Macromolecules **1993,** *26,* 597–600

Molecular Dynamics Simulation of Substituted Conjugated Ionic Polyacetylenes

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Received August 19, 1991; Revised Manuscript Received August 20, 1992

ABSTRACT: Molecular dynamics simulations were carried out on the model systems of a recently reported new class of substituted polyacetylenes possessing extensive backbone conjugation and high charge densities. Our results show that for models of these polymers with charged pyridinium substituents and bromide counterions, the polymer backbones are highly extended, which is in complete contrast to uncharged, substituted polyacetylenes. For the trans–transoidal conformer the counterions located between the positively charged pyridine rings have strong electrostatic attractive interactions with aromatic hydrogen atoms. It is shown that the enhanced electrostatic interactions are mainly responsible for the observed planar extended geometry in these ionic polyacetylenes. It is concluded that the Coulomb interactions play a dominant role in the conformation and dynamics of such systems.

Introduction

Substituted polyacetylenes are of considerable interest because of their stability, solubility, and easy processability. These polymers, however, lack the high degree of conjugation displayed by unsubstituted polyacetylene, making them poor conductors of electricity.[1] Significant interest in substituted polyacetylenes derives from the work by Masuda and Higashimura.[1] The lack of conjugation in these polymers is attributed to steric factors introduced by the substituents, which force the double bonds in the polymer backbone to twist out of coplanarity. This is evidenced by their spectral characteristics in the UV region that are devoid of strong absorptions in the visible range.[1] Most substituted polyacetylenes form clear transparent or yellow solutions, in contrast to the shiny metallic films of insoluble polyacetylene itself.

Severity of the steric hindrance may in fact lead to a rigid polymer which is soluble, but whose backbone can access limited conformer states.[2] Clough et al. have carried out extensive molecular dynamic simulations for this class of substituted polyacetylenes.[2] Their calculations and experimental evidence[1] tend to support a chain conformation that is noncoplanar with several restricted conformer states as the substituents become bulkier. It was shown that as side groups increase in size and number (for example polypropyne, polybutyne, and poly(*tert*-butylacetylene)), the backbone conformations become increasingly restricted and nonplanar. For poly(1-(trimethylsilyl)-1-propyne), barriers to rotation about the backbone single bond were as large as 40 kcal/mol. It was concluded that the rigid noncoplanar conformation established during synthesis will be maintained.

More recently, Subramanyam and Blumstein described the synthesis and properties of a new family of substituted polyacetylenes displaying high degrees of conjugation and possessing high charge densities.[3,4] Their general structures are illustrated in Figure 1. These polyenes as synthesized are black solids and display large bathochromic shifts in the visible range of the electronic spectrum in comparison with the starting monomers. It is evident from the spectroscopic data that these polymers possess extensively conjugated backbones. This also confers on them a certain rigidity and brittleness. They are readily soluble and are stable up to temperatures of 250 °C analogous to polypropynes, whose structural characteristics have been previously reported.[1] Doping with either donors or acceptors resulted in substantially higher conductivities (10^{-2} S/cm) compared to the undoped state ($<10^{-9}$ S/cm), which is in support of a conjugated polyene backbone for these systems.

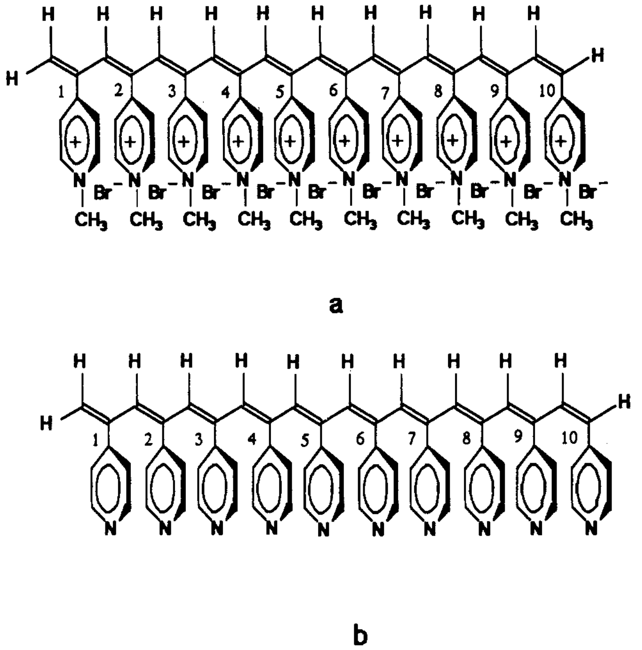

Figure 1. Substituted polyacetylene with 10 repeat units in the (a) charged and (b) uncharged states.

