Low-Energy Conformations of Isotactic Vinyl Chains Having Charged Side Chains of Equal Length

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ABSTRACT: Electrostatic energies have been calculated for regular conformations of isotactic vinyl polymers having charged side chains of equal length. For isotactic chains of acrylic acid, the conformation of minimum electrostatic energy for a long sequence of units is an extended helix having approximately $n = 5$ units per turn and an axial translation distance d of approximately 2.5 Å per unit. Similar results are obtained for ionized isotactic chains having side chains of greater length. Since the conformations of minimum *steric* energy of these chain molecules are helical sequences having $n \cong 3$ and $d \cong 2.1$ Å, the predicted conformation of these charged chains should be approximately intermediate to these two cases, with the effective dielectric constant of the medium being of crucial importance.

Circular dichroism spectra of charged poly-L-glutamic acid indicate[1] that this polypeptide chain assumes a left-handed, extended-helix conformation in the ionized state. An investigation[2] of the minimum energy conformations of ionized polypeptide chains, with respect to electrostatic as well as steric energy, substantiates this conclusion. This theoretical study shows that ionized poly-L-glutamic acid should consist of relatively short, extended, left-handed helical sequences having between $n = 2.6$ and 2.8 residues per turn (depending on the number of peptide units in the sequence) and an axial translation distance d between 3.4 and 3.1 Å per residue.

It is the purpose of the present study to determine the conformations of minimum electrostatic energy for perfectly isotactic vinyl chains bearing charges on the side chains. Such information, in conjunction with qualitative information on steric energies, should permit prediction of the preferred conformations of these chain molecules.

Theory

Chain Geometry. A schematic representation of a portion of an ionized, *d*-isotactic vinyl polymer having $(CH_2)_xCOO^-$ side chains is shown in Figure 1a. The electrostatic energy depends on the rotation angles ϕ and ψ, and on the conformation adopted by the side chain, which is shown in detail in Figure 1b for the case $x = 2$ and the side chain all-*trans*. As explained previously,[2] minimization of energy requires that the chain be helical and that all C–C bonds beyond C^α–C^β in the side chain remain *trans*. If the C^α–C^β is assumed to be in *trans* and *gauche* (±) states with equal frequency, then the charge, which we have associated with the C atom of the COO^- group, will be effectively located at point P. Thus polymers having side chains containing $x = 0$, 1, 2, 3, 4, and 6 CH_2 groups will have charges located 1.53, 2.11, 3.64, 4.21, 5.74, and 7.85 Å, respectively, from the C^α atom along the extension of the C^α–C^β bond. (The charges were located at this average position in order to make the calculations tractable. In actuality, the requirement of minimum electrostatic energy would require that each C^α–C^β bond assume the *same* rotational angle, the value of which would depend on the conformation of the chain backbone. This approximation is not involved for the case $x = 0$ and should have little effect in general for the relevant case of long sequence length, since the helix parameters are not very sensitive to small charges in the location of the charges.[2])

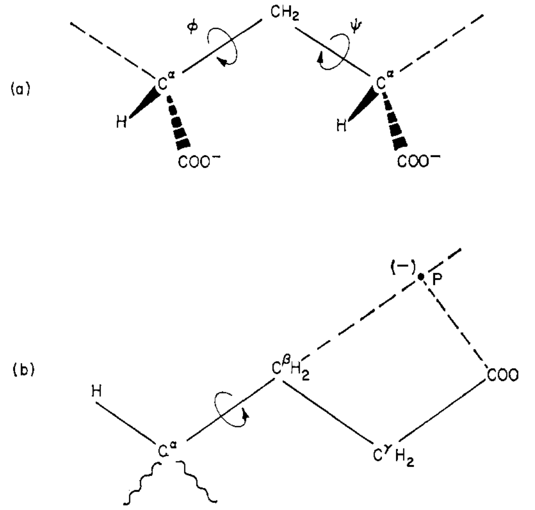

Figure 1. Structural features of the chain molecules: (a) section of a d vinyl chain bearing $(CH_2)_xCOO^-$ side chains; (b) detailed specification of the bonds in the side chain and location of the charge.

