Comb-like polymers inside nanoscale pores

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1 Introduction

A new method of polymer characterization, based on permeation studies using nanoscale pores, was recently proposed by Brochard and de Gennes [1]. In the present paper, we study how this method, initially developed for star polymers, can be extended to comb-like polymers [2]. The present study is based on the Flory free energy approach and therefore does not provide the more complete description of chain conformations that can be obtained in simple geometries through self-consistent field methods. Furthermore, our scaling analysis leaves numerical factors undetermined. The crossovers between the different regimes we obtain are expected to extend over a factor of two or so in the parameters.

2 A comb in a good solvent: from worm to star

Consider a comb homopolymer made of $n$ segments, each containing $N$ monomers along the backbone and $P$ monomers in a side-chain. The various possible chain conformations in good solvent can be derived from a classical
Flory free energy approach. They are described by the quantities listed in the following Table and are pictured on the Figure. $R$ is the radius of gyration of the whole molecule, $R_{nN}$ is that of the main chain and $R_P$ is that of the side-chains. Where it is relevant, $R_C$, $n_C$ and $P_C$ are the size, number of side-chains or number of monomers from each side-chain in the central region of the molecule described later in the text.

| Overall molecule conformation | Radius of gyration | Backbone conformation REGIME | Other characteristics |
|--------------------------------|---------------------|------------------------------|-----------------------|
| Decorated Chain $R = R_{nN}$ | $R = a(nN)^{3/5}$ (Flory) | flexible DC | $R_P = aP^{3/5}$ |
| Worm $R = R_{nN}$, $R_C = R_P$, $R = R_C \left(\frac{n}{n_C}\right)^{3/5}$ | $R = an^{3/5}P^{2/5}N^{1/5}$ | flexible FBW | $P = n_C^2N$, $R_P = aP^{3/5}n_C^{1/5}$ |
| id. | $R = an^{3/5}N^{1/2}P^{3/10}$ | stretched SBW | $P = n_C^{4/3}N^{5/3}$, $R_P = anCN$ |
| Star $R = R_P$, $n_C = n$, $R_C = R_{nN}$ | $R = aP^{3/5}n^{1/5}$ (Daoud-Cotton) | flexible FBS | $P_C = n^2N$, $R_C = aP^{3/5}n^{1/5}$ |
| id. | id. | stretched SBS | $P_C = n^2N$, $R_C = anN$ |

These various regimes can be understood quite simply. When side-chains are short ($P < N$), the whole comb behaves like a simple chain of $nN$ monomers, decorated with swollen side-chains. The gyration radii of both the side-chains and the overall molecule follow a Flory scaling law (regime DC). If side-chains are very long, they expand far away from the backbone, and the overall conformation of the comb molecule is that of a star with $n$ arms of length $P$ (regimes FBS and SBS). Its radius of gyration is that given by Daoud and Cotton \[3\]. The central region of the star contains the backbone (core of size $R_C$). If the number of monomers along the backbone between side-chains is small ($N < n$), the backbone is completely stretched ($R_C = anN$). This is the stretched backbone star regime (SBS). For larger...
Figure 1: Behavior of a comb-like polymer (made of $n$ segments, each containing $N$ monomers along the backbone and $P$ monomers in a side-chain) in a good solvent.

Values of $N$, the backbone is weakly stretched (flexible backbone star (FBS) regime). The smaller core size $R_C$ can be obtained from the following Flory free energy which takes into account the side-chain and backbone elastic free energy and the excluded volume interactions in the core region:

$$F = \frac{R_C^2}{nN\alpha^2} + n\frac{R_C^2}{P_C\alpha^2} + \frac{(nP_C)^2\alpha^3}{R_C^3}$$

(1)

where $P_C \leq P$ is the number of monomers from each side-chain that are within the core. Note $P_C$ can also be obtained from the continuity of the osmotic pressure $kT/\xi^3$ between the core interior (with $\xi = a\phi^{-3/4}$ where $\phi \simeq nP_C\alpha^3/R_C^3$) and the core boundary, where the arms of the star depart from one another (where $R_C^2 = n\xi^2$, see reference [3]).

