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Helical structure of linear homopolymers

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Abstract. The aim of our research was to conduct a computational study on helical geometries of several homopolymers. Simple helix of polymers with seventeen (poly(lactic acid)) or eighteen (poly(1-chloro-trans-1-butenylene), poly(1-methyl-trans-1-butenylene), poly(1,4,4-trifluoro-trans-1-butenylene), polyacrylonitrile and respectively polychlorotrifluoroethylene) monomers were investigated. The X, Y, and Z coordinates obtained after optimization of the geometry of polymers were used as input data to identify the rotation and translation of the coordinates and respectively the coefficient of the helix. The values of interest were calculated by minimization of residuals using two different protocols. The first protocol investigated the whole polymer by imposing (step 1) or not (step 2) a fixed value of the helix coefficient. The second protocol investigated by minimization of residuals if the monomer (one or two) from each end of the polymer is or not an outlier of the helical geometry of the polymer.

Introduction

The conformation of natural polymers goes back in 1937 when the helical structure of α-amylose was proposed by Hanes [1, 2] and further investigated by Freudenbers [3]. Linus Pauling and Robert B. Corey [4] showed in the 1950s that proteins chain form by monomeric units of proteins represented by amino-acids twists into a helix (α-helix) called secondary structure. These discoveries along with the identification of double-helical structure of DNA by James Watson and Francis Crick [5] were major breakthroughs.

Simulations studies conducted on some synthetic polymers (e.g. m-terphenyl-based π-conjugated polymer [6], poly(ethylene glycol) (PEG) [7], poly(ethylene imine) (PEI) [8], squaraine polymers [9]) shown their tendency to form helixes.

The helical shape translation of biopolymers in synthetic materials could lead to identification of materials with desired properties.

Ten linear chained homopolymers (polymers made by identical units) were subject to the investigation of shaping in a helix form. The aim of the study was to identify the helix parameters where helix shapes appears.

Polymers Generic Structures and Their Main Characteristics

The repeated sequence, abbreviation when existent, name and the feasibility to provide helix [10] are given in Table 1.

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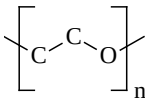
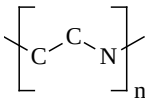
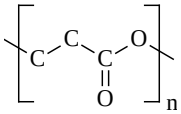
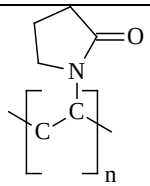
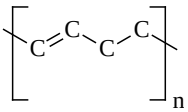
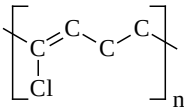
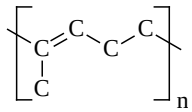
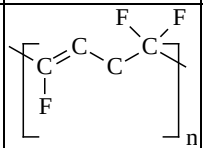
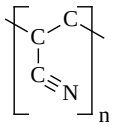
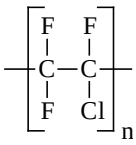
Table 1. Generic structure of polymers

No	Structure	Formula, abbreviation, name and remarks
#1		$(C_2H_4O)_n$ PEG Name: poly(ethylene glycol) Likely to provide helix: No, is purely linear
#2		$(C_2H_5N)_n$ PEI Name: polyethyleneimine Likely to provide helix: No, is purely linear
#3		$(C_3H_4O_2)_n$ PLA Name: poly(lactic acid) Likely to provide helix: Yes, internal helix
#4		$(C_6H_9NO)_n$ PVP Name: poly(N-vinyl-pyrrolidone) Likely to provide helix: Yes, double helix
#5		$(C_4H_6)_n$ Name: poly(trans-1-butenylene) Likely to provide helix: No, is purely linear
#6		$(C_4H_5Cl)_n$ Name: poly(1-chloro-trans-1-butenylene) Likely to provide helix: Yes

No	Structure	Formula, abbreviation, name and remarks
#7		$(C_5H_8)_n$ Name: poly(1-methyl-trans-1-butenylene) Likely to provide helix: Yes
#8		$(C_4H_3F_3)_n$ Name: poly(1,4,4-trifluoro-trans-1-butenylene) Likely to provide helix: Yes
#9		$(C_3H_3N)_n$ PAN Name: polyacrylonitrile Likely to provide helix: Yes, internal helix
#10		$(CF_2CClF)_n$ PCTFE / PTFCE Name: polychlorotrifluoroethylene Likely to provide helix: Yes, internal helix

Poly(ethylene glycol) or PEG, available in different geometries such as branched (3 to 10 PEG), star (10 to 100 chains) or comb (multiple PEG chains grafted onto a polymer backbone) is a compound with applications in different fields from industry to medicine.

PEGs are used as the basis of laxative [11], excipient in pharmacological products, or delivery systems [12-15]. PEGs are also used as the basis of skin creams [16], toothpaste or as an anti-foaming agent in food [17], and despite the fact that is considered biologically inert and safe can be responsible by contact dermatitis [16].

