Structural Defects in Polythiophenes: Monte Carlo Simulations with Quantum Mechanical Growth Probabilities

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Thermodynamical stability of all possible isomers of small oligomers of thiophene including branched forms is studied by ab initio calculations. The relative energetics of isomers is fitted to an additive potential function. The probability of various growth mechanisms for polythiophene can be understood in terms of Boltzmann factors derived from this potential function. A Monte Carlo type simulation is employed for growing in a canonical ensemble of polythiophenes. The conformational properties of such grown polymers are analyzed in terms of temperature and the length of the chain. Specifically, the extent of mislinkages such as $\alpha-\beta$ bondings and the branching ratio is discussed. The results are compared to those obtained from polypyrrole for ab initio and density functional theory generated potential functions. In polythiophene, 10% branching is predicted at room temperatures whereas similar figures for polypyrrole is about 20%.

I. Introduction

There has been an avalanching interest in developing new materials with relatively high density and durability of plastics and the conductivity of metals.[1,2] There are a number of conjugated polymers, such as polyacetylene (PA), polypyrrole (PPy), polythiophene (PT), and polyphenylenevinyledine (PPV), which seem to present an answer to such a need. In their doped forms the conductivities in the order of >1 S/cm are reported. The doping process involves exposure of the polymer to electron donor (such as alkali metals) or electron acceptors (such as I_2 or AsF_5), and it is expected that the charge-transfer (or electron excitation) processes result in significant local modifications (relaxations) of the chain geometry.

The basic problems in obtaining reliable information on the structure of conjugated polymers are their low solubility in common organic solvents and the difficulties in growing high quality crystals. In fact in cases such as polypyrrole, there are very few scant data obtained from various NMR (especially with solid state ^{15}N NMR) experiments which could provide some clues. In addition, the electrochemically or chemically prepared samples display a large variety of structural properties depending heavily on the method of preparation. The commonly accepted structures for polypyrroles and polythiophenes are linear chains composed of $\alpha-\alpha$ (or alternatively $2-2'$) linkages where the heteroatoms lie in antiposition. The planarity of rings is assumed for higher conjugation lengths which is thought to provide the basic mechanism for the conductance. However, it is expected that polymers will also have a certain amount of defects due to the nonideal bondings involving β carbons.[3] Even though polypyrrole is historically the first conducting polymer of five-membered rings,[4] lately the attention has turned mostly to polythiophene and its oligomers due to their relatively higher environmental stability, processability, and the ease of modulation of their electronic properties upon substitutions of the backbone. Nowadays oligothiophenes are used in electronic or opto-electronic devices such as organic transistors, light-emitting diodes, or spatial light modulators.[5]

Oligothiophenes display more uniform structural properties compared to polythiophenes[6] and usually show enhanced optical and electrical properties; hence, they could be used in molecular electronics applications and optical devices. Alkyl-oligothiophenes are soluble if the alkyl side chains are sufficiently long, i.e., longer than butyl group, making alkyl-oligothiophenes processable from solution. The similarity of both geometrical and electronic properties of oligomers and polymers of thiophene may be used to obtain reliable information related to the structures of polymers.

A great deal of computational work has appeared on the structure of oligomers of thiophene in unsubstituted and substituted forms.[7] In the pioneering study of PT,[8] ab initio Hartree−Fock (HF) and valence electron hamiltonian (VEH) calculations on dimers and polymer chains are given where the evolution of electronic properties such as ionization potential, bandgap, and width of highest occupied bands and C−C bond length between rings are examined as functions of torsional angle between consecutive rings. This investigation is motivated by the fact that many derivatives of these compounds have substituents that lead increase of the torsional angle between adjacent rings, as a result of steric interactions. As expected, on going from a coplanar to a perpendicular conformation, the ionization potential and the bandgap values increase and the width of the highest occupied bands decreases. This makes it more difficult to ionize or reduce the polymer chains and can result in achieving lower maximum conductivities on doping. However, it is found that the ionization potential value for a 40° torsion angle is about 0.4 eV larger than the coplanar conformation value. Therefore, substituents that lead to torsional

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TABLE 1: SCF Energy and Geometrical Parameters of Thiophene[a]

