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A Two-Dimensional Monte Carlo Polymerization of 5-Membered Rings

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A modification of the kinetic growth model in two dimensions for the polymerization of 5-membered rings is presented. The preliminary results reveal the validity of the modified model.

Introduction

Among the polymers of five-membered rings polypyrroles generate tremendous interest due to their high conductivity upon doping, but their insolubility in conventional solvents hinders detailed structural analysis. Solid state ^{15}N NMR^{1,2} FTIR³, Raman⁴, STM⁵ and X-ray diffraction studies⁶ have been reported but there is no conclusive evidence mostly due to different experimental conditions. Therefore, there is a rather large number of theoretical attempts, most of them on pristine polypyrrole, but a majority of them deal with $\alpha - \alpha$ linkages which exclude branching or grafting. In a recent semiempirical study⁷ it has been shown that for unsubstituted pyrrole all linkages $\alpha - \alpha$, $\alpha - \beta$ and $\beta - \beta$ are favored almost equally which implies the possibility of high degree of branching in the polymerization.

In this work we modify the kinetic growth model in a way to include the above fact, and simulate the two-dimensional growth of a polymer from five-membered rings in a dilute solution. Boltzmann averages for the characteristic properties radius of gyration, end-to-end distance and degree of branching are calculated at a constant temperature.

Model

For linear polymerization in dilute solutions self-avoiding walk (SAW) is a well known model where the SAW consists of all configurations of nonintersecting random walk^{8,9}. Moreover, large SAW can be generated by Kinetic Growth Walks KGW¹⁰ where at each step a random walker can move to neighbor site that has not

been visited before. This model is also extended such as to include branching^{11,12}. Within the present modified model each monomer unit is a nonvibrating planar pentagon. The geometrical parameters are obtained from optimum structures within AM1 parametrization belonging to C_{2v} symmetry group. Each monomer is denoted by an index *i*, each atom is defined by an running index *k*.