Polyethyleneimine (PEI) is a synthetic polymer, weakly basic and non-toxic that can take linear, branched or dendrimeric forms [18]. PEIs have been successfully used as drug carriers [19,20], gene delivery system [21,22], or growth inhibitors of microbial species [23] or cancer cells [24].

Poly(lactic acid) (polylactic acid or polylactide, PLA) is a biodegradable polyester obtained from renewable resources [25] and used in 1974 in combination with polyglycolic acid (PGA) as suture materials [26]. Due to biocompatibility and dissolvability in the body, PLA and its co-polymers were used in tissue engineering [27,28], or as carriers for bone morphogenetic proteins [29], in suture materials [30], and delivery systems [31,32].

Poly(N-vinyl-pyrrolidone) (polyvidone or povidone, PVP) is a water-soluble synthetic polymer used as a blood plasma substituent due to its hemocompatibility [33]. Poly(N-vinyl-pyrrolidone) nanoparticles have shown potential as drug delivery systems for hydrophobic drugs [34,35].

Poly(trans-1-butenylene), poly(1-chloro-trans-1-butenylene), poly(1-methyl-trans-1-butenylene), and poly(1,4,4-trifluoro-trans-1-butenylene) are polyalkadienes. They have a glass transition temperature (T_g/K) from 207 (poly(1-methyl-trans-1-butenylene)) to 238 (poly(1,4,4-trifluoro-trans-1-butenylene)) [36].

Polyacrylonitrile (PAN) is a synthetic, semicrystalline organic polymer resin, first synthesized in 1930 by Dr. Hans Fikentscher and Dr. Claus Heuck [37]. Because is hard, relatively insoluble, and a high-melting material [38], PAN is used to develop carbon fibers by stabilization, carbonization, and graphitization under controlled conditions [39,40]. PAN is also used in development of nanofibers [41,42], microcapsules/microspheres with diverse application (such as foam targets, carbon molecular sieve, cargo storage, or medical instruments) [43], semiconductor PAN powder (10^{-10} S/cm < conductivity < 10^{-3} S/cm when treated at 285-300°C) [44], or in the treatment of metals [45].

Polychlorotrifluoroethylene (PCTFE or PTFCE) is a thermoplastic chlorofluoropolymer discovered in 1934 by Fritz Schloffer and Otto Scherer [46]. PTFCE is nonflammable, has a high optical transparency, is chemical resistant, and has near-zero moisture absorption and excellent electrical properties [47-49]. The co-deposition of PCTFE (at a concentration less than or equal to 4 g/l) into Ni-W coating proved a feasible manufacturing of fluid lubricant [50]. The conductivity of PTFCE was double by treatment with nano-size copper iodide [51]. In pharmaceutical and medical industry, the PCTFE is used for packaging [52,53]. PCTFE find its application in many sectors such as chemical industry, manufacturing, electronics, architecture, energy, health and domestic sectors [54].

Helix Coefficients by Minimization of Residuals

The problem of finding the helixes determined by the atoms positions was investigated on those structures presented in Table 1 that are likely to provide a helix. Finding the helixes on these polymers is essentially a double problem. The proper rotations (eq1) and translation (eq2) of the coordinate system in such way that the helix to be aligned to the z-coordinate must be identify before and after identification of the helix (eq3).

$$\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} \cos(a_0) & \sin(a_0) & 0 \\ -\sin(a_0) & \cos(a_0) & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix} \quad (1a)$$

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos(a_1) & 0 & -\sin(a_1) \\ 0 & 1 & 0 \\ \sin(a_1) & 0 & \cos(a_1) \end{bmatrix} \cdot \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} \quad (1b)$$

$$\begin{bmatrix} x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(a_2) & \sin(a_2) \\ 0 & -\sin(a_2) & \cos(a_2) \end{bmatrix} \cdot \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} \quad (1c)$$

$$\begin{bmatrix} x_4 \\ y_4 \\ z_4 \end{bmatrix} = \begin{bmatrix} x_3 \\ y_3 \\ z_3 \end{bmatrix} - \begin{bmatrix} a_3 \\ a_4 \\ a_5 \end{bmatrix} \quad (2)$$

$$\begin{cases} x_4 = a_7 \cdot \sin(a_6 \cdot t) \\ y_4 = a_8 \cdot \cos(a_6 \cdot t) \\ z_4 = a_9 \cdot t \end{cases} \quad (3)$$

where (x_0, y_0, z_0) are the raw Cartesian coordinates of the atoms belonging to the helix, (x_1, y_1, z_1), (x_2, y_2, z_2) and (x_3, y_3, z_3) are new Cartesian coordinates obtained through elementary rotations, and (x_4, y_4, z_4) includes a translation. In eq1-eq3, a_i ($0 \le i \le 9$) are unknown coefficients (a_0, a_1 and a_2 are angles of rotation; a_3, a_4 and a_5 are scalars of a translation; a_6, a_7, a_8 and a_9 are the helix parameters; for circular-based helixes $a_7 = a_8$), and *t* is the changing parameter defining the evolution of the helix.

