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DFT study of molecular structure and electronic properties of fluoromethylpyrrole oligomers including di-, tri- and tetramer

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Abstract

Structural and electronic properties of oligomers including dimer, trimer and tetramer of fluoromethylpyrroles (FMPs), $NC_4H_4–CH_nF_{3-n}$ with $n = 0, 1, 2, 3$, and their radical cations have been studied using DFT-B3LYP method with 6–31G(d, p) basis set. FMPs are proposed in this research as candidate monomers for conducting polymers with modified characteristics compared to polypyrrole and polymethylpyrrole. A preliminary study using a set of *ab initio* computations (HF) with medium basis set was carried out on di-, tri- and tetramer in order to investigate the stability of configuration of polymer chains for FMPs. The B3LYP/6-31G** optimized geometry and stereochemistry show that the selectivity of branching of the propagating polymer chain is affected by the characteristics of the substitutions of monomer and, therefore, the growth pattern of the polymer chain can be predicted upon characterization of different centers of the monomers. Also, the results of this study, including *quinoid* coefficients, orbital energy spacing, charge- and spin-density distributions and electric dipole moment vectors show that conducting polymers consisted of trifluoromethyl pyrrole ($Py-CF_3$), compared with the other FMPs, are the most favorable to be used as monomers for conducting polymer structural and electronic properties.

Keywords: B3LYP; Electric charge; Dipole moment; Fluoromethylpyrrole; Conducting polymer

1. Introduction

Electronically conducting polymers possess different properties related to their electrochemical behavior. The importance and the potentiality of this class of materials were recently recognized by the world scientific community when H. Shirakawa, A.J. Heeger and A.G. MacDiarmid were laureated in 2000 with the Nobel Prize in Chemistry by their research in this field [1–4].

Conducting polymers are frequently called "synthetic metals" because they present electric, electronic, magnetic and optical properties inherent to metals or semiconductors, while retain the mechanical properties of conventional polymers. In intrinsic conducting polymers, the conductivity is assigned to the delocalization of π-bonded electrons over the polymeric backbone, exhibiting unusual electronic characteristics, such as low energy optical transitions, low ionization potentials and high electron affinities [5]. Electron delocalization is a consequence of the presence of conjugated double bonds in the polymer backbone.

Electrochemical synthesis of electrically conducting organic polymers, first described in detail for polypyrrole, has proven important roles in allowing development of new polymeric materials with electrical properties similar to metals [1–3]. The reversibility of charging/discharging processes and high specific capacitance of the polymers in their oxidized states has stimulated suggestions for a variety of applications such as rechargeable batteries, super-capacitors and electrochromic devices, etc. [6–15].

The main objective in the design and preparation of new materials is to improve the desired electrical and electrochemical properties. It is of high industrial importance to increase the conductivity of polymers and their solubility in certain solvents. Conducting polymers with modified solubility in some industrially important solvents were recently synthesized by introducing alkyl and other substituents on the monomers [16,17]. Since a conducting polymer has a π-conjugate system along the polymer chain, both electronic and structure of a

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substituent contribute to the delocalization of the polymer π-conjugate system, while its steric factor (which is important for substituents like *n*-alkyls) is usually not determining [18,19]. Substitution of pyrrole monomers with appropriate β-substituents induces a *push–pull* effect on the π-electrons and alters the electrical conductivity of the corresponding polymers compared with that of polypyrrole [2,20].

In the previous report [21], we have studied halomethylpyrroles as potential monomers for the synthesis of conductive polymers with modified physical and electrical characteristics respect to those of pyrrole. These substituents can effectively change packing parameter and the density of the polymer blend as well as its pyrolysis temperature and environmental recycle period. We have then concluded that the choice of a proper substitution on the pyrrole ring can change electrical conductivity of the corresponding polymers effectively.

The main goal of this research is theoretical study of the structural and electronic properties of oligomers including dimer, trimer and tetramer of fluoromethyl pyrroles (FMPs) for the preparation of corresponding conducting polymers with improved electrical and mechanical properties. Also, we carry out theoretically the electronic and structural effects of substitutions on polymerization process and isomerism of the FMP oligomers. We used oligomers consisted of pyrrole and methylpyrrole monomers as reference compounds for all comparative studies.

