Scaling Theory of Molten Polymers in Small Pores

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ABSTRACT: One long, flexible coil (N monomers) is dissolved in a melt of shorter, chemically identical chains (P monomers per chain). (1) For *bulk* melts, two regimes are known to exist. (a) $N < N_{C3} = P^2$: The monomer–monomer interactions of the N chain are screened out and the size R is ideal $R = R_0 = aN^{1/2}$. (b) $N > N_{C3}$: The coil is partially swollen and behaves like a string of subunits, each of N_{C3} monomers. Within one subunit the behavior is ideal, and the subunit size is $aN_{C3}^{1/2} = aP$. Different subunits repel each other and the size is $R_3 = (N/N_{C3})^{3/5}aP$. (2) For a melt confined in a *slit* of width $D < R_3$ we find two regimes. (a) $D > aP$: We expect to find a two-dimensional swollen chain, made of superunits of size D; at scales $r < D$ each superunit is a self-avoiding walk as described in (1b). (b) $D < aP$: The behavior at scales $r < D$ is ideal. If $N < N_{C2} = PD/a$ the whole N chain is ideal. If $N > N_{C2}$ we find a two-dimensional self-avoiding behavior, based on ideal "pancakes" of size $aN_{C2}^{1/2}$ that are mutually self-avoiding. (3) For a melt in a *tube* of diameter $D < R_3$ we expect three regimes. (a) $D > aP$: We expect a one-dimensional (1d) swollen chain, again made of superunits, each of which is a 3d self-avoiding walk. (b) $aP^{1/4} < D < aP$: If $N < C_{C1} = P^{2/3}(D/a)^{4/3}$ the whole chain should be ideal. If $N > N_{C1}$ we expect a 1d sequence of mutually avoiding "sausages" of length $aN_{C1}^{1/2}$. Inside each sausage the behavior should be ideal. (c) $D < aP^{1/4}$: Here all chains segregate and the N chain completely fills a portion of the tube of length $L \simeq Na^3/D^2$. Our analysis is restricted to scaling laws; the exact prefactors in all our formulas remain unknown.

1. Introduction

When one long flexible coil (N monomers) is immersed in a melt of shorter, chemically identical chains (P monomers per chain), the monomer–monomer interactions of the N chain are screened out. The excluded-volume parameter v is then given by

$$v = v_0/P \qquad (1)$$

where $v_0 \sim a^3$ is the bare excluded volume ("a" being a monomer size). Result (1) was first stated by Flory,[1] but its physical interpretation in term of screening is due to Edwards.[2] It can be simply deduced from the Flory–Huggins free energy of polymer mixtures.[3] For two chemically identical polymers, the free energy of mixing (per site) is purely entropic:

$$\frac{F_{site}}{kT} = \frac{\Phi}{N} \log \Phi + \frac{1-\Phi}{P} \log (1 - \Phi) \qquad (2)$$

where Φ is the volume fraction of the N monomers. In the limit of small Φ, eq 2 leads to

$$\frac{F_{site}}{kT} = \frac{\Phi}{N} \log \Phi + \frac{1}{2P}\Phi^2 + ... \qquad (3)$$

Equation 3 shows that the excluded-volume parameter is indeed given by eq 1.

The screening of the monomer–monomer interaction of the N chain leads to a partial deswelling of the chain. Following Flory, the free energy of the chain can be written as