If the side-chain length $P$ is reduced, then at some point, the side-chains do not extend beyond the core region, precisely, when $P = P_C$. The star is now reduced to its core. Let $n_C = n$ be the number of segments. If the total number $n$ of side-chains is now increased beyond $n_C$, the molecule develops into a self-avoiding walk of such cores whose size is $R_C$ (strongly or weakly stretched) and thus resembles a wiggling worm (regime SBW or FBW) whose radius of gyration is therefore equal to $R = R_C (n/n_C)^{3/5}$ (where $n_C$
is the number of segments per core). This result is confirmed by the fact that in the FBW regime (flexible backbone), the overall radius of gyration \( R = R_C \left( \frac{n}{n_C} \right)^{3/5} = an^{3/5}N^{1/5}P^{2/5} \) can be obtained directly by minimizing a simple Flory free energy \[ F = \frac{kT}{nNa^2} + \frac{(nP)^2a^3}{R^3}. \] (2)

### 3 Confined comb and injection threshold

As shown above, depending on the molecular parameters, the overall conformation of a comb in good solvent is similar to that of a swollen linear chain if side-chains are short or intermediate in length, and it is similar to that of a star if side-chains are long. The way in which such a comb may permeate through a nanopore (diameter \( D \)) due to a solvent flow is therefore expected to be quite different in these various conformation regimes. Indeed, the critical solvent flow that is necessary to force a linear chain into the nanopore is molecular weight independent \[ J_c = \frac{kT}{\eta} \equiv J_{c1} \] (3)

This applies to the comb molecule in the decorated chain regime (\( P < N \)) or in the weak confinement worm regime (\( R_C < D < R \)).

Conversely, the threshold current for stars is sensitive to the number of arms and to their molecular weight, depending on the nanopore diameter \[ J_{c}^{\text{star}} = J_{c1} \text{ if } D < aN/n^{3/2} \] (4)
\[ J_{c}^{\text{star}} = J_{c1} \cdot n \left( \frac{D}{Na} \right)^{2/3} \text{ if } aN/n^{3/2} < D < aN/n^{3/2} \] (5)

where in the first case the molecule penetrates the pore with just one forward arm at first, and in the second case the number of forward arms is \( n_0 \approx n^{1/2}(D/Na)^{1/3} \). These results apply as such to the comb molecule in the star regimes (FBS and SBS) as long as the core of the comb is smaller than the tube diameter (\( R_C < D < R \)), and even somewhat beyond \( D \approx R_C \), as we shall see.

We now wish to investigate situations where the pore diameter is smaller, in order to determine to what extent comb molecules can be characterized
by such a method. The first step is to determine the conformation of a comb molecule in such intermediate regimes, once it has completely entered the nanopore. As can be seen from Figure 2, if side-chains are long, the total length \( L \) of the object is essentially their length \( L_P \) which can be deduced from a Flory argument. The elastic energy of the side chains is balanced by the excluded volume free energy:

\[
\frac{F}{kT} \simeq \frac{n L_P^2}{P a^2} + \frac{(nP)^2 a^3}{L_P D^2}
\]

Minimizing this energy yields the length of the comb molecule which is proportional to the side-chain molecular weight \( P \):

\[
L \simeq L_P \simeq a P n^{1/3} (a/D)^{2/3}
\]

Conversely, if the side-chains are shorter, the length of the object is the length of the backbone and its elasticity is the dominant elastic contribution:

\[
\frac{F}{kT} \simeq \frac{L_{nN}^2}{nN a^2} + \frac{(nP)^2 a^3}{L_{nN} D^2}
\]

The length of the comb molecule is now proportional to the number \( n \) of molecule segments:

\[
L \simeq L_{nN} \simeq a n P^{2/3} N^{1/3} (a/D)^{2/3}
\]

The crossover between equations (7) and (9) occurs for \( P \simeq N n^2 \) and provides the basic ingredient for a finer description of the comb conformation, as we now see.

Consider a star in the regime of equation (7) and suppose that side-chains \( P \) are now shorter. The central region of the molecule is not affected. In fact, it will start to be affected when the side chain length has decreased to the backbone length \( L_{nN} \), i.e., when we reach the worm regime of equation (9). In other words, the length \( L_{nN} \) of the central region is given by equation (7) where \( P \) is chosen as \( N n^2 \), i.e. \( L_{nN} \simeq a N n^{7/3} (a/D)^{2/3} \).

Let us now consider a worm in the regime of equation (9). The side-chains located near the end of the backbone have extra space and are extended outwards. How far into the molecule does this edge effect penetrate can be estimated by decreasing the number \( n \) of molecule segments: when \( n \) is such that \( P \simeq N n^2 \), the molecule crossovers to the star regime and the edge effect has
Figure 2: Conformation of a comb-like polymer molecule inside a nanopore. (a) Star-like conformation: the overall length $L$ is comparable to the arm length $L_P$, and the backbone (length $L_{nN} \ll L$) may be weakly or strongly stretched (regime C-FBS or C-SBS). (b) Worm conformation: the overall length of the molecule is essentially that of the backbone ($L \simeq L_{nN}$) which is either weakly or strongly stretched (regime C-FBW or C-SBW), and about $n_{edge} \simeq n_C$ arms stretch away from the backbone along the tube axis (edge effect).
invaded the whole molecule conformation. Turning back to the worm regime, this yields the extension \( L_P \simeq a P n_{\text{edge}}^{1/3} (a/D)^{2/3} \simeq a P^{7/6} N^{-1/6} (a/D)^{2/3} \) of the edge effect, where the number of side-chains involved is given by:

\[
n_{\text{edge}} \simeq (P/N)^{1/2}
\]  