Structures and the numbering scheme used for FMP monomers and their oligomers in this study are illustrated in Fig. 1. It is noticeable that carbons adjacent to heteroatom in the pyrrole-ring, $C_2(\alpha)$ and $C_3(\alpha')$, are branching centers in the electropolymerization process and therefore control the stereochemistry of the polymer chains. Also, both $C_5(\beta)$ and $C_6(\beta')$ carbons are appropriate positions for substitutions, however, in this study, the fluoromethyl substitution is fixed on β-position in all compounds. For easier comparative studies and similar to monomer structures, in all oligomer chins, α-carbon is close to the substituent position and α'-carbon is away from it at the head and the tail of an oligomer chain.

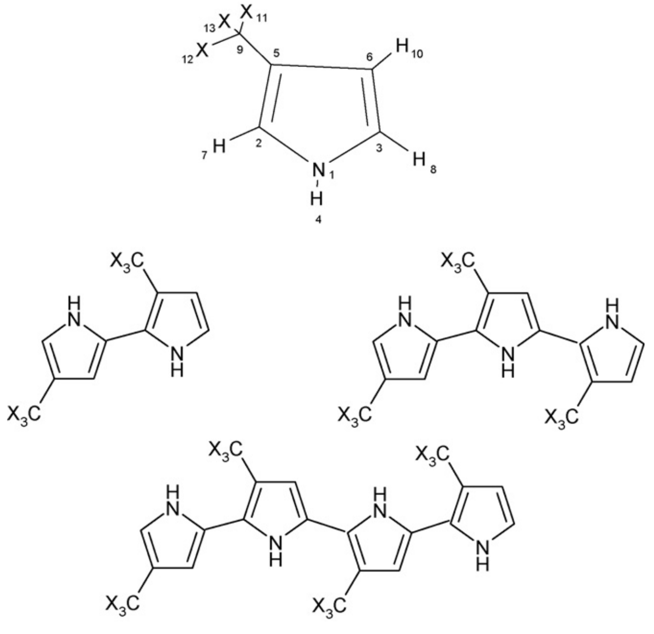

Fig. 1. Structure and numbering scheme used for the FMP monomers and their oligomers where $-CX_3$ stands for $-CH_3$, $-CH_2F$, $-CHF_2$ and $-CF_3$.

2. Results and discussion

2.1. Characteristics of monomers

It is well known that electrical conductivity of conducting polymer films depends on the characteristics of their monomers in the polymer chain backbone. In this section, in order to complete our discussion about oligomers, it is necessary to review some characteristics of monomers which we identified from our previous work [21].

Some of geometrical parameters corresponding to the optimized structures of FMP monomers and their radical cations were obtained using the B3LYP/6-31G(d, p) level of theory. Structural studies show that the C–H bond length on α and α′ positions are identical for pyrrole monomer, but they change effectively for FMPs. Values of the dihedral angle defining torsion of the fluoromethyl groups ($-CH_2F$, $-CHF_2$ and $-CF_3$) with respect to the molecular plane are very close to 0°, with a maximum deviation of 1.8° for Py–CHF_2. This indicates that the referenced atom (F and H for the two sets of groups, respectively) lies in the ring plane, and the other two atoms of the fluoromethyl group lie symmetrically above and below the pyrrole ring plane. It can thus be said that the local dipole moment of the fluoromethyl groups are aligned with the molecular plane. This allows one to determine interactions between neighboring FMP polymer chains based on the planar structure of the pyrrole rings. In other words, fluoromethyl group contribution appears as a pure steric effect only.

It is known that the formation of the intermediate radical cations from the monomers, first step in the polymerization mechanism of conductive polymers, has the important role in their polymerization process. This reaction can be considered as ionization reaction [2–5]. In this way, the calculated values of ionization potential (IP) for FMP monomers show that methylpyrrole monomer has the lowest IP. This may be due to the electron donor character of the substituent $-CH_3$ on the pyrrole ring, and so its radical cation in the gas phase has the highest stability among all FMP radical cations. This behavior is in agreement with the lower oxidation potential measured experimentally for methylpyrrole [22].