$$F_{ch}/kT = Nv\bar{C} + (R/R_0)^2 \qquad (4)$$

where $v\bar{C}$ is the repulsive energy per monomer, $\bar{C}$ being the mean local concentration of N monomers: $\bar{C} = N/R^3$. The second term in eq 4 is an elastic term corresponding to a chain elongation R ($R_0 = aN^{1/2}$ is the ideal chain radius).
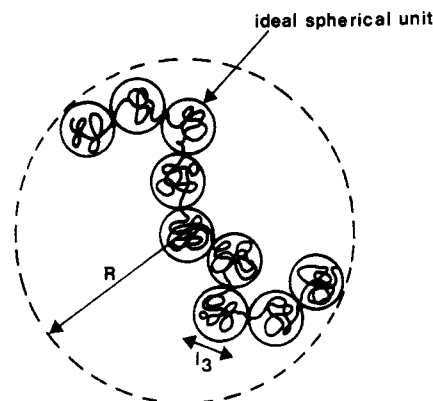
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Figure 1. Conformation of one single, partially swollen N chain dissolved in a melt of smaller P chains. The N chain can be described as a self-avoiding walk of N/N_{C3} units of size $l_3 = aP$.

From eq 4 one can define a perturbation parameter ζ_3 as

$$\zeta_3 = Nv\bar{C}_0 = \frac{N^2}{R_0^3}\frac{v_0}{P} \qquad (5)$$

where $\bar{C}_0 = N/R_0^3$ is the mean local concentration for an ideal chain. The threshold length N_c between an ideal and a swollen chain is obtained by setting the parameter ζ_3 equal to one:

$$N_{C3} = P^2 \qquad (6)$$

If $N < N_{C3}$, the N chain is ideal. One the other hand, if $N > N_{C3}$, the N chain is partially swollen: short segments of the chain (with a number of monomers smaller than N_{C3}) will show internal correlation of an *ideal* chain, but larger segments repel each other. The chain thus behaves like a string of subunits, each containing N_{C3} monomers (Figure 1). Within one subunit, the behavior is ideal, leading to a subunit size $l_3 = aN_{C3}^{1/2} = aP$. Different subunits repel each other and the resulting self-
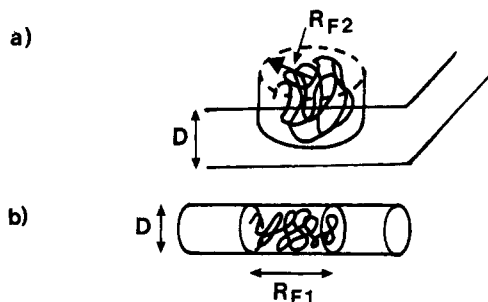
Figure 2. Conformations of a single flexible N chain trapped into a slit (a) or a capillary (b) for the case $P = 1$.

avoiding chain (of unit step l_3) has a size

$$R_3 = (N/N_{C3})^{\nu_3} l_3 \qquad (7)$$

where $\nu_3 = 3/5$ is the Flory three-dimensional exponent.

The size R_3 of the N chain can also be directly obtained by minimizing eq 4. Omitting all numerical coefficients, we find

$$R_3 = aN^{3/5}P^{-1/5} \qquad (8)$$

in agreement with eq 7.

Our aim here is to study how the deswelling of the N chain by the P chains (eq 6 and 7) is modified when the chains are confined to pores (slits or capillaries) of diameter D, comparable to the coil radius R_3 (eq 8).

The statistics of macromolecular solutions trapped in small pores has been discussed by Daoud and de Gennes[4] for the case of N chains dissolved in a good solvent of small molecules ($P = 1$). It shows many different regimes, depending on the concentration of the N chains and on the diameter D of the pore. Let us briefly recall the single-chain problem:

(a) in a *slit* of width D smaller than the free coil radius $R_{F3} = aN^{3/5}$ (where F stands for Flory and 3 for three-dimensional), the chain is squeezed into a flat "pancake" of thickness D and radius R_{F2} (Figure 2a). The chain can be described as a sequence of superunits, each of volume D^3. Inside one superunit, the chain behaves like a three-dimensional self-avoiding walk: the number of monomers per superunit is thus given by $g = (D/a)^{5/3}$. For long-range properties, the chain can be pictured as a two-dimensional (2d) self-avoiding walk of unit step D:

$$R_{F2} = D(N/g)^{\nu_2} = aN^{3/4}(a/D)^{1/4} \qquad (9)$$

where $\nu_2 = 3/4$ is the 2d Flory exponent.

