

Injection Threshold for a Statistically Branched Polymer inside a Nanopore

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ABSTRACT: A nonadsorbing, flexible polymer (in dilute solution with a good solvent) enters a pore (of diameter D smaller than its natural size, R) only when it is sucked in by a solvent flux, J , higher than a threshold value, J_c . For linear polymers $J_c \sim kT/\eta$ (where T is the temperature and η the solvent viscosity). We discuss here the case of statistically branched polymers, with an average number, b , of monomers between branch points. We find that there are two regimes, “weak confinement” and “strong confinement”, depending on the tube diameter. By measuring J_c in both regimes, we should determine both the molecular weight and the number b .

I. Introduction

Thanks to suitable metallocene catalysts,¹ it is now possible to produce polyolefins with adjustable average molecular weights, $M = XM_0$ (X , polymerization index; M_0 , monomer molecular weight), and with adjustable average levels of branching. But standard rheological measurements are not quite sufficient to characterize the resulting complex mixtures. This led us recently to propose another, complementary method of characterization, based on permeation studies using nanopores.² The discussion in ref 2 was restricted to a very simple family of branched objects, namely star molecules. We found that stars can be sucked in a narrow pore when the solvent flux J inside the pore exceeds a certain threshold, $J_c(\text{star})$:

$$J_c(\text{star}) \cong \frac{kT}{\eta} f \left(\frac{D}{Na} \right)^{2/3} \quad (1)$$

(whenever $f > (Na/D)^{2/3}$)

where f is the number of arms in the star ($f \gg 1$), and $N = Xf$ is the arm length. k is the Boltzmann constant, a is the monomer size, T is the temperature, and η is the solvent viscosity. (Equation 1 should hold when the molecules do *not* adsorb on the pore walls.) The critical current predicted by eq 1 is very sensitive to the amount of branching (i.e. to f).

In the present paper, we present a theoretical discussion (at the level of scaling laws) for the more usual case: a *statistically branched* polymer. In section II, we discuss the statistics of confined chains. The main idea here is based on what we call the “Ariadne length” of a cluster. The principle was discovered first by Vilgis et al.,³ using a slightly different language, in relation with what is called the spectral dimension, d_s of clusters (see Appendix A for a discussion of d_s). Our approach in section II is based on a simple Flory argument, and predicts in fact the value $d_s = 4/3$, which is currently recognized to be an excellent approximation.⁴ In section III, we set up the hydrodynamics and compute the critical current. Section IV extends the discussion to cases of “weak branching”, where the number of mono-

mers between adjacent branch point has a large average value b : this is the most useful case in practice. Section V analyses all the results.

For readers inclined to somewhat more mathematical discussions, the case of branched objects with more general spectral dimensions d_s is studied in Appendix B.

II. Statistics of Branched Clusters

(1) Overall Size in Dilute Solution, R . An interesting approach, based on a Flory type of calculation, was set up by Lubensky and Isaacson;⁵ a lucid description (incorporating many physical phenomena) was set up by Daoud and Joanny.⁶

An *ideal* branched structure (with no steric interactions) would have a size $R_0 \sim X^{1/4}a$.^{7,8} If we now incorporate excluded volume (with a volume per monomer of a^3), we can write a coil energy $F(R)$ depending on the size R as follows:

$$F(R) \cong kT \left[\frac{R^2}{R_0^2} + \frac{X^2 a^3}{R^3} \right] \quad (2)$$

Here, the first term is an elastic energy, and the second term is the effect of intermonomer repulsions (Xa^3/R^3 is the internal volume fraction). Optimizing (2) with respect to R , we arrive at:

$$R \cong X^{1/2} a \quad (3)$$

Some verifications of eq 3 have been obtained (on dilute solutions of branched polymers) by M. Adam et al.⁹ In the following, we shall be concerned with pores of diameter $D \ll R$.

