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(RECOMMENDED CITATION)

STUDY OF GEOMETRICAL SHAPING OF LINEAR CHAINED POLYMERS STABILIZED AS HELIXES

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ABSTRACT. The hypothesis of the study was that linear chained polymers have a natural chance to stabilize as a helix. Ten linear chained polymers, poly(ethylene glycol), polyethyleneimine, poly(lactic acid), poly(N-vinyl-pyrrolidone), poly(trans-1-butenylene), poly(1-chloro-trans-1-butenylene), poly(1-methyl-trans-1-butenylene), poly(1,4,4-trifluoro-trans-1-butenylene), polyacrylonitrile, polychlorotrifluoroethylene, were investigated. The structure of polymers was drawn and then optimized at Hartree-Fock, 6-31G* level of theory. The helix parameter was extracted from the optimized geometries using a home-made program. Seven out of ten polymers are likely to have a helical structure; the polymers with oxygen shown the highest residual error. The helix coefficient and rotation step per monomer were also calculated. The top three polymers according to rotation step per monomer behaved same as the one according to the helix coefficient. The top three non-increasing order was: polychlorotrifluoroethylene-Cl, polyacrylonitrile-N, and poly(lactic acid)-C-methyl. The smallest rotation step per monomer was associated with the smallest value of the helix coefficient (this being linearly related to rotation step per monomer). The highest helix radius was identified for poly(1-chloro-trans-1-butenylene), followed by poly(1-methyl-trans-1-butenylene) and poly(1,4,4-trifluoro-trans-1-butenylene).

Keywords: *linear chained polymer, helix radius, computational study*

INTRODUCTION

The polymer term is derived from Greek poly- 'many' & -mer 'parts' and identifies a molecule constructed by many repeated subunits [1] (Table 1).

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Polymer based materials have different properties, such as resistive memory [2], physical and electronic properties [3], and a variety of uses (see Table 2 [4,5]).

Table 1. Basic structure of polymers

Monomer			Polymer	
Structure	**Name**	**CID**	**Repeating unit**	**Name**
$CH_2=CH_2$	Ethene	6325	$(\text{-CH-CH-})_n$	Polyethylene
$CH_2=CHCl$	Chloroethene	6338	$(\text{-}CH_2\text{-CH(Cl)-})_n$	Polyvinyl chloride
$F_2C=CF_2$	Tetrafluoroethene	8301	$(\text{-}F_2C\text{-}CF_2\text{-})_n$	Polytetrafluoroethylene

Table 2. Applications of polymers

	Polymer	Monomer unit	Uses
1	polypeptides	-NH-CO- (amino acids)	proteins, wool, silk, steric stabilizers, colloidal additives
2	polyvinyls	$\text{-}CH_2\text{-CH(X)-}$	plastics
3	polyesters	-CO-O-	clothing, containers
4	polysiloxanes, silicones	-Si-O-	lubricants, rubbers, paints
5	polyamide	-NH-CO-	nylon, fabrics, auto parts
6	polyurethanes	-NH-CO-O-	adhesives, flexible furniture
7	cellulose	-C-O-	paper, photographic film
8	polycarbonates	-O-CO-O-	optical equipment, CDs
9	polyethylene oxide (PEO, PEG)	$\text{-}CH_2\text{-O-}CH_2\text{-}$	detergents, cosmetics
10	polyacrylamide (PAA)	$\text{-}CH_2\text{-CH(}CONH_2\text{)-}$	plastics, textiles, diapers
11	polyvinyl alcohol (PVA)	$\text{-}CH_2\text{-CH(OH)-}$	fibers, adhesives, textiles
12	polyethylene (PE)	$\text{-}CH_2\text{-}CH_2\text{-}$	coating, containers, films
13	polystyrene (PS)	$\text{-}CH_2\text{-CH(}C_6H_5\text{)-}$	packing (fast-food containers), housewares
14	polybutadiene (PBD)	$\text{-}CH_2\text{=CH-CH=}CH_2\text{-}$	latex paints, rubbers
15	polydimethylsiloxane (PDMS)	$\text{-Si(}CH_3\text{)}_2\text{-O-}$	silicone oil, lubricants
16	polypropylene (PP)	$\text{-}CH_2\text{-CH(}CH_3\text{)-}$	carpets, bottles, wrap films, microwaveable containers
17	polymethylmethacrylate (PMMA)	$\text{-}CH_2\text{-}CCH_3\text{(}CO_2CH_3\text{)-}$	transparent windows, plexiglass, perpex
18	polytetrafluoroethylene (PTFE)	$\text{-}CF_2\text{-}CF_2\text{-}$	teflon
19	polyvinyl chloride (PVC)	$\text{-}CH_2\text{-CH(Cl)-}$	plastic sheet, insulation, pipes

