



# Physical CHEMISTRY

*An Indian Journal*

*Full Paper*

PCAIJ, 9(1), 2014 [15-23]

## Spectroscopic study of a series of fluorine-pyrrole oligomers using the density functional theory

Hossein Nikoofard

Faculty of Chemistry, Shahrood University of Technology, Shahrood 36199-95161, (IRAN)

E-mail : hnikoofard@shahroodut.ac.ir

### ABSTRACT

In one of the works previously reported by our research team [J. Fluor. Chem. 128 (2007)], we used a DFT-B3LYP method in order to study the structural and electronic properties of the oligomers including the dimer, trimer, and tetramer of fluoromethylpyrroles (FMPs),  $\text{NC}_4\text{H}_4\text{-CX}_3$  (where  $\text{-CX}_3$  stands for  $\text{-CH}_2\text{F}$ ,  $\text{-CHF}_2$  and  $\text{-CF}_3$ ), and their radical cations. In the work mentioned above, FMPs were proposed as candidate monomers for conducting polymers with modified characteristics compared to polypyrrole and polymethylpyrrole. In the present work, the method mentioned above is applied to predict the vibrational frequencies and NMR properties of FMPs and their corresponding oligomers. The optimized structural parameters of these compounds are used in the vibrational spectra and chemical shift calculations. Analysis of the vibrational frequencies and NMR chemical shifts for the mono-, di-, tri-, and tetramer of FMPs supports their structural and electronic properties. The results obtained from the computational studies carried out confirm that selectivity of the configuration of FMP oligomers in the polymerization process is most affected by characteristics of the  $\text{CX}_3$ -substituted monomer ring. The chemical shift data obtained show that the nucleation of FMP monomers occurs most probably at the  $\alpha'$ -position, far away from the group substituted on the monomer ring, while growth of the corresponding oligomers progresses more from the  $\alpha$ -position of the oligomer chain, close to the substitution position. Also the results obtained from the spectroscopic studies carried out show that FMP oligomers consist of  $\text{Py-CF}_3$  compared with other FMP monomers, and that they have the most potential for electropolymerization.

© 2014 Trade Science Inc. - INDIA

### KEYWORDS

DFT-B3LYP;  
Vibrational frequencies;  
NMR chemical shift;  
Conducting polymer.

### INTRODUCTION

Electrical conductivity is a consequence of the presence of conjugated double bonds in a polymer backbone. In intrinsic conducting polymers, conductivity is

due to the delocalization of  $\pi$ -bond electrons over the polymeric backbone, exhibiting unusual electronic properties such as low energy optical transitions, low ionization potentials, and high electron affinities<sup>[1-4]</sup>.

Electrochemical synthesis of electrically conduct-

## Full Paper

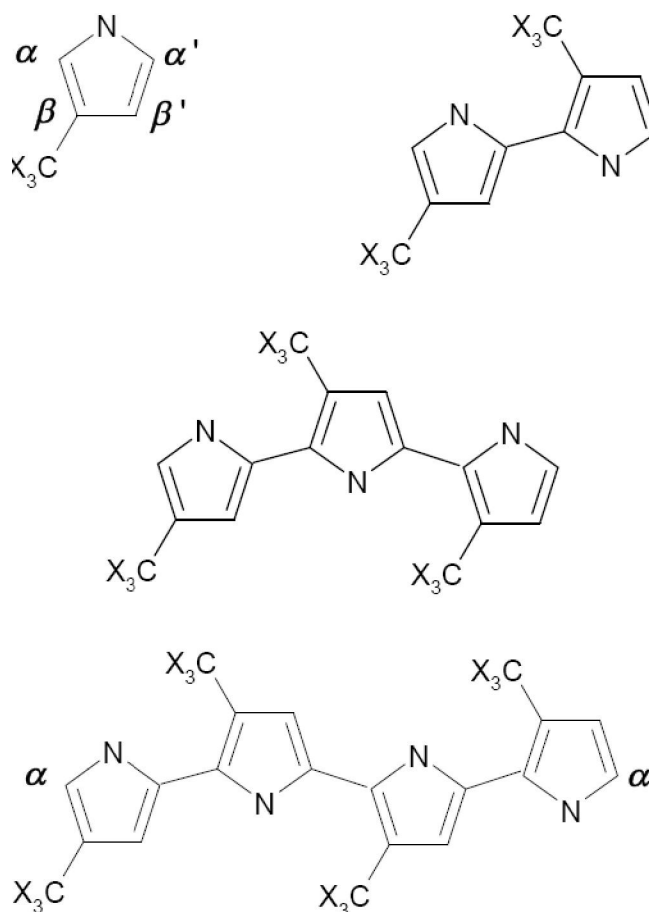
ing organic polymers has played important roles in allowing the development of new polymeric materials with electrical properties similar to metals. The reversibility of charging/discharging processes and high specific capacitance of the polymers in their oxidized states has led scientists to propose them for a variety of appliances such as rechargeable batteries, super-capacitors, and electrochromic devices<sup>[5-15]</sup>. However, for commercial applications, poor processing ability and low conductivity of many accessible conductive polymers have inhibited their widespread use. In order to avoid these disadvantages, composites of conductive polymers and other polymers or inorganic materials have been developed<sup>[16,17]</sup>.