(b) in a *capillary* of diameter $D < R_{F3}$ the chain is squeezed into a long "cigar" of diameter D and length R_{F1} (Figure 2b). The chain can now be described as a linear sequence of N/g superunits ($g = (D/a)^{5/3}$), each of volume D^3:

$$R_{F1} = (N/g)D = aN(a/D)^{2/3} \qquad (10)$$

The conformations of individual chains for a *monodisperse melt* confined in a tube have been studied by Brochard and de Gennes.[5] For $D < aP^{1/4}$ (D being the tube diameter and P the number of monomers per chain), the chains are spatially segregated. This result can be easily understood by the following argument: when D is large, we are dealing with a three-dimensional system; the chains are ideal, with size $R_0 = aP^{1/2}$. For $D < R_0$, each chain is confined in two directions and spans a length R_0 in the direction parallel to the tube axis. As D decreases, the internal filling fraction $f = Pa^3/R_0 D^2$ increases up to $f = 1$ for $D = aP^{1/4}$. For $D < aP^{1/4}$, the chains lie in sequence one after the other, each occupying a given length $L = Pa^3D^{-2}$ of the tube.

In this paper we analyze the configuration of a *single* N chain confined in a pore (diameter D) filled by a melt of shorter P chains (the regime of N chains overlapping will be published elsewhere[6]). In particular we derive the threshold length N_C, which separates the ideal regime from the swollen regime as a function of P and D. The size of the N chain is derived by two methods: (i) by using an argument of the Flory type, which gives the correct size but not the correct free energy; (ii) by a "blob approach" where the chain is divided into smaller units. In section 2 we discuss the single-chain problem for a slit. The capillary case is discussed in section 3. In section 4 we derive the partition coefficient for pores exchanging chains with a bulk solution.

Long capillaries of circular cross section can be realized in various ways, for instance in porous glass or polymeric films by leaching[7,8] or with open crystallographic structures such as zeolites.[9] The case of slits might be found with a cleavage fracture in mica.

2. Chain in a Slit

Let us start from a slit of diameter D filled by a melt of P chains. We now bring one single N chain inside the slit ($N > P$).

If $D \gg R_3 = aN^{3/5}P^{-1/5}$, no change in the behavior of the N chain is expected: the chain remains a spherical coil and the threshold length N_C is still given by $N_{C3} = P^2$ (eq 6).

But if $D < R_3$, the coil is squeezed into a flat pancake of thickness D and radius R. The Flory free energy of the pancake is given by eq 4 with the mean concentration $\bar{C}$ now equal to N/R^2D:

$$\frac{F_{ch}}{kT} = \frac{v_0}{P}\frac{N^2}{R^2D} + \left(\frac{R}{R_0}\right)^2 \qquad (11)$$

From eq 11 one can define a perturbation parameter as $\zeta_2 = aN/PD$. The threshold length N_c is obtained by setting ζ_2 equal to one: $N_{C2} = PD/a$. If $P < (D/a)$, ζ_2 is always greater than one (since we have assumed $D < R_3$), and the chain is swollen (i.e., $R > R_0$). If $P > (D/a)$, the chain is ideal (i.e., $R = R_0$) for $N < P(D/a)$ and swollen (i.e., $R > R_0$) for $N > P(D/a)$. The radius R of the chain can be derived directly by minimizing the free energy (eq 11). This leads to

$$R = a\frac{N^{3/4}}{P^{1/4}(D/a)^{1/4}} \qquad (12)$$

The radius of the chain (eq 12) can also be derived by a microscopic approach. We have seen that a free chain is built from ideal spheres of size l_3 that exclude each other (section 1). If the chain is confined ($D < R_3$), two different behaviors are expected.