(2) Flory Argument in a Tube. Let us now modify eq 2 for a confined polymer, extended over a length, L (Figure 1). The allowed volume is now LD^2 , and we have

$$\frac{F}{kT} = \frac{L^2}{X^{1/2} a^2} + \frac{X^2 a^3}{LD^2} \quad (4)$$

Optimizing with respect to L , we find

$$\frac{L}{D} = X^{5/6} \left(\frac{a}{D} \right)^{5/3} \equiv \left(\frac{R}{D} \right)^{5/3} \quad (5)$$

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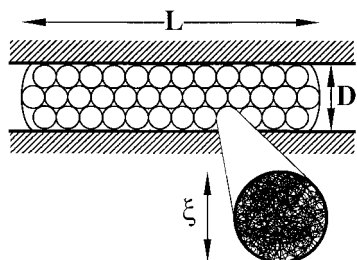


Figure 1. A branched polymer forced in a pore of diameter D smaller than its natural size, R . The interior of the polymer is a semidilute solution of correlation length ξ .

and the internal concentration is

$$\phi = \frac{Xa^3}{LD^2} = \left(\frac{D_{\min}}{D}\right)^{4/3} \quad (6)$$

The diameter

$$D_{\min} = aX^{1/8} \quad (7)$$

corresponds to maximum squeezing ($\phi = 1$).¹⁰ Of particular interest is the corresponding value of L :

$$L_{\max} = aX^{5/6} \left(\frac{a}{D_{\min}}\right)^{5/3} \quad (8a)$$

Ariadne helped Theseus through the Minoan labyrinth, by giving him a reel of thread, which kept a track of his march. l_A represents the length of the shortest path, from the starting point, to the monster which is to be killed—in our context, the thread distance between two arbitrary points on the cluster (see Appendix A). In the squeezed polymer, assuming that there are *no loops*, the corresponding path becomes completely stretched, and thus:

$$l_A = L_{\max} = aX^{3/4} \quad (8b)$$

As usual for semidilute solutions in good solvents, we can think of the squeezed polymer as a compact stacking of blobs, each with a diameter (ξ) and a number of monomers (g). The relation between g and ξ inside one blob is derived from the size of a single cluster (eq 3):

$$\xi = ag^{1/2} \quad (9)$$

Writing that $\phi = ga^3/\xi^3$ (compact arrangement) and comparing with eq 6, we ultimately find the correlation length:

$$\xi = a\left(\frac{D}{a}\right)^{4/3} X^{-1/6} \quad (10)$$

For weak confinement ($D = R$) we recover $\xi = R$, and for very strong confinement ($D = D_{\min}$) we have $\xi \sim a$.

III. Suction into the Tube

We now force our polymer through the pore and assume that a certain length (y) of the squeezed structure has entered, as shown in Figure 2. The free energy required for this may be written as

$$F = F_c y - \int_0^y dy F_h(y) \quad (11)$$

where F_c is a force resulting from confinement, while F_h is a hydrodynamic force. We can write simply

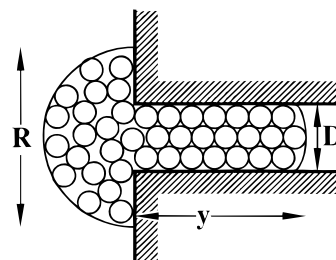


Figure 2. The entry process for the branched polymer: only a certain length, y , has penetrated in the tube.

$$F_c = \Pi D^2 \quad (12)$$

where Π is the osmotic pressure of the squeezed object, given by the usual scaling law,

$$\Pi = kT\xi^3 \quad (13)$$

and D^2 is the cross sectional area of the tube. The hydrodynamic force is equivalent to a Stokes force per blob,

$$F_h \cong \eta \xi V \frac{D^2 y}{\xi^3} = \frac{\eta J y}{\xi^2} \quad (14)$$

where $V = J/D^2$ is the local solvent velocity and $D^2 y/\xi^3$ is the number of blobs inside the pore.