If the worm backbone is stretched \( (L = L_n N \simeq anN) \), the same approach yields the detailed conformation:

\[
n_{\text{edge}} \simeq (P/N)^{3/2} a/D \quad L_P \simeq P^{3/2}/N^{1/2} a^2/D
\]

It can be seen from all these results that in the confined geometry, the extension of the various regimes are altered because confinement may stretch the backbone completely: the limit between the confined flexible backbone worm regime (C-FBW) and the stretched backbone worm (C-SBW) is now \( P \simeq N D/a \) instead of \( P \simeq N^3 \), the limit between the flexible backbone star (C-FBS) and the stretched backbone star (C-SBS) is now \( n \simeq (D/a)^{1/2} \) instead of \( n \simeq N \), and the limit between the stretched backbone star and worm (C-SBS and C-SBW) is \( n = (P/N)^{3/2} a/D \) instead of \( n \simeq P^{3/4}/N^{5/4} \).

The results of reference [1] for the threshold current (see equations 4, 5) can be easily transposed here. Indeed, the edge of the confined worm has the same conformation as one half of a star with \( 2n_{\text{edge}} \) arms. This is also true before the molecule enters the pore since the expression for \( n_{\text{edge}} \) is the same as that for \( n_C \). The threshold current for the worm can thus be obtained simply by using the equivalent number of star arms \( n_{\text{edge}} \) (flexible worm regime C-FBW, equation 10) instead of \( n \) in equations (4, 5):

\[
J_{c-\text{FBW}}^C = J_{c_1} \quad \text{if} \quad \frac{D}{a} < \frac{N^{7/4}}{P^{3/4}}
\]

\[
J_{c-\text{FBW}}^C = J_{c_1} \cdot \left( \frac{P^{1/2}}{N^{1/2}} \right) \left( \frac{D}{N a} \right)^{2/3} \quad \text{if} \quad \frac{D}{a} > \frac{N^{7/4}}{P^{3/4}}
\]

Similarly, for the stretched backbone case (regime C-SBW):

\[
J_{c-\text{SBW}}^C = J_{c_1} \quad \text{if} \quad \frac{D}{a} > \frac{P^{9/2}}{N^{13/2}}
\]

\[
J_{c-\text{SBW}}^C = J_{c_1} \cdot \left( \frac{P^{3/2}}{N^{5/2}} \right) \left( \frac{N a}{D} \right)^{1/3} \quad \text{if} \quad \frac{D}{a} < \frac{P^{9/2}}{N^{13/2}}
\]

By comparing the various threshold current values obtained with Figure 1, we find the regimes where they are relevant. They essentially correspond to
the confined regimes described above. Indeed, as soon as \( R > D > Na \), the star threshold of equation (5) applies to regimes C-FBS and C-SBS, and the worm thresholds of equations 13 and 15 apply in regimes C-FBW and C-SBW respectively. If the pore diameter is smaller (\( aN^{4/7} < D < Na \)), the non-sensitive regime \( J_c = J_{c1} \) includes not only the decorated chain regime DC, but also a portion of the star and worm regimes (namely \( n < (Na/D)^{2/3} \) and \( P < N^{7/3}(a/D)^{4/3} \)). If the diameter is even smaller (\( D < aN^{4/7} \)), the non-sensitive regime \( J_c = J_{c1} \) includes \( n < (Na/D)^{2/3} \) and \( P < N^{13/9}(D/a)^{2/9} \), and equations (5,15) are valid beyond these limits.

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References

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[4] The fact that we obtain \( R = R_C (n/n_C)^{3/5} \) through the overall Flory argument for the whole molecule implies that the persistence length \( \lambda \) of the worm is of the order of its radius \( R_C \). This question is by no means obvious and has been much debated in recent years. It is addressed more fully in a separate study [3], whose essential argument can be expressed qualitatively in the following terms. One could imagine that the osmotic pressure of the side-chains could induce a higher worm rigidity: consider that the worm of radius \( R_C \) behaves like some continuous elastic medium whose modulus is given by the osmotic pressure \( \pi \), then the bending rigidity \( \mu \) is on the order of \( \pi R_C^4 \). The persistence length is then given by \( \lambda \simeq \mu/kT \simeq R_C^4/\xi^3 \), which can be much larger than \( R_C \). Such an elastic worm model is in fact too crude, since side-chains are free to rotate about the main chain when the worm is subjected to flexion, in
order to relieve compression on the inner side and expansion on the outer side. Similarly, the chains are free to adjust how far they extend away from the backbone. We show in reference [5] that the combination of these two effects lead to negligible bending rigidity on length scales larger than $R_C$.

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