Classification of polymers is done according to vary criteria, such as synthesis method, molecular structure (linear or branched), chemical family (organic or inorganic), etc. [6].

According to their structure, polymers are classified as [7]:

- Linear: a single continuous chain of repeated unit (such as acrylics, nylons, polyethylene, polyvinyl chloride).
- Branched: side chains of repeated unit connecting into the main chain of repeated unit (such as polyethylene). A linear polymer may show branching points and side chains (parts out of the linear chain, like branches off the trunk of a tree).
- Cross-linked: interconnections between chains (such as rubbers)
- Network: many interconnections between chains such that the entire sample is a single molecule (such as epoxies, phenolics)
- Configuration: 3D structure of polymer based on orientations that can be changed just by breaking the bonds

Linear polymers may include different atoms in the main chain and may or may not have rings (cyclolinear polymers):

- Just carbon atoms (C) in the main chain: saturated main chain (polyethylene, polypropylene), unsaturation of the main chain (natural rubber, polyacetylene), or polar side groups (PVC, PMMA, Teflon)
- Oxygen (O) in the main chain: polyformaldehyde (acetal), epoxy polymers (PEO, PPO), polyesters, polycarbonates
- N in the main chain: polyamines, polyamides (polypeptides), polyurethanes
- Other atoms in the main chain: polysulfones, polysiloxanes (silicones), polyphosphazenes
- Rings in the main chain: poly(p-phenylene), polyaniline, cellulose

After a while, linear constructions of polymers (such is a hose) have the natural tendency to bend. The expose of hoses to biodiesel, for example, led to decrease of its tensile strength [8], while the sterilization of surgical silicone hose led to modification of the structure of polymer [9]. The main question is in which degree this tendency to bend is a natural tendency?

A series of studies shown that some synthetic polymers (m-terphenyl-based π-conjugated polymer [10], poly(ethylene glycol) (PEG) [11-13], poly(ethylene imine) (PEI) [14], squaraine polymers [15]) or natural polymer-like compounds (functional polymers like DNA [16], RNA [17], globular proteins [18]) have the tendency to form a helix. Of course, the most important case is the helix of DNA, but the question about the tendency of other polymers to form helix even if was investigated [19-22] it still needs more attention. The present study takes into account a series of polymers, from both biological and synthetic groups having as the subject of investigation the tendency of polymers to form a helix.

RESULTS AND DISCUSSION

The residual errors obtained by applying (3) varied from 0.0016 to 0.4428 with highest residuals for oxygen atom in any position (even, odd, or all – polymer #4, Table 3). Systematically, the polymers with oxygen had highest values of residuals, followed by the polymers with C-methyl group. The highest value of residual errors is thus observed in the polymer that tend to form a double helix and all investigated structures of #4 proved to have outliers. Furthermore, the sample size after removal of the outliers (if any) proved inversed linearly related to residual errors (Pearson's correlation coefficient R = -0.8969, p-value = 7.68e-5). Accordingly, with some exceptions (see #4 O-all, Table 3), when the sample size increases, the residual error decreases.