The main objective for the design and preparation of new conductive polymer materials is to improve the desired electrical and electrochemical properties. It is clearly observed that substitution of pyrrole monomers with appropriate  $\beta$ -substituents induces a *push-pull* effect on the  $\pi$ -bond electrons, and alters electrical conductivity of the corresponding polymers compared to that of polypyrroles<sup>[18,19]</sup>. In our previous works carried out in this area<sup>[20,21]</sup>, we studied some new materials as potential monomers for the synthesis of conductive polymers with modified physical and electrical characteristics compared to those of polypyrrole. It was found that a proper substitution on the pyrrole ring could significantly affect electrical conductivity of the corresponding polymers. We also showed that positions of both the  $\alpha$ - and  $\alpha'$ -carbon atoms in the pyrrole ring, as branching centers in the electropolymerization process, were equivalent, although this equality was altered with the attachment of substituent groups on the  $\beta$ -position of the pyrrole ring.

In this work, the vibrational frequencies and NMR properties of FMP oligomers including dimer, trimer, and tetramer chains were studied using quantum chemical computational techniques. With the aid of spectral property calculations, we studied the electronic and structural effects of substitutions on some structural features of FMP oligomers. The reason for preferring fluorine-pyrroles over other conductive polymer materials for this study is as follows: fluoropolymers are characterized by their excellence in resisting chemical attacks, very good thermal stability, chemical inertness, outstanding electrical properties, and excellent weathering rate<sup>[22]</sup>.

These properties differentiate fluoropolymers from their hydrocarbon analogues, and make them preferable materials for high energy radiation environments in the chemical, microelectronic, and nuclear industries as well as in the medicine and aerospace fields<sup>[23]</sup>. We used oligomers consisting of pyrrole (Py) and methylpyrrole (Py-CH<sub>3</sub>) monomers as reference compounds for all comparative studies.

The structural scheme used in this study for FMP monomers and their oligomers are illustrated in Figure 1. It is noticeable that the carbon atoms adjacent to the heteroatom in the pyrrole-ring, C( $\alpha$ ) and C( $\alpha'$ ), are branching centers in the electropolymerization process, and control the stereochemistry of the polymer chains. Also both the C( $\beta$ ) and C( $\beta'$ ) atoms are appropriate positions for substitution. However, in this study, the fluoromethyl substituent was fixed on the  $\beta$ -position in all compounds. For easier comparative studies, and similar to the monomer structures, the  $\alpha$ -carbon atom of an



**Figure 1 :** Structures and numbering scheme used for FMP monomers and their oligomers, where  $-CX_3$  stands for  $-CH_3$ ,  $-CH_2F$ ,  $-CHF_2$ , and  $-CF_3$ .

oligomer chain is close to the substituent position, and the  $\alpha'$ -carbon atom is away from it. The structure parameters for this series of FMPs were defined based on Figure 1.

## COMPUTATIONAL PROCEDURES

The optimized structure, vibrational wave numbers, and NMR properties of the FMP oligomers were calculated at the density functional theory (DFT), utilizing Becke's three-parameter exchange functional, with the Lee-Yang-Parr non-local correlation functional (B3LYP)<sup>[24]</sup> and the 6-31G (d, p) basis set. All parameters were allowed to relax, and the calculations converged to an optimized geometry. The theoretical absolute NMR chemical shielding was calculated using the IGAIM method<sup>[25-28]</sup>. It was found that the Hartree-Fock (HF) method failed to predict reasonable values for the vibrational spectra of the representative FMPs. Based on these preliminary studies, we employed the B3LYP/6-31G(d,p) method, as implemented in the Gaussian 03 program<sup>[29]</sup>.

## RESULTS AND DISCUSSION

**TABLE 1 : Selected optimized geometry parameters of FMP oligomers obtained using B3LYP/6-31G\*\* method (Units of bond length and dihedral angle are Angstrom and degree, respectively).**

Oligomer	C $_{\alpha}$ -H	C $_{\alpha'}$ -H	$\hat{D}_{R-CX_3}$	$\hat{D}_{R_1-R_2}$	$\hat{D}_{R_2-R_3}$	$\hat{D}_{R_3-R_4}$	R $_1$ -R $_2$	R $_2$ -R $_3$	R $_3$ -R $_4$
Di-Py	1.0794	1.0794	-	0.0	-	-	1.4483	-	-
Di-PyCH $_3$	1.0801	1.0794	0.0	0.0	-	-	1.4484	-	-
Di-PyCH $_2$ F	1.0785	1.0791	0.6	26.4	-	-	1.4485	-	-
Di-PyCHF $_2$	1.0791	1.0785	1.2	26.5	-	-	1.4496	-	-
Di-PyCF $_3$	1.0794	1.0789	0.0	26.3	-	-	1.4501	-	-
Tri-Py	1.0793	1.0794	-	0.0	0.0	-	1.4456	1.4453	-
Tri-PyCH $_3$	1.0802	1.0796	0.0	0.0	0.0	-	1.4459	1.4460	-
Tri-PyCH $_2$ F	1.0803	1.0792	2.9	25.9	24.5	-	1.4469	1.4471	-
Tri-PyCHF $_2$	1.0785	1.0791	2.0	26.4	25.2	-	1.4484	1.4482	-
Tri-PyCF $_3$	1.0790	1.0789	0.0	0.0	0.0	-	1.4477	1.4473	-
Tet-Py	1.0795	1.0795	-	0.0	0.0	0.0	1.4453	1.4427	1.4453
Tet-PyCH $_3$	1.0801	1.0794	0.0	0.0	0.0	0.0	1.4455	1.4427	1.4455
Tet-PyCH $_2$ F	1.0801	1.0795	3.7	38.1	23.4	30.7	1.4503	1.4440	1.4493
Tet-PyCHF $_2$	1.0785	1.0791	3.3	26.0	24.4	25.1	1.4482	1.4468	1.4481
Tet-PyCF $_3$	1.0790	1.0789	0.0	0.0	0.0	0.0	1.4472	1.4447	1.4467