Results also show that the IP of these compounds increases when the electron-pull effect of the substituent increases, that is, the oxidation potential of FMPs series increases in the order of $-CH_2F < -CHF_2 < -CF_3$. In general, it may be concluded that initiation step of electropolymerization of FMP monomers needs higher applied potential as the number of the substituted fluorine atoms increase.

2.2. Isomerism of oligomers

Let us begin our study of isomerism of FMP oligomers with a dimer structure. A monomer, Py–CH_3 for example, can be

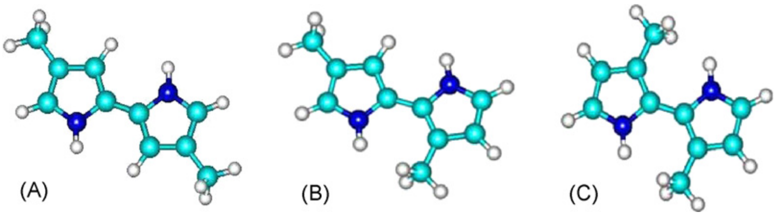

Fig. 2. Three different of possible arrangements for a Py–CH_3 dimer which can be considered as a unit block of the polymethyl pyrrole.

dimerized to one of the arrangements **A**, **B** and **C** shown in Fig. 2. A preliminary study using a set of DFT computations with B3LYP/6-31G** level of theory was carried out in order to identify the stability of these structure isomers. The result of this study showed that the arrangement **A** is 3.2 and 4.4 kJ/mol more stable than **B** and **C** arrangements, respectively.

Similar investigations were carried out for all type of trimer and tetramer of FMP oligomers using optimized geometry structure obtained at B3LYP/6-31G** level of theory. As the length of an oligomer chain increases the number of their possible arrangements increase considerably. For brevity, details of the structural analysis for all likely arrangements of the FMP trimers and tetramers are not reported here. These results showed that the FMP oligomer chains with substituent groups alternating regularity from side to side are more stable than other isomers with all substituent groups on side of an extended chain or distributed at random on it (except for Py–CHF_2 oligomer chains). For example, the stabilities of the two important structure isomers of Py–CF_3 tetramer are compared in Fig. 3. It is likely that substituent groups in a FMP oligomer chain tend to take those positions at which the most favorable dipole–dipole interactions. We can observe that the selectivity of the oligomer conformation during the propagation step of polymerization is affected by the characteristics of the substituent group on the monomer ring in oligomer chain.

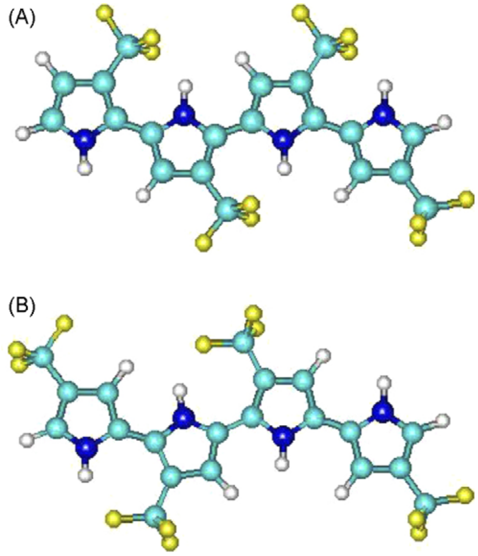

Fig. 3. Structure isomer of the Py–CF_3 tetramer (A) is 3.39 kcal/mol more stable than the structure isomer (B).

2.3. Some structural features of FMP oligomers

It has been already found that branching of monomers and corresponding oligomers in the polymerization process is initiated from α and α′-positions of monomer ring [2–5]. Thus, it is interesting to consider the important structural parameters that related to the substitution positions and the ring geometries of FMP oligomer chain (Fig. 1). Table 1 reports some of the optimized values of bond lengths and dihedral angles for all FMP oligomers using B3LYP/6-31G** level of theory.