Table 3. Residual errors for investigated polymers likely to have a helical structure

Polymer	Atom	*n*	*n*'	Residual error (SS)	Remarks
#3	C-methyl	17	15	0.0393	SS 100 times higher with the ends ➔ the ends are outliers (2)
#4	O-even	11	9	0.3123	SS 46 times higher with the ends ➔ the ends are outliers (2)
	O-odd	12	10	0.4428	SS 66 times higher with the ends ➔ the ends are outliers (2)
	O-all	21	17	0.1255	SS 100 times higher with the ends ➔ the ends are outliers (4)
#6	Cl	18	18	0.0127	Ends are not outliers
#7	C-methyl	18	18	0.0684	Ends are not outliers
#8	C-1	18	18	0.0033	Ends are not outliers
	C-2	18	18	0.0016	Ends are not outliers
	C-3	18	18	0.0019	Ends are not outliers
	C-4	18	18	0.0016	Ends are not outliers
#9	N	18	16	0.0285	SS 4 times higher with the ends ➔ the ends are outliers (2)
#10	Cl	18	16	0.0047	SS 37 times higher with the ends ➔ the ends these are outliers (2)

n = sample size; *n*' = sample size after removal of the outliers

The rotation step (coefficient c_0 in (2)) and the rotation step/monomer were obtained for each investigated polymer and are given in Table 4. All other calculated coefficients of the helix of the investigated polymers are given in Table 5.

Table 4. The coefficient of the helix and rotation step

Polymer (atom type)	Helix coefficient (c_0)	Rotation step (/monomer) (°)
#3 (- C-methyl)	2.972e-1	107
#4 (- O-even)	9.288e-2	33.4
#4 (- O-odd)	9.193e-2	33.1
#4 (- O-all)	9.183e-2	33.1
	1.233e-1	44.4 (odd/even)
#6 (- Cl)	2.148e-2	7.73
#7 (- C-methyl)	3.085e-2	11.1
#8 (- C-1)	2.743e-2	9.87
#8 (- C-2)		
#8 (- C-3)		
#8 (- C-4)		
#9 (- N)	3.347e-1	120.5
#10 (- Cl)	3.609e-1	129.9

Table 5. Helix coefficients – see (2)

Polymer (atom type)	Helix coefficients for axial projection					
		x axis		y axis		z axis
#3	c_1	3.9983e-2	c_5	3.2314e0	c_9	3.2505e+0
	c_2	-2.2040e+0	c_6	-6.7020e-1	c_{10}	9.0419e-1
	c_3	-1.7105e+0	c_7	5.3824e-3	c_{11}	-3.0941e-2
	c_4	1.5932e+1	c_8	-1.2359e-1	c_{12}	2.1275e-1
#4 (even)	c_1	3.257e+0	c_5	2.088e0	c_9	4.026e+0
	c_2	-1.807e+0	c_6	-1.724e0	c_{10}	-3.349e+0
	c_3	1.345e+0	c_7	-2.036e0	c_{11}	-1.073e-1
	c_4	-1.640e+1	c_8	2.487e+1	c_{12}	1.270+0
#4 (odd)	c_1	2.584e+0	c_5	1.555e+0	c_9	2.906e+0
	c_2	-3.290e+0	c_6	-3.228e+0	c_{10}	-4.865e+0
	c_3	1.306e+0	c_7	-2.039e+0	c_{11}	-9.570e-2
	c_4	-1.525e+1	c_8	2.358e+1	c_{12}	1.162e+0
#4 (all)	c_1	2.9031e+0	c_5	1.8583e+0	c_9	3.4290e+0
	c_2	-2.5169e+0	c_6	-2.4382e+0	c_{10}	-4.0614e+0
	c_3	1.3204e+0	c_7	-2.0466e+0	c_{11}	-1.0094e-1
	c_4	-1.5757e+1	c_8	2.4304e+1	c_{12}	1.2071e+0
	c_{13}	4.1484e-1	c_{14}	2.5537e-1	c_{15}	5.3846e-1
	c_{16}	-4.0826e-1	c_{17}	6.6823e-1	c_{18}	2.4509e-2
# (6)	c_1	2.48427e1	c_5	3.19611e+1	c_9	1.79865e+1
	c_2	-2.88747e0	c_6	-1.34873e+0	c_{10}	1.64965e-1
	c_3	1.74459e0	c_7	-1.01784e-1	c_{11}	1.90010e+0
	c_4	-1.68632e1	c_8	-2.24718e+1	c_{12}	-1.90634e+1
# (7)	c_1	1.82640e1	c_5	2.33646e+1	c_9	1.41794e+1
	c_2	2.93375e0	c_6	1.33951e+0	c_{10}	-1.99841e-1
	c_3	1.57034e0	c_7	6.32800e-2	c_{11}	1.93730e+0
	c_4	-1.46022e1	c_8	1.16876e+1	c_{12}	-1.77684e+1