Returning now to the energy, $F(y)$ (eq 11), we see that it is a maximum for

$$y = y^* = \frac{F_c \xi^2}{J\eta} \quad (15)$$

corresponding to an energy barrier,

$$E^* = \frac{1}{2} F_c y^* = \frac{(kT)^2}{J\eta} \left(\frac{D}{\xi}\right)^4 \quad (16)$$

Aspiration occurs when $E^* \sim kT$; this gives a critical current,

$$J_c \cong \frac{kT(D)}{\eta \left(\frac{D}{\xi}\right)^4} \quad (17)$$

Equations 16 and 17 are a natural extension of the result for the "symmetric mode" of stars (ref 2). For the stars in this mode, we had $f/2$ branches in parallel, each occupying a cross section $\xi^2 = 2D^2/f$, and the barrier energy was proportional to $(f/2)^2/J$, as in eq 16.

We can now insert the results of section II on the correlation length (eq 10), and we find:

$$J_c = \frac{kT(R)}{\eta \left(\frac{D}{a}\right)^{4/3}} \quad (18)$$

$$= \frac{kT}{\eta} X^{2/3} (a/D)^{4/3} \quad (19)$$

IV. Extension to Weaker Branching

Our discussion assumed a very high density of branching. In a more chemical language, if we make our polymer via condensation reactions, using a mixture of two and three functional units, we were assuming that the initial concentrations of these species were comparable.

In practice, we often operate with a much smaller fraction of three functional unit species, and the average number of difunctional monomers between two adjacent

branch points (b) is much larger than unity. Then, our formulas have to be adjusted as follows.

(1) An unconfined polymer in dilute solution will have a size

$$R = aX^{1/2}b^{1/10} \quad (20)$$

and an Ariadne length

$$l_A = aX^{3/4}b^{1/4} \quad (21)$$

One may check these exponents by noticing that if $b = X$ (i.e.: when we return to linear polymers), we have the standard values $R = aX^{3/5}$ (the Flory radius) and $l_A = aX$.

(2) The length L of the confined polymer is still given by the second form of eq 5

$$L = D\left(\frac{R}{D}\right)^{5/3} = a\left(\frac{a}{D}\right)^{2/3} X^{5/6} b^{1/6} \quad (22)$$

where R is now taken from eq 20. At maximum stretching, we must have $L = l_A$, and this corresponds to a size

$$D_{\min} = X^{1/8} b^{-1/8} a \quad (23)$$

(3) There is one complication, however: there are two regimes, depending on the size of the correlation length (ξ) when compared to the size (ξ_b) of one linear piece of b monomers. In good solvents, ξ_b is given by the Flory law:

$$\xi_b = ab^{3/5} \quad (24)$$

(a) When the tube diameter D is larger than a certain crossover value, D^* , we have $\xi > \xi_b$. We call this “*weak confinement*”. In this regime, the results of section II can then easily be transposed, using blobs of b monomers (and size ξ_b) instead of monomers. (This leads, in particular, to a derivation of eq 22). The correlation length is

$$\xi = a\left(\frac{D}{a}\right)^{4/3} X^{-1/6} b^{-1/30} \quad (25)$$

(b) The crossover occurs when $\xi = \xi_b$. Using eq 25, we find that the corresponding tube diameter is

$$D^* = aX^{1/8} b^{19/40} \quad (26)$$

(Conversely, if one type of nanopore (fixed diameter D) is being used to separate a polydisperse mixture, it is useful to rewrite eq 26 in terms of a critical molecular weight: $X^* = (D/a)^8 b^{-19/5}$).

Note that (from eqs 23 and 26)

$$\frac{D^*}{D_{\min}} = b^{3/5} > 1 \quad (27)$$

(c) In the interval $D^* > D > D_{\min}$, we have a new regime of *strong confinement*. We retain the same law for L (eq 22), but the blob structure is different. There are many blobs between two adjacent branch points, and the correlation length ξ versus volume fraction ϕ follows the classical law for semidilute solutions of *linear* polymers $\xi = a\phi^{-3/4}$. The concentration ϕ can be derived

from

$$\phi = \frac{Xa^3}{LD^3} \quad (28)$$

Using eq 22 for L , we then arrive at a very simple result:

$$\xi = a\frac{D}{D_{\min}} \quad (29)$$

(4) Knowing these static properties, we can now return to the critical current, J_c (eq 17), and we find

$$\frac{\eta}{kT} J_c = \begin{cases} X^{2/3} (a/D)^{4/3} b^{2/5} & (D > D^*) \\ (X/b)^{1/2} & (D < D^*) \end{cases} \quad (30a)$$

$$(30b)$$

In the second regime (strong confinement), J_c is independent of the tube diameter.

