm^{-1}). However, the characteristic vibration band of the C=C moieties (around 1600 cm^{-1}) is not so intense as it usually appears in polypyrrole and is slightly shifted toward higher energies.[20,21]

Spectroelectrochemistry. Figure 7 shows the spectra recorded between 400 and 800 nm at various electrode potentials, starting from the fully oxidized state. One can see clearly the strong decrease of absorption, especially in the red part of the spectrum, when the applied potential becomes more cathodic, corresponding to the annihilation of the charged carriers (polarons, bipolarons) in the polymer chains (see ref 22 and references cited therein). Simultaneously the absorption increases in the blue part of the spectrum ($\lambda_{max} = 470$ nm), corresponding to the $\pi \rightarrow \pi^*$ transition. The band gap energy of PDFP can be evaluated to ca. 2.6 eV, which is 0.6 eV below the polypyrrole value,[23] as expected from the stabilizing effect of fluorine on the cation radical. Except for 1.4 V, the spectra cross at a quasi isosbestic point in the 570−580 nm interval, indicating the transformation of charged segments into neutral ones during the reduction process. All these features are coincident with the mechanism of doping well-known for conducting polymers.

Conductivity Measurements. In situ conductivity of a PDFP film, synthesized in dichloromethane under argon

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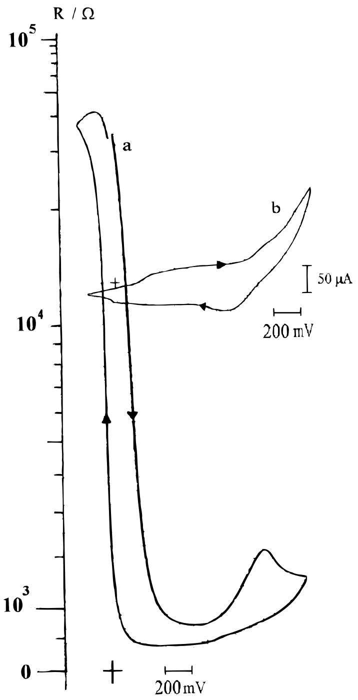


Figure 8. Variation of resistance (a) in log units and current (b) as a function of potential, for a PDFP film coated on Pt microelectrodes, and synthesized in dichloromethane + (TBA)PF$_6$ under argon atmosphere (glovebox). Scan rate: 5 mV/s. Direction of scanning indicated in the figure.

atmosphere, is shown in Figure 8, as a function of applied potential (curve a). A simultaneous cyclic voltammogram, recorded between − 0.2 and +1.4 V, is shown in the same figure (curve b). PDFP exhibits a clear transition between an insulating reduced state and a conductive oxidized state, with a quite small variation of conductivity (about 2 orders of magnitude) between both states. The conductivity of the oxidized polymer can be derived from the measured resistance (400 Ω) and the estimated film thickness (2 μm, calculated from the polymerization charge[8]). A value of 2×10^{-2} S·cm^{-1} was obtained for the film conductivity, which is higher than for other halopyrroles.[2]

For PDFP, the evolution of resistance as a function of potential gives the surprising result that resistance tends to slightly decrease at high oxidation potentials (>1 V). This feature is reproducible, even if the polymer is cycled to very positive potentials. No loss of conductivity has been found for PDFP cycled as far as 2 V, which indicates a very good stability of the film against oxidative degradation. This follows the trend observed for the evolution of the degradation potential of other polyhalopyrroles.[2] These observations are consistent with the higher electronegativity of fluorine and the greater strength of the carbon−fluorine bond, both of which stabilize the polymer against overoxidation.

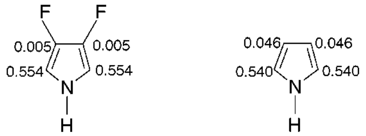
On the other hand, a pressed pellet of polymer has been prepared from the powder recovered from electrolyzation of relatively large polymer films (the limitation is only due to the available platinum electrode surface). The four probes measured conductivity reaches 0.2 ± 0.05 S·cm^{-1}. This value is in good accordance with the one measured in situ. Since, in ex situ measurements on pellets, the presence of grain junctions often leads to the underestimation of the conductivity, we believe that, in the in situ experiments, on the contrary, the film thickness was overestimated and that the conductivity of as-grown polymer films is in the range 0.1−0.2 S·cm^{-1}. This value is remarkably high for a poly(halopyrrole) and shows that the fluorine substituents do not impede delocalization of the charge along the polymer segments.