Table 5. (Continued)

Polymer (atom type)	**Helix coefficients for axial projection**					
	x axis		y axis		z axis	
#8 (-C1)	c_1	-9.14110e+0	c_5	1.51182e+1	c_9	1.70206e+1
	c_2	-1.46653e-1	c_6	-6.30651e-1	c_{10}	1.07360e+0
	c_3	3.29307e+0	c_7	1.82544e+0	c_{11}	7.95252e-1
	c_4	-3.25477e+1	c_8	-2.22678e+1	c_{12}	2.49521e+0
#8 (-C2)	c_1	-9.46739e+0	c_5	1.57384e+1	c_9	1.76728e+1
	c_2	-9.44889e-2	c_6	-5.76774e-1	c_{10}	1.12318e+0
	c_3	3.29773e+0	c_7	1.83040e+0	c_{11}	8.01570e-1
	c_4	-3.20550e+1	c_8	-2.20244e+1	c_{12}	2.53498e+0
#8 (-C3)	c_1	-9.40050e+0	c_5	1.56074e+1	c_9	1.75550e+1
	c_2	-7.59906e-2	c_6	-5.58858e-1	c_{10}	1.13939e+0
	c_3	3.29710e+0	c_7	1.82896e+0	c_{11}	8.05768e-1
	c_4	-3.07980e+1	c_8	-2.12904e+1	c_{12}	2.81228e+0
#8 (-C4)	c_1	-9.18430e+0	c_5	1.53022e+1	c_9	1.71931e+1
	c_2	6.26188e-3	c_6	-4.76742e-1	c_{10}	1.22481e+0
	c_3	3.30040e+0	c_7	1.82834e+0	c_{11}	8.03362e-1
	c_4	-3.06020e+1	c_8	-2.12218e+1	c_{12}	2.87783e+0
#9 (-N)	c_1	-3.21292e+0	c_5	1.08286e-2	c_9	3.22894e+0
	c_2	-2.35726e+0	c_6	-2.48275e+0	c_{10}	2.35661e+0
	c_3	3.07394e-3	c_7	2.21476e+0	c_{11}	7.50670e-4
	c_4	-2.71106e-2	c_8	-1.96284e+1	c_{12}	1.54767e-3
#10 (-Cl)	c_1	2.42189e+0	c_5	-3.60496e-2	c_9	-2.41754e+0
	c_2	-7.72781e-1	c_6	-7.46450e-1	c_{10}	-2.34239e+0
	c_3	2.90532e-2	c_7	2.32023e+0	c_{11}	3.25795e-3
	c_4	-2.59285e-1	c_8	-2.07402e+1	c_{12}	1.17230e-2

The smallest coefficient of the helix was observed on polymers with highest size (n=18, see Table 4); and without outliers while the highest coefficient of the helix was observed in polymers #3, #9 and #10. As expected, the smallest rotation step per monomer was associated with the smallest value of the helix coefficient, which is linearly related to the rotation step per monomer (R = 0.9999, p-value = 8.55e-25).

Several coefficients, such as c_4, c_8, c_{12} (and c_{16}, c_{17}, c_{18} for the double helix) are not of interest since represent the position of the helix relative to the origin of the coordinates system, position which is arbitrary. The rest of coefficients represent the projection of the helix on a coordinate system rotated relatively to the convenient direction of the helix propagation.