basis	energy	$R(\mathrm{S{-}C_\alpha})$	$R(\mathrm{C_\alpha{-}C_\beta})$	$R(\mathrm{C_\beta{-}C_\beta})$	$\mathrm{S{-}C_\alpha{-}C_\beta}$	$\mathrm{C_\alpha{-}C_\beta{-}C_\beta}$	$\mathrm{C_\alpha{-}S{-}C_\alpha}$
experimental[6]		1.723	1.36	1.43	111.62	112.55	91.67
4-31	−550.603 460 7	1.7964	1.3362	1.4431	111.61	113.81	89.16
6-31	−551.190 757 8	1.7903	1.3426	1.4448	111.73	113.57	89.40
6-31(d)	−551.290 351 7	1.7257	1.3452	1.4369	111.81	112.54	91.30
6-31(d,p)	−551.297 791 1	1.7252	1.3451	1.4366	111.80	112.54	91.32
6-311	−551.236 893 4	1.7892	1.3405	1.4445	111.71	113.58	89.42
6-311(d)	−551.339 224 1	1.7246	1.3445	1.4358	111.87	112.51	91.24
6-311(d,p)	−551.347 117 2	1.7242	1.3448	1.4355	111.82	112.54	91.28
6-311(2d,p)	−551.355 935 6	1.7214	1.3416	1.4320	111.70	112.61	91.38
6-311(df,p)	−551.356 907 3	1.7213	1.3432	1.4331	111.79	112.54	91.34
6-311(3d,p)	−551.309 671 3	1.7168	1.3458	1.4339	111.77	112.44	91.58
6-311(2df,p)	−551.366 703 2	1.7161	1.3423	1.4306	111.69	112.54	91.54
6-311(3df,p)	−551.370 187 2	1.7123	1.3435	1.4303	111.69	112.47	91.68
6-311(d,pd)	−551.349 465 6	1.7239	1.3445.	1.4350	111.79	112.54	91.34
6-311(2d,pd)	−551.356 930 3	1.7215	1.3416	1.4322	111.70	112.61	91.38
6-311(df,pd)	−551.357 794 3	1.7215	1.3431	1.4331	111.80	112.54	91.32
6-311(2df,pd)	−551.367 263 9	1.7161	1.3422	1.4305	111.69	112.54	91.54
6-311(3df,pd)	−551.371 039 0	1.7123	1.3433	1.4301	111.70	112.46	91.68

[a] The energy is in au, bond lengths are in angstroms, and angles are in degrees.

angles between consecutive rings smaller than 40° are quite acceptable.[9] The electron diffraction data on bithiophene also shows that the torsional angle to be around either 148° or 36°,[10] and the X-ray study at 133 K has shown that the structure is planar.[11] The ab initio calculations with varying sophistications have also dealt with the torsional angle problem. The majority of these results show that indeed the minimum energy conformation is the twisted form with angles 145°. SCF and density functional theory (DFT) result in slight differences in bond lengths and valence angles. Additional caution is required when one deals with DFT on these systems as it is recently pointed out that the DFT methodology is inappropriate to study torsional motion in conjugated polymers.[12]

The majority of the theoretical work on PT deals with geometry and vibrational spectra of isolated ideal $\alpha{-}\alpha$ linked oligomers. Very few calculations are reported on simulations or crystal packing of oligomers or polymers. The unusual linkages which result in shortening of the conjugation length and branching are mostly analyzed in bithiophene. We have previously reported semiempirical calculations on all possible isomers of pyrrole[13] and thiophene oligomers[14] up to tetramers to understand the thermodynamical stability of mislinkages.

Here we would like to present a combination of ab initio quantum mechanical results and a Monte Carlo type growth approach. We have previously applied this method to PPy[15,16] and have reported that at room temperature up to 20% branching is thermodynamically allowed. In this study we would like to present results on polythiophene and compare to those obtained for PPy. The energetics obtained from ab initio calculations on all possible bonding types in oligomers is used to form a basis which can guide the growth of a macromolecule. Employing this basis we are able to deduce the relative abundance of defects, such as $\alpha{-}\beta$ type bondings and various branching possibilities.

II. Energetics of Oligomers

Ab initio calculations of molecular structure have been carried out with Gaussian 94[17] and Gaussian 98.[18] The geometrical parameters are fully optimized so that nonplanar structures can also be obtained. As it will be discussed later, the idealized planar structures do not allow branching due to large steric hindrances. Electronic structure of the monomer has been discussed in detail previously.[19] We did a similar study of the effects the basis sets on the geometrical parameters for the purpose of obtaining the most cost-effective basis set to be used in larger oligomers. We started by optimizing the geometry of the monomer with a large number of basis sets starting with a small split valence set of 4-31G to a large set of 6-311(3df,pd) with d and f polarization functions on heavy atoms and p and d on hydrogens. It is observed that basis sets without d functions on heavy atoms result in too long S−C bonds. Similarly, the CCC angles are found to be 1.5° too large compared to experimental values. Once the d functions are employed, then a relatively small basis set of 6-31(d) is found to give reasonably correct geometrical parameters. It has also been reported that this basis set is sufficiently well balanced for the calculation of rotational barriers of bithiophene with various levels of theory.[12] DFT calculations are carried out with three-parameter hybrid method using the LYP correlation functional of Becke.[20] Calculations with the same basis sets provide parallel results except that both C−C bond lengths agree with experiment values better than those obtained from SCF. A summary of these results is given in Tables 1 and 2.

For three linkage types of bithiophene, a smaller group of basis sets is tried. The experimental geometry is known for $\alpha{-}\alpha$ (2−2′) bithiophene from electron diffraction data[10] and in the same report it is emphasized that d orbitals on heavy atoms must be included for predicting correct conformations. The rotational potential has two minima where the anti-like conformation is the global minimum. Experimentally these minima are observed at 36° and 148°. In semiempirical calculations these minima have been found at 30° and 150°, respectively.[21] More detailed quantum mechanical calculations result in a large range of structures where the syn-like conformation is found to vary between 22−48° and anti-like at 138−161°.[12] The transition state is observed at 90°, and the barrier to anti-like structure is 1.7−2.9 kcal/mol and to syn-like structure is 1.0 to 2.1 kcal/mol. NMR experiments show that the barrier is 5.0 ∓ 2.0 kcal/mol[22,23] and the energy difference between two minima is proposed to be 0.2 kcal/mol. In Figure 1 we present our rotational potential function obtained from 6-31(d) basis set in comparison with that of bipyrrole. We calculate the relative stability of anti-like conformation as 0.7 kcal/mol and the barrier to be 1.7 kcal/mol. Zero-point corrections lower the energy barrier by 0.05 kcal/mol. The geometrical parameters and ground state energy from various basis sets are given in Tables 3 and 4, where it is seen that 6-31(d) basis is sufficient for obtaining reliable geometrical information.