R $_{i-j}$  = Length of bond between an adjacent pair monomer ring of an extended chain;  $\hat{D}_{R-CX_3}$  = Dihedral angle between -CX $_3$  group and monomer ring of an extended chain;  $\hat{D}_{R_1-R_2}$  = Dihedral angle between an adjacent pair monomers ring of an extended chain.

## Full Paper

However, it is likely that the dihedral angles depend noticeably on the characteristics of the substituent group. The values for the dihedral angle defining torsion of the substituent group ( $-CX_3$ ) with respect to the monomer ring plane (R) at  $\alpha$ -position of the oligomer chain,  $\hat{D}_{R-CX_3}$ , are very close to  $0^\circ$ . The small deviation ( $\leq 3.7^\circ$ ) for the Py-CH<sub>2</sub>F and Py-CHF<sub>2</sub> oligomers may be due to the low symmetry of their fluorinated substituents ( $-CH_2F$  and  $-CHF_2$  groups). However, the  $-CF_3$  and  $-CH_3$  groups lie completely in the ring plane.

The ring geometries of an extended oligomer chain are interesting. As it can be seen in TABLE 1, the connecting length between an adjacent pair monomer ring of an extended chain,  $R_i-R_j$ , is affected by the substituent groups. Insertion of fluorine substituents on these compounds increases the  $R_i-R_j$  bond length compared to the pyrrole and methylpyrrole oligomers. This is due to the polarity of fluorine substituents in the oligomer chains. Moreover, the geometrical data presented in TABLE 1 shows that the  $R_i-R_j$  bond length decreases when the number of monomers increase in an oligomer chain. The values for the dihedral angle defining torsion between an adjacent pair ring plane of an extended chain,  $\hat{D}_{R_i-R_j}$ , are exactly, except for the Py-CH<sub>2</sub>F and Py-CHF<sub>2</sub> oligomers. Since planarity of the polymer

chains is important for the electrical properties of conducting polymers<sup>[2-5]</sup>, we expect Py-CF<sub>3</sub> oligomers to have a preferred structure for producing a conducting polymer with higher conductivity. Of course, we may predict that values of dihedral angles in other FMP oligomers decreases when the length of the polymer chain increases.

### Vibrational frequencies

The fundamental vibrational frequencies for all the FMP monomers were calculated using the B3LYP/6-31G\*\* level of theory. All wavenumbers show real frequencies confirming that the structures correspond to the equilibration points on the potential energy surfaces. Frequency calculations for the fluoromethyl-substituted pyrroles show 33 normal vibrational modes, and this is an algebraic consequence of the fact that there are  $3N-6$  vibrational degrees of freedom for non-linear molecules with  $N$  atoms. For brevity, the normal vibrational modes with the IR band intensities higher than 10 km/mol are listed in TABLE 2. The data reported in this table show that the number of strong IR bands increases with the size of monomer corresponding to their number of fluorine atoms ( $-CF_3 > -CHF_2 > -CH_2F$ ). This behavior may be a result of the charge delocalization redistributed in the pyrrole ring. In the other words, the charge redistribution of fluorine substituents on the pyr-

**TABLE 2 Transition frequencies (intensities) in cm<sup>-1</sup> (km/mol) for FMP monomers (only the intense bonds are reported here).**

Py-CF <sub>3</sub>		Py-CHF <sub>2</sub>		PyCH <sub>2</sub> F		Py-CH <sub>3</sub>		Pyrrole	
499	(84)	489	(84)	479	(88)	432	(91)	461	(78)
703	(25)	698	(15)	727	(45)	764	(51)	734	(111)
729	(11)	773	(70)	791	(39)	1087	(24)	1042	(26)
802	(40)	831	(18)	1036	(103)	1095	(14)	1076	(23)
940	(43)	856	(14)	1087	(47)	3031	(48)	3689	(55)
1102	(28)	1074	(23)	1100	(13)	3081	(30)		
1159	(46)	1097	(105)	1430	(30)	3111	(24)		
1165	(183)	1111	(90)	1440	(11)	3690	(58)		
1176	(281)	1124	(125)	1476	(13)				
1191	(177)	1392	(11)	1540	(24)				
1392	(162)	1412	(108)	3036	(58)				
1442	(12)	1451	(15)	3080	(42)				
1477	(20)	1478	(14)	3687	(64)				
1543	(55)	1538	(38)						
1630	(41)	1628	(18)						
3685	(73)	3049	(71)						
499	(84)	3687	(67)						
703	(25)								

role ring and its variation during vibrational modes contribute significantly to many of the IR bands.