Three coefficients (among those provided in Table 5) are of interest: c_1, c_5 and c_9 since they allow computing the approximation of the helix radius, by formula:

$$helix\,radius = \frac{\sqrt{c_1^2 + c_5^2 + c_9^2}}{\sqrt{2}} \tag{5}$$

The smallest helix radius was evaluated for #10 (internal helix), followed by #4odd (double helix), and #3 (internal helix) (see Table 6). The highest value was estimated for the polymer #6, followed by #7 and #8, all polymers being with sample size of 18 and without any outlier.

Starting from the values obtained in this research, the coefficients of the 'classical' helix equation (0) could be obtained. Furthermore, the results obtained here could be used to investigate other polymers likely to form helixes.

CONCLUSIONS

Seven out of ten investigated polymers are likely to form helixes (internal and double helix). The polymer with the highest coefficient of the helix and highest rotation step per monomer was a polymer with internal helix, polychlorotrifluoroethylene-Cl. The coefficient of the helix proved to be linearly related to the rotation step per monomer (p-value < 0.0001).

Table 6. Radius of the helix approximated by (5)

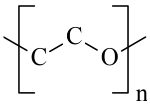
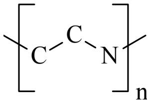
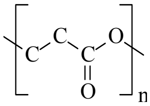
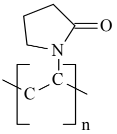
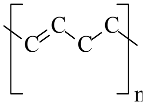
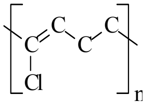
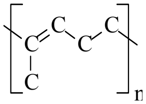
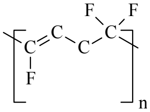
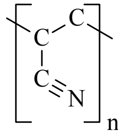
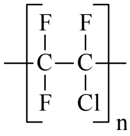
Polymer (atom type)	Radius (Angs)
#3	3.24
#4 (even)	3.95
#4 (odd)	2.96
#4 (all)	3.44
#6	31.32
#7	23.24
#8 (-C1)	17.35
#8 (-C2)	18.02
#8 (-C3)	17.89
#8 (-C4)	17.52
#9 (-N)	3.22
#10 (-Cl)	2.42

The highest helix radius was identified for poly(1-chloro-trans-1-butenylene) while the smallest helix radius was calculated for polychlorotrifluoroethylene-Cl.

EXPERIMENTAL SECTION

Hypothesis: Linear chained polymers have a good chance to stabilize as a helix. A series of linear polymers were included into this study. Not all of them have enough steric constraints to provide a 'regular irregularity', the essential ingredient of the helix form. Table 7 gives the series of investigated polymers, along with this first level of approximation revealed for instance by a simple geometry built at any level of theory.

Table 7. Structural characteristics and use of the investigated linear polymers

	Name	Structure	Remarks	Likely to provide helix
1	poly(ethylene glycol)		PEG - biological interest (laxative [23], improvement of action potential after spinal cord injury [24], drug delivery [25])	[NO] purely linear
2	polyethyleneimine		PEI - biological interest (gene delivery [26], drug carrier [27])	[NO] purely linear
3	poly(lactic acid)		PLA - biological interest [28] (tissue engineering [29], suture materials [30], delivery systems [31])	[YES], internal helix (see Fig. 2)
4	poly(N-vinyl-pyrrolidone)		PVP - other interest (beverages, disinfectant, in complexation with of iodine, film forming agents [32,33])	[YES] double helix (see Fig. 3)
5	poly(trans-1-butenylene)		other interest (glass transition temperature [34])	[YES]
6	poly(1-chloro-trans-1-butenylene)		other interest (glass transition temperature [34])	[YES]
7	poly(1-methyl-trans-1-butenylene)		other interest (glass transition temperature [34])	[YES]
8	poly(1,4,4-trifluoro-trans-1-butenylene)		other interest (glass transition temperature [34])	[YES]
9	polyacrylonitrile		PAN - other interest (nanofibers [35,36], treatment of metals [36])	[YES] internal helix (see Fig. 4)
10	Polychlorotrifluoroethylene		PCTFE or PTFCE - other interest (chemical industry, manufacturing, electronics, architecture, energy, health and domestic sectors [37])	[YES] internal helix (see Fig. 5)

Spartan optimized geometries are shown in Figure 1.