TABLE 2: DFT Energy and Geometrical Parameters of Thiophene[a]

basis	energy	R(S−C$_\alpha$)	R(C$_\alpha$−C$_\beta$)	R(C$_\beta$−C$_\beta$)	S−C$_\alpha$−C$_\beta$	C$_\alpha$−C$_\beta$−C$_\beta$	C$_\alpha$−S−C$_\alpha$
4-31	−552.345 710 6	1.8048	1.3584	1.4375	111.48	113.87	89.3
6-31	−552.931 749 6	1.8035	1.3642	1.4402	111.54	113.18	89.14
6-31(d)	−553.002 633 2	1.7361	1.3673	1.4298	111.50	112.75	91.50
6-31(d,p)	−553.009 304 3	1.7357	1.3672	1.4294	111.49	112.75	91.52
6-311	−552.991 729	1.8057	1.3605	1.4387	111.55	113.82	89.26
6-311(d)	−553.061 979 9	1.7338	1.3647	1.4270	111.59	112.72	91.38
6-311(d,p)	−553.069 687 7	1.7336	1.3647	1.4269	111.55	112.74	91.42
6-311(2d,p)	−553.077 471 7	1.7290	1.3623	1.4239	111.45	112.77	91.56
6-311(df,p)	−553.078 630 3	1.7309	1.3624	1.4242	111.54	112.75	91.42
6-311(3d,p)	−553.081 339 4	1.7227	1.3650	1.4241	111.47	112.63	91.80
6-311(2df,p)	−553.086 338 8	1.7237	1.3625	1.4222	111.44	112.70	91.72
6-311(3df,p)	−553.090 118 0	1.7193	1.3636	1.4213	111.44	112.63	91.86
6-311(d,pd)	−553.072 009 8	1.7332	1.3644	1.4264	111.52	112.76	91.44
6-311(2d,pd)	−553.078 523	1.7291	1.3622	1.4239	111.44	112.78	91.56
6-311(df,pd)	−553.079 858 7	1.7308	1.3623	1.4241	111.55	112.75	91.40
6-311(2df,pd)	−553.087 170 1	1.7237	1.3624	1.4220	111.45	112.70	91.70
6-311(3df,pd)	−553.091 481 4	1.7192	1.3634	1.4212	111.45	112.63	91.84

[a] The energy is in au, bond lengths are in angstroms, and angles are in degrees.

TABLE 3: SCF Energy and Bond Lengths of Bithiophene[a]

basis	energy	R(S−C$_\alpha$)	R(S−C$_\alpha$)	R(C$_\alpha$−C$_\beta$)	R(C$_\alpha$−C$_\beta$)	R(C$_\beta$−C$_\beta$)	R(T−T)
experimental[6]		1.7330	1.7190	1.3700	1.3630	1.4520	1.4560
4-31	−1100.060 859 0	1.8130	1.7943	1.3433	1.3355	1.4372	1.4400
6-31	−1101.233 956 8	1.8092	1.7880	1.3493	1.3414	1.4395	1.4471
6-31(d)	−1101.430 485 6	1.7392	1.7250	1.3515	1.3444	1.4336	1.4647
6-31(d,p)	−1101.441 699 9	1.7389	1.7247	1.3515	1.3443	1.4334	1.4647
6-311	−1101.323 900 9	1.0857	1.7872	1.3473	1.3396	1.4394	1.4494
6-311(d)	−1101.526 057 3	1.7363	1.7243	1.3505	1.3439	1.4328	1.4655
6-311(d,p)	−1101.537 843 5	1.7359	1.7241	1.3506	1.3439	1.4325	1.4655
6-311(2d,p)	−1101.556 344 5	1.7330	1.7216	1.3473	1.3407	1.4292	1.4617
6-311(df,p)	−1101.558 010 8	1.7331	1.7214	1.3491	1.3423	1.4300	1.4362

[a] The energy is in au; bond lengths are in Å.

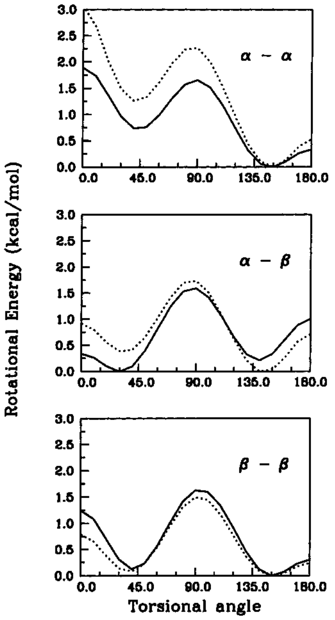

Figure 1. Rotational potentials for three isomers of bipyrrole (dotted lines) and bithiophene (solid lines).