In the present calculations, carbon–carbon bond lengths of 1.53 Å were employed;[3] bond angles along the chain backbone were taken to be 112°,[4] and those along the side chain, 109.5°.[3]

Calculation of the Electrostatic Energy. The total electrostatic energy E of a sequence of N side chain

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Table I

Conformations of Minimum Electrostatic Energy for Isotactic Vinyl Chains with Charged Side Chains[a]

	x					
N	0	1	2	3	4	6
2	120, −120[b] 3.27	85, −155 2.73	65, −175 1.87	65, −175 1.66	60, −180 1.28	55, −185 0.97
3	95, −95 6.24	95, −95 5.27	100, −100 3.74	100, −105 3.37	95, −110 2.67	80, −120 2.07
4	70, −70 9.15	70, −75 7.85	75, −80 5.69	75, −80 5.16	80, −80 4.12	80, −80 3.22
6	85, −10 14.14	80, −15 12.60	45, −55 9.61	50, −50 8.82	50, −50 7.22	50, −55 5.77
8	85, 10 17.59	85, 10 15.91	80, 5 12.73	80, 5 11.87	75, 5 10.05	35, −40 8.31
16	70, 35 26.17	70, 35 24.24	65, 40 20.37	60, 40 19.27	55, 40 16.89	50, 40 14.52
32	65, 40 35.12	65, 40 33.03	55, 45 28.76	55, 40 27.51	50, 40 24.78	45, 40 21.99
64	55, 40 44.26					

[a] *N* is the number of units in the helix and *x* is the number of CH_2 groups in the side chain. [b] The first part (*a*, *b*) of each entry represents a *pair* of minima of identical coulombic energy at $\phi = a$, $\psi = b$ and $\phi = -b$, $\psi = -a$; the second, the coulombic energy at the minima, in kilocalories per mole of charges.

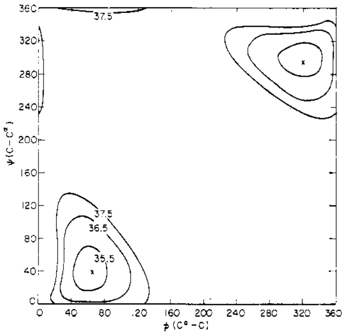

Figure 2. The coulombic energy as a function of bond rotation angles for a vinyl chain of $N = 32$ units each having a side chain with $x = 0$ CH_2 groups between the C^α atom and the charged carboxyl group. Energy contours are in kilocalories per mole of charges and energy minima are marked by ×.

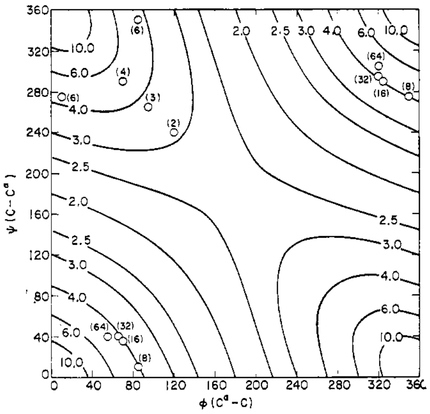

Figure 3. Locations of coulombic energy minima as a function of *N* for $x = 0$; values of *N* for each point are given in parentheses. Contours represent values of the helix parameter *n*, the number of units per turn.

charges of magnitude $|Q|$ in a medium of dielectric constant ϵ was taken to be the sum of terms

$$E_{ij} = Q^2/\epsilon R_{ij} \qquad (1)$$

for each pair of charges separated by the distance R_{ij}.

The magnitude of *Q* was taken to be the electronic charge. The dielectric constant ϵ, which is associated with the medium intervening between the charges (primarily the chain itself), was arbitrarily set equal to 10. Intercharge distances R_{ij} were calculated in the usual manner[5] by means of orthogonal transformation matrices. Since the conformation of minimum electrostatic energy of a long sequence of charges must be helical,[2] all pairs of skeletal bonds must adopt the same values of ϕ and ψ. (For reasons given previously,[2] this restriction should also be a reasonable approximation for a short helical sequence bounded by disruptions, *i.e.*, changes in the axial direction of the helix.)

In this manner, electrostatic energies were calculated at intervals of 20° in ϕ and ψ. Regions near minima in the energy were reexamined at 5° intervals, thus locating these minima to within a few degrees.

Results

A typical plot of electrostatic energy *vs.* ϕ and ψ, that for the case $x = 0$ [poly(acrylic acid)] and $N = 32$, is shown in Figure 2. Energy contours, located by linear interpolation, are given in kilocalories per mole of charges. Similar plots were used to locate energy minima for other values of *x* and *N*; the positions of these minima and the corresponding energies are given in Table I. Results for $x = 0$ are shown as a function of *N* in Figures 3 and 4. As is the case for steric energies[4,6] such plots have a symmetry axis defined by $\psi = -\phi$, and thus a minimum at $\phi = a$, $\psi = b$ is associated with another minimum of identical energy at $\phi = -b$, $\psi = -a$.