The presently described polymers are unique with respect to their long conjugation in spite of high degrees of substitution. The extensive conjugation observed in this polymer class is surprising. It is postulated that the arrangement of the charged species in the side group architecture and the dominant Coulomb interactions play an important role in dictating the backbone conformation and dynamics. In contrast, the dispersive–repulsive forces play a dominant role in dictating the nonplanar conformations in the uncharged substituted polyacetylenes investigated earlier.[2]

In an effort to determine the structural characteristics responsible for these phenomena, modeling studies were extended to a representative polymeric system.[2] In particular, it is of interest to understand the factors

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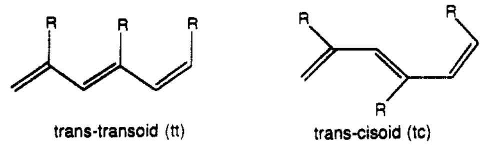
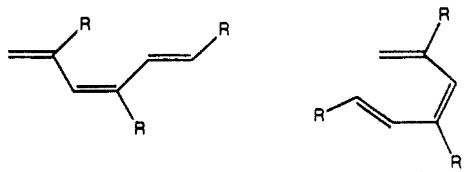


trans-transoid (tt)

trans-cisoid (tc)



cis-transoid (ct)

cis-cisoid (cc)

Figure 2. Various conformations of polyacetylene.

responsible for the coexistence of high degrees of substitution and extensive conjugation of the polymer chain, as well as the role played by the ionic charges in stabilization of such planar structures.

Calculations

Bond lengths, bond angles, force constants, and force field parameters employed in the present calculations were supplied by Polygen Corp. These parameters were used either as supplied or after a suitable modification, which was used in our earlier studies on dynamics simulation of substituted polyacetylenes.[2] Molecular mechanics and molecular dynamics results were obtained using Polygen Corp.'s QUANTA/CHARMm software on a Stellar GS1000 graphics computer in our Molecular Design Laboratory. The dynamics simulation employed the Verlet algorithm.[5,6]

The charged and uncharged forms of the representative polymeric system (including the end groups) used in the study are shown in Figure 1. Figure 2 shows the four possible conformations of each form that were considered for the calculations.

The calculated potential energy (E_{pot}), kinetic energy (E_{kin}), and total energy (E_{total}) are given by eqs 1, 2, and 3, respectively.

$$E_{\text{pot}} = E_{\text{bond length}} + E_{\text{bond angle}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der Waals}} \quad (1)$$

$$E_{\text{kin}} = \sum_{i=1}^{N} m_i \langle v_i^2 \rangle = {}^3/_2 NkT \quad (2)$$

$$E_{\text{total}} = E_{\text{pot}} + E_{\text{kin}} \quad (3)$$

where m_i and v_i are the mass and velocity of the ith atom, respectively, N is the total number of atoms in the system, and k is the Boltzmann constant.

The polymer models were created by ChemNote in QUANTA. Calculations were performed on a chain of ten repeat units. The charges of the atoms on the side group were reassigned based on the results from AM1[7] calculations on a model compound representing one repeat unit. The models underwent steepest descents energy minimization to remove bad contacts. The optimized structures were then heated to 300 K followed by an equilibration period. Heating was accomplished by initially assigning random velocities according to a Gaussian distribution appropriate for that low temperature and then running dynamics. The temperature was gradually increased by assigning greater random velocities to each atom at predetermined time intervals. During equilibration, the system was allowed to evolve spontaneously for a specific period of time by integrating the equations of motion until the average temperature and structure remained unchanged. Typically, runs were made with intervals of 50–100 ps and a step size of 1 fs. For the charged polymer, an additional 200 ps of dynamics simulation was carried out on the trans–transoid (tt), trans–cisoid (tc), cis–transoid (ct), and cis–cisoid (cc) conformers. Additionally, 2400 ps of simulation was performed on selected structures.

