

Flory page 111 equation

$$\langle R^2 \rangle_{Linear\ Chain} = 2nl l_p - nl^2 \quad (1)$$

for a linear chain. This equation arises from the definitions of $\langle R^2 \rangle$ and l_p . l_p is defined as the average of the dot product of a vector at position i with itself and all chain steps of higher index, where i is randomly chosen. On average l_p begins at the midway point of the chain so the total chain is composed of two of these average chains. This line of reasoning yields the first term in equation (1), $\langle R^2 \rangle = 2Ll_p$. Since l_p involves the step “ i ” itself and all later steps, doubling this over counts $\langle R^2 \rangle$ by one pair of $j = i$, or nl^2 so this must be subtracted from the first term yielding equation (1).

Equation (1) reflects the condition for a linear chain. For a cyclic, each chain step is at the beginning of the chain and all steps are identical. Further, if random steps are chosen the entire chain is counted for l_p , so we do not need to double the first term in equation (1) and there is no over counting,

$$\langle R^2 \rangle_{Cyclic} = nll_p \quad (2)$$

So this approach can yield the relative size between a linear and a cyclic, linear always being larger or equal to a cyclic in size,

$$\left(\frac{\langle R^2 \rangle_{Linear\ Chain}}{\langle R^2 \rangle_{Cyclic}} \right) = 2 - \frac{l}{l_p} \quad (3)$$

For the smallest degree of persistence $l_p = l$ and the cyclic is the same size as the linear chain. When persistence is large, $l_p \Rightarrow \infty$, and the cyclic is half the size of the linear since it must fold in half for the two ends to be linked.

The change in the size of a chain with topological constraints compared to a linear chain is governed by the ratio between the persistence length and the chemical bond length. For short persistence lengths the chains are of identical size.