(1) $D > aP$. As long as D is greater than $l_3 = aP$, the chain can still be pictured as a sequence of ideal spheres of size l_3 that exclude each other. At scales smaller than D, we have a 3d self-avoiding walk (unit step l_3), independent of the confining slit. At scales greater than D, the chain can be described as a 2d sequence of superunits of size D, each containing g_D monomers ($g_D = (D/a)^{5/3}P^{1/3}$). The N/g_D superunits repel each other and form a 2d self-avoiding walk (unit step D) of size

$$R = (N/g_D)^{\nu_2}D \qquad (13)$$

where ν_2 is the two-dimensional exponent. By using the (approximate) Flory value $\nu_2 = 3/4$, we recover result (12).

(2) $D < aP$. Since $D < aP$, it is no longer possible to describe the chain as a sequence of ideal spheres of size
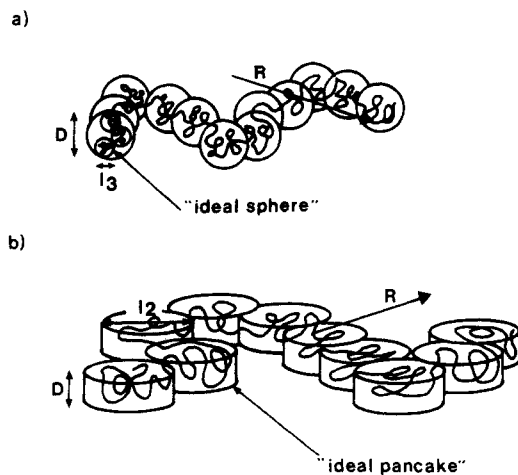
a)

b)

Figure 3. Conformations of one single N chain dissolved in a melt of smaller P chains, the system being confined to a slit of width D. (a) For $D > aP$ the N chain is built from "ideal spheres" of size l_3, which exclude each other and generate a 3d self-avoiding walk at scales smaller than D and a 2d self-avoiding walk at larger scales. (b) For $D < aP$, a large chain ($N > N_{C2} = P(D/a)$) is a 2d sequence of N/N_{C2} self-avoiding "pancakes" of size $l_2 = aN_{C2}^{1/2}$.
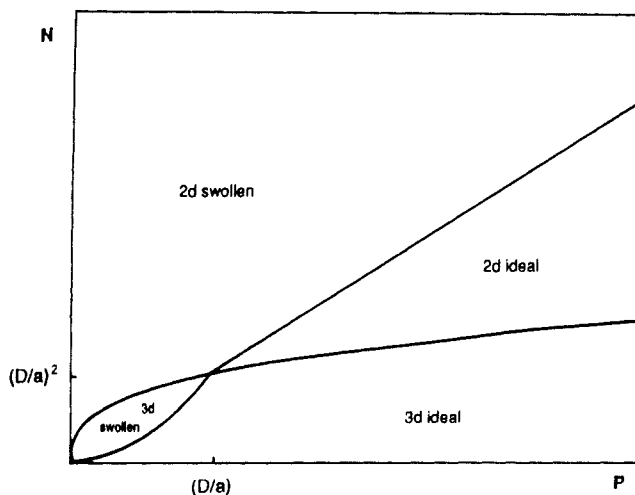

Figure 4. Various regimes for an N chain immersed in a melt of smaller P chains, the system being confined into a slit of width D.

$l_3 = aP$. One must build new fundamental units, "ideal pancakes", which are now sensitive to the confinement. To achieve mutual exclusion, such pancakes must contain $N_{C2} = PD/a$ monomers (corresponding to $\zeta_2 = 1$). Depending on the size of the N chain, two regimes are expected: (a) if $N < N_{C2}$, the whole chain is ideal (i.e., $R = R_0$), (b) if $N > N_{C2}$, the chain can be pictured as 2d self-avoiding walk of ideal pancakes (Figure 3); the size of one pancake is $l_2 = aN_{C2}^{1/2}$, leading to a total radius of the chain

$$R = (N/N_{C2})^{\prime 2} l_2 \qquad (14)$$

which again corresponds to (12).

Conclusion. The different regimes are summarized in Figure 4.