V. Concluding Remarks

(1) The critical current $J_c(X)$ of branched polymers ($J_c \sim X^{2/3}$) is a signature of their Ariadne length (or equivalently of their spectral dimension, as defined in the appendices). For instance, if we had not a statistically branched object but a spheroidal clump taken from a three-dimensional gel ($X \sim R^3$), we would expect $J_c \sim X^{4/3}$.

(2) If we return to the general formulas (30a,b) for statistically branched clusters with weak branching levels ($b \gg 1$), we see that one measurement of J_c in each regime ($D > D^*$ and $D < D^*$) should allow us to determine *both* the molecular weight (X) and the chemical distance between branch points (b). Thus the permeation may be a rather powerful characterization method; it may also have separation potentialities.

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Appendix A: Fractal and Spectral Dimensions of Branched Objects

(1) The *fractal* dimension of our clusters describes the relation between the size, R and the polymerization index, X :

$$X \cong \left(\frac{R}{a}\right)^{d_f}$$

For our branched systems in good solvents, $d_f = 2$ (eq 3)

(2) The *spectral* dimension of a cluster, d_s , depends on its chemical formula (describing linear sequences and branch points), but is independent of the exact conformation of the polymer (e.g. its linear segments may be rigid or flexible, d_s will be the same). The concept was introduced by Alexander and Orbach,⁴ and exploited by Rammal and Toulouse.¹¹ Here, we shall present it qualitatively, using an acoustic model as a tool.

Let us assume that our bonds can propagate sound, with a velocity c measured along the chemical sequence: the transit time between adjacent, bonded, monomers is a/c . We choose an “emitter” site (one particular monomer) and we send a signal at time 0. After a certain time, t , all the monomers which have a curvilinear distance to the emitter smaller than ct , have

received the signal. Their number is called $m(t)$. Clearly, $m(t)$ increases with time. For "self similar" situations (i.e. when $m < X$), it is correct to postulate a power law for $m(t)$:

$$m(t) = \left(\frac{ct}{a}\right)^{d_s} \quad (\text{A1})$$

The exponent d_s is characteristic of the chemical structure: a linear polymer has $d_s = 1$ (be it flexible or rigid). A sheet (like a graphite layer) has $d_s = 2$, even if it is crumpled, etc.

After a certain time, t^* , our whole cluster (X monomers) has received the acoustic signal. t^* is defined by

$$X = \left(\frac{ct^*}{a}\right)^{d_s} \quad (\text{A2})$$

The length

$$l_A = ct^* \quad (\text{A3})$$

is what we call the Ariadne length. From eq A2, we see that

$$\begin{aligned} l_A &= aX^{1/d_s} \\ &= aX^{3/4} \end{aligned} \quad (\text{A4})$$

Comparing this with eq 8b for our statistically branched clusters, we get $d_s = 4/3$.

(3) We now derive the cluster conformation (L and ξ , eqs 5 and 10) using the Ariadne length.

(a) Vilgis et al.³ assumed that the maximum stretched length of a confined cluster would scale like l_A (eq A4). Using the scaling form derived from the Flory argument for the length of the confined object (eq 5), they find the corresponding minimum tube diameter, D_{\min} (eq 7).

(b) Conversely, the maximum stretching ($L_{\max} \equiv l_A$) is due to confinement; it is thus reasonable to assume $\phi \sim 1$ in this situation (which defines some tube diameter $D \equiv D_{\min}$, eq 7). Assuming the existence of a unique scaling law from the unperturbed regime $L \sim R \sim D$ to the maximum stretching ($L = l_A$, $D = D_{\min}$), we recover eq 5.

