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Contribution to the Conformational Study of Regularly Alternating Copolymers

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Self-avoiding random walks (SARW) on lattices have long been used as models for flexible macromolecules. These models allow description of the thermodynamic properties of dilute solutions of polymers, taking into account the effect of volume exclusion. A great amount of information about such walks has been gathered by means of Monte-Carlo methods, exact enumeration for short chain lengths, and approximate theories.

In preceding works,[1,2] we established rigorous analytical recurrence formulas for a five-choice SARW on a cubic lattice. Several coefficients characterize such a walk, particularly C_n, the total number of configurations that a chain of n segments can take on the lattice (or the number of self-avoiding walks of $n - 1$ steps) and $\langle r_n^2 \rangle$, the mean-square end-to-end distance of these configurations.

Determination of C_n and $\langle r_n^2 \rangle$

We briefly recall our preceding results. Earlier,[1] we proposed recurrence formulas for the calculation of accurate values of C_n for a three-dimensional cubic lattice. This quantity was obtained as a sum of partial terms. Each of these partial terms corresponds to the population of configurations having a given value of x, the number of primary contacts between nearby segments. A primary contact occurs between segments of the chain if the distance between them is equal to the side of the lattice cell (Figure 1). The value of x can vary between 0 and $(n - 2)/2$ for n even and 0 and $(n - 3)/2$ for n odd. Configurations having a given value of x can present different numbers of primary contacts between segments distant on the chain (segments p and $p + i$, with $i > 3$). Their number, designated by u, can vary between $u = 0$ and $u = u_{\max}$, the latter being a function of x that can be calculated.[1] Our independent variable is y, the number of secondary contacts between nearby segments (segments p and $p + 2$). The distance between these segments is equal to the diagonal of the lattice cell (Figure 1), and y varies between 0 and $n - 2$.

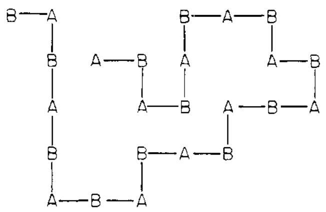

Figure 1. Configuration that can exist when the monomers A and B are compatible with each other in solution and both soluble (identical with a soluble homopolymer configuration). Secondary contacts between nearby segments occur between segments of the same nature and primary contacts between segments of different nature (also true for a cubic lattice).

Let us note that by the manner we have established our recurrence formulas, we can determine separately the number of configurations of a chain n having given values of x and u. Earlier,[2] we have given the following recurrence formula:

$$\langle r_n^2 \rangle = \gamma \langle r_n^2 \rangle_0 + (1 - \gamma) \langle r_{n-2}^2 \rangle \tag{1}$$

where $\langle r_n^2 \rangle_0$ is the mean-square end-to-end distance of the class of configurations of the chain n with $x = 0$ primary contacts, $\langle r_{n-2}^2 \rangle$ is the mean-square end-to-end distance for all the configurations of a chain $n - 2$, and $\gamma = [N]_n^{x=0}/C_n$, where $[N]_n^{x=0}$ is the number of configurations of the chain n having $x = 0$ primary contacts. Also, C_n is the total number of configurations of this chain.

In order to make use of eq 1 we have to establish algebraic relations to determine $\langle r_n^2 \rangle_0$, for each value of n. Letting $\log \langle r_n^2 \rangle_0 = E_n^0 \log n$, the exponent E_n^0 can be calculated with the help of eq 2 and 3 of ref 2.

Regularly Alternating Copolymers

We now apply the preceding results to the study of two types of regularly alternating copolymers. We shall suppose that the constituent monomers A and B are incompatible with each other in solution. We represent this situation by stipulating that two segments A and B cannot be primary neighbors. On a square lattice or on a cubic lattice, primary contacts are of type AB. The configurations with $x \neq 0$ and $u \neq 0$ will then disappear. We now investigate two cases.

(a) A and B are soluble. In this case

$$C_n = \sum_{y=0}^{y=n-2} [N]_n^{x=0,y} \tag{2}$$

and

$$\langle r_n^2 \rangle = \langle r_n^2 \rangle_0 \tag{3}$$

For this type of copolymer and $n = 15$, we find

$$C_{15} = 984\,003\,000$$

$$\langle r_{15}^2 \rangle = 40.37$$

while for a homopolymer we had

$$C_{15} = 4\,468\,955\,764$$

$$\langle r_{15}^2 \rangle = 25.33$$

(b) A and B are poorly soluble. A monomer unit will now have a tendency to draw near a segment of the same nature. The configurations will then reduce to those corresponding to $y = y_{\max} = n - 2$, and

$$C_n = [N]_n^{x=0,y=n-2} \tag{4}$$

These configurations obviously have a helicoidal structure. To evaluate their mean-square end-to-end distance,

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we made drawings. This is rather easy up to $n = 10$. Indeed, the configurations divide into symmetrical groups and present geometrical properties which much simplify the work. For $10 < n \leq 15$, we made an exact enumeration with a computer. The numerical values so obtained show that $\langle r_n^2\rangle_0^{y=n-2} < \langle r_n^2\rangle_0$ and that $\langle r_n^2\rangle_0^{y=n-2}$ rapidly tends toward $\langle r_n^2\rangle_0$.

