

Partie III
Autres problèmes

Chapitre 6

Caractérisation de polymères branchés par perméation

Introduction

It was emphasized in chapter 1 that the synthesis of homopolymers most often leads to undesired effects like polydispersity and branching. Characterization and separation methods (paragraph 1.2.6) are therefore essential. The work reported in the present chapter sets the basis for a purely physical separation method that is sensitive to branching. It is a generalization of a former work by de Gennes that deals with star polymers (ref 2 of the paper). Used alone or as a complement to other methods, it could provide a useful tool for polymer engineering.

Introduction

Comme nous l'avons indiqué au chapitre 1, le produit d'une polymérisation est rarement exempt de polydispersité et de branchement et nécessite l'emploi de méthodes de caractérisation et de séparation (paragraphe 1.2.6). De Gennes a élaboré une méthode de séparation fondée sur des effets purement physiques, pour une solution diluée de polymères en étoile [123]: le procédé permet de séparer les étoiles selon leur nombre de bras. Dans l'article reproduit ci-dessous [8] (section 6.2), nous appliquons cette méthode de séparation à des polymères branchés statistiques, et montrons ainsi qu'elle est, plus généralement, sensible au degré de branchement des molécules. Seule ou en association avec d'autres procédés, une telle méthode de séparation pourrait donc s'avérer utile dans l'industrie des polymères.

6.1 Version brève de l'article

Considérons une membrane perméable constituée de pores de taille (nanométrique) bien calibrée, séparant un compartiment contenant une solution diluée du polymère et un compartiment de solvant pur. On suppose qu'il n'y a aucune interaction particulière (telle qu'une propension à l'adsorption) entre le polymère et la membrane. En l'absence de toute différence de pression de part et d'autre, les petites molécules diffusent librement de part et d'autre de la membrane. Les grosses ne peuvent la traverser car cela nécessiterait un confinement important pour la pénétration dans un pore, défavorable du point de vue entropique. Il n'y a donc pas de perméation spontanée. Cela pourrait constituer en soi une méthode de séparation. Cependant, les temps mis en jeu sont très longs. De plus, la sélectivité concerne seulement le rayon de giration de la molécule, et très peu son degré de branchement.

La méthode proposée consiste à établir un flux de solvant à travers les pores (par une différence de pression appliquée entre les deux compartiments). Ce courant de solvant rend possible le passage de la molécule à travers le pore s'il est suffisamment important ($J > J_c$). Dans le cas d'un polymère en étoile (f bras), il s'avère (référence 2 de l'article ci-dessous) que le courant critique dépend de la connectivité de l'étoile (équation 1). L'article montre que cette sensibilité au branchement est plus générale dans cet effet de perméation.

On suppose que la dimension spectrale des polymères branchés statistiques est $d_s = 4/3$. On n'envisage d'autres valeurs que dans la seconde annexe.

Statistique des polymères branchés

X désigne le nombre de monomères de la molécule.

Rayon de giration en solution diluée

Le rayon de giration idéal de l'objet (s'il est fantôme, c'est-à-dire en l'absence de volume exclu) est $R_0 = aX^{1/4}$. A l'aide d'une énergie de Flory (équation 2), on obtient le rayon de giration de l'objet en bon solvant (équation 3).

Confinement dans un tube: argument de Flory

Une énergie de Flory modifiée (équation 4) fournit la conformation de l'objet dans un tube (équations 5 et 6). Il ne peut pas être confiné au-delà d'une certaine limite, correspondant à une densité maximale $\phi = 1$ (équations 7 et 8). La conformation en blobs est donnée par les équations 9 et 10.

Seuil de succion

La pénétration du polymère dans le pore, sur une longueur y , est gênée par la pénalité de confinement $F_c y$, mais favorisée par le travail de la force hydrodynamique F_h due au flux de solvant à travers le polymère confiné. De par ces deux effets, le polymère doit

franchir une barrière E^* (équation 16). Celle-ci est franchie si elle n'excède pas l'énergie thermique kT , ce qui correspond à un courant critique J_c (équations 17 à 19).

Cas d'un branchement moindre

Considérons maintenant le cas où les branchements du polymère sont moins fréquents: ils interviennent tous les b monomères en moyenne (b est par exemple le rapport du nombre d'unités difonctionnelles usuelles au nombre d'unités multifonctionnelles). Le polymère est donc linéaire aux échelles inférieures à b monomères, et de dimension spectrale égale à $4/3$ au-delà. Les relations établies précédemment sont modifiées.