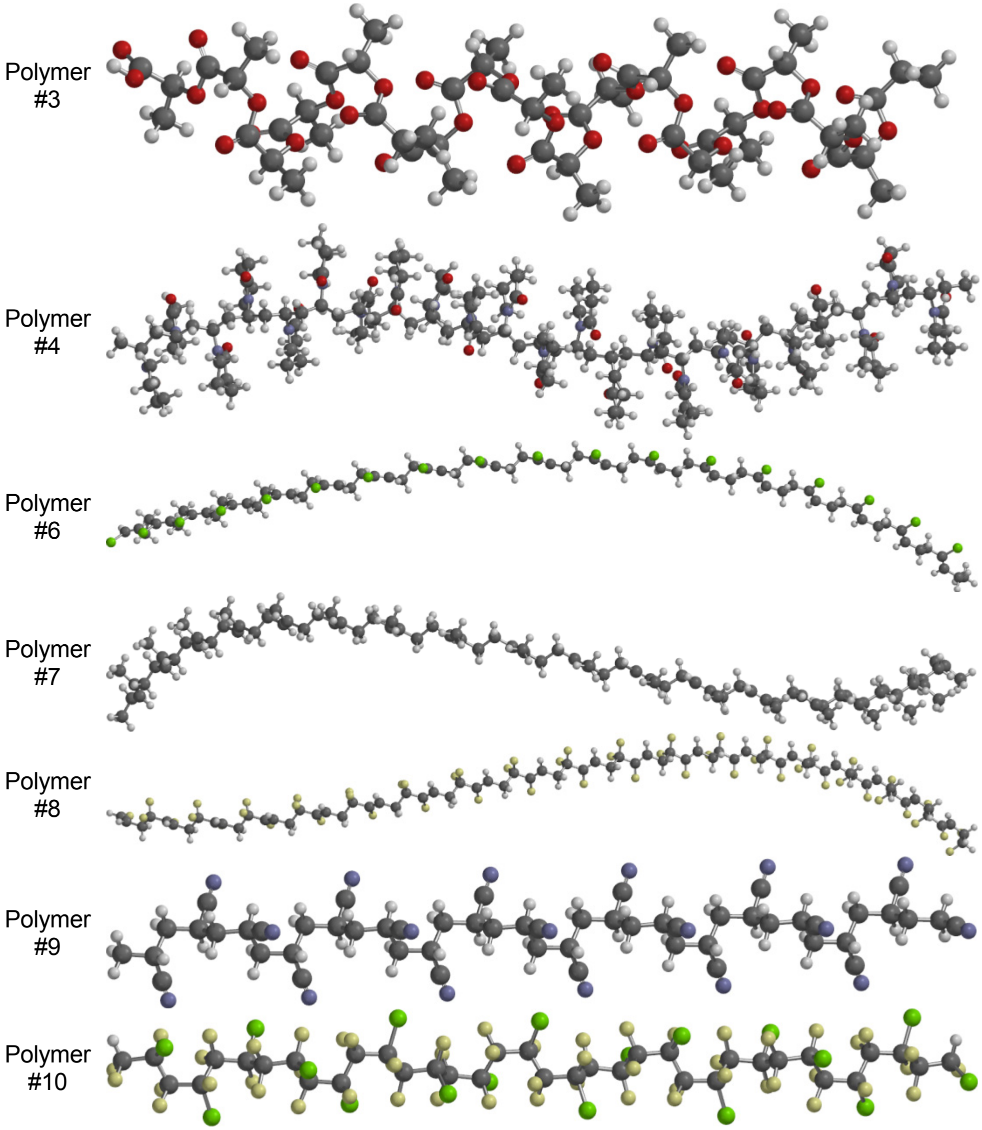


Figure 1. Spartan images of the studied polymers with optimized geometry

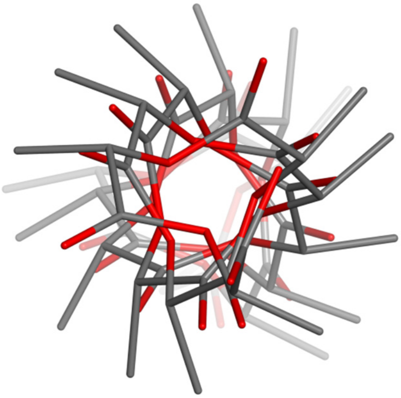


Figure 2. Internal helix of poly(lactic acid) (O atoms, red)

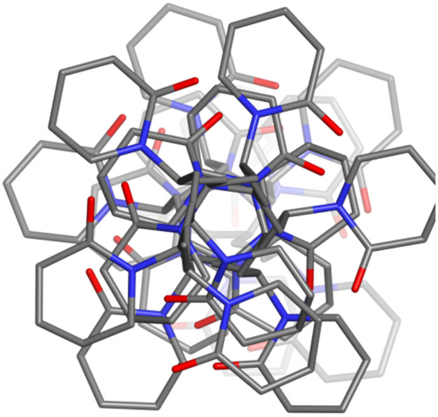


Figure 3. Double helix of poly(N-vinyl-pyrrolidone) (N atoms, blue; O atoms, red)

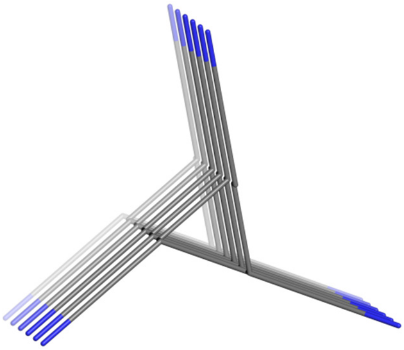


Figure 4. Internal helix of polyacrylonitrile (N atoms, blue)

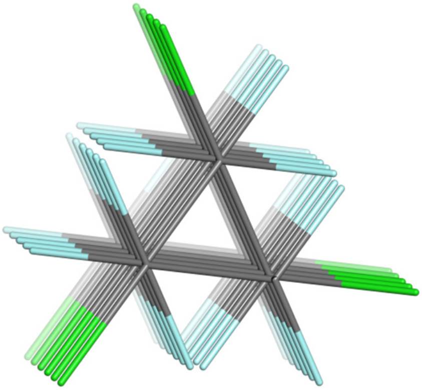


Figure 5. Internal helix of polychlorotrifluoroethylene (chlorine atoms, green, fluorine atoms, cyan)

The 10 polymers of interest were drawn by HyperChem and the geometry of each polymer was optimized. The optimization was done by Spartan software, at Hartree-Fock (HF [38]) level of theory (6-31G* [39]). A home-made program, that extracts from the optimized geometry the parameters of the helix.

Recall that a helix is defined as in Eq 0:

$$\begin{aligned} x &= a_1 + a_2 \cdot \sin(a_0 \cdot t) \\ y &= a_3 + a_4 \cdot \cos(a_0 \cdot t) \\ z &= a_5 + a_6 \cdot t \end{aligned} \qquad (0)$$

where x, y, and z are the axial projections of the helix, and a_i ($0 \leq i \leq 6$) are unknown coefficients (a_1, a_3 and a_5 expressing a translation of the reference system relative to the helix, by keeping the direction of the axis the same; a_0, a_2, a_4 and a_6 are helix parameters; for circular-based helixes $a_2 = a_4$); t defines the evolution of the helix.