The helix is rotated and translated such that its xOy projection is a circle when $a_7 = a_8$ while $a_7 \neq a_8$ provides an ellipse. The main difficulty is given that starting roughly from atoms coordinates (x_0, y_0, z_0), all coefficients (from a_0 to a_9) must be identified at once.

The problem defined by the eq1 to eq3 is a problem of optimization. If *n* represents consecutive points (atoms positions) from the polymer converged as helix, the residual sum $\Sigma_{1 \le i \le n} f_0$ should be minimized (f_0 in eq4, $t \leftarrow i$).

$$f_0 = \Sigma\{[a_7 \sin(a_6 \cdot i) - x_4(i)]^2 + [a_8 \cos(a_6 \cdot i) - y_4(i)]^2 + [a_9 i - z_4(i)]^2\} \quad (4)$$

Since some of the unknowns are inside of periodic functions (especially concerns should be taken for a_6), it is essential that the starting values of the coefficients to be good.

In the case of a double helix, the eq3 can be changed to include a double time-dependence (eq5).

$$\begin{cases} x_4 = a_7 \cdot \sin(a_6 \cdot t) + a_{11} \cdot \sin(a_{10} \cdot t) \\ y_4 = a_8 \cdot \cos(a_6 \cdot t) + a_{12} \cdot \cos(a_{10} \cdot t) \\ z_4 = a_9 \cdot t \end{cases} \quad (5)$$

Going back to the problem of minimization (eq4), for fixed values of the a_0, a_1, a_2, a_6 (and a_{10} for eq5) coefficients, the problem may be simplified (by embedding eq3 or eq5 in eq4) to correspond to triple linear regression (eq6 for embedding eq3 in eq4; for embedding eq5 in eq4 is similar).

$$0 = \frac{\partial f_1}{\partial a_3} = \frac{\partial f_1}{\partial a_7}, \; f_1 = \sum_{i=1}^{n} \left(x_3(i) - a_3 - a_7 \cdot \sin(a_6 \cdot i)\right)^2 \quad (6a)$$

$$0 = \frac{\partial f_2}{\partial a_4} = \frac{\partial f_2}{\partial a_8}, \; f_2 = \sum_{i=1}^{n} \left(y_3(i) - a_4 - a_8 \cdot \cos(a_6 \cdot i)\right)^2 \quad (6b)$$

$$0 = \frac{\partial f_3}{\partial a_5} = \frac{\partial f_3}{\partial a_9},\ f_3 = \sum_{i=1}^{n} \left(z_3(i) - a_5 - a_9 \cdot i\right)^2 \tag{6c}$$

The solutions of eqs6 are therefore easily obtained (eqs7):

$$a_7 = \frac{n\sum_{i=1}^{n} x_3(i)\sin(a_6 i) - \sum_{i=1}^{n} x_3(i)\sum_{i=1}^{n}\sin(a_6 i)}{n\sum_{i=1}^{n}\sin(a_6 i)\sin(a_6 i) - \sum_{i=1}^{n}\sin(a_6 i)\sum_{i=1}^{n}\sin(a_6 i)} \tag{7a1}$$

$$a_3 = \left(\sum_{i=1}^{n} x_3(i) - a_7\sum_{i=1}^{n}\sin(a_6 i)\right)/n \tag{7a2}$$

$$a_8 = \frac{n\sum_{i=1}^{n} y_3(i)\cos(a_6 i) - \sum_{i=1}^{n} y_3(i)\sum_{i=1}^{n}\cos(a_6 i)}{n\sum_{i=1}^{n}\cos(a_6 i)\cos(a_6 i) - \sum_{i=1}^{n}\cos(a_6 i)\sum_{i=1}^{n}\cos(a_6 i)} \tag{7b1}$$

$$a_4 = \left(\sum_{i=1}^{n} y_3(i) - a_8\sum_{i=1}^{n}\cos(a_6 i)\right)/n \tag{7b2}$$

$$a_9 = \frac{n\sum_{i=1}^{n} z_3(i)i - \sum_{i=1}^{n} z_3(i)\sum_{i=1}^{n} i}{n\sum_{i=1}^{n} i^2 - \sum_{i=1}^{n} i\sum_{i=1}^{n} i} \tag{7c1}$$

$$a_5 = \left(\sum_{i=1}^{n} z_3(i) - a_9 \cdot \sum_{i=1}^{n} i\right)/n \tag{7c2}$$

The complexity of finding the helix was reduced from a problem of optimum with 10 (eq3) or respectively 11 (eq5) unknown coefficients to a problem of optimum with 4 (eq3) or respectively 5 (eq4) unknown coefficients that must be determined.