There are very few scant information on structural defects in PT. Previously we have reported AM1 results where all three linkage types for bithiophene are energetically almost degenerate.[14] The effects of such mislinkages on the conjugation length have been discussed within the tight bonding approach, and it has been reported that such defects results in shorter conjugation lengths and modified band gaps as expected.[24] We also recently reported that introduction of α−β linkages hinder the formation and mobility of polarons in oligothiophenes.[25]

TABLE 4: Angular Parameters of Bithiophene[a]

basis	C$_\alpha$−S−C$_\alpha$	S−C$_\alpha$−C$_\beta$	C$_\alpha$−C$_\beta$−C$_\beta$	torsion
experimental[6]	91.70	111.80	111.90	148.00
4-31	89.49	110.32	114.62	169.87
6-31	89.74	110.35	114.43	169.89
6-31(d)	91.58	110.76	113.19	147.31
6-31(d,p)	91.58	110.77	113.17	147.50
6-311	89.78	110.41	114.37	155.75
6-311(d)	91.56	110.84	113.16	143.78
6-311(d,p)	91.58	110.85	113.14	144.61
6-311(2d,p)	91.64	110.73	113.24	143.98
6-311(df,p)	91.64	110.78	113.18	146.77

[a] In degrees.

In order to calculate the extent of mislinkages and branching, a through study of various isomers of oligothiophenes must be carried out. The relative stability of three isomers of 2T again with various basis sets are given in Table 5. Similarly the plots of rotational potentials for α−β and β−β bithiophenes are plotted in Figure 1. The anti-like positions of heteroatoms are favored as assumed except that in α−β bithiophene. Rotational barriers of all three isomers change only slightly going from pyrrole to thiophene. A detailed discussion of the rotational motion is given by Karpfen,[12] and we have also reported the coefficients of rotational potentials for three isomers of bipyrrole.[15] Similar to AM1 results, the ground state energy of three isomers in gas phase are very close to each other if d orbitals are included. Even for DFT calculations where the α−α bithiophene has the lowest energy, the relative stability is no more than 0.5 kcal/mol. This is remarkably different than that of pyrrole, where α−α bipyrrole is always the most stable one to the degree of 1.5 to 2.0 kcal/mol.[15]

On the basis of this extensive set of calculations, we decided to proceed with 6-31(d) basis for 3T, 4T, and 5T.

TABLE 5: SCF and DFT Ground State Energy(au) of Three Isomers of Bithiophene and Relative Stabilities (kcal/mol)

basis	$E_{\alpha\alpha}$	$E_{\alpha\beta}$	$E_{\beta\beta}$	$E_{\alpha\beta}-E_{\alpha\alpha}$	$E_{\beta\beta}-E_{\alpha\beta}$	$E_{\beta\beta}-E_{\alpha\alpha}$
			SCF			
4-31	−1100.060 859 0	−1100.058 252 8	−1100.056 373 3	1.635	1.179	2.815
6-31	−1101.233 956 8	−1101.231 718 9	−1101.230 375 7	1.404	0.843	2.247
6-31(d)	−1101.430 485 6	−1101.430 343 3	−1101.430 563 9	0.089	−0.138	−0.049
6-31(d,p)	−1101.441 699 9	−1101.441 534 1	−1101.441 708 6	0.104	−0.110	−0.005
6-311	−1101.323 900 9	−1101.322 357 5	−1101.321 043 0	0.969	0.825	1.793
6-311(d)	−1101.526 057 3	−1101.525 927 8	−1101.525 987 0	0.081	−0.037	0.044
6-311(d,p)	−1101.537 843 5	−1101.537 754 2	−1101.537 900 9	0.056	−0.092	−0.036
6-311(2d,p)	−1101.556 344 5	−1101.556 259 3	−1101.556 471 8	0.053	−0.133	−0.080
6-311(df,p)	−1101.558 010 8	−1101.557 803 2	−1101.557 925 9	0.130	−0.077	0.053
			DFT			
4-31	−1103.505 761 8	−1103.502 245 0	−1103.500 265 7	2.207	1.242	3.449
6-31	−1104.676 450 2	−1104.673 309 5	−1104.671 782 4	1.971	0.958	2.929
6-31(d)	−1104.816 713 0	−1104.815 828 5	−1104.815 671 4	0.555	0.099	0.654
6-31(d,p)	−1104.826 562 2	−1104.825 794 7	−1104.825 566 4	0.482	0.143	0.625
6-311	−1104.792 514 0	−1104.789 598 0	−1104.787 692 0	1.830	1.196	3.026
6-311(d)	−1104.931 120 9	−1104.930 653 6	−1104.930 159 0	0.293	0.310	0.604
6-311(d,p)	−1104.943 189 3	−1104.942 161 6	−1104.941 682 5	0.645	0.301	0.946

TABLE 6: Ground State Energy(au) of Oligothiophenes and Relative Stability (kcal/mol) with Respect to Linear Forms: Linear Trimers

oligomer type (3T)	energy	stability
αα−αα	−1651.57 0870 3	
αα−αβ	−1651.570 717 7	0.0958
αα−βα	−1651.570 259 8	0.3831
αα−ββ	−1651.570 644 2	0.1419
αβ−αβ	−1651.570 342 8	0.3310
αβ−βα	−1651.566 198 2	2.9318
αβ−ββ	−1651.566 981 6	2.4402
βα−αβ	−1651.570 834 5	0.0225
βα−ββ	−1651.570 462 7	0.2558
ββ−ββ	−1651.566 504 4	2.7396