(1) If $P < D/a$, the threshold length N_C is given by the usual expression $N_{C3} = P^2$. The line $N = P^2$ separates two three-dimensional regimes (ideal sphere versus swollen sphere). For $N > (D/a)^{5/3}P^{1/3}$, the confined chain can be pictured as a two-dimensional swollen chain made of superunits of size D; at scales smaller than D each superunit is a 3d self-avoiding walk.

(2) If $P > D/a$, the threshold length N_C is *reduced*: $N_{C2} = P(D/a)$. If $N < P(D/a)$, the whole N chain is ideal. If $N > P(D/a)$, the chain is a self-avoiding walk of ideal pancakes of size $a(PD/a)^{1/2}$. Note that for $D = a$ we recover the true two-dimensional behavior for which $N_C = P$ (see ref 10).

3. Chain in a Capillary

Let us start from a capillary of diameter D, filled by a melt of P chains. We now bring one single N chain inside the capillary ($N > P$).

If $D \gg R_3 = aN^{3/5}P^{-1/5}$, no change in the behavior of the N chain is expected: the chain remains a spherical coil and the threshold length N_C is still given by $N_{C3} = P^2$ (eq 6).

But if $D < R_3$, the chain is squeezed into a "cigar" of length R. The Flory free energy of the confined chain is given by

$$\frac{F_{ch}}{kT} = \frac{v_0}{P} \frac{N^2}{RD^2} + \left(\frac{R}{R_0}\right)^2 \qquad (15)$$

from which one can define a perturbation parameter $\zeta_1 = N^{3/2}a^2/PD^2$. The threshold length is obtained by setting ζ_1 equal to one: $N_{C1} = P^{2/3}(D/a)^{4/3}$. If $P < D/a$, ζ_1 is always greater than one (since $D < R_3$) and the chain is swollen ($R > R_0$). If $P > D/a$, the chain is ideal (i.e., $R = R_0$) for $N < P^{2/3}(D/a)^{4/3}$ and swollen (i.e., $R > R_0$) for $N > P^{2/3}(D/a)^{4/3}$. By minimizing eq 15 one obtains the length R:

$$R = a\frac{N}{P^{1/3}(D/a)^{2/3}} \qquad (16)$$

As in the previous case (section 2), the radius of the chain (eq 16) can also be derived by a microscopic approach. We know that a free chain is built from ideal spheres of size l_3 that exclude each other (section 1). When the diameter of the tube becomes smaller than the coil size R_3, three different behaviors are expected.

(1) $D > aP$. As long as D is greater than $l_3 = aP$, the chain can still be pictured as a sequence of ideal spheres of size l_3 that exclude each other. At scales smaller than D, we have a 3d self-avoiding walk (unit step l_3), independent of the confining capillary. At scales greater than D, the chain can be described as a sequence of superunits of size D, each containing $g_D = (D/a)^{5/3}P^{1/3}$ monomers. The N/g_D superunits repel each other, leading to a length

$$R = \frac{N}{g_D}D \qquad (17)$$

One can check that eqs 16 and 17 do coincide.

(2) $aP^{1/4} < D < aP$. Since $D < aP$, it is not more possible to describe the chain as a sequence of ideal spheres of size $l_3 = aP$. One must built new fundamental units, ideal sausages, which are now sensitive to the confinement. To achieve mutual exclusion, such sausages must contain $N_{C1} = P^{2/3}(D/a)^{4/3}$ monomers (corresponding to $\zeta_1 = 1$). Depending on the size of the N chain, two regimes are expected: (a) if $N < N_{C1}$, the whole chain is ideal ($R = R_0$); (b) if $N > N_{C1}$, the chain can be pictured as a 1d self-avoiding walk of ideal sausages (Figure 5); the size of one sausage is $l_1 = aN_{C1}^{1/2}$, leading to a total length of the chain