The study was conducted with polymers that embedded seventeen (#3, Table 1) or eighteen monomers (#4, #7, #8, #9, #10, Table 2) to assure the reliability of the calculation with the available calculation power. The polymers of interest were drawn with HyperChem and their geometries were optimized with the Spartan program at Hartree-Fock [55] 6-31G* level of the theory [56].

X, Y, and Z coordinates resulted after optimization of the geometry were used to shape the helixes. These data were used as input data to identify the rotation and translation of the coordinates and respectively the coefficients of the helix. The graphical representation of these input data is presented in Fig. 1 where each triangle is made from the coordinates of a monomer.

The above-presented equations were used to identify the optimum solution by using a guess value for the a_6 coefficient and the same initial starting values for all other coefficients. The guess value for a_6 coefficient was obtained by inspection of the graphical representations of the molecules.

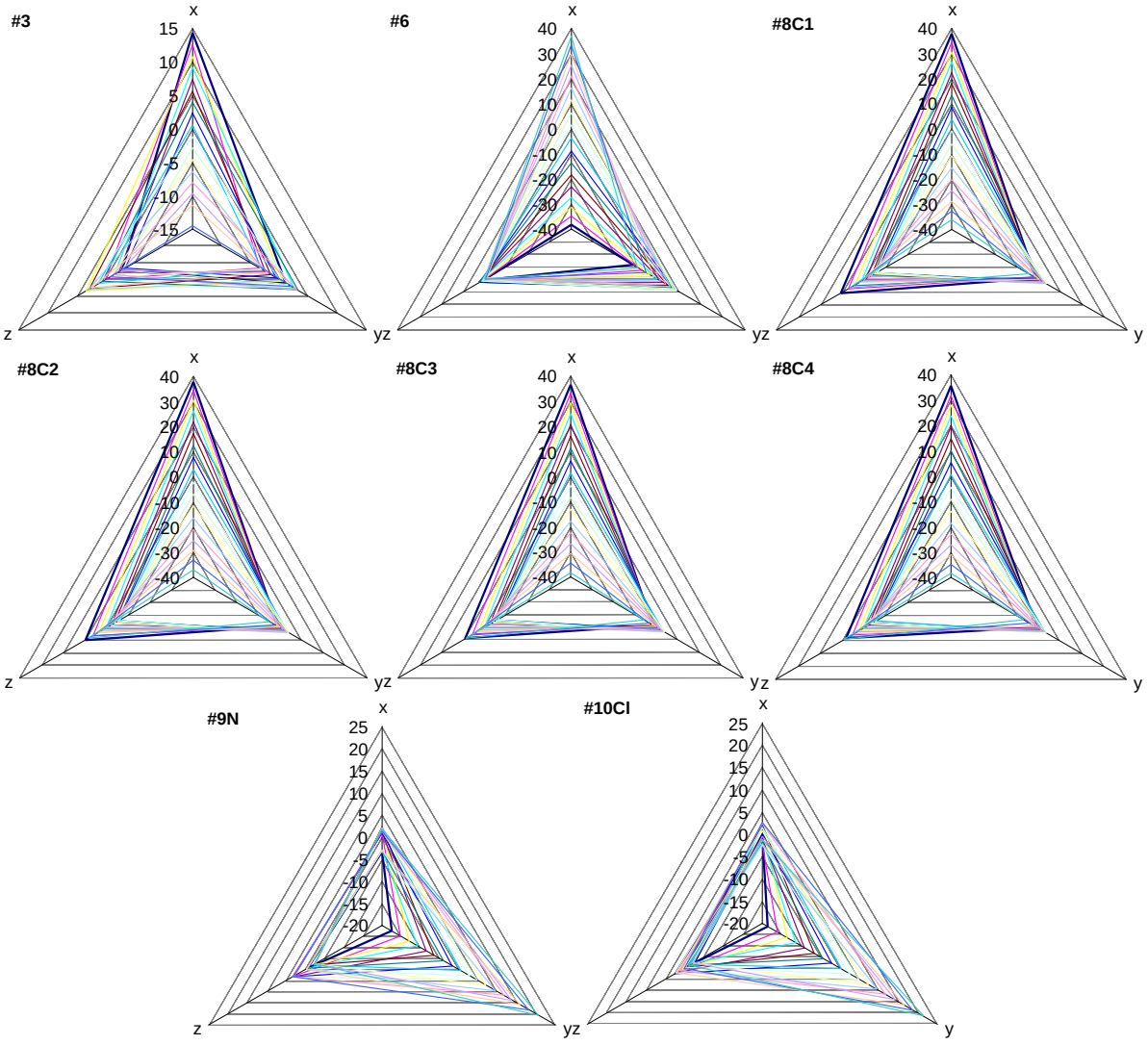


Fig. 1. Distribution of coordinates as resulted from geometry optimization.