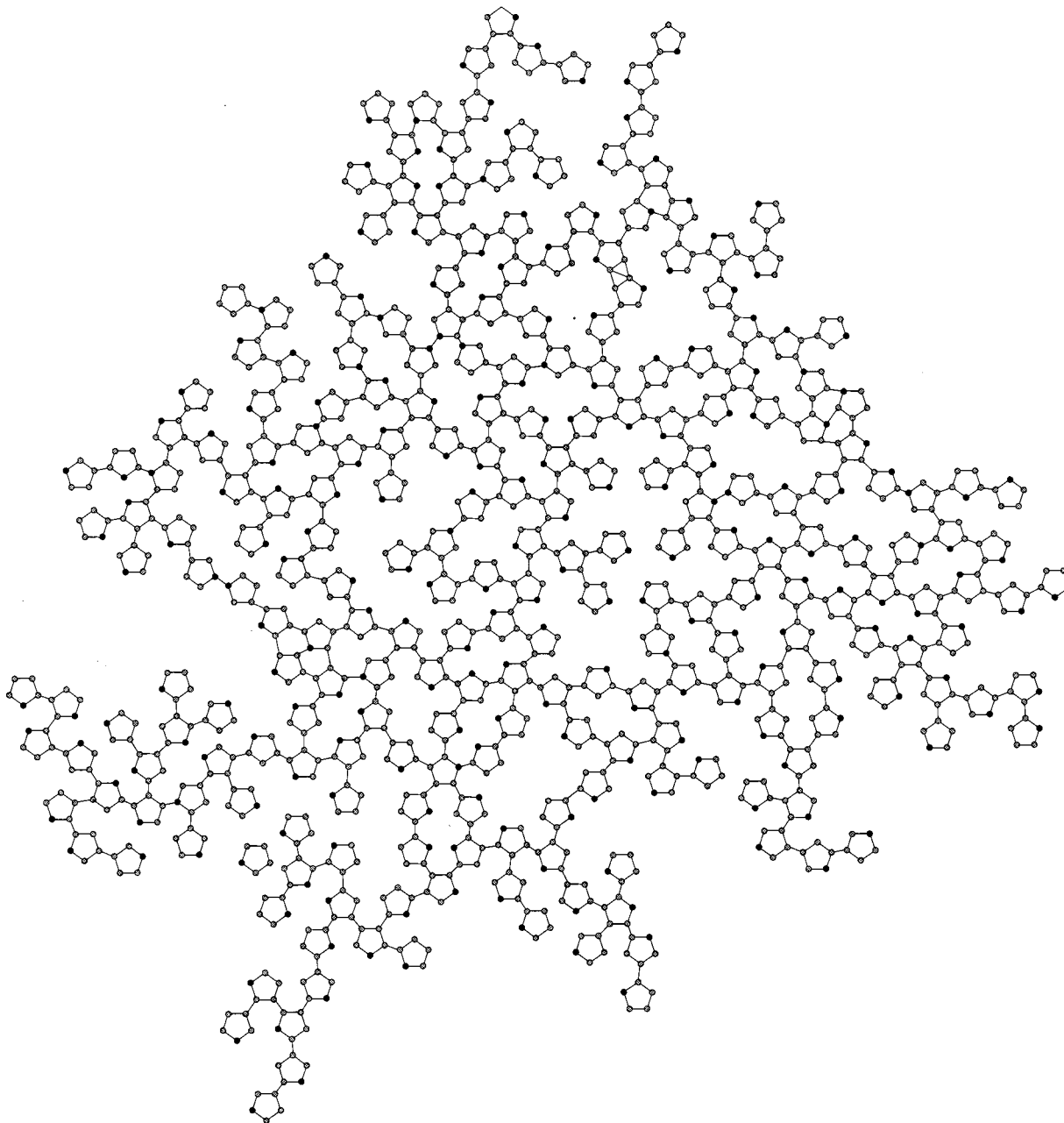


Figure 1. A sample conformation from N=250.

Let us assume that a chain composed of *N* monomers is already generated. A vector *IB* with the length $5N$ also accompanies this chain. If the atom *k* is a nitrogen or an already bonded atom then the corresponding element $IB(k)=1$, otherwise it is zero. In this manner we can keep track of all positions which are available to bonding. Since we assume equal probabilities to all sites, and if the number of available sites is $S(N)$, then each site has a probability of $1/S(N)$. We proceed to build a probability vector as:

$P(1)=0$ (Since the first atom is a nitrogen)
 $P(k)=P(k-1)+1/S(N)$ if k is available for bonding
 $P(k)=P(k-1)$ otherwise.

In this manner, there is a probability band for every atom either as zero or $1/S(N)$. A random number R between 0 and 1 is selected which falls into the band $P(m) < R < P(m+1)$. The number m is then the position of the site for the linkage. In actual computations P vector has a second index with dimension 4 (2α and 2β positions) which determines the binding site of the new monomer numbered $(N+1)$. However the algorithm retains the logic described before since all sites have equal probabilities. We are in the process of calculating the energy differences between various linages using highly accurate ab-initio quantum mechanical methods. In that case the components of the P vector will be computed from different formulas but the strategy will remain the same.

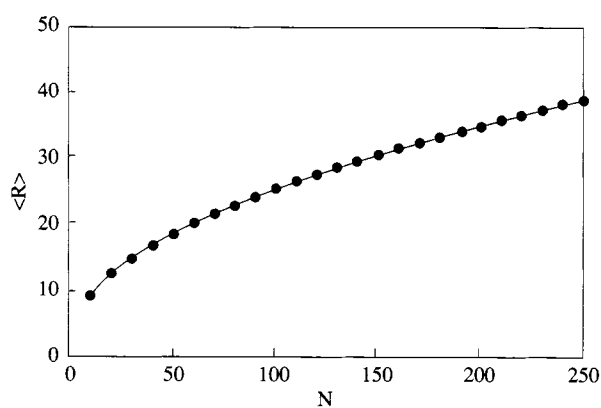


Figure 2. Variation of the $\langle R \rangle$ as a function of the length N .