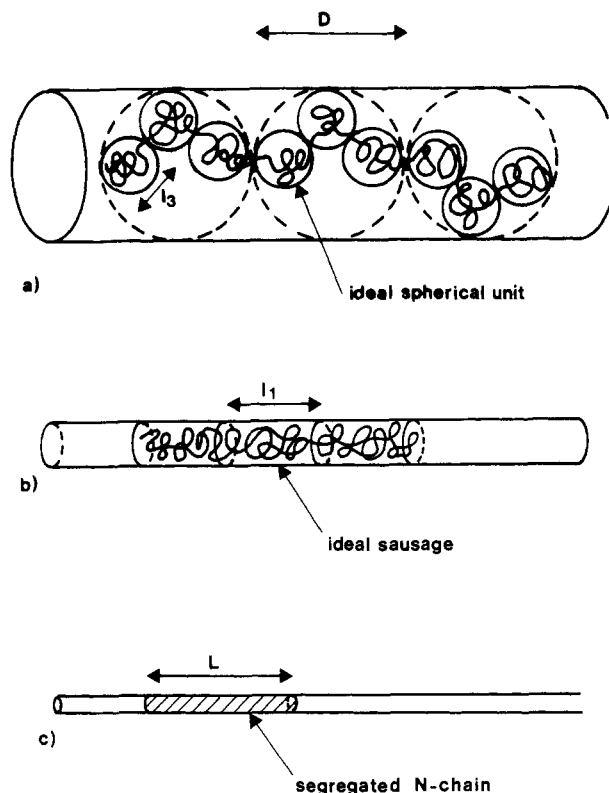$$R = (N/N_{C1})l_1 \qquad (18)$$

which again corresponds to (16).

Figure 5. Conformations of one single N chain dissolved in a melt of smaller P chains, the system being confined to a capillary of diameter D. (a) For $D > aP$, the N chain is built from "ideal spheres" of size l_3, which exclude each other and generate a 3d self-avoiding walk at scales smaller than D and a 1d self-avoiding walk at larger scales. (b) For $aP^{1/4} < D < aP$, a large chain ($N > N_{C1} = P^{2/3}(D/a)^{4/3}$) is a 1d sequence of N/N_{C1} self-avoiding sausages. (c) For $D < aP^{1/4}$, all the chains segregate and the N chain completely fills a portion of the tube of length $L = Na^3/D^2$.

(3) $D < aP^{1/4}$ (Segregation Regime). As D decreases, the volume fraction of the N chain

$$f = \frac{Na^3}{D^2R} = P^{1/3}(a/D)^{4/3}$$

increases up to $f = 1$ for $D = aP^{1/4}$. For $D < aP^{1/4}$, all the chains (i.e., the N chain and the P chains (see section 1)) are spatially segregated, lying in sequence one after the other. The N chain then occupies a portion of the tube of length

$$L = Na^3/D^2 \qquad (19)$$

One can check that eqs 16 and 19 coincide for $D = aP^{1/4}$.

Conclusions. A. The different regimes are summarized on Figure 6.

(1) If $P < D/a$ the threshold length N_C is given by the usual expression $N_{C3} = P^2$. The line $N = P^2$ separates two three-dimensional regimes (ideal sphere versus swollen sphere). For $N > (D/a)^{5/3}P^{1/3}$, the confined chain can be pictured as a linear sequence of superunits of size D; at scales smaller than D, each superunit is a 3d self-avoiding walk.

(2) If $aP^{1/4} < D < aP$, the threshold length N_C is reduced: $N_{C1} = P^{2/3}(D/a)^{4/3}$. If $N < P^{2/3}(D/a)^{4/3}$, the whole N chain is ideal. If $N > P^{2/3}(D/a)^{4/3}$, the chain behaves like a string of ideal sausages of size $aP^{1/3}(D/a)^{2/3}$.

(3) If $D < aP^{1/4}$, all the chains are spatially segregated, the N chain occupying a length $L = Na^3/D^2$. Note that for $D = a$ we obtain $L = Na$ as expected.