Two different protocols were applied to calculate the values of interest:

- *Protocol I* was dedicated to the evaluation of the whole polymer. In the first step, the helix coefficient (a_6) was kept fixed and the values of the remaining coefficients were iterated to minimize the value of residuals until convergence. In the second step, the algorithm was applied again, starting with the final values obtained in the first step and the values of all coefficients (including helix coefficient a_6) were iterated to minimize the residuals until convergence.
- Since usually at the end the geometrical constrains are different than in the middle of the polymer, the *Protocol II* was dedicated to the evaluation of a smaller inside portion of the polymer and was done by exclusion of one or two monomers from each end. The starting values in the calculation of

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the values of coefficients were the values obtained as optimum values at the end of the first protocol. The coefficients were iterated until convergence.

The input data were the atom coordinates. Thus, for #3 the checkpoint was the double bonded oxygen, for #6 the chlorine, for #7 the carbon from methyl position. Four different checkpoints (C1 - carbon connected with one fluorine atom, and C2, C3, and C4 - the other carbon atoms) were used for #8. The checkpoint for #9 was the nitrogen atom, while for the #10 was chlorine atom.

Convergence Analysis

The pattern of convergence to the minimum value of residuals was different for the applied steps in the Protocol I. The starting values for the angular coefficients (a_0-a_2) were 0.1 in all cases. The number of iterations until the convergence ranged between 26 and 41 (Fig. 2) when the value of a_6 was fixed and was between 5 and 46 when all coefficients were calculated (Fig. 3).

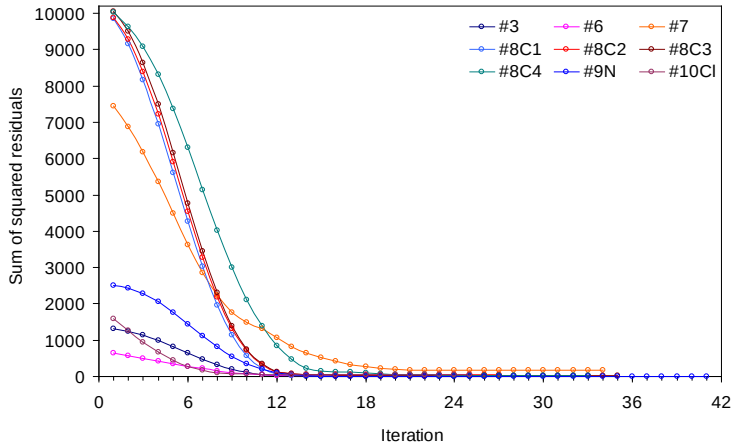

Fig. 2. Residuals convergence for helix coefficient fixed.

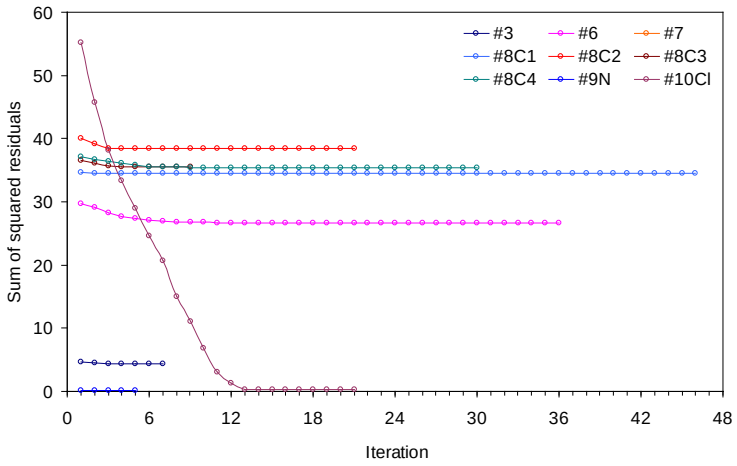

Fig. 3. Residuals convergence for helix coefficient also optimized.

In the case with fixed value of a_6, a similar (#8C4 similar with all other #8s, Fig. 2) and sometimes overlapping (#8C1, #8C2, and #8C3) behavior was observed for polymer #8 when different carbon atoms were imposed as a checkpoint. The residuals have the tendency to significant decrease until around the 12th iteration and after this iteration, the changes in the values of residuals are small (Fig. 2).

The minimization of residuals in the second step mimic a change in a plateau with small differences between iteration on the same polymer with one exception represented by #10Cl (Fig. 3). The residuals of the #10Cl follow a change similar to the one observed in the first step with significant decrease until the 12th iteration follows by a plateau where the changes are very small.