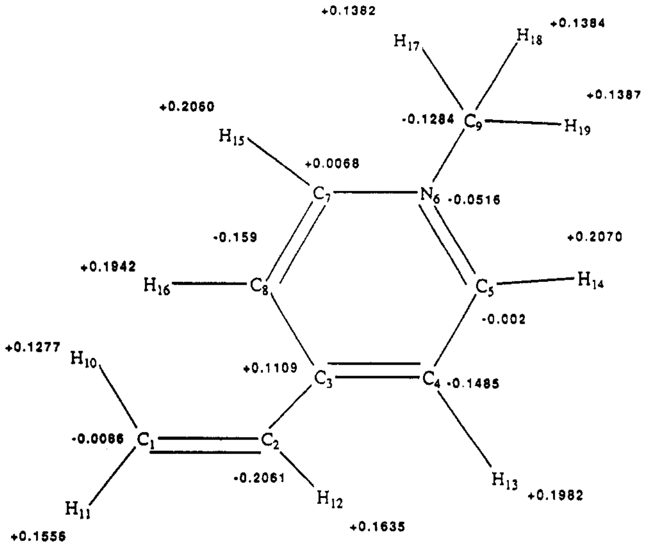


Figure 3. Charges on the individual atoms on the pyridinium ring calculated by AM1.

Results and Discussion

Charge Distribution. The AM1 method was used to calculate the charges on the individual atoms for the model compound representing one repeat unit (Figure 3). The hydrogen atoms bonded to the ring have the highest positive charge (0.2), while those of the N-methyl groups have a smaller value (0.14). A charge of −1 was assigned to each Br^- ion. Further, the results indicate that the substituent (ethyl or ethylene) at the para position with respect to nitrogen has little effect on the charge distribution in the ring and the N-methyl group. When defining the charge distribution for the polymer, two hydrogen atoms (one each from carbons C_1 and C_2) were deleted, which resulted in the polymer being negatively charged. To make the system electrically neutral, the charge on carbon C_2 in the resulting ethylene group was, therefore, changed arbitrarily from −0.2061 to +0.02.

The charge distribution as calculated by AM1 was extended to the ionic polyacetylene shown in Figure 1a containing ten repeat units for three conformations, namely, trans–transoid (tt), trans–cisoid (tc), and cis–transoid (ct). As expected, the cis–cisoid (cc) conformer had slightly higher energy, with the chain coiling back on itself, and is omitted in further discussions. The chain conformations of the tt and ct forms with the associated counterions after 300 ps of dynamics simulation is shown in Figure 4. The Br^- anions that were arbitrarily placed in the plane of the polyene backbone prior to the simulation underwent a positional change during the dynamics simulation, as is evident from the figure. The location of the anion prior to and after simulation for the ct conformer is illustrated in Figure 5.

In the tt conformer, the Br^- ions underwent a positional change (with respect to their initial placement) such that they are displaced from the plane of the polyene backbone. They are closely associated with aromatic ring hydrogens of adjacent pyridinium rings (Figure 4a). There are 24 close Br^-–H interaction pairs whose average distance is less than 3 Å. Twenty of these are from Br^-–H_{aromatic} pairs

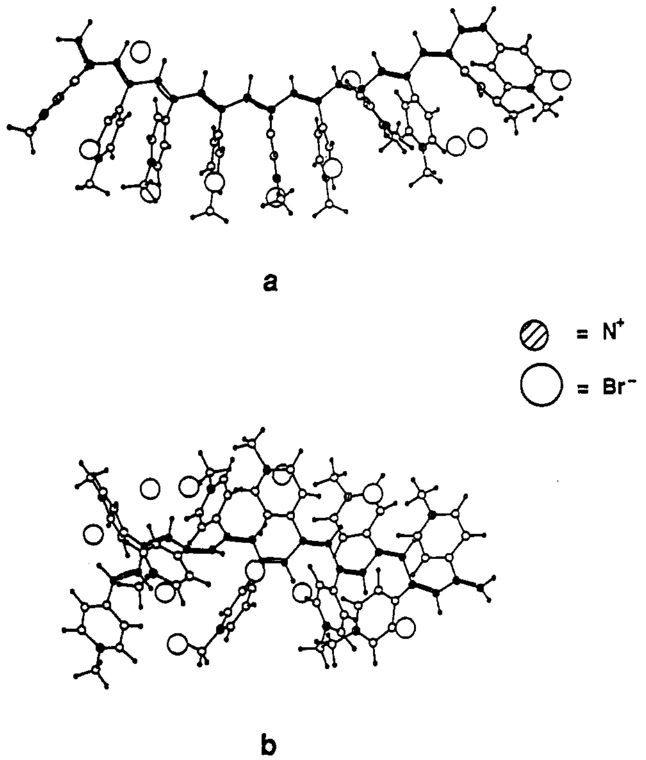


Figure 4. Chain conformations of (a) tt and (b) ct conformers with associated counterions after 300-ps dynamics simulation.