B. The problem of a chain confined to a capillary is related to that of chains that are densely grafted onto a
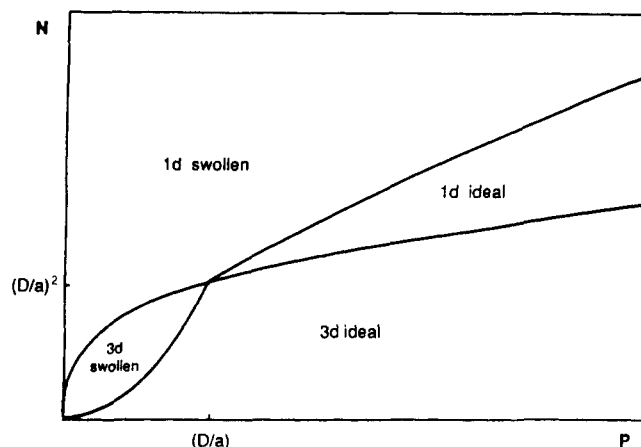

Figure 6. Various regimes for an N chain immersed in a melt of a smaller P chain, the system being confined to a capillary of diameter D. For simplicity, the segregation regime has not been represented.

flat surface. Most of the above results are indeed similar to those obtained by de Gennes[11] for the behavior of densely grafted N chains in a melt of shorter P chains. However, the transition to the segregation regime is sharper in our case: in a tube, even the small chains are confined and segregated for $D < aP^{1/4}$, whereas they remain ideal in a grafted layer.

4. Concluding Remarks

A. As one long flexible N chain is dissolved in a melt of shorter, chemically identical P chains, the monomer–monomer interactions of the N chain are screened out by the P chains ($v = v_0/P$, v_0 being a monomer volume). This screening leads to a threshold length N_C below which excluded-volume effects are absent: if $N > N_C$, the N chain is partially swollen whereas for $N < N_C$ the chain is ideal. In this paper we have studied how this deswelling of the N chain by the P chains is modified when the chains are confined into slits or pores of size D. Our principal results are the following.

(1) As long as D is larger than l_3, the threshold length N_C is not sensitive to the confinement and $N_C = N_{C3} \equiv P^2$. The conformation of the confined N chain can be simply deduced from the case $P = 1$ (ref 4) by picturing the chain as a sequence of ideal units of size $l_3 = aP$. The N chain is then a string of N/g_D superunits of size D ($D = aP(g_D/P^2)^{3/5}$) and its total size is given by $R = (N/g_D)^{v_2}D$ in the case of a slit and by $R = (N/g_D)D$ in the case of a capillary. The free energy $\mathcal{F}_N$ of the N chain, measured from the state with $D = \infty$, is given by

$$\mathcal{F}_N = \frac{N}{g_D}kT \qquad (20)$$

It measures the lose of entropy due to the confinement of N/g_D superunits. Expression 20 can be derived from scaling arguments by writing[4]

$$\mathcal{F}_N \cong kT(R_3/D)^x \qquad (21)$$

where $R_3 = aP(N/P^2)^{3/5}$ is the radius of the free chain. The value of x is obtained from the requirement that $\mathcal{F}_N$ be an extensive function of N:

$$\left(\frac{R_3}{D}\right)^a = \frac{N^{3x/5}}{P^{x/5}}\left(\frac{a}{D}\right)^x$$

$$3x/5 = 1$$

$$\frac{\mathcal{F}_N}{kT} \cong \frac{N}{P^{1/3}}\left(\frac{a}{D}\right)^{5/3} \qquad (22)$$

The free energy $\mathcal{F}_N$ can be obtained by measuring the partition coefficient (i.e., the ratio of concentration inside the pore to the concentration outside) for a pore exchanging chains with a bulk solution:[7]

$$\frac{C_{pore}}{C_{bulk}} \sim \exp\left(-\frac{\mathcal{F}_N}{kT}\right) \qquad (23)$$

We have thus a process to separate long versus small chains from a blend of chemically identical chains.