According to Table 1, the C–H bond length on α and α′-positions of an extended chain, C^{α}–H and $C^{\alpha'}$–H, are slightly affected by substituent group. However, the bond length of C^{α}–H is longer than $C^{\alpha'}$–H bond. The reason for this difference might be due to the FMP substitution effect that is reflected in substantial charge difference on α and α′-carbon atoms. Also, it is likely that the dihedral angles depend noticeably on the substituent group. Values of the dihedral angle defining torsion of substituent groups (S) with respect to the monomer ring plane (R) at α-position of oligimer chain, $\hat{D}^{\alpha}_{\mathrm{R-S}}$, and α′-position, $\hat{D}^{\alpha'}_{\mathrm{R-S}}$, are very close to 0°. The small deviation ($\leq 3.7^{\circ}$) for Py–CH_2F and Py–CHF_2 oligomers may return to the low symmetry of their fluorinated substituents (–CH_2F and –CHF_2 groups). However, the –CF_3 and –CH_3 groups lies completely in the ring plane.

The ring geometries of an extended oligimer chain are interesting. As it can be seen from Table 1, the connecting length between an adjacent pair monomer ring of an extended chain, R_i–R_j is affected by substituent groups. Fluorine substitutions in the FMP oligomers increase the R_i–R_j respect to the pyrrole and methylpyrrole oligomers. It is due to the polarity of fluorine substitutions in oligomer chains. Also, the geometrical data from Table 1 show that the R_i–R_j bond decreases when the number of monomers increase in an oligomer chain. Values of the dihedral angle defining torsion between an adjacent pair ring plane of an extended chain, $\hat{D}_{\mathrm{R}_i-\mathrm{R}_j}$ are exactly 0°, except for Py–CH_2F and Py–CHF_2 oligomers. Of course, we expect these distortions to decrease if the length of a polymer chain increases. Since, the planarity of polymers chain is a necessary factor for electrical conducting of polymers [2–5], we predict the Py–CF_3 oligomers to have preferred structure for producing conducting polymer.

The fundamental vibrational frequencies for all FMP monomers were calculated using optimized structures at B3LYP/6-31G** level of theory. The real frequencies of FMP monomers confirm their optimized structures corresponded to equilibration points on potential energy surfaces.

Table 1
Some of the optimized geometrical parameters of FMP oligomers obtained at B3LYP/6-31G** method (units of bond length and dihedral angle are Angstrom and degree, respectively)

Oligomer	C^{α}–H	$C^{\alpha'}$–H	R_1–R_2	R_2–R_3	R_3–R_4	$\hat{D}^{\alpha}_{R-S}$	$\hat{D}^{\alpha'}_{R-S}$	$\hat{D}_{R1-R2}$	$\hat{D}_{R2-R3}$	$\hat{D}_{R3-R4}$
Di-Py	1.0794	1.0794	1.4483	–	–	–	–	0	–	–
Di-$PyCH_3$	1.0801	1.0794	1.4484	–	–	0.0	0.0	0.0	–	–
Di-$PyCH_2F$	1.0785	1.0791	1.4485	–	–	0.6	2.5	26.4	–	–
Di-$PyCHF_2$	1.0791	1.0785	1.4496	–	–	1.2	3.3	26.5	–	–
Di-$PyCF_3$	1.0794	1.0789	1.4401	–	–	0.0	0.0	0.0	–	–
Tri-Py	1.0793	1.0794	1.4456	1.4453	–	–	–	0.0	0.0	–
Tri-$PyCH_3$	1.0802	1.0796	1.4459	1.4460	–	0.0	0.0	0.0	0.0	–
Tri-$PyCH_2F$	1.0803	1.0792	1.4469	1.4471	–	2.9	1.1	25.9	24.5	–
Tri-$PyCHF_2$	1.0785	1.0791	1.4484	1.4482	–	2.0	3.0	26.4	25.2	–
Tri-$PyCF_3$	1.0790	1.0789	1.4477	1.4473	–	0.0	0.0	0.0	0.0	–
Tetra-Py	1.0795	1.0795	1.4453	1.4427	1.4453	–	–	0.0	0.0	0.0
Tetra-$PyCH_3$	1.0801	1.0794	1.4455	1.4427	1.4455	0.0	0.0	0.0	0.0	0.0
Tetra-$PyCH_2F$	1.0801	1.0795	1.4403	1.4440	1.4493	3.7	3.7	38.1	23.4	30.7
Tetra-$PyCHF_2$	1.0785	1.0791	1.4484	1.4468	1.4484	3.3	3.6	26.0	24.4	25.1
Tetra-$PyCF_3$	1.0790	1.0789	1.4472	1.4447	1.4467	0.0	0.0	0.0	0.0	0.0

R: bond length between an adjacent pair monomers ring of an extended chain. $\hat{D}_{R-S}$: dihedral angle between $-CX_3$ group and monomer ring of an extended chain. $\hat{D}_{R_i-R_j}$: dihedral angle between an adjacent pair monomers ring of an extended chain.