With no exception, the values of residuals reduced significantly at the end of the first step (Table 2). The highest reduction was observed for the #9 polymer (its monomer contain a triple bond -C≡N) when the value of residual was 20,731 times lower at the end of the first step compared with the start value. The value of residuals at the end of the second step is less than 190 times as compared with the value of residuals at the end of the first step.

Table 2. The values of residuals and coefficients: first protocol

		residuals	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	Iteration
#3	start	1316.371	0.100	0.100	0.100	0.450	0.435	1.480	1.867	1.372	2.818	-0.177	0
	end-1	4.720	1.538	0.923	1.521	0.059	0.061	16.081		3.276	3.091	-1.736	27
	end-2	4.410	1.545	0.843	1.527	0.026	0.028	16.082	1.876	3.264	3.103	-1.736	7
#6	start	10562.800	Identical with #3			-18.547	-2.735	-2.541	0.155	25.095	2.612	0.319	0
	end-1	29.772	1.536	-0.064	1.587	-16.419	0.479	-44.933		25.049	1.022	4.624	37
	end-2	26.670	1.600	-0.073	1.580	-13.788	0.535	-44.939	0.165	22.452	1.088	4.633	36
#7	start	7444.306	Identical with #3			15.736	-0.745	-3.299	0.194	-27.304	2.934	0.374	0
	end-1	177.895	1.431	-0.037	1.637	11.725	-0.222	-37.635		-22.925	-1.005	4.074	34
	end-2	124.517	1.622	-0.041	1.639	19.548	0.019	-38.459	0.165	-30.481	-1.455	4.143	18
#8C1	start	9846.996	Identical with #3			-8.205	-1.086	6.253	-0.172	-14.596	-3.541	-0.662	0
	end-1	34.633	1.363	1.214	1.361	-11.097	-0.186	44.230		-17.638	-0.694	-4.533	27
	end-2	34.452	1.420	1.214	1.417	-11.884	-0.142	44.256	-0.168	-18.362	-0.577	-4.535	46
#8C2	start	9879.200	Identical with #3			-11.256	-1.619	4.242	-0.176	-18.787	-3.461	-0.461	0
	end-1	40.091	1.463	1.143	1.490	-10.456	0.551	43.714		-17.387	0.118	-4.556	27
	end-2	38.377	1.589	1.142	1.607	-12.553	0.598	43.790	-0.165	-19.356	0.214	-4.562	21
#8C3	start	10042.268	Identical with #3			-12.599	-2.999	3.398	-0.176	-18.747	-3.476	-0.417	0
	end-1	36.508	1.487	1.139	1.483	-10.503	-0.109	42.449		-17.505	-0.973	-4.565	26

	end-2	35.542	1.585	1.131	1.575	-12.112	-0.024	42.526	-0.167	-19.058	-0.850	-4.571	9
#8C4	start	10025.977	Identical with #3			-12.690	-3.337	2.918	-0.175	-17.411	-2.597	-0.323	0
	end-1	37.168	-1.578	2.051	-1.573	-10.648	0.127	41.182		-16.974	0.093	-4.518	33
	end-2	35.331	-1.464	2.057	-1.475	-12.656	0.175	41.234	-0.164	-18.981	0.019	-4.523	30
#9N	start	2510.015	0.100	0.100	0.100	0.132	0.113	1.910	2.103	-2.119	1.882	-0.215	0
	end-1	0.121	0.000	-0.782	1.571	0.002	0.002	19.676		-3.221	-3.212	-2.220	41
	end-2	0.121	0.000	-0.785	1.571	0.002	0.002	19.676	2.104	-3.220	-3.212	-2.220	5
#10CL	start	2680.676	Identical with #3			0.117	0.102	1.668	2.103	-1.120	2.215	-0.196	0
	end-1	55.205	-0.008	-0.792	1.582	-0.072	-0.073	20.803		-1.723	-1.564	-2.328	30
	end-2	0.290	-0.010	-2.342	1.564	0.036	0.035	20.805	2.268	-2.415	-2.382	-2.328	21

end-1: the values obtained by minimizing the residuals when a_6 is fixed;

end-2: the values obtained by minimizing the residuals when all coefficients are calculated

The lowest value of residuals is obtained at the end of the second step while the values of the coefficients of the helixes have generally the tendency to increase (see Table 2). However, for the #7 and #8 polymers, the coefficient of the helix decrease at the end of the second step compared with the value obtained at the end of the first step.

The smallest absolute value of the helix coefficient a_6 when the first protocol was applied was of 0.155 (#6, poly(1-chloro-trans-1-butenylene)) at the end of the first step and 0.164 (#8C4, poly(1,4,4-trifluoro-trans-1-butenylene)) at the end of the second step. The highest absolute value of the helix coefficient a_6 was of 2.103 (#9N - polyacrylonitrile and #10Cl - polychlorotrifluoroethylene) at the end of the first step and 2.268 (#10Cl - polychlorotrifluoroethylene) at the end of second step in this first protocol.