Vibrational analysis of FMP oligomers are very complex due to low symmetry of the oligomer chains, especially when the chain length increases. Frequency calculations for FMP oligomers show 66, 99, and 132 normal vibrational modes for the dimer, trimer, and tetramer chains, respectively. For all FMP oligomers, the number of low frequencies ( $\nu < 1000 \text{ cm}^{-1}$ ) and the corresponding zero point energies (ZPEs) with their vibrational energies (at 298.15 K) are listed in TABLE 3. According to this table, all the oligomer chains including the dimer, trimer, and tetramer types that consist of the Py-CF<sub>3</sub> monomer have higher numbers of low frequencies. It is known that molecules with the highest low frequencies correspond to their largest force constants for the bending vibrations<sup>[18,19]</sup>. We may therefore predict that Py-CF<sub>3</sub> oligomers have a higher protection from thermal disintegration. On the other hand, this indicates that Py-CF<sub>3</sub> oligomers can pose a higher thermodynamic stability compared to other FMP oligomers; this is also supported by their ZPE and vibrational energy values, indicated in TABLE 3.

As mentioned above, positions of  $\alpha$  and  $\alpha'$  carbon atoms in both sides of the oligomer chains are the reactivity sites in the polymerization of the conducting poly-

mer, and therefore, we considered vibrations of the C <sub>$\alpha$</sub> -H and C <sub>$\alpha'$</sub> -H bonds in these compounds. Vibrational analysis showed that frequencies for the  $\nu(\text{C}_{\alpha}\text{-H})$  and  $\nu(\text{C}_{\alpha'}\text{-H})$  stretching modes are equivalent for the pyrrole oligomers, and that the length of the oligomer chain has no substantial effect on the  $\nu(\text{C-H})$  vibrational frequencies due to their point group symmetry. The frequencies for the  $\nu(\text{C}_{\alpha}\text{-H})$  and  $\nu(\text{C}_{\alpha'}\text{-H})$  stretching modes change slowly in the presence of the substituted groups (-CX<sub>3</sub>). However, this frequency variation is not considerable (the maximum value of frequency deviation is less than 30  $\text{cm}^{-1}$ ) but displacement of the C-H bonds in their stretching motion at the  $\alpha$ -position, shown in TABLE 4, are considerable respect to  $\alpha'$  positions. According to the data reported in this table, displacement of the C-H bond at the  $\alpha$ -position for all FMP oligomers is larger than that for the C-H bond at the  $\alpha'$ -position which is supported with lower force constants. This may be due to the presence of the fluorine substituent, which is closer to the  $\alpha$ -position.

#### Chemical shift data

It is clear that the chemical shielding data can be used to predict the ring current and to estimate the aromaticity of molecules with conjugated  $\pi$ -bond electrons<sup>[30]</sup>. In this way, chemical shielding plays an impor-

**TABLE 3 : Number ( $n$ ) and percent ( $n\%$ ) of IR transitions with frequencies lower than 1000  $\text{cm}^{-1}$  for FMP compounds, with their ZPEs and vibrational energies.**

Compound	$n$ ( $\nu < 1000 \text{ cm}^{-1}$ )	$n\%$ ( $\nu < 1000 \text{ cm}^{-1}$ )	ZPE (kcal/mol)	$E_{\text{vib}}$ (kcal/mol)
PyCH <sub>3</sub>	12	36.36	69.09	71.00
PyCH <sub>2</sub> F	13	39.39	64.92	67.18
PyCHF <sub>2</sub>	15	45.45	60.35	62.81
PyCF <sub>3</sub>	17	51.52	55.07	57.98
Di-PyCH <sub>3</sub>	28	42.42	126.14	130.52
Di-PyCH <sub>2</sub> F	32	48.48	118.31	124.21
Di-PyCHF <sub>2</sub>	31	46.97	108.68	115.44
Di-PyCF <sub>3</sub>	37	56.06	98.06	105.69
Tri-PyCH <sub>3</sub>	43	43.43	183.17	190.69
Tri-PyCH <sub>2</sub> F	49	49.50	171.36	181.20
Tri-PyCHF <sub>2</sub>	50	50.50	156.83	168.03
Tri-PyCF <sub>3</sub>	57	57.58	140.2	151.30
Tet-PyCH <sub>3</sub>	58	43.94	239.91	250.68
Tet-PyCH <sub>2</sub> F	60	45.45	229.95	238.51
Tet-PyCHF <sub>2</sub>	68	51.52	204.87	219.48
Tet-PyCF <sub>3</sub>	77	58.33	182.73	197.81

## Full Paper

**TABLE 4 : Displacement (in Angstrom) of the H atoms in the stretching mode of vibration of the C<sub>α</sub>-H and C<sub>α'</sub>-H bonds with their force constants (in Nm<sup>-1</sup>), FCs, for FMP oligomers.**