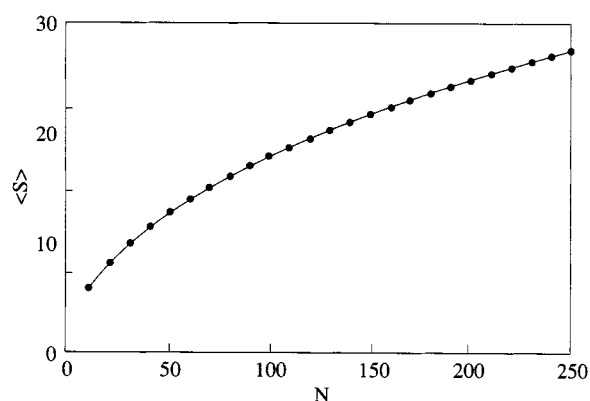


Figure 3. Variation of the $\langle S^2 \rangle^{1/2}$

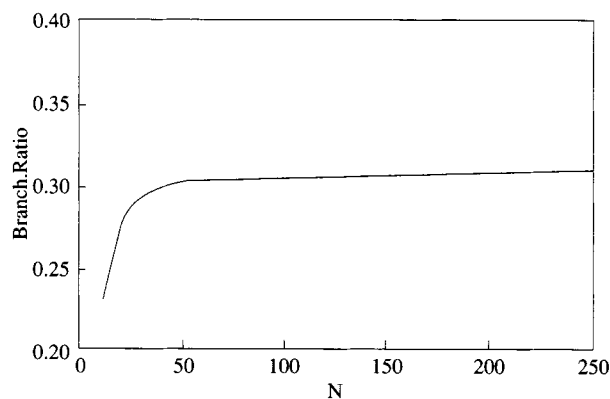


Figure 4. Variation of the branching ratio as a function of the length N .

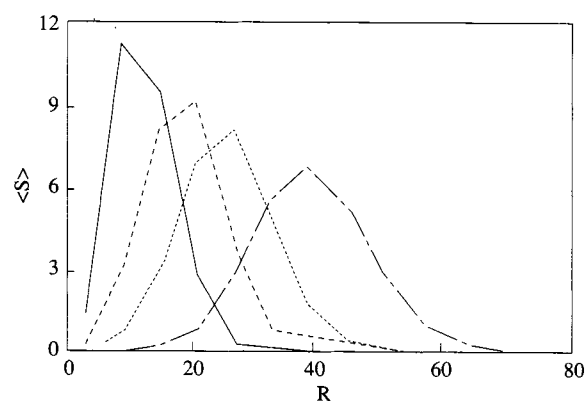


Figure 5. Distribution of the $\langle R \rangle$ for various N .

— $N=20$, - - - $N=50$, $N=100$, - · - · $N=250$

The bond distance between monomers is taken to be as 1.46 Å which is an average value for various linkage types (again obtained from AM1 optimum geometries). The final point to be noted in the growth process is the excluded volume effect. It is always possible when the new monomer is added according to the above mentioned recipe, the distances between this monomer and another one from the chain may be very small or even the rings may overlap. In the case that the distances between the center of masses are below a certain threshold, we discard that monomer and try a new position. The final structure does not include

any grafting but allows branching.

After every preselected length of the chain is reached, radius of gyration, end-to-end distance, and the branching ratios are calculated and stored. The growth process is repeated 25000 times which is sufficiently large to give converged values for all properties of interest. A statistical analysis package calculates averages and distributions.

Results and Discussion

Polymers do not have single, fixed values for any physical property but have some distributions. Therefore, these properties can only be measured or computed as average values over appropriate ensembles. The quantities we have calculated are the two standard measures of the size of the polymer. One of these is the average end-to-end distance, $\langle R \rangle$, which is the distance between the two ends of polymer:

$$\langle R \rangle = 1/M \sum_i |(r_N - r_1)_i|,$$

where r_N and r_1 are the coordinates of the last and the first monomers of the chain, i , M being the number of chains in the ensemble. The second quantity is the mean-square radius of gyration, $\langle s^2 \rangle$:

$$\langle s^2 \rangle = 1/M \sum_i^2 s_i^2$$

where s_i denotes the distance from the i th monomer to the center of the gravity of the polymer. We proceed to define a measure for the branching ratio which expresses the extent of the deviations from linearity. This is achieved by assigning weights to each monomer (w_i) according to its number of linkages. This can be done in various ways but we decide to give zero weight to all monomers which are at the end of some side chains (1 linkage) or exist in linear forms (2 linkages). If a monomer has three sites occupied its weight is 1 and those with all sites bonded to other monomers have the weight of 2. The other types of assignments did not show a considerable qualitative differences. The final measure of the branching for a given chain is defined as:

$$BR(i) = 1/N \sum w_i$$

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