There are 10 distinct bonding possibilities for 3T. Ground state energy of these isomers are calculated with optimization of all geometrical parameters so that nonlinear structures are obtained. For 4T the number of isomers is 35 for the linear form and 12 for the branched form. In the case of 5T, we only calculated the fully linear α−α bonded form and the branched structures where all carbons on the central ring are connected to another thiophene(10 isomers can be obtained according to the linkage types). The ground state energy and relative stability of 67 such structures are given in Tables 6−9. In a majority of these cases, there exists a number of local minima according to the syn-like and anti-like positions of heteroatoms and a through search of these minima are carried out to find the global minimum of each structure. As it will be discussed in the next section, these structures are sufficient to generate thermodynamical growth probabilities for a given polymer.

From the energetics of these oligomers, we have found out that all structures are strongly nonplanar. Mislinkages introduce kinks and branch formation results in a variety of deviations from linearity (Figure 2). Even though the structures in gas phase can be considerably different than the solid phase, the energetics and geometrical structures of these oligomers should be sufficient to be used in determining the morphology of polymer chains.

In order to be able to predict the probability of various growth mechanisms, we fit an empirical growth function to the relative stability of isomers with respect to the fully linear α−α isomer. There are several functional forms which could be used for this purpose. We have found out that a partitioning of the energy in terms of ring types worked very well in case of pyrrole.[15,16] In a polymer consisting of five-membered rings, each ring can be labeled as one of the eight distinct types according to the number of positions used in bonding to other rings. Monomers at the ends of chains are either of type α if they are connected to the backbone from 2 or 5 position or type β if 3 or 4 is used. Similarly rings which are in the backbone (or one of the side chains) are labeled as αα, αβ, or ββ. If a ring is growing a branch, then it is either type ααβ or an αββ. Finally, there is one more ring type where all four positions are attached to other

TABLE 7: Stability of Linear Tetramers

oligomer type (linear 4T)	energy	stability	oligomer type	energy	stability
αα−αα−αα	−2201.711 239 6		αα−αα−αβ	−2201.711 101 4	0.0867
αα−αα−βα	−2201.710 987 4	0.1583	αα−αα−ββ	−2201.710 858 7	0.2390
αα−αβ−αα	−2201.710 625 8	0.3852	αα−αβ−αβ	−2201.710 713 2	0.3303
αα−αβ−βα	−2201.707 188 5	2.5421	αα−αβ−ββ	−2201.708 435 8	1.7594
αα−βα−αβ	−2201.710 461 3	0.4884	αα−βα−βα	−2201.710 264 9	0.6116
αα−βα−ββ	−2201.710 451 5	0.4945	αα−ββ−αα	−2201.710 703 0	0.3367
αα−ββ−αβ	−2201.710 680 2	0.3510	αα−ββ−βα	−2201.706 411 1	3.0299
αα−ββ−ββ	−2201.708 069 8	1.9891	αβ−αα−αβ	−2201.710 887 1	0.2212
αβ−αα−βα	−2201.710 396 7	0.5289	αβ−αα−ββ	−2201.710 368 7	0.5465
αβ−αβ−αβ	−2201.710 330 3	0.5706	αβ−αβ−βα	−2201.706 648 5	2.8810
αβ−αβ−ββ	−2201.707 931 8	2.0757	αβ−βα−αβ	−2201.706 809 9	2.7797
αβ−βα−ββ	−2201.702 718 9	5.3468	αβ−ββ−αβ	−2201.708 311 4	1.8375
αβ−ββ−βα	−2201.702 442 0	5.5206	αβ−ββ−ββ	−2201.702 718 9	5.3468
βα−αα−ββ	−2201.710 726 4	0.3220	βα−αβ−αβ	−2201.710 828 2	0.2582
βα−αβ−ββ	−2201.708 140 2	1.9449	βα−βα−ββ	−2201.710 336 3	0.5668
βα−ββ−αβ	−2201.710 718 2	0.3272	βα−ββ−ββ	−2201.707 703 9	2.2187
ββ−αα−ββ	−2201.710 755 3	0.3039	ββ−αβ−ββ	−2201.707 039 7	2.6355
ββ−ββ−ββ	−2201.704 072 8	4.4972			

TABLE 8: Stability of Branched Tetramers

oligomer type (branched 4T)	energy	stability
αα–αα(βα)	−2201.706 447 8	3.0069
αα–αα(ββ)	−2201.706 883 8	2.7333
αα–αβ(βα)	−2201.707 157 4	2.5616
αα–αβ(ββ)	−2201.708 147 5	1.9403
αα–βα(βα)	−2201.701 150 7	6.3309
αα–βα(ββ)	−2201.702 734 3	5.3372
αα–ββ(ββ)	−2201.703 608 1	4.7888
αβ–αβ(αβ)	−2201.707 148 4	2.5673
αβ–αβ(βα)	−2201.702 238 4	5.6483
αβ–αβ(ββ)	−2201.703 376 3	4.9343
βα–αβ(ββ)	−2201.708 394 6	1.7853
βα–ββ(ββ)	−2201.704 951 9	3.9456