Oligomers	C <sub>α</sub> -H					C <sub>α'</sub> -H				
	ΔX	ΔY	ΔZ	Δr	FCs	ΔX	ΔY	ΔZ	Δr	FCs
Di-Py	-0.50	0.50	0.00	0.71	700	0.50	-0.50	0.00	0.71	700
Di-PyCH <sub>3</sub>	-0.86	0.50	0.00	0.99	689	0.84	0.45	0.00	0.95	698
D-iPyCH <sub>2</sub> F	0.41	-0.89	0.20	1.00	691	-0.37	0.86	0.20	0.96	699
Di-PyCHF <sub>2</sub>	0.40	0.90	0.20	1.00	701	0.26	0.63	-0.01	0.68	705
Di-PyCF <sub>3</sub>	0.35	0.89	0.28	1.00	702	0.22	0.72	-0.03	0.75	706
Tri-Py	-0.81	0.36	0.00	0.89	700	0.81	0.36	0.00	0.89	700
Tri-PyCH <sub>3</sub>	0.01	1.00	0.00	1.00	689	0.69	-0.65	0.00	0.95	698
Tri-PyCH <sub>2</sub> F	-0.87	0.39	0.30	1.00	690	0.86	0.26	-0.30	0.95	700
Tri-PyCHF <sub>2</sub>	0.86	0.34	-0.37	1.00	699	0.59	-0.22	-0.29	0.69	705
Tri-PyCF <sub>3</sub>	0.52	0.85	0.00	1.00	701	-0.19	0.68	0.00	0.71	707
Tet-Py	0.00	0.80	0.00	0.80	700	0.00	0.80	0.00	0.80	700
Tet-PyCH <sub>3</sub>	-0.25	0.96	0.00	0.99	689	-0.20	0.92	0.00	0.94	698
Tet-PyCH <sub>2</sub> F	-0.82	0.56	0.02	0.99	630	0.61	-0.46	-0.02	0.76	630
Tet-PyCHF <sub>2</sub>	0.83	-0.53	0.14	0.99	690	0.44	-0.29	-0.12	0.54	703
Tet-PyCF <sub>3</sub>	0.96	-0.27	0.00	1.00	694	-0.58	0.13	0.00	0.59	708

$$\Delta r = (\Delta X^2 + \Delta Y^2 + \Delta Z^2)^{1/2}$$

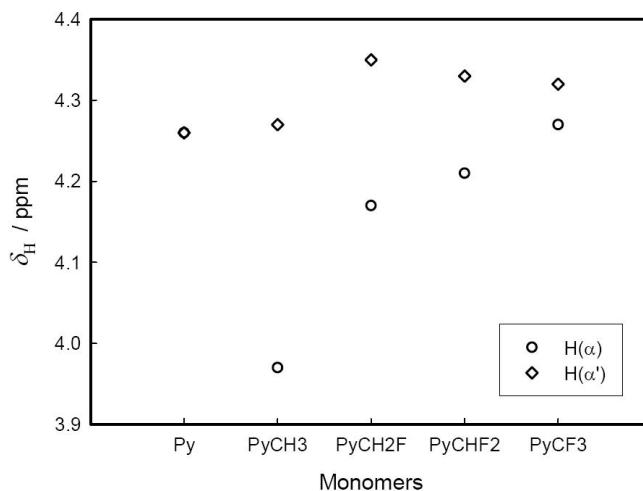
tant role in studying the molecular structure and electropolymerization process of FMP oligomers. For all compounds, the corrected isotropic chemical shifts of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR referred to TMS pertinent were calculated at the B3LYP/6-31G (d,p) level of theory. NMR chemical shielding of nuclei of FMP oligomers have been calculated using the same level of theory based on the IGAIM, SGO, and CSGT methods<sup>[25-28]</sup>. Analysis of the results obtained show that the IGAIM and CSGT methods predict equivalent shielding, while the shielding values obtained via the SGO method are considerably different. We selected the results obtained via the IGAIM method for the analysis of NMR properties of FMP oligomers.

The <sup>1</sup>H and <sup>13</sup>C shieldings for TMS calculated using the same level of theory were used as references for comparative analysis of the chemical shielding. In this study, the relative shielding constant or chemical shift, for a nucleus *n* is defined as:

$$\delta_n = \sigma_n(\text{ref.}) - \sigma_n \quad (1)$$

where (ref.) and  $\sigma_n$  are chemical shieldings of the nucleus *n* in the reference and the FMP oligomers, respectively.

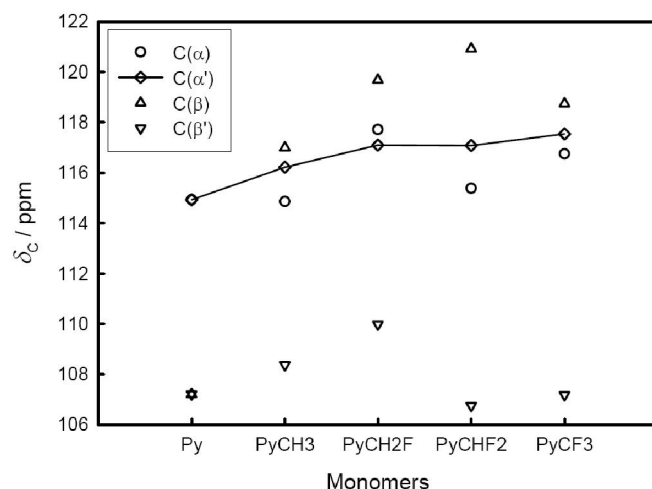
The values calculated for NMR chemical shifts for the <sup>1</sup>H and <sup>13</sup>C atoms on α- and α'-positions in FMP monomers are shown in Figures 2 and 3, respectively.



**Figure 2 : IGAIM <sup>1</sup>H-NMR chemical shifts for the H atoms in the α and α' positions.**

Analysis of the <sup>1</sup>H-NMR chemical shifts shows that and are equivalent in pyrrole monomer but the presence of substituent on the monomer ring alters this equality. Electron-inductive substituents such as -CH<sub>3</sub> displace to lower field, while electron-withdrawing substituents such as -CF<sub>3</sub> displace to higher field. Displacement of, which is away from the substitution position, is less affected by the type of substituent (i.e. number of fluorine atoms).

