Comb-like polymers inside nanoscale pores

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Abstract

A new method of polymer characterization, based on permeation studies using nanoscale pores, was recently proposed by Brochard and de Gennes. In the present paper, we study (at the level of scaling laws) how this method, initially developed for star polymers, can be extended to comb-like polymers. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A new method of polymer characterisation, 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

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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 Table 1 and are pictured in Fig. 1. 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. 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. 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 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:

$$\frac{F}{kT} = \frac{R_C^2}{nNa^2} + n\frac{R_C^2}{P_C a^2} + \frac{(nP_C)^2 a^3}{R_C^3} \tag{1}$$

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/ξ^3 between the core interior (with $\xi = a\phi^{-3/4}$ where $\phi \simeq nP_C^{a^3}/R_C^3$) 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

Table 1

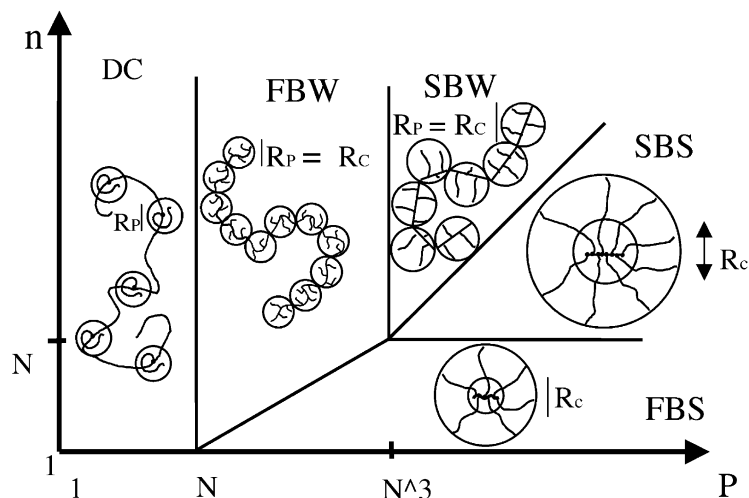| Overall molecule conformation	Radius of gyration	Backbone conformation REGIME	Other characteristics
Decorated chain $R = R_{nN}$	$R = a(nN)^{3/5}$ (Flory)	Flexible DC	$R_P = aP^{3/5}$
Worm $R = R_{nN}$, $R_c = R_P$, $R = R_C \left(\dfrac{n}{n_C} \right)^{3/5}$	$R = an^{3/5}P^{2/5}N^{1/5}$	Flexible FBW	$\dfrac{P = n_C^{\,2}N}{\begin{array}{l} R_P = aP^{3/5}n_C^{1/5} \\ \quad = aP^{7/10}N^{-1/10} \end{array}}$
i.d.	$R = an^{3/5}N^{1/2}P^{3/10}$	Stretched SBW	$\dfrac{P = n_C^{\,4/3}N^{5/3}}{\begin{array}{l} R_P = an_C N = aP^{3/5}n_C^{1/5} \\ \quad\quad = aP^{4/3}N^{-1/4} \end{array}}$
Star $R = R_P$, $n_C = n$, $R_C = R_{nN}$	$R = aP^{3/5}n^{1/5}$ (Daoud–Cotton)	Flexible FBS	$\dfrac{P_C = n^2N}{\begin{array}{l} R_C = aP_C^{3/5}n^{1/5} \\ \quad = aN^{3/5}n^{7/5} \end{array}}$
i.d.	i.d.	Stretched SBS	$\dfrac{P_C = n^2N}{\begin{array}{l} R_C = anN \\ \quad = aP_C^{3/5}n^{1/5} \end{array}}$

Fig. 1.   Behaviour 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.

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 $R = R_C(n/n_C)^{3/5} = an^{3/5}N^{1/5}P^{2/5}$ can be obtained directly by minimising a simple Flory free energy:[1]

$$\frac{F}{kT} = \frac{R^2}{nNa^2} + \frac{(nP)^2 a^3}{R^3} \tag{2}$$

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[1]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 λ 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 [4], 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 π, then the bending rigidity μ in on the order of πR_C^4. The persistence length is then given by $\lambda \simeq \mu/kT \simeq \pi R_C^4/\xi^3$ 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 [4] that the combination of these two effects lead to negligible bending rigidity on length scales larger than R_C.

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 [5]:

$$J_c = \frac{kT}{\eta} \equiv J_{c1} \tag{3}$$

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 [1,2]:

$$J_c^{star} = J_{c1} \text{ if } D < aN/n^{3/2} \tag{4}$$

$$J_c^{star} = J_{c1} \cdot n \left(\frac{D}{Na} \right)^{2/3} \text{ if } aN/n^{3/2} < D < aN/n^{3/2} \tag{5}$$

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 $n_0 \simeq n^{1/2}(D/Na)^{1/3}$. 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 $D \simeq R_C$, 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 characterised 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 Fig. 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:

$$\frac{F}{kT} \simeq n \frac{L_P^2}{Pa^2} + \frac{(nP)^2 a^3}{L_P D^2} \tag{6}$$