Table 2
The total energies (and ZPE) for the FMP monomers and their oligomers obtained with B3LYP/6-31G** method (units are in kcal/mol)

	E				
	Pyrrole	$PyCH_3$	$PyCH_2F$	$PyCHF_2$	$PyCF_3$
Monomer	54.4 (51.9)	72.8 (69.1)	69.0 (64.9)	64.6 (60.4)	59.8 (55.1)
Dimer	96.0 (91.5)	132.3 (126.1)	126.0 (118.3)	117.2 (108.7)	107.5 (98.1)
Trimer	137.6 (131.0)	192.5 (183.2)	183.0 (171.4)	169.8 (156.8)	153.1 (140.2)
Tetramer	179.2 (170.4)	252.5 (239.9)	240.3 (130.0)	221.3 (204.9)	199.6 (182.7)

Vibration analysis of FMP oligomers is very complex due to the low symmetry of polymer chains when the length of oligomer chain increases. This is not discussed here but the total energies and the zero point energy (ZPE) of all FMP oligomers listed in Table 2. As seen in Table 2, all oligomers including dimer, trimer and tetramer which consist of Py–CF_3 monomer have lower values of energies and we may therefore predict that Py–CF_3 oligomers are capable of having higher thermodynamic stability than other FMP oligomers which is supported by their ZPE values. Furthermore, it is clear that in the electropolymerization of conducting polymer, the applied oxidation potential is reduced with the growth of the polymer film on the working electrode surface which is related to the extension of the π-conjugation system. A critical geometrical parameter determining the ease of cationic electropolymerization is the *quinoid* coefficient defined as $f = 2 \times R_{56}/(R_{25} + R_{36})$; the closer the *quinoid* coefficient f to 1, the easier the cationic polymerization [23–25]. The calculated values of *quinoid* coefficient f for FMP oligomers are demonstrated in Fig. 4.

It can be clearly seen from Fig. 4 that all monomers of FMP have approximately similar *quinoid* coefficient (with maximum deviation of ±3%). However, with the growth of the polymer chain, these coefficients decrease towards unity. Also, among the FMP oligomers, the Py–CF_3 tetramer has the closest *quinoid* coefficient to unity. Thus, it can be concluded that this monomer undergoes cationic electropolymerization much easier than the most of the monomers.

2.4. Electronic characteristics of oligomers

It is known that energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), or simply HLG, is a key parameter which determines the molecular admittance because it is a

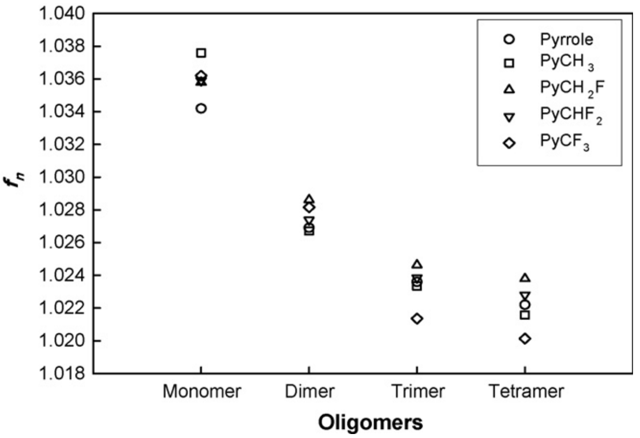

Fig. 4. The *quinoid* coefficient, f_n, of mono-, di-, tri- and tetramer of the FMPs.