Analysis of the <sup>13</sup>C-NMR chemical shifts of FMP



**Figure 3 :** IGAIM <sup>13</sup>C-NMR chemical shifts for the C atoms in the  $\alpha$ - $\alpha'$  and  $\beta$ - $\beta'$  positions.

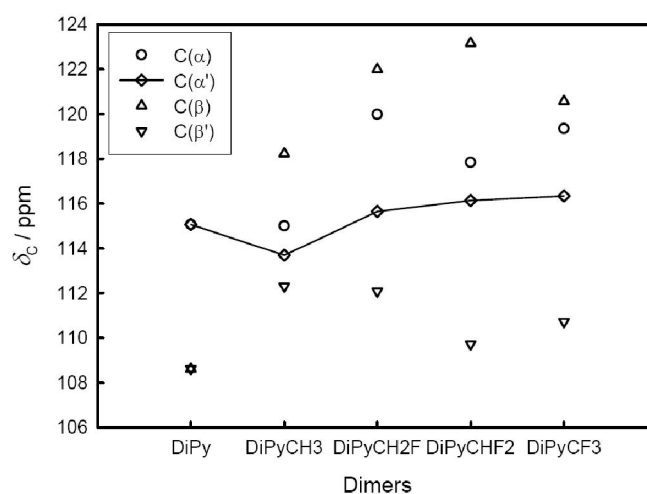
monomers in Figure 3 reveal that the chemical shift of the  $\beta$ -carbon atom has the largest values because it is linked directly to the substituted group. Also comparison between and shows that the values for are higher than those for (variations of are marked with a line graph). According to the polymerization mechanism of conducting polymers<sup>[3]</sup>, one can predict that nucleation of the monomer rings can be initiated by higher probability from  $\alpha'$ -position resulting in a preferred stereochemistry of oligomer chains.

These results also show that a fluoromethyl substituent can affect the chemical shielding of FMPs, mainly via inductive effects rather than contributing to the ring current. Introduction of the fluoromethyl group at the  $\beta$ -position induces a positive charge on the  $\alpha$ -carbon atom, which results in higher chemical shifts as compared to  $\alpha'$ -carbon atom. This is evident from the data demonstrated in Figures. 2 and 3.

It is known that the electropolymerization of substituted pyrroles will proceed via the  $\alpha$ - and  $\alpha'$ -carbon atoms<sup>[1-3]</sup>, and thus the hydrogen atoms linked to these carbon atoms cannot be used as probes or as references for studying the synthesized polymer. However, the chemical shifts of both pairs of ( $\alpha$ - $\alpha'$ ) and ( $\beta$ - $\beta'$ ) carbon nuclei are excellent probes to evaluate the extent of polymerization, stereochemistry, and packing of the synthesized polymers. In this way, variations in the calculated values for IGAIM based on DFT-B3LYP/6-31G(d,p) optimized geometry and wave functions for di-, tri-, and tetramers were shown in Figures. 4-6, respectively.

Analysis of the chemical shifts for  $\alpha$ - $\alpha'$  and  $\beta$ - $\beta'$  carbon atoms of the FMP oligomers in Figs. 4-6 show that oligomers consisting of pyrrole monomer render only two chemical shift values because the electronic density of  $\beta$ - $\beta'$  pair and also  $\alpha$ - $\alpha'$  pair carbon atoms is equivalent. Introduction of a fluoromethyl group on the pyrrole ring induces more positive charge on the  $\beta$  and  $\alpha$  carbon atoms, which results in higher chemical shifts as compared to  $\beta'$  and  $\alpha'$  carbon atoms. This is an evidence for the substituent effect. Comparison between and shows that  $\alpha$ -carbon atom favors larger positive charge to contribute to the polymerization process which may determine the favored path of polymerization and configuration of the polymer chains. It is also known that the process initiates and propagates through a radical cation intermediate mechanism<sup>[1-3]</sup>. Similarly, it was found that the steric repulsion of substituent on the monomer ring has an important effect in determining the configuration of the polymer chains. In this way, we expect polymer chains to propagate substantially from  $\alpha'$ -carbon position (far away from the substituted group position).

Also Figures 4-6 show that the chemical shift values are less affected by increasing the length of the oligomer chain (from dimer to tetramer) but they are varied mainly by substitution effects such as the number of fluorine atoms. This means that the fluoromethyl substituents contribute to the chemical shielding mainly via inductive effect rather than changing the ring current. Thus we can find that oligomers corresponding to the Py-CF<sub>3</sub> monomer have a higher chemical shielding for



**Figure 4 :** IGAIM <sup>13</sup>C-NMR chemical shifts for the C atoms in the  $\alpha$ - $\alpha'$  and  $\beta$ - $\beta'$  positions.