For $n = 15$, as an example, we obtain

$$C_{15} = 7\,489\,728$$

$$\langle r_{15}^2\rangle = 36.55$$

Let us note that in the case of a poor solvent we account for increased interactions between two nearby second-neighbor segments (segments p and $p + 2$) but ignore equally increased interactions of type $(p, p + 4)$, $(p, p + 6)$, ... etc. Nevertheless, we have separately measured the end-to-end distance of the drawn configurations presenting second contacts between segments distant on the chain. The mean-square end-to-end distance of this group is inferior but rapidly approaches the value of this coefficient for all the configurations having $y = n - 2$ (the difference is about 10% for $n = 15$). The probability of the minimum end-to-end value $\langle r_n^2\rangle = 2$ (corresponding to the maximum number of second contacts between distant segments) also rapidly decreases when n increases.

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Communications to the Editor

Electron Paramagnetic Resonance Method for the Determination of Orientation in the Amorphous Regions of Polymers

In order to completely characterize the orientation induced in partially crystalline polymers, one must obtain the amorphous orientation function $f_{\mathrm{am}} = \langle(3 \cos^2 \alpha - 1)/2\rangle$, where α is the angle between the stretching direction and the polymer chain axis. This parameter has generally been determined by combining birefringence or sonic modulus measurements with a knowledge of the sample crystallinity and the corresponding orientation function for the crystalline region.[1,2] A shortcoming of this indirect procedure is that the value of f_{am} so obtained may be subject to cumulative errors, and consequently there is a need for more direct methods of measuring this important parameter. In this communication we report an EPR method which exploits the angular dependence of the spectrum obtained from a spin probe incorporated into the partially ordered amorphous regions of low-density polyethylene.

The present study was initiated as a result of recent work in our laboratory showing very dramatic effects of sample orientation on the EPR spectra of trapped radicals in partially aligned matrices.[3,4] In particular, the relative intensity of the parallel and perpendicular features in the EPR spectrum of $C_2F_4^-$ in the methylcyclohexane-d_{14} matrix showed a pronounced angular dependence,[4] suggesting that this sensitive anisotropic property could be used to determine low degrees of orientation. This technique has now been applied to oriented polymers, the basic requirements being (i) the incorporation of C_2F_4 into a well-defined morphological region and (ii) that the EPR spectrum of $C_2F_4^-$ generated by γ irradiation should not be masked by signals from other radiation-produced radicals. As will be evident from the results, both of these requirements are met by polyethylene.

A low-density polyethylene (Aldrich) supplied in the form of pellets was heated to 175 °C and pressed to form a film which was subsequently stretched at 70 °C to obtain stretch ratios between 2 and 5. This elongated film (ca. 1-mm thick) was then cut into narrow strips which were stacked together and placed in a Suprasil or Spectrosil sample tube. As shown in Figure 1, samples were prepared with the stretching direction in the film stack being either parallel (A) or perpendicular (B) to the axis of the sample tube. Tetrafluoroethylene (PCR, Inc.), which had been degassed on a vacuum line, was condensed into the sample tube at −196 °C from a storage bulb held at −78 °C. The amount of C_2F_4 transferred into the tube was about 10 mol % of the C_2H_4 repeating units in the polyethylene sample, and this was sufficient to generate a pressure of ca. 5 atm in the sealed tube at room temperature. The sample tubes were stored for 1 week at ambient temperature and then irradiated at −196 °C with ^{60}Co γ rays for a total dose of ca. 1 Mrd. EPR measurements were made on the γ-irradiated samples at 80 K and higher temperatures as previously described.[5]

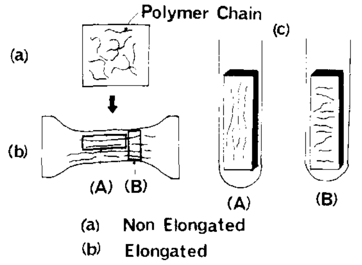

Figure 1. Schematic representation of polymer chains before (a) and after (b) elongation showing the development of orientation along the stretching direction. The two configurations A and B of the elongated polymer film in the EPR tube are shown in c.

The solid line in Figure 2a shows the EPR spectrum of a nonelongated polyethylene film which had been treated with C_2F_4 and irradiated in the same way as the elongated samples. The prominent outer features marked by the stick diagrams correspond closely to those obtained for the spectrum of $C_2F_4^-$ in a methyltetrahydrofuran (MTHF) glass. As discussed elsewhere,[4,6] this powder spectrum consists of parallel and perpendicular features resulting from hyperfine interaction with four equivalent fluorines. Assuming the values of $g_\parallel$ (2.0022) and $g_\perp$ (2.0033) reported previously,[4] the anisotropic hyperfine couplings $^{19}A_\parallel$ (4) and $^{19}A_\perp$ (4) were found by spectral simulation to be 133.2 and 74.8 G, respectively, in good agreement with the values obtained for $C_2F_4^-$ in the MTHF glass.[6] In accordance with previous interpretations,[4,6] the axial and parallel hyperfine

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