For the second protocol, the exclusion of the monomers from the ends of the polymer was investigated to identify the outliers of helix on the investigated polymers.

As expected, the behavior to the convergence to the minimum value of residuals was different when the second protocol was applied compared with the first protocol.

The number of iterations ranges from 7 to 80 when one monomer from each end of the polymer was excluded (the number of monomers in the polymers decreased with two, Fig. 4) and from 7 to 168 when two monomers from each end of the polymer were excluded (the number of monomers in the polymers decreased with four, Fig. 5).

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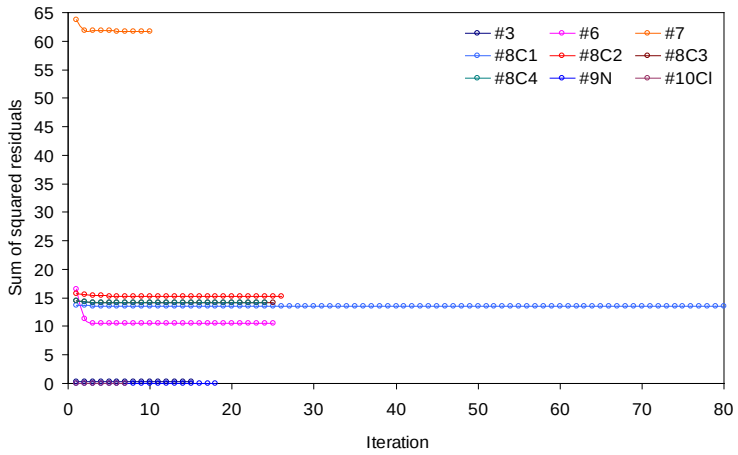

Fig. 4. Convergence of residuals for exclusion of one monomer from each end.

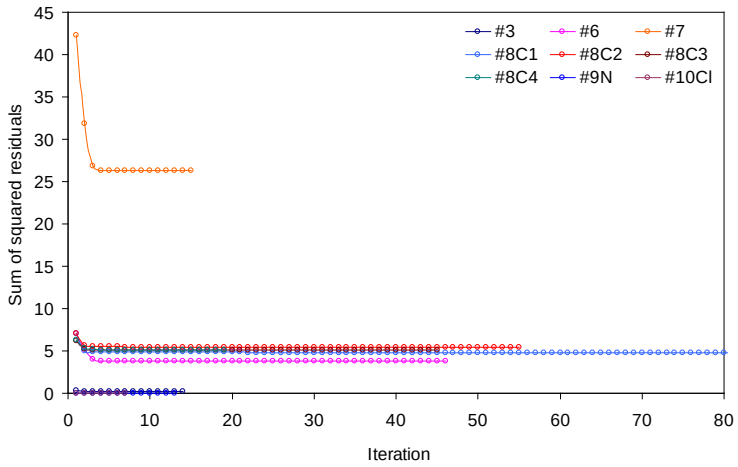

Fig. 5. Convergence of residuals for exclusion of two monomers from each end.

The changes in the residuals were smaller in the case of the second protocol compared with the first protocol. The minimization of residuals led to different values when one monomer is excluded compared with the case when two monomers are excluded (Table 3). The analysis of the values of residuals could let to the identification of the existence of outliers of the helix on the investigated polymers.

The values of residuals are similar after the exclusion of a monomer from each end of the polymer; as compared with the initial value, this indicates that the ended monomers are not outliers.

In two cases (#9N & #10Cl) the residual data were lower than 0.1 and the values of the helix coefficients were different at a value of 0.001 when compared the exclusion of a monomer relative to the baseline value and identical for exclusion of one monomer or two monomers (see Table 3).

For #9N, the exclusion of two monomers in each end of the polymer decrease the residuals 4 times (from 0.030 to 0.008) compared with the exclusion of one monomer, but in this case the ended monomers could not be considered outliers since the residuals are in all investigated cases very small.

In three investigated polymers (#3, #6, and #7), one monomer from each end of the polymers could be considered as outlier of the helix since the value of residuals were three times lower compared with

the values of residuals without any exclusion. Furthermore, the values of helix coefficient (a_6) are very closed for #6 and #7 to the start values and identical if one or two monomers at the end of each polymer were excluded (see Table 3).