La taille $\xi_b = ab^{3/5}$ des brins linéaires (équation 24) délimite un régime de confinement faible, dans lequel les blobs dus au confinement (dont la taille est donnée par l'équation 25 qui est une généralisation de l'équation 10) sont plus gros que ξ_b et contiennent donc des branchements; et un régime de confinement fort dans lequel les blobs de confinement (équation 29) sont plus petits que ξ_b et sont en général constitués d'un brin de chaîne linéaire.

Ces deux régimes de confinement conduisent à un seuil d'injection différent (équation 30).

Remarques

1. L'exposant $X^{2/3}$ du courant critique (équations 19 et 30a) est une signature de la dimension spectrale de l'objet.
2. Pour un polymère monodisperse à caractériser, deux mesures du courant critique (avec deux membranes différentes), une dans chaque régime de confinement (équations 30a et 30b), doit permettre de déterminer à la fois la masse totale X du polymère et son taux de branchement (quantité b). Si l'on veut au contraire extraire une fraction bien définie d'un polymère polydisperse, le nombre d'opérations est multiplié par deux: on ajuste le flux de solvant un peu en-dessous du seuil choisi, on élimine le polymère qui est passé; on ajuste le flux au-dessus du seuil, et le polymère recueilli a les caractéristiques requises.

Annexe A: Dimensions fractale et spectrale

- (1) Définition de la dimension fractale.
- (2) Dimension spectrale et longueur d'Ariane.
- (3) Conformation d'un polymère confiné de dimension spectrale donnée.

Annexe B: Seuil d'injection pour un polymère de dimension spectrale arbitraire

Les exposants obtenus dans l'expression du courant critique J_c (équation B3) dépendent de la dimension de l'objet.

6.2 Article: Injection Threshold for a Statistically Branched Polymer inside a Nanopore

Injection threshold for a statistically branched polymer inside a nanopore

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(Abstract) : A non adsorbing, 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 molecular weights $M = X M_0$ (X : polymerization index, M_0 : monomer molecular weight) and with adjustable levels of branching. But standard rheological measurements are not quite sufficient to characterize the resulting complex mixtures. This led one of 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 :

$$J_c(\text{star}) \equiv \frac{kT}{\eta} (f/2)^2 \quad (1)$$

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where f is the number of arms in the star ($f \gg 1$). (The result (1) should hold when the molecules do not adsorb on the pore walls). The critical current predicted by eq. (1) is independent of the arm length (provided that the arms are long $R > D$), but is very sensitive to the amount of branching (ie 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 statics 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 the 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 monomers 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 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 ($X a^3 / R^3$ is the internal volume fraction). Optimizing (2) with respect to R , we arrive at :

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

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 (fig. 1). The allowed volume is now $L D^2$, and we have :

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

Optimizing with respect to L , we find :

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

and the internal concentration is :

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

The diameter :

$$D_{\min} = a X^{1/3} \quad (7)$$

corresponds to maximum squeezing ($\phi = 1$). Of particular interest is the corresponding value of L , which we call Ariadne length l_A :

$$l_A = a X^{5/6} \left(\frac{a}{D_{\min}}\right)^{5/3} = X^{3/4} a \quad (8)$$

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 language, the thread distance between two arbitrary points on the cluster. In the squeezed polymer, the corresponding path becomes completely stretched, and thus $l_A = L_{\max}$.

As usual for semi dilute 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) :

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

Writing that $\phi = g a^3 / \xi^3$ (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. Succion 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 on fig. 2. The free energy required for this may be written as :

$$f = F_c y - \int_0^y d y' F_h(y') \quad (11)$$

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

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

where Π is 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 :

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

Eqs (16, 17) are a natural extension of the result for stars (ref. 2). For the stars, we had $f / 2$ branches in parallel, each occupying a cross section $\xi^2 = 2 D^2 / f$, 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 :

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

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

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 2 functional and 3 functional units, we were assuming that the initial concentrations of the 2 f. and 3 f. species were comparable.

In practice, we often operate with a much smaller fraction of 3 f species, and the average number b of difunctional monomers between two adjacent branch points 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 :

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

and an Ariadne length :

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

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

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 :

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

a) When the tube diameter D is larger than a certain cross-over 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 cross-over occurs when $\xi = \xi_b$. Using eq. (25), we find that the corresponding tube diameter is :

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

(Conversely, if one type of nanopores (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 semi dilute solutions of linear polymers $\xi = a \phi^{-3/4}$. The concentration ϕ can be derived from :

$$\phi = \frac{X a^3}{L D^3} \quad (28)$$

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 :

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

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 3 dimensional gel ($X \sim R^3$), we would expect $J_c \sim X^{4/3}$.

2) If we return to the general formulas (30 a, 30 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 to determine both the molecular weight (X) and the chemical distance between branch points (b). Thus the permeation method may be rather powerful.