TABLE 9: Stability of Branched Pentamers

oligomer type (5T)	energy	stability
linear	−2751.851 601 8	
branched		
αααα	−2751.837 099 8	9.1001
ααβα	−2751.838 211 0	8.4029
αββα	−2751.839 002 4	7.9062
αααβ	−2751.839 171 3	7.8003
ααββ	−2751.839 405 1	7.6535
αβαβ	−2751.839 956 6	7.3075
αβββ	−2751.840 176 6	7.1694
βααβ	−2751.840 320 4	7.0792
βαββ	−2751.840 582 7	6.9146
ββββ	−2751.843 315 9	5.1995

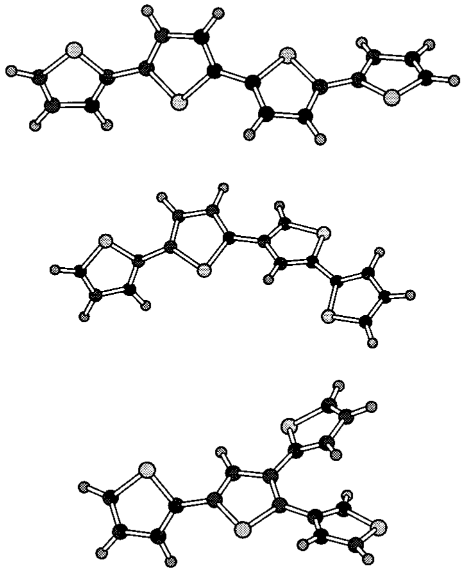

Figure 2. (a) Structures of an ideal tetramer. (b) A tetramer with an α–β linkage. (c) Structure of a branched form.

TABLE 10: Energy Parameters for PPy and PT from SCF and DFT/SCF Calculations (kcal/mol)

	pyrrole		thiophene	
type	SCF	DFT	SCF	DFT
E_{α}	−0.054 100	−0.001 358	0.018 975	0.050 450
E_{β}	1.772 600	1.994 692	−0.005 575	0.232 850
$E_{\alpha\alpha}$	−0.347 267	−0.072 134	0.026 033	0.187 300
$E_{\alpha\beta}$	1.189 825	1.956 166	0.264 550	0.915 075
$E_{\beta\beta}$	3.300 367	4.079 599	2.690 467	3.660 333
$E_{\alpha\alpha\beta}$	1.069 317	1.565 982	2.412 350	3.408 133
$E_{\alpha\beta\beta}$	33.432 133	3.762 116	5.144 083	6.626 517
$E_{\alpha\alpha\beta\beta}$	4.098 160	4.403 372	7.451 050	9.210 350

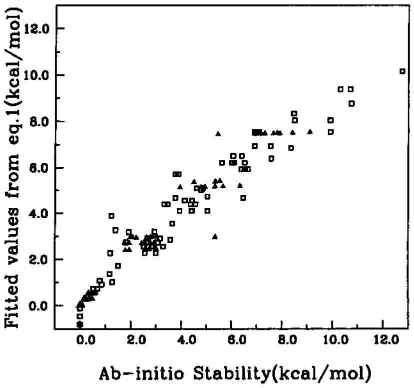

Figure 3. The relative stability of pyrrole and thiophene isomers obtained from eq 1. The open squares are for thiophene, and the filled triangles are for pyrrole.

rings, and it is labeled as ααββ. Once the number of each monomer type is known for a given randomly generated polymer, then its relative stability with respect to linear form can be written as

$$E = \sum\nolimits_k n_k E_k \tag{1}$$

where n_k are the number of monomer type k and E_k fitted parameters obtained from the results in Tables 5–9. From the energetics of the dimer, we obtain E_{α} and E_{β}. Using these two parameters, we proceed to fit $E_{\alpha\alpha}$, $E_{\alpha\beta}$, and $E_{\beta\beta}$ to trimers. The branched forms 4T and 5T are then used to generate final three parameters. The set of parameters for pyrrole and thiophene are given in Table 10. We have also carried out DFT calculations using Becke's three-parameter functional[20] on SCF optimized geometry, and the resulting energy parameters are presented in the same table. The geometry optimization on small oligomers within DFT did not considerably change the parametrization. In fact as it will be shown in the next section, the qualitative results are not sensitive to small changes in parametrization. The fit between quantum mechanically calculated energy stability and the stabilities obtained from eq 1 are shown in Figure 3 for pyrrole and thiophene oligomers. Except for highly unstable cases, we are able to obtain a very good representation of relative stability of oligomers from a simple functional form.