Table 3. The values of residuals and coefficients: second protocol

		residuals	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	Iteration
#3	start	0.711	1.545	0.843	1.527	1.876	0.010	15.932	0.012	3.255	3.220	-1.711	0
	excl-1	0.240	1.548	0.895	1.545	0.012	0.011	15.935	1.868	3.249	3.233	-1.711	15
	excl-2	0.205	1.544	0.897	1.545	0.020	0.019	15.939	1.868	3.238	3.245	-1.713	14
#6	start	28.438	1.600	-0.073	1.580	-13.525	1.626	-45.839	0.165	22.133	1.481	4.728	0
	excl-1	10.547	1.603	-0.075	1.539	-13.363	0.615	-45.687	0.166	21.978	2.873	4.716	25
	excl-2	3.764	1.605	-0.075	1.506	-13.094	0.666	-46.281	0.166	21.673	4.258	4.782	46
#7	start	167.269	1.622	-0.041	1.639	19.883	-2.457	-40.294	0.165	-30.886	-0.518	4.337	0
	excl-1	61.771	1.625	-0.041	1.756	20.026	0.253	-39.945	0.164	-31.030	-4.198	4.296	10
	excl-2	26.278	1.623	-0.046	1.850	20.329	0.411	-41.187	0.164	-31.383	-6.314	4.423	15
#8C1	start	19.043	1.420	1.214	1.417	-11.900	0.509	44.871	-0.168	-18.382	-1.269	-4.602	0
	excl-1	13.498	1.352	1.216	1.321	-11.015	-0.201	44.738	-0.173	-17.562	-2.331	-4.591	80
	excl-2	4.790	1.348	1.220	1.292	-11.016	-0.240	45.138	-0.173	-17.563	-3.620	-4.638	168
#8C2	start	21.448	1.589	1.142	1.607	-12.600	1.281	44.478	-0.165	-19.412	-0.527	-4.634	0
	excl-1	15.234	1.538	1.143	1.531	-11.758	0.607	44.421	-0.169	-18.597	-1.481	-4.629	26
	excl-2	5.441	1.524	1.147	1.494	-11.574	0.582	44.913	-0.170	-18.423	-2.844	-4.683	55
#8C3	start	19.882	1.585	1.131	1.575	-12.140	0.632	43.175	-0.167	-19.092	-1.553	-4.640	0
	excl-1	14.102	1.544	1.135	1.511	-11.500	-0.003	43.066	-0.170	-18.458	-2.438	-4.631	25
	excl-2	5.059	1.538	1.138	1.484	-11.451	0.007	43.508	-0.171	-18.411	-3.689	-4.681	45
#8C4	start	19.798	-1.464	2.057	-1.475	-12.699	0.825	41.890	-0.164	-19.033	-0.700	-4.591	0
	excl-1	14.166	-1.506	2.057	-1.536	-11.971	0.241	41.839	-0.168	-18.282	-1.468	-4.587	24
	excl-2	5.094	-1.521	2.054	-1.570	-11.753	0.265	42.312	-0.169	-18.061	-2.711	-4.639	19
#9N	start	0.037	0.000	-0.785	1.571	0.007	0.007	19.630	2.104	-3.218	-3.223	-2.215	0

	excl-1	0.030	-0.002	-0.785	1.571	0.006	0.006	19.629	2.103	-3.219	-3.224	-2.215	18
	excl-2	0.008	-0.002	-0.794	1.570	0.007	0.006	19.632	2.104	-3.224	-3.217	-2.215	13
#10Cl	start	0.076	-0.010	-2.342	1.564	0.029	0.029	20.740	2.268	-2.422	-2.416	-2.320	0
	excl-1	0.056	-0.010	-2.337	1.568	0.028	0.028	20.740	2.267	-2.422	-2.418	-2.320	7
	excl-2	0.048	-0.009	-2.350	1.567	0.027	0.027	20.756	2.268	-2.416	-2.417	-2.322	7

Summary

Helical geometries are natural in biological polymers structures as seen in DNA [5], RNA [57], or globular proteins [58]. The understanding of how this natural helical geometry occurs could guide the design of material at macro and nano-scale levels with specific desired uses and properties [59].

Our computational study showed that some of the investigated homopolymers have a good chance to stabilize as helical geometries and for these structures, several coefficients were calculated by minimization of residuals applying two different protocols. In our analysis, the polymer with the highest helix coefficient was the one formed by 18 polychlorotrifluoroethylene monomers with chlorine as checkpoint of the helix. Opposite, the polymer with the lowest helix coefficient was the one formed by 18 poly(1-chloro-trans-1-butenylene) monomers. The second protocol was applied to identify if the monomers (one or two) from the ends of the polymers are or not outliers of the helical geometry. In other words, this second protocol analyzed if helical geometry of investigated polymers are of 15/16 monomers instead of 17/18 monomers (a monomer in each end of the polymer was excluded) or respectively 13/14 (two monomers from each end of the polymer). The investigation of the helical geometry pattern with more monomers in the polymer could bring more sounds in the knowledge of their behavior.

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