(2) For D smaller than $l_3 = aP$, the threshold length N_C becomes sensitive to the confinement.

In the case of a slit, N_C is given by $N_C \equiv N_{C2} \equiv PD/a$. For $N < N_{C2}$, the chain is ideal. For $N > N_{C2}$, the chain can be pictured as a sequence of ideal pancakes (of size $l_2 = aN_{C2}^{1/2}$) that exclude each other: $R = (N/N_{C2})^{\nu_2}l_2$. By analogy with the previous case, we postulate that the free energy of confinement is proportional to the number N/N_{C2} of units[12]

$$\mathcal{F}_N = \frac{N}{N_{C2}}kT = \frac{N}{P(D/a)}kT \qquad (D/a < P) \qquad (24)$$

For a true two-dimensional problem, we obtain $\mathcal{F}_N = (N/P)kT$.

In the case of a capillary, $N_C = N_{C1} \equiv P^{2/3}(D/a)^{4/3}$ if $P^{1/4} < D/a < P$. For $N < N_{C1}$, the chain is ideal. For $N > N_{C1}$, the chain is a sequence of ideal sausages (of size $l_1 = aN_{C1}^{1/2}$) that exclude each other: $R = (N/N_{C1})l_1$. The free energy of confinement should be given by[13]

$$\mathcal{F}_N = \frac{N}{N_{C1}}kT = \frac{N}{P^{2/3}(D/a)^{4/3}} \qquad (P^{1/4} < D/a < P) \qquad (25)$$

For a very small capillary, all the chains are spatially segregated. The N chain fills a portion of the tube of length $L = Na^3/D^2$. The confinement energy can be

expected to be given by $\mathcal{F}_N = (N/P)kT$, which does coincide with (25) for $D = aP^{1/4}$.

B. Since the role of the P chains is to reduce the monomer–monomer interactions of the N chain, our theory should apply equally to dilute polymer solutions with small excluded-volume parameters $(0 \ll v \leqslant a^3)$.

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(12) One cannot simply justify eq 24 by the lose of entropy due to the confinement since the structures at small scales of the free chain (spheres of size l_3) and of the confined chain (pancakes of size l_2) are different. By definition, the repulsive energy per unit (l_3 or l_2) is given by kT. The increase in the number of subunits from N_{c3} to N_{c2} leads thus to a contribution to $\mathcal{F}_N$: $((N/N_{c2}) - (N/N_{c3}))kT \sim (N/N_{c2})kT$, which is of the same oder as the entropic term.
(13) One can use the same argument as in ref 12 provided that one replaces N_{C2} by N_{C1}.

Configurational Characteristics and Scaling Behavior of Starburst Molecules: A Computational Study

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ABSTRACT: The growth of starburst molecules having trifunctional branch points and flexible spacers of P (= 1, 3, 5, 7, 9, and 11) steps are studied by a computer simulation. A self-avoiding walk algorithm is employed to kinetically grow the molecules. The center-to-branch-end distance is found to scale with the radius-of-gyration of the molecule throughout growth. Intramolecular density profiles indicate that the ends of the branches traverse the entire molecule and are not confined to its surface. This branch growth behavior indicates highly folded branches throughout all stages of growth. In general, kinetically grown models of starburst molecules behave as modified Cayley trees. The radius of gyration, R_g, of the molecule is found to scale with the molecular weight M and the spacer length P according to $R_g \sim M^\nu P^\beta$. The exponents β and ν change throughout growth with $\nu = 0.22 \pm 0.02$ and $\beta = 0.50 \pm 0.02$ in the high molecular weight scaling region.

Introduction

The scaling behavior of "starburst" growth was originally considered by Zimm and Stockmayer in their study

of branched polymers.[1] The resulting structural form has fallen under the nomenclature of a Cayley tree or Bethe lattice in much of the physics literature, especially in percolation theory.[2,3] Generalizations of the Zimm–Stock-