III. Monte Carlo Growth of Polymers

Once it is established that the relative stability of any polymer can be obtained from a simple additive potential, we proceed to generate an NVT ensemble of polythiophene to statistically analyze the linkage types and the branching as functions of the chain length and temperature. The method employed here is analogous to the kinetic growth problem.[26,27]

Let us assume that a polymer of m units has already been grown. Since there are four positions on each ring, the total number of positions for a new growth possibility is 4m; however, some of these positions will be already filled. In fact, in any randomly grown single chain, this number is $2(m+1)$. An addition of a new monomer to any of these $2(m+1)$ position will change the number of rings of types n_k of the eq 1. As an example, we connect a new monomer to a ring which was of type αα. The $n_{\alpha\alpha}$ will be reduced by 1, and since the new monomer can only attach to the 3 or 4 position, $n_{\alpha\alpha\beta}$ will increase by 1. If one of the α positions of the new monomer is to be connected to the backbone, also n_{α} will be increased by one. Therefore a relative stability value for this specific growth can be written as

$$\Delta E_i = -E_{\alpha\alpha} + E_{\alpha\alpha\beta} + E_{\alpha} \tag{2}$$

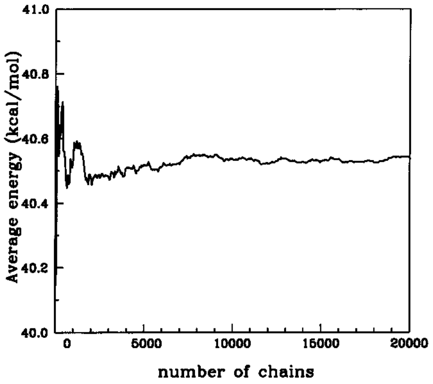

Figure 4. The convergence of the average energy of a thiophene simulation at 300 K.

A Boltzmann probability function for a specific growth mechanism i is defined as:

$$P_i = \frac{e^{-\Delta E_i/kT}}{Z} \tag{3}$$

where Z is the partition function or the sum over all probabilities. The elements of the function P_i are zero if the position is already occupied by a ring. At every step, the function P_i is computed for 4 ($2(m+1)$) possibilities and a random addition is selected from this probability distribution, namely a random number between 0 and 1 is chosen and the corresponding addition is obtained from eq 3. The excluded volume is included in the growth mechanism; that is, if the new monomer comes very near to one of the rings of the chain, that connection is ignored, the corresponding probability is set to zero, P is renormalized, and a new random addition is tried. The effects of anti- or syn-conformations are not introduced into our method so positions 2 and 5 of the new monomer have the same probability of being connected. Similarly, positions 3 and 4 are equivalent. Actually, the definition of syn- or anti-conformations lose their simple meanings in large chains. There are various branching possibilities and one monomer may be neighboring more than one ring. However, we attach the new monomer always with a torsional angle of 148°; hence, in the linear portions both conformations may exist.

Once a sufficiently large number of such grown chains is collected, we have calculated averages and distributions of several conformational properties. For chains containing up to 100 rings, a sample size of 20000 chains is observed to converge for energy or size related properties. In Figure 4, we plot the convergence of the energy (relative to the linear chain) with the sample size for $n = 100$ and at 300 K.

The structural changes of polymer coils are best understood in terms of the end-to-end distance,

$$R = \langle r^2\rangle^{1/2} = \frac{1}{N}\sum_k r_{1m}^k \tag{4}$$

or radius of gyration,

$$S = \langle s^2\rangle^{1/2} = \frac{1}{Nm}\sum_k \sum_j r_j^k \tag{5}$$

N is the size of the sample, m is the length of the chain, r_{1m}^k is the distance between the first and the last monomer, and r_j^k is the distance from each ring to the center of mass. In addition to these two standard measures, we have defined a branching ratio:

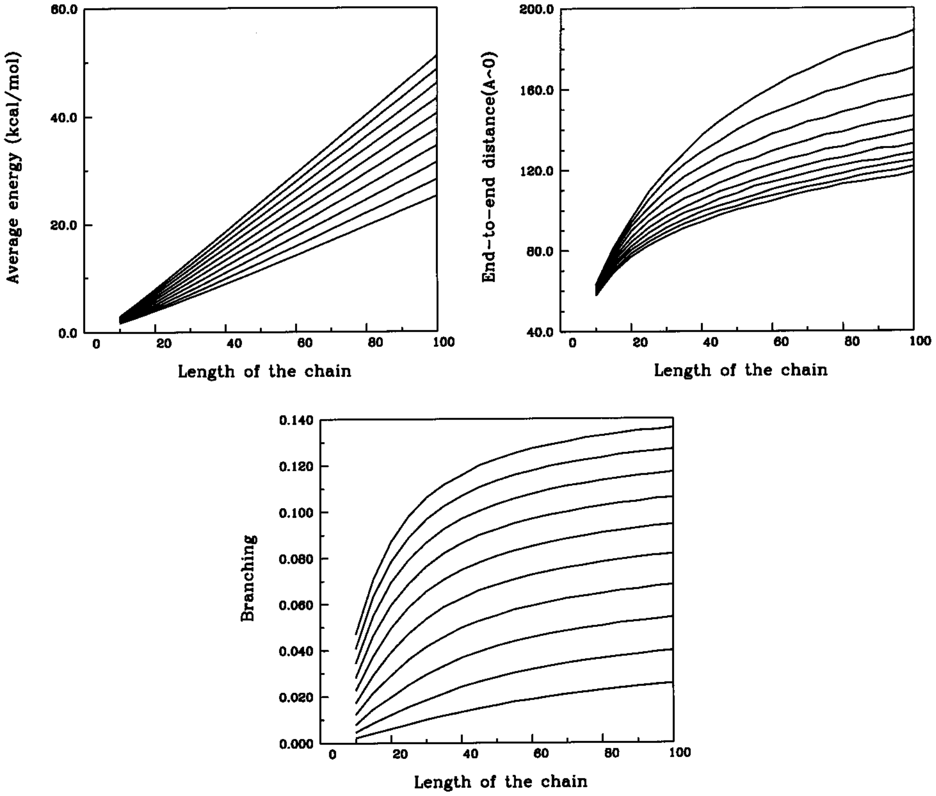

Figure 5. (a) Average energy as a function of the length of the chain. Each line corresponds to a different temperature between 175 and 400 K, where the lower lines correspond to lower temperatures. (b) Variation of S as a function of the length. (c) Variation of the branching ratio B, as a function of the length.