The regular structures which result when each C^α–C–C^α bond pair adopts that set of values of ϕ and ψ giving minimum electrostatic energy can be

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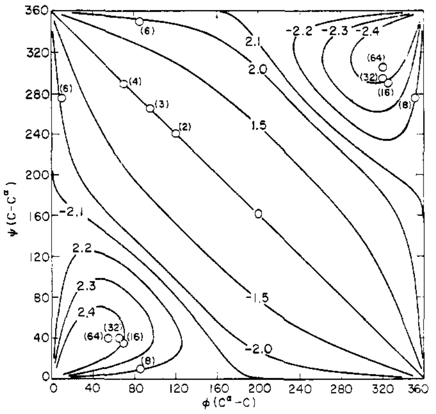

Figure 4. The points given in Figure 3 with superposed contours of the residue repeat distance d. Negative values of d are associated with left-handed helices.

characterized by the symmetry parameters n and d of the helix passing through *alternate* skeletal atoms. Values of n, calculated from the equation of Hughes and Lauer,[7] are incorporated in Figure 3, and values of d, from the equation of Miyazawa,[8] in Figure 4.

Discussion

In order to predict the most stable conformations of these ionized isotactic vinyl polymers, the *sum* of the coulombic and steric energies must be minimized. It is obvious that of the steric interactions of a linear side chain, those involving the group β to the C$^\alpha$ carbon atom, are of predominant importance, the length of the side chain being of minor effect. For the chains under consideration, this group is CH_2 except for the case $x = 0$, where it is COO. Calculations of steric energies of interaction involving COO groups have not been carried out, but two pieces of experimental evidence support the assumption that CH_2 and COO groups do not differ greatly in their effective size. Of the five isotactic acrylate polymers which have been studied in the crystalline state by X-ray diffraction analysis, all were found to adopt the same conformation (the Natta–Corradini 3_1 helix)[9] as that of crystalline poly(propylene).[10] The second pertinent fact involves highly isotactic poly(isopropyl acrylate) which, on the basis of Bovey's recent reinterpretation[11] of nmr spectra, typically contains approximately 5% of steric irregularities. For such a polymer of isopropyl acrylate, the random coil dimensions were found[12] to be in good agreement with the value[4] predicted for vinyl chains bearing $(CH_2)_xH$ side chains and having 5% of such irregularities.

Steric energies have been calculated for perfectly isotactic vinyl polymers with $(CH_2)_xH$ side chains.[4] For such polymers, helical disruptions generally require a large amount of energy[4] and thus must occur very infrequently at temperatures at which the molecules are chemically stable. (This is in contrast[5] to the case of most polypeptides, for which large regions of the conformational energy map are associated with relatively low energies.) Thus the regions of primary interest in Figures 3 and 4 are the locations (55, 40 and −40, −55°) corresponding to conformations of minimum coulombic energy in the limit of *long* helical sequences. As shown in these figures, this pair of conformations corresponds to right-handed and left-handed helices of otherwise identical symmetry. Furthermore, as is obvious from Table I, the locations of coulombic energy minima are not very sensitive to x for large values of the sequence length N and thus the following analysis should hold for chains having ionized side chains of any uniform length. In addition, in all cases the most appropriate value of the electrostatic energy per unit is that corresponding to the longest helical sequences.[2]

In the determination of the low energy conformations of these long helical sequences, a compromise must be struck between the conformation of lowest coulombic energy and that of lowest steric energy. For a perfectly isotactic d chain, the regions of minimum steric energy lie in the vicinity of 120, 0° and 0, −120°, giving rise to helices with symmetry parameters $n \leqq 3.0$ and $d \leqq \pm 2.1$ Å, where negative values of d refer to left-handed helices. (Because of the short-range character of the steric interactions, the locations of these minima are not dependent on the length of the helical sequence.) In the hypothetical case in which coulombic energies greatly predominate over steric energies, the low energy conformation would be extended helical sequences having approximately 5 units per turn and a significantly larger axial repeat distance of approximately ±2.5 Å. In the more realistic case where steric energies cannot be ignored, the relative magnitudes of the steric and coulombic energies would determine the values of n and d. Thus the effective dielectric constant of the intervening medium would assume crucial importance.[13]

Similar arguments apply, of course, to perfectly isotactic l chains. Locations of steric or coulombic energy minima for these chains may be obtained from the transformations $\phi(l) = \psi(d)$ and $\psi(l) = \phi(d)$.

In the case of chains having high, but not perfect isotacticity, the helical sequence length would be relatively short because of the occurrence of disruptions of low steric energy which are made possible by the presence of the structural irregularities.[4] As can be seen in Figures 3 and 4, coulombic effects would again favor highly extended helical arrangements, but with parameters closer to those of the 3_1 helix than would be the case for perfectly isotactic charged molecules.

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(13) There does not seem to be, at present, a reliable means of determining the value of this constant for a given system.