Minimizing this energy yields the length of the comb molecule which is proportional to the side-chain molecular weight P:
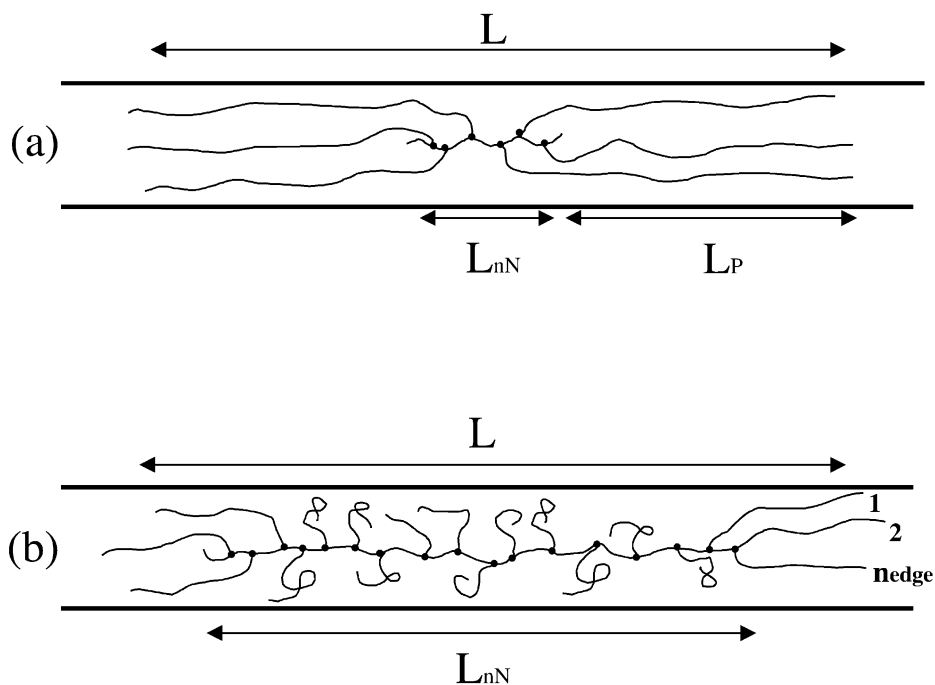
$$L \simeq L_P \simeq aPn^{1/3}(a/D)^{2/3} \tag{7}$$

Fig. 2.   The conformation of a comb-like molecule inside a nanopore. (a) Star-like conformations: 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 approximately $n_{edge} \simeq n_c$ arms stretch away from the backbone along the tube axis (edge effect).

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:

$$\frac{F}{kT} \simeq \frac{L_{nN}^2}{nNa^2} + \frac{(nP)^2 a^3}{L_{nN}D^2} \tag{8}$$

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

$$L \simeq L_{nN} \simeq anP^{2/3}N^{1/3}(a/D)^{2/3} \tag{9}$$

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

Consider a star in the regime of Eq. (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 Eq. (9). In other words, the length L_{nN} of the central region is given by Eq. (7) where P is chosen as Nn^2, i.e. $L_{nN} \simeq aNn^{7/3}(a/D)^{2/3}$.

Let us now consider a worm in the regime of Eq. (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 $P \simeq Nn^2$, the molecule crossovers to the star regime and the edge effect has invaded the whole molecule conformation. Turning back to the worm regime, this yields the extension $L_P \simeq aPn_{edge}^{1/3}(a/D)^{2/3} \simeq aP^{7/6}N^{-1/6}(a/D)^{2/3}$ of the edge effect, where the number of side-chains involved is given by:

$$n_{edge} \simeq (P/N)^{1/2} \tag{10}$$

If the worm backbone is stretched ($L = L_{nN} \simeq anN$), the same approach yields the detailed conformation:

$$n_{edge} \simeq (P/N)^{3/2} a/D \qquad L_P \simeq (P^{3/2}/N^{1/2})a^2/D \tag{11}$$

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 $P \simeq ND/a$ 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 Eqs. (4) and (5)) can be easily transposed here. Indeed, the edge of the confined worm has the same conformation as one half of a star with $2n_{edge}$ arms. This is also true before the molecule enters the pore since the expression for n_{edge} is the same as that for n_C. The threshold current for the worm can is thus obtained simply by using the equivalent number of star arms n_{edge} (flexible worm regime C–FBW, Eq. (10)) instead of n in Eqs. (4) and (5):

$$J_c^{C-FBW} = J_{c1} \text{ if } \frac{D}{a} < \frac{N^{7/4}}{P^{3/4}} \tag{12}$$

$$J_c^{C-FBW} = J_{c1} \cdot \frac{P^{1/2}}{N^{1/2}}\left(\frac{D}{Na}\right)^{2/3} \text{ if } \frac{D}{a} > \frac{N^{7/4}}{P^{3/4}} \tag{13}$$

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

$$J_c^{C-SBW} = J_{c1} \ \text{if} \ \frac{D}{a} > \frac{P^{9/2}}{N^{13/2}} \tag{14}$$

$$J_c^{C-SBW} = J_{c1} \cdot \frac{P^{3/2}}{N^{5/2}} \left(\frac{Na}{D} \right)^{1/3} \ \text{if} \ \frac{D}{a} > \frac{P^{9/2}}{N^{13/2}} \tag{15}$$

By comparing the various threshold current values obtained with Fig. 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 Eq. (5) applies to regimes C−FBS and C−SBS and the worm thresholds of Eq. (13) and Eq. (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 Eqs. (5) and (15) are valid beyond these limits.

Acknowledgements

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