Acknowledgments : this program was initiated by discussions at the DSM meeting on Polymer Rheology (Isaac Newton Institute, Cambridge, May 1996). We are especially thankful for the remarks of T. Mc Leish and S. Milner during this symposium.

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 (eg its linear segments may be rigid, or may be flexible : d_s will be the same). The concept was introduced by Alexander and Orbach ⁽⁴⁾, and exploited by Rammal and Toulouse ⁽⁹⁾. 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 (ie when $m < X$), it is correct to postulate a power law for $m(t)$:

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

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^* , all our cluster (X monomers) has received the acoustic signal. t^* is defined by :

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

The length :

$$l_A = ct^* \tag{A3}$$

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

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

for our statistically branched clusters. Hence, $d_s = 4/3$.

3) We now derive the cluster confirmation (L and ξ , eqs 5, 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, ie 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 $L D^2 \equiv (X/x) \xi^3$ (ie, $\phi_\xi \sim 1$), 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**

1) A useful picture for the Ariadne length l_A is the following. The fractal object, made of monomers, can be parametrized ⁽³⁾ by a function $\vec{R}(x)$, where \vec{R} is the monomer position in real space ($d = 3$), and where 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, ie, $L_A \cong Na$. (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 $R_0 = a X^{1/4}$ (eq. 2). Indeed, the Edwards Hamiltonian ⁽¹⁰⁾ can be generalized ⁽³⁾ as :

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

The corresponding mean-field Flory Free Energy :

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

gives the correct radius of gyration in good solvent $R = a M^{(2+d_s)/5d_s}$ (with $d_s = 4/3$, 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 length ⁽³⁾ is made clear through the parametrization (paragraph B1) : since a monomer cannot be stretched beyond extension a , the fractal cannot be stretched beyond $L_{max} \cong Na = l_A$. From this we deduce, as in paragraph A3, another derivation of scaling law for L (eq. 5), and the blob size $\xi = D(D/R)^w$ (compare with eq. 10), where $w = (d_s - 1) / (2 d_s / d_f + 1 - d_s)$ (or $w = 5(d_s - 1) / 3(3 - d_s)$), using the fractal dimension derived from the Flory argument, $d_f = 5 d_s / (2 + d_s)$. 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) :

$$J_c = \frac{kT}{\eta} \left(\frac{D}{\xi} \right)^4 = \frac{kT}{\eta} \left(\frac{a}{D} \right)^{4w} M^{4w/df} \quad \text{B3}$$

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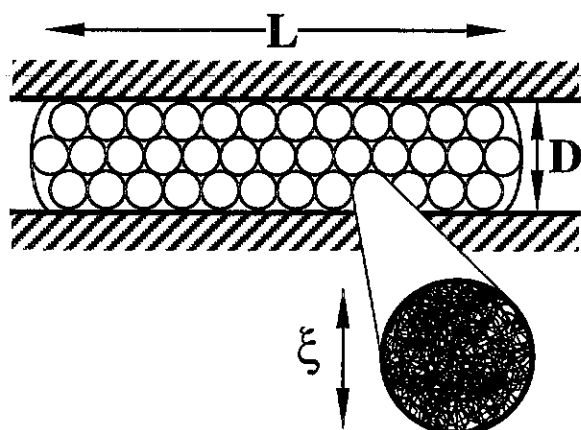


Figure 6.1: A branched polymer forced into a pore of diameter D smaller than its natural size R . The interior of the polymer is a semi-dilute solution of correlation length ξ .

Figure 6.1: On force un polymère branché à entrer dans un pore de diamètre D inférieur à son extension naturelle R . L'intérieur est une solution semi-diluée de longueur de corrélation ξ .

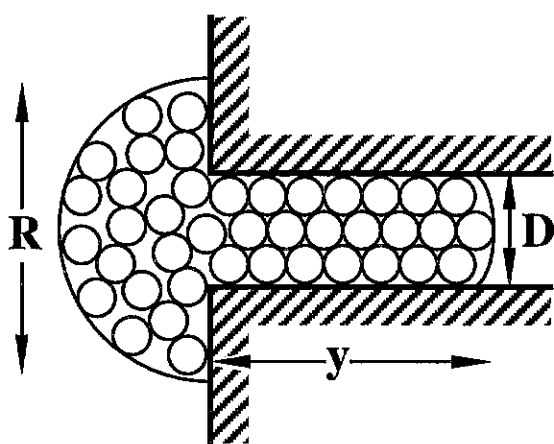


Figure 6.2: The entry process for the branched polymer: only a certain length y has penetrated in the tube.

Figure 6.2: L'entrée du polymère branché: seule une certaine longueur y a pénétré dans le tube.