

SHORT COMMUNICATIONS

Chain Dimensions of a Poly(macromonomer) in a Good Solvent

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A poly(macromonomer) is one type of comb polymer. The number of branches which it has is very large, because each monomeric unit has a long side chain. Its physical properties differ greatly from those of usual linear polymers. Recently, the chain dimensions of poly(macromonomer)s have been reported by several authors.¹⁻³ Wintermantel *et al.* reported the molecular weight dependency of the radii of gyration of poly(macromonomer)s using GPC with a multi-angle light-scattering detector.¹ They concluded that the poly(macromonomer) could be excellently described as a stiff worm-like chain whose Kuhn length is very long, about 100 nm. This value is much larger than that of polystyrene, which has a value of about 1.2 nm.⁴ Nemoto *et al.* measured the dynamic light-scattering and sedimentation velocities for wide ranges of degree of polymerization, D_p , of the main chain and side chain.² They showed that the poly(macromonomer) could be quantitatively described as a rotatory ellipsoid, in which the main chain extended in a zigzag conformation and in which the side chains behaved as Gaussian chains. Wataoka *et al.* measured small-angle X-ray scattering.³ They reported that the poly(macromonomer) resembled a rotatory ellipsoid, while the radius of gyration of the cross section of the ellipsoid was independent of D_p of the main chain. They also found that the exponent in the power-law

relation between the radius of gyration and D_p of the side chains was 0.64. This value is larger than that predicted for a self-avoiding chain in 3-dimensional space, which is 0.60.

The chain dimension of the poly(macromonomer) depends not only on D_p of the main chain, but also on D_p of the side chains. However, a theoretical prediction concerning the relation between the chain dimension and D_p has not been reported. In this communication, we present three chain shapes of a poly(macromonomer), and describe the dependency of the mean dimensions of the main chain and side chains on D_p using a simple Flory type mean-field theory.

MODEL

The poly(macromonomer) consists of N segments of unit length which form the main chain. Each segment in the main chain has a side chain of $n-1$ segments. The values of N and n are so large that we can apply chain statistics to them. The end-to-end distances of the main chain and side chains are denoted by R and r , respectively. We assume that the values of r are equal, regardless of their position.

In the case of free-rotational chains, the contributions of entropies to the partition function of the poly(macromonomer) are $\exp(-3R^2/2N)$ for the main chain, and $\exp(-3r^2/2n)$ for

each of the side chains. The contributions of the excluded volume to the partition function are evaluated as $\exp(-v/2 \int d\tau \rho^2)$ using the mean-field approximation, where v is the excluded volume of a segment, ρ is the segment density, and $d\tau$ is the volume element. If we assume that the segments are distributed uniformly in the equivalent volume of the poly-(macromonomer), V , the contribution of the excluded volume can be expressed as

$$\exp(-vN^2n^2/2V)$$

In the following, we study extreme cases for convenience.

COIL STATES

If the main chain is in the coil state, we can assume that the radius of an equivalent sphere of a polymer chain is proportional to the end-to-end distance of the chain, according to Flory. Then V is proportional to $(R+2r)^3$, where $2r$ represents contributions from the side chains attached to the end segments of the main chain. The partition function of the poly-(macromonomer), Q , is expressed as,

$$Q = \exp(-3R^2/2N - N3r^2/2n - cvN^2n^2/(R+2r)^3) \quad (1)$$

where c is a numerical constant. The mean values of R and r can be evaluated using this partition function. In this communication, we concentrate our attention on power-law relations of R and r on N , n , and v . Numerical prefactors are approximated as 1.

Minimizing the free energy of the chain, $-\ln(Q)$, with respect to R and r (R and r are taken as order parameters in this method), the following relations are derived

$$R/N \sim vN^2n^2/(R+2r)^4 \quad (2)$$

and

$$r/n \sim vNn^2/(R+2r)^4 \quad (3)$$

1) The case where $R \gg r$:

In this case, the denominator in the right

hand side of eq 2 can be approximated as R^4 . Then we get

$$R \sim v^{1/5} N^{3/5} n^{2/5} \quad (4)$$

Equation 4 predicts that the main chain behaves as a self-avoiding chain in 3-dimensional space. The poly(macromonomer) is similar to the usual linear polymer in this case. However, the apparent excluded volume of the segment is vn^2 . The value of R increases with n . Finally, we get $R \sim N$ when $n = N$. This means that the chain changes from coil to extension with increasing n . However, eq 2 cannot apply to the extended state.

