Supporting Information

For

Research Progress on the Conformational Property of Comb-like Polymers in dilute Solution

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Main Approach used by Flory Approximation and Scaling Analysis

1 Approach of Fredrickson[1]

Different from the simplified Flory theory method, Fredrickson considers the details of the sidechain conformation when analyzing the average conformation of the whole comb chain in the range of medium σ, and no longer simply equates the main sidechain as a unified unit. At this time, the expression of the comb whole chain free energy is as follows:

$$\Delta F = \Delta F_{el} + \Delta F_{ex,\,b\text{-}b} + \Delta F_{ex,\,b\text{-}g} + \Delta F_{ex,\,g\text{-}g}$$
$$;\ k_B T \left[\frac{R_g^2}{N_b b^2} + \frac{b^3 N_b^2}{R_g^3} + \frac{(R_{g,g} + b^3 \sigma N_b^2}{R_g^3} + \frac{R_{g,g}^3 (\sigma N_b)^2}{R_g^3} \right] \tag{S1}$$

Similar to eq 1 in main text, the first, second, third and fourth terms on the right side of the equation in turn represents the contribution from the elastic entropy of backbone, the excluded volume interaction of backbone-backbone monomer, the excluded volume interaction of backbone monomer-graft, and the excluded volume interaction of graft-graft, respectively. In this case, the sidechain is no longer a discrete monomer unit, but a polymer with connection is substituted into eq S1 to consider its excluded volume effect. In addition, Fredrickson believes that in the very low σ range, the conformational evolution behavior of the bottlebrush chain is the same as that of the linear chain, which follows the scaling law of $R_g \sim N_b^{3/5}$. This is because the side linkage is too sparse to cause the conformational change of the bottlebrush chain.

In the medium σ range, by assuming that the radius of gyration of sidechain satisfies the true "swollen" chain conformation scaling law $R_{g,g} \sim N_g^{3/5}$ in a good solvent and ignoring the excluded volume interaction between the backbone monomer unit and the sidechain, Fredrickson using the derivation of eq S1 to obtain the extreme value, the scaling law of the bottlebrush polymer is derived to satisfy $R_g \sim N_b^{3/5} \sigma^{1/25} (N_g \sigma)^{9/25}$ at the lowest energy. By combining the two R_g expressions of the low σ interval and the medium σ interval, the turning point of the low to medium graft density interval can be obtained as $\sigma = N_g^{-9/10}$.

In the high σ range ($\sigma > N_g^{-3/5}$), i.e., in the case of assuming a real "swollen" conformation of sidechain,

the σ is high enough that sidechains can overlap each other, the configuration of the bottlebrush gradually changes from that of a coil toward a more extended rod. To calculate the l_p of this rod-like bottlebrush structure, Fredrickson follow the Daoud-Cottont approach for calculating the free energy of aggregates, which is modified by considering the influence of the different distribution of sidechain tails on both sides of the backbone when the bottlebrush is considered as a gently linear curved aggregate.[2] Finally, the free energy per unit contour length of the bottlebrush is given by

$$\Delta F_{unit} : k_B T \left[\sigma^{13/8} N_g^{3/8} \psi(\frac{\sigma^{1/4} N_g^{3/4}}{\rho}) \right] \tag{S2}$$

Where $\psi(\sigma^{1/4} N_g^{3/4} \rho^{-1})$ is a function of N_g, σ and the radius of curvature ρ when the bottlebrush is bent. Next, we can use eq S2 to derive an expression for l_p of bottlebrush polymer, if the bottlebrush polymer is viewed as a wormlike chain, it follows that the free energy change on bending per unit contour length is related to l_p by the simple scaling relation

$$\Delta F_{unit} : k_B T (\frac{l_p}{\rho^2}) \tag{S3}$$

Comparison of eqs S2 and S3 leads to an explicit expression for the l_p

$$l_p : \sigma^{17/8} N_g^{15/8} \tag{S4}$$

The bottlebrush polymer appears rod-like when viewed on scales comparable to that given by eq S4 and coil-like when viewed on much larger scales ($L_c \gg l_p$). The overall dimension of bottlebrush polymer, which is a self-avoiding random walk with steps of length l_p, thus scales as

$$R_g : l_p (N_b / l_p)^{3/5} \tag{S5}$$

Combine with the eq S4, the expression of R_g are summarized in table 1.

2 Approach of Birshtein et al.[3]

It can be seen from Fredrickson's discussion above that l_p is not obtained through Flory theory, Obviously, for the local structure of bottlebrush polymer, such as D, h and l_p cannot be extracted by Flory theory.

However, the establishment of P. de Gennes' scaling method opened a way for the theoretical study of polymer systems with complex structures. Combining the "Flory theory" and scaling method, Alexander first derived the 2D polymer brush conformation as the balance between the elastic energy of an entropic spring and an excluded volume repulsion between segments in 1977.[4-6] The elastic energy is considered increases quadratically with their end-to-end distance of grafts ($R_{e,g}$). In contrast, the excluded volume originates from uniformly distributed monomer segments and is proportional to their volume fraction. By minimization, the scaling equation $R_{e,g} \sim N_b\sigma^{1/3}$ was derived. In the following decades, different hypotheses and theoretical approaches have been adapting to analyze the influence on the brush conformation in the community, but led to different theoretical predictions.