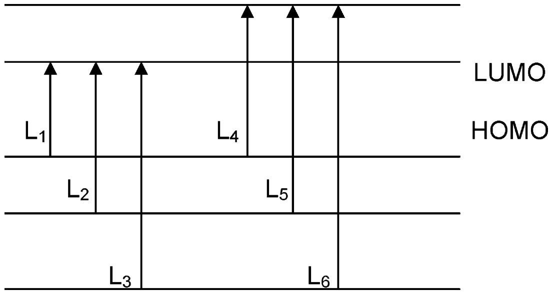

Fig. 5. Presentation of the calculated energy gaps, L_i, studied in this research for oligomers including the HOMO-LUMO gaps (HLG), L_1.

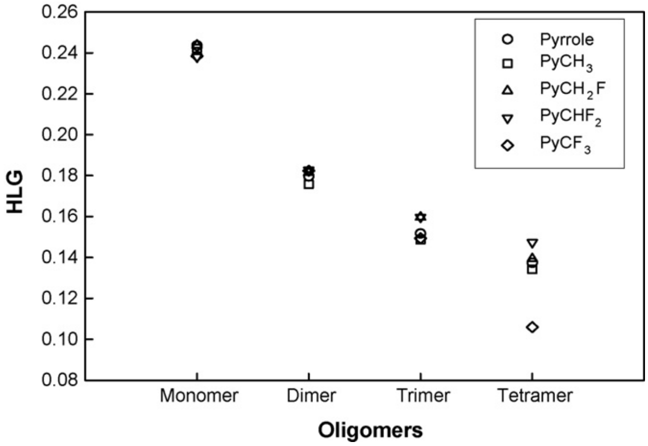

Fig. 6. The HLG (L_1) values obtained for all FMP monomers and their oligomers using B3LYP/6-31G** method.

measure of the electron density hardness [26,27]. The HLG values and some other orbital energy spacing of FMP oligomers, defined in Fig. 5, are calculated at B3LYP/6-31G** level of theory. For brevity, only HLG values (L_1) are shown in Fig. 6. As shown in this figure, the HLG values of the monomers decrease slowly with the number of fluorine atoms. Therefore, we predict that those of the oligomers consisting of Py–CF_3 monomer to have the highest conductivity. This is proved by comparing the trend of the HLG values of the FMP oligomers which have same number of monomers. As seen from Fig. 6, HLG values for the Py–CF_3 tetramer is considerably lower than that of the other FMP tetramers.

Since the charge density of the α and α′ carbons at both sides of the oligomer chains is an important factor in the polymerization mechanism of conductive polymer, charge and spin density distribution on these carbons in all radical cations were calculated and listed in Table 3. These data show that both α and α′ carbons in pyrrole monomer and their oligomers (di-, tri- and tetrapyrrole) have equivalent positive charge and spin densities, but with the addition of a fluorinated substitution on pyrrole ring, this equality is altered. For the larger oligomer chains, the positive charge on the α-carbon which is close to the $-CH_nF_{n-3}$ substitution, is higher than that on the α′-carbon. Conversely, spin density is distributed mainly on the α′-carbon. This is due to the fact that the distributed charge is positive while the spin density is carried by electrons whose charge is negative.

Table 3
Distribution of charge (spin) density on the branching centers in the radical cations of the FMP monomers and their oligomers

Radical cation	C(α)	C(α′)
Pyrrole	0.198 (0.538)	0.198 (0.538)
$PyCH_3$	0.195 (0.521)	0.175 (0.482)
$PyCH_2F$	0.198 (0.534)	0.184 (0.499)
$PyCHF_2$	0.208 (0.535)	0.201 (0.535)
$PyCF_3$	0.222 (0.532)	0.207 (0.532)
Di-Py	0.167 (0.310)	0.167 (0.310)
Di-$PyCH_3$	0.149 (0.348)	0.162 (0.293)
Di-$PyCH_2F$	0.160 (0.342)	0.163 (0.284)
Di-$PyCHF_2$	0.176 (0.312)	0.167 (0.294)
Di-$PyCF_3$	0.194 (0.304)	0.171 (0.297)
Tri-Py	0.143 (0.195)	0.143 (0.195)
Tri-$PyCH_3$	0.120 (0.228)	0.139 (0.182)
Tri-$PyCH_2F$	0.135 (0.235)	0.132 (0.161)
Tri-$PyCHF_2$	0.150 (0.203)	0.141 (0.174)
Tri-$PyCF_3$	0.168 (0.199)	0.146 (0.178)
Tetra-Py	0.129 (0.131)	0.129 (0.131)
Tetra-$PyCH_3$	0.104 (0.158)	0.125 (0.120)
Tetra-$PyCH_2F$	0.109 (0.160)	0.126 (0.122)
Tetra-$PyCHF_2$	0.134 (0.139)	0.126 (0.109)
Tetra-$PyCF_3$	0.155 (0.140)	0.131 (0.113)