(c) The same scaling argument as in b can be used to provide a description of the confined fractal in terms of blobs. Let us assume that confining the fractal into a tube of diameter D leaves its structure unperturbed at small length scales, i.e. that blobs of a certain size $\xi(D)$ retain their unaltered structure. Renormalizing these blobs as monomers, we can look at the confined object as a cluster in a tube of minimum diameter: $D \equiv D_{\min}(\xi(D))$. More precisely, we have $L \equiv \xi(X/x)^{1/d_s}$ (similarly to eq A4), and $LD^2 \equiv (X/x)\xi^3$ (i.e., $\phi_\xi \sim 1$), where $x = (\xi/a)^2$ is the mass of one blob (eq 3). The resulting blob size is given by eq 10.

Appendix B : Injection Threshold for Statistically Branched Polymers of Arbitrary Spectral Dimensions

(1) A useful picture for the Ariadne length, l_A , is the following. The fractal object, made of monomers, can be parametrized³ by a function $\bar{R}(x)$, where \bar{R} is the monomer position in real space ($d = 3$) and x is a vector in the discrete, $d_s -$ dimensional, parameter space $\{1, 2, \dots, N\}^{d_s}$. The parameter space describes the object connectivity, independently of how it is embedded in real space (loose or dense, crumpled or stretched). It is clear from this picture that N represents the maximum distance between two points in the object, i.e., $l_A \approx Na$.

(This is obvious with the particular cases $d_s = 1$, linear polymer, and $d_s = 2$, crumpled sheet). Obviously, the fractal molecular weight is also $X = N^{d_s}$.

(2) A generalized Flory approach yields the object radius of gyration, without use of the ideal size of a branched polymer $R_0 = aX^{1/4}$ (eq 2). Indeed, the Edwards Hamiltonian¹² can be generalized³ as

$$\frac{F}{kT} = \int d^d x (\nabla_x \bar{R}(x))^2 + \int d^d x \int d^d x' (a^3 \delta^3(\bar{R}(x) - \bar{R}(x'))) \quad (\text{B1})$$

The corresponding mean-field Flory free energy,

$$\frac{F}{kT} = \frac{R^2 N^{d_s}}{a^2 N^2} + \frac{a^3 N^{2d_s}}{R^3} = \frac{R^2}{a^2 X^{(2-d_s)/d_s}} + \frac{X^2 a^3}{R^3} \quad (\text{B2})$$

gives the correct radius of gyration in good solvent, $R = aX^{(2+d_s)/5d_s}$ (when $d_s = 4/3$, we recover eq 3).

(3) The conformation of the fractal confined in a tube can be worked out in the same way as in the main text. The Flory approach gives directly the exponent $5/3$ for the dependence of L (eq 5). The assumption that the Ariadne length is the maximum stretched length³ is made clear through the parametrization (paragraph B1): since a monomer cannot be stretched beyond extension a , the fractal cannot be stretched beyond $L_{\max} \approx Na = l_A$. From this we deduce, as in paragraph A3, another derivation of the scaling law for L (eq 5) and the blob size $\xi = D(D/R)^w$ (compare with eq 10), where $w = (d_s - 1)/(2d_s/d_f + 1 - d_s)$ (or $w = 5(d_s - 1)/3(3 - d_s)$), using the fractal dimension derived from the Flory argument, $d_f = 5d_s/(2 + d_s)$. Note that $w = 0$ for linear polymers ($d_s = 1$, $d_f = 5/3$, $\xi = D$), and $w = 1/3$ for statistically branched polymers ($d_s = 4/3$, $d_f = 2$; see eq 10).

(4) The critical solvent current for the injection of such a fractal into a nanopore is derived in the same way as for a statistically branched polymer (section III):

$$J_c = \frac{kT(D/\xi)^4}{\eta} = \frac{kT(a/D)^{4w}}{\eta} X^{4wd_f} \quad (\text{B3})$$

References and Notes

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