Accordingly, the research on 1D polymer brush, namely bottlebrush polymer, which involves scaling argument is mainly based on the work of Birshtein et al. and Borisov et al.[3, 7] To analyses the local structure of the bottlebrush polymer, the free energy of the sidechain in the bottlebrush polymer can be expressed as:

$$\Delta F_g = \Delta F_{conc} + \Delta F_{el, g} + \Delta F_{el, b} \tag{S6}$$

Obviously, the mutual repulsion of the closely situated side branches (in the layer near the backbone) determines the local conformational structure of the sidechain. Then, the corresponding contribution of ΔF_{conc} to the free energy of the sidechain is equal to the free energy of this chain in semi-dilute solution. To reduce the concentration in the layer near the backbone, the sidechains and backbone must be stretched. Hence, $\Delta F_{el,g}$ and $\Delta F_{el,b}$ are the free energies of stretching of the sidechain and the backbone, respectively. Owing to the minimization of free energy ΔF_g, equilibrium values of the parameters such as D and h of the local bottlebrush structure were found, and the equilibrium free energy ΔF_g per sidechain (see Table1) were also derived. where τ is the reduced temperature $\tau = (T - \theta)/T$ with T and θ being the absolute and θ temperature, respectively.

Table S1. Power dependences of the characteristics of the structure of a bottlebrush chain.

Conditions	ΔF_g	h	D	R_g
θ solvent	$(N_g\sigma)^{1/4}$	$\sigma^{-1/2}(N_g\sigma)^{1/8}$	$N_g^{1/2}(N_g\sigma)^{1/8}$	$N_b^{3/5}\sigma^{1/10}(N_g\sigma)^{13/40}$
Good solvent	$(N_g\sigma)^{1/10}$	$\sigma^{-3/5}\tau^{1/5}(N_g\sigma)^{3/25}$	$N_g^{3/5}\tau^{1/5}(N_g\sigma)^{3/25}$	$N_b^{3/5}\tau^{1/5}(N_g\sigma)^{9/25}$

Furthermore, by considering the change in the free energy on bending of the backbone with the grafted chains, Birshtein et al. proved that when the curvature radius is larger than D of the bottlebrush polymer, the free energy of the system will not be increased. This result may serve as further confirmation of the quite natural assumption that the length of the rigid portion (ξ) of a comb-like chain is of the order of its thickness, i.e. $\xi \sim D$. Thus, one bottlebrush chain can be actually regarded as a linear sequence of freely reticulated blobs with interaction energy on the order of k_BT and blob size of D, and the blobs are not permeable for each other not only in a good but also a θ solvent. Therefore, the overall chain size can be further expressed as:

$$R_g \approx (L')^{3/5}D^{2/5} = (\frac{N_b h}{N_s})^{3/5}D^{2/5} \tag{S7}$$

where L' is the effective contour length of the chain ($L' = N_b h/N_s$). By combining eq S7 and the result of D in Table S1, the expressions of R_g can be derived in Table 1.

3 Approach of Borisov et al.[7]

In addition, in 1996, Borisov et al. further considered the influence of induced stiffness of the backbone on bottlebrush chain under good solvent condition. The induced persistent length of a bottlebrush chain with a flexible backbone is given by:

$$l_p \approx D(N_g\sigma)^{9/10} \approx N_g^{81/50}\sigma^{51/50} \tag{S8}$$

The equilibrium conformation of the bottlebrush chain on a large scale depends on the ratio between l_p and L'. In particular, when $D < L' < l_p$, which is the case at $N_b < N_g(N_g\sigma)^{1/2}$, the bottlebrush chain has a rod-like conformation with a characteristic size $R_g = L'$. When $L' > l_p$, the bottlebrush chain acquires the conformation of a Gaussian or of a swollen coil with a size given by

$$R_\mathrm{g} = L'^{1/2}\, l_\mathrm{p}^{1/2} \qquad\qquad\qquad L' = l_\mathrm{p}^3 D^{-2} \qquad\qquad (S9)$$

$$R_\mathrm{g} = L'^{3/5}\, D^{1/5} l_\mathrm{p}^{1/5} \qquad\qquad\qquad L' ?\ l_\mathrm{p}^3 D^{-2} \qquad\qquad (S10)$$

Combining the result of D in Table S1, the expressions of R_g can be summarized as Table 1.

To sum up, by comparing the results of Fredrickson and Borisov et al., it is found that: 1) Compared with the results derived from the consideration of backbone induced stiffness effect (l_p), the Rg results obtained by simplified Flory theory are much less dependent on the number and length of the sidechains of the grafts; 2) Birshtein et al. combined the Flory theory with the scaling method, and the results obtained without considering the backbone induced stiffness were very close to those obtained by simplified Flory theory (9/25 and 2/5); 3) In the range of wide solvent quality (theta solvent to good solvent), the whole chain size of bottlebrush always meets the scaling relationship of $R_\mathrm{g} \sim N_\mathrm{b}^{3/5}$; 4) Except that the local conformation parameters h and D of the polymer chain satisfy the same scaling law basis as the linear chain with the intrinsic degree of polymerization N_s and N_g, they are also affected by the size expansion caused by the existence of the excluded volume of the graft sidechain, and the expansion factor is the same, both of which are $(N_\mathrm{g}\sigma)^{3/25}$. These theoretical predictions are of great significance to the subsequent experimental study of the conformational evolution behavior of comb polymers.

Reference

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