## Full Paper

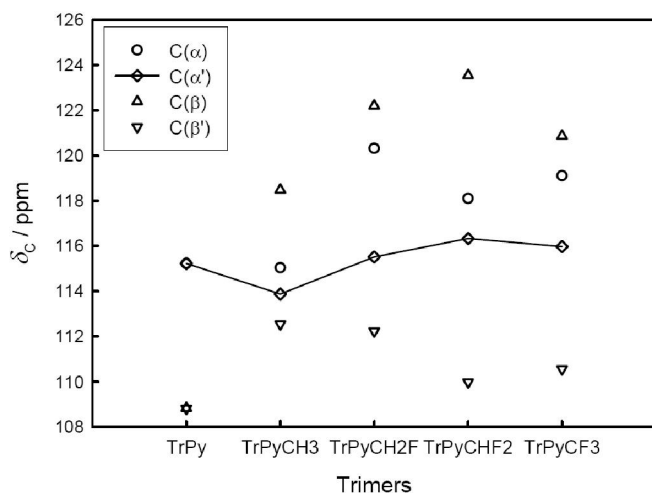


Figure 5 : IGAIM <sup>13</sup>C-NMR chemical shifts for the C atoms in the  $\alpha$ - $\alpha'$  and  $\beta$ - $\beta'$  positions.

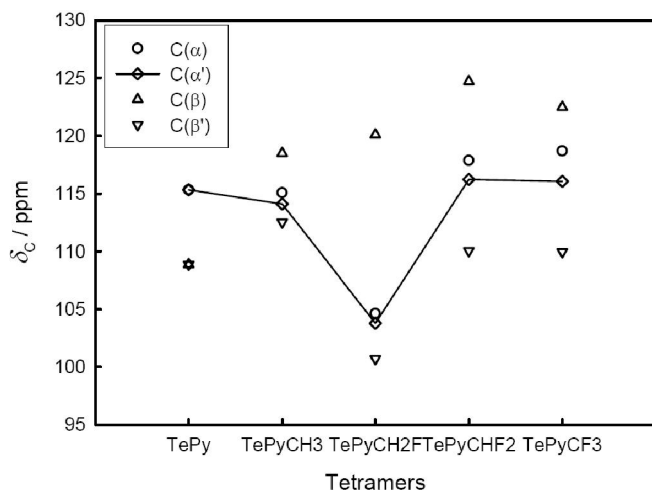


Figure 6 : IGAIM <sup>13</sup>C-NMR chemical shifts for the C atoms in the  $\alpha$ - $\alpha'$  and  $\beta$ - $\beta'$  positions

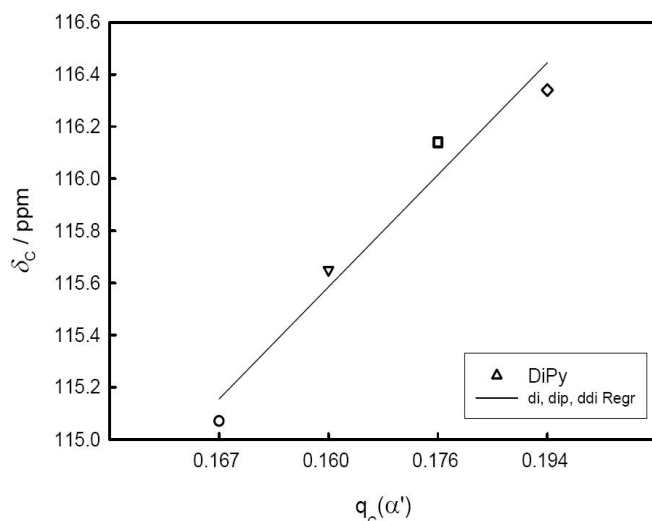


Figure 7 : Correlation between <sup>13</sup>C-NMR chemical shifts and charge density calculated for the  $\alpha'$ -carbon of the FMP dimers

$\alpha$ - $\alpha'$  carbon atoms, which is related to reduced electronic density at these sides.

In this way, we calculated the charge distribution of the radical cations for all FMP oligomers. For the sake of brevity, the correlation between  $\delta_C$  values for natural charge of  $\alpha'$ -carbon,  $q_C(\alpha')$ , are shown in Figure 7 for the dimer type. This figure shows that values for  $\delta_C$  correlate reasonably well with those for  $q_C(\alpha')$ . On the other hand, among the FMP oligomers, the Py-CF<sub>3</sub> oligomers have higher values, and thus  $\alpha'$ -carbon atom has a more positive charge. This causes oligomers consisting of Py-CF<sub>3</sub> to have the most appropriate conditions for synthesis of conducting polymers.

## CONCLUSION

The present study shows that the DFT-B3LYP/6-31G\*\* method is capable of effectively describing fluorinated compounds, and delivers valuable additional information about spectroscopic properties including NMR and IR spectra as well as structural and electronic properties. It was found that the spectroscopic data obtained in this work can support the structural and electronic properties of FMP oligomers. Analysis of the NMR properties including corrected isotropic hydrogen and carbon chemical shifts for mono-, di-, tri-, and tetramer rings of FMPs confirm their comparative structural and electronic properties. Chemical shift data showed that nucleation of monomers occur at  $\alpha'$ -position, far away from the substituent group, while growth of polymer chains progress effectively from  $\alpha$ -position, close to substitutions.

Analysis of the results obtained shows that FMPs can be regarded as possible candidates for the synthesis of corresponding conducting polymers with improved properties as compared to the polymers of methylpyrrole and pyrrole. It was also found that characteristics of the fluorinated substitutions play an important role in the polymerization process of FMPs. In addition, spectroscopic studies showed that the Py-CF<sub>3</sub> oligomers have higher capability for conducting polymers than other FMP oligomers because Py-CF<sub>3</sub> oligomers have higher planarity, higher stability, and other properties that are all appropri-



ate for electropolymerization of FMPs.

## ACKNOWLEDGEMENT

The author wish to thank Shahrood University of Technology for the financial support of this work.