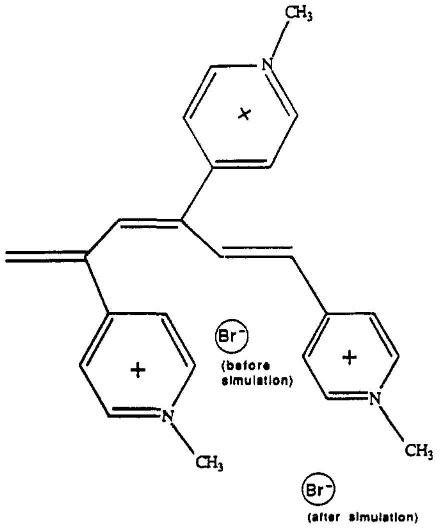


Figure 5. Position of Br^- ion with respect to the pyridinium rings before and after simulation for the ct conformer.

and four are from Br^-–$H_{methylene}$ pairs. There are no interaction pairs involving Br^-–H_{methyl} pairs; this is attributed to the repulsion between the anions that would occur if they were to be spatially situated for such an interaction. In the ct conformer, the Br^- anions were also displaced from their initially assigned position after dynamics simulation. However, in contrast to the tt conformer, they are located closer to the *N*-methyl groups for the ct conformer (Figure 4b), resulting in strong attraction with the methyl hydrogens. It was also observed that the Br^- and the methyl hydrogens exhibit strongly correlated motions. (The distance between two methyl groups on adjacent pyridinium rings was calculated to be 6.3 Å.)

It was observed that the average distance between a Br^- ion and the H atoms on the pyridine rings (numbered 13, 14, 15, and 16 in Figure 3) is in the range 2.63–2.91 Å for all the conformers being discussed, with fluctuations in the range 0.13–0.23 Å. No significant fluctuations in the backbone rotation were observed after 2400 ps of simulation performed on selected conformers.

Simulations were also carried out on the corresponding polymeric system on the corresponding uncharged polymer, i.e., with the charges "turned off", as well as a charged system with excess Br^- ions (20 Br^- for 10 repeat units of the polymer). The latter is analogous to a doped system. The calculated energies and the various components of these energies are listed in Table I. It is evident from the large increase in $E_{electrostatic}$ that attractive electrostatic interactions increase substantially upon introduction of charge compared to the uncharged system. The charged side groups with the associated counterions in the ionic polyacetylene, therefore, play a significant role in stabilizing an extended, planar backbone conformation in such systems. The data also suggest that introduction of excess Br^- ions leads to an additional increase in the electrostatic component, indicating greater stabilization of such planar conformations in doped systems. The irreversible dopant uptake of, e.g., iodine observed for these polymers[8] supports this inference.

Chain Conformation. The computed energies listed in Table I have been used for chain conformation comparisons for the tt, ct, and tc conformers. The average calculated energies for all three conformers were similar and were within a difference of only ~5 kcal/mol, per repeat unit. The average fluctuation of the dihedral angles and the rotations of the backbone single and double bonds from planarity are shown in Table II. It is observed that for each of these structures, the deviation of the backbone conformation from planarity is not significantly large. Also, the average deviation of the dihedral angle from planarity for the backbone single bond is smaller for the charged polymer than that for the unchanged one, which is indicative of an additional stabilization of the planar structure in the charged polymer. This deviation is also smaller than those calculated for polyacetylenes substituted with uncharged bulky side groups.[2]

An alternative method was also employed to confirm the extended chain structure in these ionic polyacetylenes. It involved an estimation of the end-to-end distance of the chains of finite length (ten repeat units). The end-to-end distance is defined by the length of the straight line joining the mass centers of the two end groups of the model polymers. This distance was estimated to be between 19 and 21 Å for all three conformers that were investigated, which is indicative of an extended conformation. This observation is also consistent with the spectral characteristics of these polymers, which confirm an extended backbone π conjugation.