For the side chain, we obtain the next relation by substituting eq 4 into eq 3,

$$r \sim v^{1/5} (n/N)^{7/5} \quad (5)$$

The value of r tends to 0 with decreasing n/N . This is interpreted as follows. The segment densities of side chains in the equivalent sphere (whose radius is determined by the size of the main chain) are low, and so the contribution of the excluded volume is negligible compared with that of the entropies of the side chains. However, approximation for deriving eq 3 may be poor, because the segments are connected to each of the side chains. A side chain is located very close to each main chain segment. Then the effective excluded volume of the main chain segment can be approximated as vr^2 . (The side chain spreads into 2-dimensional space, but not into 3-dimensional space, due to hindrance resulting from neighboring side chains.) Equation 4 predicts that the apparent excluded volume of the main chain is vn^2 . Then we get

$$r \sim n \quad (6)$$

Equation 6 predicts that the side chain is in the extended state.

The ratio of eq 4 to 6 shows

$$R/r \sim v^{1/5} (N/n)^{3/5} \quad (7)$$

Following eq 7, the condition $R \gg r$ is satisfied in the case of $N \gg n$.

2) The case where $R \ll r$:

The denominator in eq 3 is approximated to r^4 , then we get

$$r \sim v^{1/5} n^{3/5} N^{1/5} \quad (8)$$

This relation predicts that side chains can be treated as self-avoiding chains in 3-dimensional space. Then the poly(macromonomer) behaves as a star polymer with N arms. The value of the exponent on N , $1/5$, is the same as that predicted by Daoud and Cotton using the scaling argument.⁵

In this case, the value of R is proportional to $N^{1/5}$, as can be shown using eq 2 and 8. However, segments of the main chain are connected in a linear fashion. The radius of the equivalent sphere of the main chain is proportional, not to $R+2r$, but to R . The number of segments in this sphere is much larger than N , because segments of the side chains are included in this sphere. Then approximation in deriving eq 2 is poor in this case. The extended main chain model is more suitable.

EXTENDED STATES

When the main chain is in the extended state, there is no contribution from the entropy of the main chain. The poly(macromonomer) is approximated as a rod (or rotatory ellipsoid) with length, $R+2r$ and the radius of the cross section, r . The partition function is obtained as

$$Q = \exp(-N3r^2/2n - c'vN^2n^2/(R+2r)r^2) \quad (9)$$

where c' is the numerical coefficient. Values of all numerical prefactors are assumed to be 1, as assumed previously. Minimizing the free energy with respect to r , the mean value of r is obtained using the next relation.

$$r/n \sim vNn^2(R+3r)/(R+2r)^2r^3 \quad (10)$$

1) The case where $R \gg r$:

The value of R is N in this case. Disregarding the values of r in the parentheses of eq 10, we get the next relation.

$$r \sim v^{1/4} n^{3/4} \quad (11)$$

Equation 11 predicts that the value of r is independent of the value of N . The value of the exponent on n , $3/4$, coincides with the value for a self-avoiding chain in 2-dimensional space. It is interpreted that the side chain is confined within a thin disc perpendicular to the main chain by neighboring side chains.

2) The case where $R \ll r$:

Disregarding the value of R in eq 10, we get

$$r \sim v^{1/5} n^{3/5} N^{1/5} \quad (12)$$

This relation is the same as that of eq 8. Equations 8 and 12 predict that the poly(macromonomer) behaves as a star polymer in the case $R \ll r$, regardless of the shape of the main chain. However, as was discussed previously, the main chain is in the extended state.

DISCUSSION

The mean dimensions of a poly(macromonomer) are derived using Flory type mean-field theory. The calculated values of exponents in the power-law relations of over-all dimensions are physically reasonable, though the segments are crowded near the roots of side chains. Chains can spread into space where the excluded volume interaction between segments is dominant. The over-all dimensions are determined by these spreaded chains. Some values of the exponents for local dimensions are unreasonable (for example, eq 5). The cause in part is the inadequate assumption of the uniform segment density in the equivalent volume of polymers.

We have shown that the shape of the poly(macromonomer) can be classified as a coil, rod-like and star-like. The crossover line between the coil and rod can be obtained using eq 4 and the relation $R \sim N$ in the rod,

$$n = v^{-1/2} N \quad (13)$$

From eq 11 and 12, we get the crossover line between the rod and star as,

Table I. Poly(macromonomer) shape presentations

	Main chain	Side chain	Crossover line
Coil	$v^{1/5}N^{3/5}n^{2/5}$ (3D Self-avoiding)	n (Extend)	$n=v^{-1/2}N$
Rod	N (Extend)	$v^{1/4}n^{3/4}$ (2D Self-avoiding)	$n=v^{-1/3}N^{4/3}$
Star	N (Extend)	$v^{1/4}n^{3/5}N^{1/5}$ (3D Self-avoiding)	

$$n = V^{-1/3}N^{4/3} \quad (14)$$

The power-law dependencies of dimensions of the main chain and of the side chains on the chain length are summarized in Table I.

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