## REFERENCES

- [1] R.J.Waltman, A.F.Diaz, J.Bargon; *J.Phys.Chem.*, **88**, 4343 (1984).
- [2] H.Shirakawa, E.J.Louis, A.G.MacDiarmid, C.K.Chiang, A.J.Heeger; *Chem.Soc.Chem. Commun.*, **16**, 578 (1977).
- [3] S.Sadki, P.Scotland, N.Brodie, G.Sabouraud, *Chem.Soc.Rev.*, **29**, 283 (2000).
- [4] <http://nobelprize.org/noble-prizers/chemistry/laureates/2000/heeger-lecture.html>
- [5] J.C.Vidal, E.Garcia, J.R.Castillo; *Anal.Chim.Acta*, **385**, 213 (1999).
- [6] T.E.Campbel, A.J.Hodgson, G.G.Wallace; *Electroanalysis*, **11**, 215 (1999).
- [7] D.Kincal, A.Kamer, A.D.Chield, R.J.Reynold; *Synth.Met.*, **92**, 53 (1998).
- [8] N.T.Kemp, G.U.Flanagan, A.B.Kaiser, H.J.Trodahl, B.Chapman, A.C.Partridge, R.G.Buckley; *Synth.Met.*, **101**, 434 (1999).
- [9] E.Smela; *J.Micromech.Microeng.* **9**, 1 (1999).
- [10] W.H.Meyer, H.Kiess, B.Binggeli, E.Meier, G.Harbeke; *Synth.Met.*, **10**, 255 (1985).
- [11] T.A.Skothiem, R.Elsenbaumer, J.Reynolds; *Handbook of Conducting Polymers*, Marcel Dekker, New York, (1998).
- [12] G.G.Wallace, G.Spinks, P.R.Teasdale; *Conductive Electroactive Polymers*, Technomic, New York, (1997).
- [13] G.Torres-Gomez, S.Skaarup, K.West, P.Gomez-Romero; *J.Electrochem.Soc.*, **147**, 2513 (2000).
- [14] C.K.Chiang; *Polymer*, **22**, 1454 (1981).
- [15] X.-L.Wei, Y.Z.Wang, S.M.Long, C.Bobeczko, A.J.Epstein; *J.Am.Chem.Soc.*, **118**, 2545 (1996).
- [16] M.Tsuchiya, S.Matsui, K.Sano, T.Kojima, *J.Appl.Polym.Sci.*, **70**, 471 (1998).
- [17] M.Charton; *J.Am.Chem.Soc.*, **97**, 1552 (1975).
- [18] H.Sabzyan, A.Omrani; *J.Phys.Chem.*, **A 107**, 6476 (2003).
- [19] A.Omrani, H.Sabzyan; *J.Phys.Chem.* **A 109**, 8874 (2005).
- [20] H.Sabzyan, H.Nikoofard; *Chem.Phys.*, **306**, 105 (2004).
- [21] H.Nikoofard, H.Sabzyan; *J.Fluid.Chem.*, **128**, 668 (2007).
- [22] S.Mitov, A.Panchenko, E.Roduner; *Chem.Phys.Lett.*, **402**, 485 (2005).
- [23] C.Sperati; *Handbook of plastic Materials and Technology*, Irvin I.Rubin, Editor; John Wiley & Sons, New York, (1990).
- [24] A.D.Becke; *J.Chem.Phys.*, **98**, 5648 (1993).
- [25] K.Wolinski, J.F.Hinton, P.Pulay; *J.Am.Chem.Soc.*, **112**, 8251 (1990).
- [26] J.L.Dodds, R.McWeeny, A.J.Sadlej; *Mol.Phys.*, **41**, 1419 (1980).
- [27] R.Ditchfield; *Mol.Phys.*, **27**, 789 (1974).
- [28] R.McWeeny; *Phys.Rev.*, **126**, 1028 (1962).
- [29] M.J.Frisch, G.W.Trucks, H.B.Schlegel, G.E.Scuseria, M.A.Robb, J.R.Cheeseman, V.G.Zakrzewski, J.A.Montgomery Jr., R.E.Stratmann, J.C.Burant, S.Dapprich, J.M.Millam, A.D.Daniels, K.N.Kudin, M.C.Strain, O.Farkas, J.Tomasi, V.Barone, M.Cossi, R.Cammi, B.Mennucci, C.Pomelli, C.Adamo, S.Clifford, J.Ochterski, G.A.Petersson, P.Y.Ayala, Q.Cui, K.Morokuma, D.K.Malick, A.D.Rabuck, K.Raghavachari, J.B.Foresman, J.Cioslowski, J.V.Ortiz, B.B.Stefanov, G.Liu, A.Liashenko, P.Piskorz, I.Komaromi, R.Gomperts, R.L.Martin, D.J.Fox, T.Keith, M.A.Al-Laham, C.Y.Peng, A.Nanayakkara, C.Gonzalez, M.Challacombe, P.M.W.Gill, B.Johnson, W.Chen, M.W.Wong, J.L.Andres, C.Gonzalez, M.Head-Gordon, E.S.Replogle, J.A.Pople; *Gaussian03W*, Gaussian Inc., Pittsburgh PA, (2003).
- [30] N.S.Goncalves, R.Cristiano, M.G.Pizzolatti, F.S.Miranda; *J.Mol.Struct.*, **733**, 53 (2005).