The relative distances and orientations of the side group pyridinium rings with respect to each other in these ionic polyacetylenes was also estimated. Such estimates were obtained for both the charged and uncharged polyene (i.e., with the charges "turned off") and are listed in Table III. It is evident that the distances between the mass centers of any two neighboring rings generally increase when the charges are "turned off", since the steric factors force them away from one another. This results in a loss of planarity of the polymer backbone with a concomitant loss in chain extension.

The average dihedral angles between the backbone and the side group pyridinium rings are approximately 19, 32, and 57° (from 90°) for the tt, ct, and tc conformers, respectively, where 90° indicates that the ring plane is orthogonal to the backbone. The simulations suggest planar stacking of the aromatic side groups for the tt conformer (Figure 4a). The substantially larger dihedral

Table I
Components of the Potential Energy[a] of the Model Systems with 10 Repeat Units

model type (tt)	E_{total}	E_{elec}	E_{vdW}	E_{bond}	E_{angle}	E_{dihed}	E_{impr}
uncharged model	167	−15	28	31	44	46	33
charged model with 10 Br^-	26	−183	22	33	61	54	39
charged model with 20 Br^-	−126	−323	11	33	61	57	35

[a] In kcal/mol per repeat unit.

Table II
Average Backbone Rotation and Dihedral Angle Fluctuation for Various Conformers

	av backbone rotation (deg)				av dihedral angle fluct (deg)			
	single bond		double bond		single bond		double bond	
conf	chr	unchr	chr	unchr	chr	unchr	chr	unchr
tt	6.9	21.2	3.6	8.2	7.3	8.2	5.0	5.2
tc	18.5	13.8	9.3	7.5	6.9	9.1	4.7	5.2
ct	20.6	30.3	7.2	5.2	8.2	12.8	5.2	5.9

Table III
Distance between Mass Centers of Pyridine Rings for Charged and Uncharged States

		dist between mass centers (Å)	
conf	ring no.[a]	chr	unchr
tt	1 and 2	3.26	3.97
	2 and 3	3.53	4.87
	3 and 4	3.29	4.91
	4 and 5	3.53	5.15
	5 and 6	3.28	5.07
	6 and 7	3.54	4.98
	7 and 8	3.18	3.67
tc	1 and 2	5.03	6.28
	2 and 3	5.44	5.86
	3 and 4	5.61	6.09
	4 and 5	4.27	5.96
	5 and 6	3.47	5.92
	6 and 7	4.30	5.98
	7 and 8	4.72	6.29
ct	1 and 2	5.63	6.79
	2 and 3	4.90	6.34
	3 and 4	4.93	6.01
	4 and 5	5.48	6.27
	4 and 6	4.52	4.85
	6 and 8	3.97	4.91
	7 and 8	5.28	6.08

[a] The ring numbers correspond to the numbering scheme indicated in Figure 1.

angle for the tc model (i.e., 57° from orthogonal) is consistent with larger deviations of the backbone from planarity. The fact that the charged polymer model invesigated in this study displays a long-wavelength fluorescence band in its emission spectrum[9] due to intramolecular excimer formation between the pendant aromatic rings is indicative that the tt conformation is favored over the ct and tc conformers in these ionic polyacetylenes.

Conclusions

The present study shows that the preferred chain conformations of substituted polyacetylenes with ionic side groups that are associated with counterions are planar and highly extended. They resemble unsubstituted polyacetylene in this regard but are in complete contrast to their counterparts where the substituents are uncharged and bulky. In unsubstituted polyacetylene, the backbone π conjugation plays an important role in dictating the planar extended structure as the preferred conformation. In uncharged substituted polyacetylenes, the steric interaction of the side groups plays a dominant role in dictating a rigid but nonplanar backbone conformation without π conjugation. In the presently described systems, the electrostatic attractive interactions between the charged side groups and the counterions override the steric repulsive interactions between side groups, resulting in an extended and planar geometry for the backbone.

Acknowledgment. X.-F.S., A.B., and S.S. acknowledge partial support from the National Science Foundation's Polymers Program (Grant DMR-8823084) and the Office of Naval Research. S.K.T. acknowledges partial support from the Office of Naval Research. We also gratefully acknowledge support from Polygen Corp.

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