Table 1. Oxidation (eV) and Reaction (kcal·mol^{-1}) Energies from B3LYP/6-31G* and Cosmo[a]

	ΔU_{el}			
X	oxidation (eV)	dimerization (kcal·mol^{-1})	deprotonation of the cation radical of the monomer (kcal·mol^{-1})	deprotonation of the dimer (kcal·mol^{-1})
	Gas Phase			
H	7.797	31	231	352
F	8.190	29	221	332
F − H	0.393	−2	−10	−20
	Solution phase (CH$_2$Cl$_2$)			
H	5.853	−30	276	504
F	6.114	−27	270	489
F − H	0.261	3	−6	−15

[a] Definitions: ΔU_{el}(oxidation) = U_{el}(pyrrole$^{\bullet+}$) − U_{el}(pyrrole); ΔU_{el} in CH$_2$Cl$_2$(oxidation) = U_{el}(pyrrole$^{\bullet+}$) − U_{el}(pyrrole) + $\Delta G_{i_{solv}}$(pyrrole$^{\bullet+}$) − $\Delta G_{i_{solv}}$(pyrrole); ΔU_{el}(dimerization) = U_{el}(bipyrrole (2H$^+$)) − 2U_{el}(pyrrole$^{\bullet+}$); ΔU_{el} in CH$_2$Cl$_2$(dimerization) = U_{el}(bipyrrole (2H$^+$)) − 2U_{el}(pyrrole$^{\bullet+}$) + $\Delta G_{i_{solv}}$(bipyrrole (2H$^+$)) − 2$\Delta G_{i_{solv}}$(pyrrole$^{\bullet+}$); ΔU_{el}(deprotonation of the cation radical) = U_{el}(pyrrole$^\bullet$) − U_{el}(pyrrole$^{\bullet+}$); ΔU_{el} in CH$_2$Cl$_2$(deprotonation of the cation radical) = U_{el}(pyrrole$^\bullet$) − U_{el}(pyrrole$^{\bullet+}$) + $\Delta G_{i_{solv}}$(pyrrole$^\bullet$) − $\Delta G_{i_{solv}}$(pyrrole$^{\bullet+}$); ΔU_{el}(deprotonation of the dimer) = U_{el}(bipyrrole) − U_{el}(bipyrrole (2H$^+$)); ΔU_{el} in CH$_2$Cl$_2$(deprotonation of the dimer) = U_{el}(bipyrrole) − U_{el}(bipyrrole (2H$^+$)) + $\Delta G_{i_{solv}}$(bipyrrole) − $\Delta G_{i_{solv}}$(bipyrrole (2H$^+$)) (F − H, differences between difluoropyrrole and pyrrole).

Table 2. Spin Densities on the Carbon Atoms in the Cation Radicals of Pyrrole and Difluoropyrrole (B3LYP/6-31G*)



Theoretical Modeling of DFP Polymerization. We performed theoretical calculations on the radical cation of DFP to provide some explanation for the relatively sluggish polymerization reactions observed experimentally. We modeled the one-electron oxidations of DFP and pyrrole and their respective dimerization and deprotonation reactions in the gas phase and in methylene chloride; the results are displayed in the Tables 1 and 2. The oxidation reaction is relatively well-described by this theoretical treatment; the calculated difference in oxidation potentials (0.26 V) is close to the experimental value (0.31 V). A comparison of the electron spin and charge distributions for cation radicals of pyrrole and DFP indicate that there are no significant ground-state differences. Also, the free energies for the respective dimerization reactions are virtually identical. The major difference predicted by this theoretical treatment is that the DFP cation radical is expected to be a much stronger acid than the corresponding pyrrole radical cation. However, the results from the microelectrode experiments are not consistent with immediate deprotonation of the cation radical as a likely pathway for polymerization. These results indicate that the fluorine substituents slightly destabilize the transition state for the dimerization reaction. The calculations indicate that substantial positive charge resides on the reactive 2 and 5 positions of pyrrole radical cations, regardless of the nature of the substituents at the 3 and 4 positions. For dimerization to occur, significant electrostatic (charge−charge) repulsion must be overcome at the transition state. Fluorine substitution in organic molecules generally lowers their polarizability; hence the 3,4-difluorinated pyrrole radical cation is less capable of repolarizing its electron cloud to minimize charge−charge repulsion, leading to a higher activation barrier to dimerization. This molecular polarizability argument is congruent with the fact that 3,4-dimethylpyrrole and 3,4-diiodopyrrole radical cations dimerize at appreciably faster rates than 3,4-DFP, despite the significantly smaller steric bulk of fluorine compared to iodine or a methyl group.

4. Conclusion

We have demonstrated that DFP can be oxidized in organic media, giving rise to the corresponding fluorinated polypyrrole. The polymer exhibits a high redox potential (but lower than predicted by the electronic effects of the substituents), high doping levels (ca. 55%), and a high conductivity as compared with other poly(halopyrroles). Fluorine substitution imparts an unusual kinetic stability to the cation radical of DFP. However, the long lifetime and highly electrophilic and acidic nature of the electrogenerated cation radical make it very sensitive to side reactions. This obliges the use of strictly anhydrous conditions and results in a marked solvent dependence for the electropolymerization process.

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