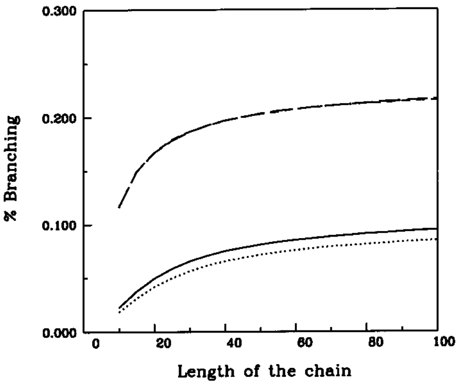

Figure 6. Branching ratio of PPy and PT from SCF- and DFT-generated parameters. The solid line is for SCF parameters for PT; dotted line is for DFT parameters of PT. Results from SCF and DFT for PPy are indistiguishable and presented in dashed lines.

$$B = \frac{1}{N}\sum_{k} [n^{k}_{\alpha\alpha\beta} + n^{k}_{\alpha\beta\beta} + 2n^{k}_{\alpha\alpha\beta\beta}] \qquad (6)$$

where n^k is the number of certain types of monomer in the kth chain. The factor 2 in the last term comes from the fact that each $\alpha\alpha\beta\beta$ type monomer results in two side branches. Now by analyzing the number of mislinkages and size-dependent properties such as R, S, and B, we can deduce the branching in both polypyrrole and polythiophene as functions of the temperature.

IV. Results and Discussion

In Figure 5 we plot the average energy, S, and B as functions of the chain length for temperatures changing from 150 to 400 K. The energy changes almost linearly with the length with positive slopes. Higher slopes correspond to higher temperatures as energetically less favorable branched forms become more accessible. Variation of R (same qualitative behavior is observed for S) can be described as a power law if very short chains are excluded:

$$R = Am^{\gamma} \qquad (7)$$

where γ is a critical exponent whose value changes from 0.257 to 0.466 as the temperature is dropped from 400 to 150 K; however, it remains reasonably constant around 0.27 above 250 K. For polypyrrole, γ has also been found to be around 0.25.[16] The average value of B for relatively large chains of 100 units, changes between 2−14% as the temperature is increased. The branching in polypyrrole is relatively higher (12−27% for the same temperature range), and also it converges much faster with respect to the chain length. These findings are in accordance with the experimental observations of the relative solubility and crystallization of PPy and PT. The extent of branching is given in Figure 6 for both PPy and PT at 300 K using the parametrization of SCF and DFT results. Both methods give indistinguishable results for PPy. The differences in case of DFT-generated probabilities for PT are also not very significant. This implies that basically normalized stability of isomers determine the extent of the branching rather than the differences in absolute thermodynamical stability. The temperature dependence of the branching is given in Figure 7, and both polymers show similar behavior. The changes in the branching ratio with chain length for PPy and PT are the same. The simulations carried out in this work only search for growth mechanisms and we have not followed up by a thermalization within the canonical or microcanonical ensembles. Because of that we are not able to study possible phase transitions.

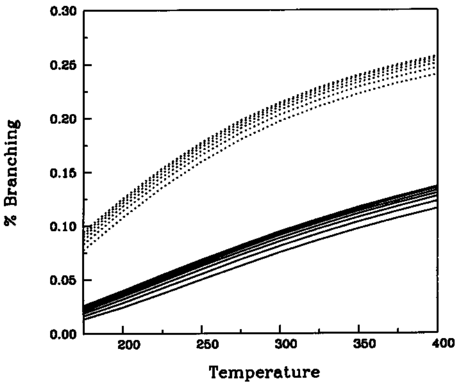

Figure 7. Variation of the branching ratio as functions of the temperature for various chain lengths. Solid lines are for PT and dotted lines are for PPy. Lower curves are for shorter chains.

We would like to conclude that thermodynamical stability of small oligomers can indeed distinguish various growth possibilities. In case of PT, such stability measures can be calculated from ab initio calculations with sufficient accuracy provided that d orbitals are included for heavy atoms. Ab initio results can be fitted to a simple additive function in terms of monomer types and corresponding energy parameters. The growth probability function based on these small molecules can be expressed as a Boltzmann distribution, and within an NVT ensemble, growing of single polymers can be accurately simulated. The kinetics of the growth mechanism is assumed to be independent of the type of the radicals generated. At the moment we do not have any evidence to support this assumption. However, the simulations based purely on the energetics of these systems provide results which agree with the general characteristics of PPy and PT. We are in the process of carrying out calculations on radical structures to obtain information on the kinetics of growth processes.

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