Equation 0 is theoretically important, but in practice there is no way to align the helix on the z-axis without the identification of the unknown coefficients ($a_0..a_6$); actually the equations of the helix are hidden behind a transformation of the system coordinates. Therefore, the equations maximizing the agreement between the model and the observation may be as follows:

$$\begin{aligned} x &= b_1 \cdot \sin(b_0 \cdot t) + b_2 \cdot \cos(b_0 \cdot t) + b_3 \cdot t + b_4 \\ y &= b_5 \cdot \sin(b_0 \cdot t) + b_6 \cdot \cos(b_0 \cdot t) + b_7 \cdot t + b_8 \\ z &= b_9 \cdot \sin(b_0 \cdot t) + b_{10} \cdot \cos(b_0 \cdot t) + b_{11} \cdot t + b_{12} \end{aligned} \qquad (1)$$

where b_i ($0 \leq i \leq 12$) are unknown coefficients (to be determined), and t is as above.

Some unknown coefficients may be incorporated inside of the periodic functions, providing a more convenient expression for the helix:

$$\begin{aligned} x &= c_1 \cdot \cos(c_0 \cdot 2\pi \cdot t + 2\pi \cdot c_2) + c_3 \cdot t + c_4 \\ y &= c_5 \cdot \cos(c_0 \cdot 2\pi \cdot t + 2\pi \cdot c_6) + c_7 \cdot t + c_8 \\ z &= c_9 \cdot \cos(c_0 \cdot 2\pi \cdot t + 2\pi \cdot c_{10}) + c_{11} \cdot t + c_{12} \end{aligned} \tag{2}$$

where again c_i ($0 \le i \le 12$) are unknown coefficients, and 2π coefficient is introduced for convenient interpretation of the c_0 and c_2, c_6 and c_{10} coefficients.

The maximization of the agreement was achieved by minimizing the squared residual sum:

$$\begin{aligned} & S^2 = S^2_{x,i} + S^2_{y,i} + S^2_{y,i} \to \min. \\ & S^2_{x,i} = \sum_{i=1}^{n} (x_i - c_1 \cdot \cos(c_0 \cdot t + c_2) - c_3 \cdot t - c_4)^2 \\ & S^2_{y,i} = \sum_{i=1}^{n} (y_i - c_5 \cdot \cos(c_0 \cdot t + c_6) - c_7 \cdot t - c_8)^2 \\ & S^2_{z,i} = \sum_{i=1}^{n} (x_i - c_9 \cdot \cos(c_0 \cdot t + c_{10}) - c_{11} \cdot t - c_{12})^2 \end{aligned} \tag{3}$$

where n is the number of observations (grid points in the supposed helix-like structure).

A simple look on (3) gives the minimal number of observations (n) to obtain a statistically significant result: $n \ge 3\times12/3$ (three coordinates - e.g. x, y, z - 12 unknowns, 3 observations per unknown). Therefore, no less than 12 monomers should be in the polymer in order to obtain statistical significant coefficients.

For a double helix, one follows equations:

$$\begin{aligned} x &= (c_1+(-1)^t \cdot c_{13}) \cdot \cos(c_0 \cdot 2\pi \cdot t + c_2 + 2\pi \cdot (-1)^t \cdot c_{19}) + c_3 \cdot t + c_4 + (-1)^t \cdot c_{16} \\ y &= (c_5+(-1)^t \cdot c_{14}) \cdot \cos(c_0 \cdot 2\pi \cdot t + c_6 + 2\pi \cdot (-1)^t \cdot c_{19}) + c_7 \cdot t + c_8 + (-1)^t \cdot c_{17} \\ z &= (c_9+(-1)^t \cdot c_{15}) \cdot \cos(c_0 \cdot 2\pi \cdot t + c_{10} + 2\pi \cdot (-1)^t \cdot c_{19}) + c_{11} \cdot t + c_{12} + (-1)^t \cdot c_{18} \end{aligned} \tag{4}$$

As can be observed, for the double helix, a series of new unknown coefficients appeared; c_{19} parameterizes a possible shift between the appearance of the helixes, while c_{16}, c_{17} and c_{18} account for the differences among the origin points of the helixes, and finally c_{13}, c_{14} and c_{15} parameterizes the differences in amplitude.

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