Larger differences between the electric charges at α and α′ positions (which are propagation centers in the electropolymerization process) will result in the higher selectivity of the tactility of the polymer chain. The syndiotactic structure of the FMP polymers corresponds to the lower steric effects between fluoromethyl groups on the neighboring monomers and the higher thermal stability of the polymer. It can, therefore, be concluded that fluoromethyl substituents increase the selectivity of the syndiotactic order of the polymer chain.

The orientation of the electric dipole moment vector of the oligomers with respect to the direction of the polymer chain determines electrochemical characteristics of the polymer on the electrode surface. In addition to their orientations, size of the electric dipole moment vector of the monomers and their interactions with the solvent and support electrolyte are the key factor in their selection for electropolymerization. Furthermore, the structure of the electrical double layer at the surface of electrodes which determines the kinetics of the diffusion-controlled electrode reactions, depends on the dipole moment of the solute molecules [11]. Thus, the study of dipole moment characteristics of oligomers is of importance and of our interest.

Table 4
The total dipole moments (in Debye) of the FMP monomers and their oligomers obtained with B3LYP/6-31G** method

	μ				
	Pyrrole	$PyCH_3$	$PyCH_2F$	$PyCHF_2$	$PyCF_3$
Monomer	1.90	1.71	3.46	3.68	4.42
Dimer	0.00	0.12	2.36	2.76	3.37
Trimer	1.81	1.61	3.71	4.81	5.70
Tetramer	0.00	0.11	1.34	4.52	5.71

The calculated values of the electric dipole moment vectors for FMP monomers and their corresponding oligomers have been listed in Table 4. The data presented in this table show that the number of fluorine atoms determines the values of electric dipole moment vector. The comparative size of the dipole moment vectors for all of monomers and their oligomers with the same size follows the following orders:

$$\mu(\mathrm{Py} - \mathrm{CH_2F}) < \mu(\mathrm{Py} - \mathrm{CHF_2}) < \mu(\mathrm{Py} - \mathrm{CF_3})$$

According to this trend, the oligomers consisting of tri-fluoromethyl pyrrole (Py–CF_3 oligomers) are expected to be more soluble in polar solvents because of the larger electric dipole moments. Also, it is observed from Table 4 that the electron donor characters of the –CH_3 substituent decreases the dipole moment vector of the methylpyrrole oligomers, if the pyrrole oligomers are taken as references.

3. Conclusion

Analysis of the results of this study show that the FMP oligomers can be regarded as the possible candidates for the synthesis of corresponding conducting polymers with improved properties as compared to the polymers of methylpyrrole and pyrrole. It was also shown that the characteristics of the fluorinated substitutions (including position and number of fluorine atom of the substitution) in these molecules have important role in the polymerization process of FMPs and their polymer products.

In this series of FMP oligomers, the Py–CF_3 oligomers have the higher capability as building blocks for conducting polymers because these oligomers have higher planarity, quinoid coefficient close to unity, higher thermochemical stability, proper tacticity, lower HLG values, higher dipole moment vectors, and appropriate charge and spin densities, which are all in favor of electropolymerization. It is also found that the increase in the number of monomers of a FMP oligomer chain provides a better condition for the synthesis of modified conducting polymers.

4. Methods of calculation

Quantum chemical density functional theory calculations were performed at B3LYP level of theory [28]. The preliminary studies showed that 6–31G (d, p) is the most suitable basis set considering computational times and our available hardware facilities. All the parameters were allowed to relax and all the calculations converged to an optimized geometry. The RHF method failed to predict reasonable values for the thermochemical stabilities of the representative FMPs. Based on these preliminary studies we employed B3LYP/6-31G(d, p) method as implemented in Gaussian 98 program [29].

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