Polymer communication

# Unified description of transportation of polymer chains with different topologies through a small cylindrical pore

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## ARTICLE INFO

## ABSTRACT

Instead of using free energy, we directly balanced confinement and hydrodynamic forces ($f_c = k_BT/\xi$ and $f_h = 3\pi\eta u l_e$) on individual "blobs" to obtain a unified description of how polymer chains with different topologies (linear, star and branched) pass through a cylindrical pore with a diameter of $D$, much smaller than its size, under a flow rate ($q$), where $k_B$, $T$, $\eta$, $\xi$, $u$ ($= q/D^2$), and $l_e$ are the Boltzmann constant, absolute temperature, viscosity, "blob" diameter, flow velocity, and the blob's effective length along the flow direction, respectively; and each "blob" is defined as a maximum portion of the confined chain whose confinement free energy becomes of order thermal energy ($k_BT$). Namely, using $f_c = f_h$, we easily locate at which minimum (critical) flow rate ($q_c$) polymer chains with different topologies are able to pass through the pore without priori consideration of chain topology, i.e., a general description, $q_c/q_{c,\text{linear}} = (D/\xi)^2$, where $q_{c,\text{linear}}$ equals $[k_BT/(3\pi\eta)](\xi/l_e)$. The only thing left here is to find $\xi$ for each topology. Obviously, for a confined linear chain, $\xi_{\text{linear}} = D$. For a confined star chain, $\xi_{\text{star}} = [2/(f + |f - 2f_{\text{in}}|)]^{1/2}D$, where $f$ is arm number and $f_{\text{in}}$ is the number of arms first inserted into the pore; and for a branched chain, $\xi_{\text{branch}} = (D/a)^{\alpha'} N_{t,\text{Kuhn}}^{\beta'} N_{b,\text{Kuhn}}^{\gamma'}$, where $a$ is the size of one Kuhn segment, $N_{t,\text{Kuhn}}$ and $N_{b,\text{Kuhn}}$ are respectively the numbers of Kuhn segments of the entire branched chain and the subchain between two neighboring branching points; and the three constant exponents ($\alpha'$, $\beta'$ and $\gamma'$) are directly related to the well-known Flory's scaling exponents between the chain size and both $N_{t,\text{Kuhn}}$ and $N_{t,\text{Kuhn}}$.

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Statistical physics tells us that the possibility of a polymer chain passes through a cylindrical pore with a diameter of $D$ much smaller than its size is extremely low because there is a confinement penalty. To overcome the confining energy barrier, one has to "pull" the chain with a kind of interaction, such as the hydrodynamic or electric (if it is charged) force. It was shown by de Gennes [1–3], Pincus [4], Casassa [5], and Edwards and Freed [6] that the minimum force (the critical flow rate, $q_c$, when the Poiseuille flow is used) depends on the chain's topology and deformability as well as the pore size, but unexpectedly not on the chain size in some cases, including linear and star chains [7–9]. In particular, de Gennes [1] and Pincus [4] showed that for a linear chain, $q_{c,\text{linear}} \sim k_BT/\eta$, independent on sizes of both the chain and pore, where $k_B$, $T$ and $\eta$ are the Boltzmann constant, absolute temperature and solution viscosity, respectively. However, our previous experimental results revealed that for linear chains, $q_{c,\text{linear}}$ decreases as $D$ increases

because the chain segment inside each "blob" should not be treated as a hard sphere with a dimension of $D$ but with an effective length ($l_e$) along the flow direction [7,8], i.e.,

$$q_{c,\text{linear}} = \frac{k_BT}{3\pi\eta}\frac{D}{l_e} \tag{1}$$

Note that here individual "blobs" with a size of $\xi$ is defined as a maximum portion of the confined chain whose center of gravity undergoes the Brownian motion under the agitation of the thermal energy; namely, within which the total energy of interest becomes of order $k_BT$; and $l_e$, depending on the chain topology, is generally longer than $\xi$ because the confined chain segments are partially draining. Such a dependence for linear chains (Eq. (1)) was supported by the recent first principle calculation [10,11].

Physically, each polymer chain confined inside a small cylindrical pore can be viewed as a number of packed blobs. Instead of considering free energy of the entire confined chain as previously done by others, we only consider the confinement and hydrodynamic forces on individual blobs ($f_c = k_BT/\xi$ and $f_h = 3\pi\eta l_e u$, where $u = q/D^2$, the flow velocity), i.e., from $f_c = f_h$, and drive the critical

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flow rate ($q_c$). Using such an approach, we have established a unified description of normalized $q_c$ without any priori consideration of the chain topology as follows.

$$\frac{q_c}{q_{c,\text{linear}}} = \left(\frac{D}{\xi}\right)^2 \tag{2}$$

It shows that the only thing left here is to find $\xi$ for each topology. Obviously, for a confined linear chain, $\xi_{\text{linear}} = D$. For a confined star chain with $f$ arms, we have to consider whether the number of forwarded and stretched arms ($f_{\text{in}}$) that are inserted into the pore is larger or smaller than that of backwarded and coiled arms ($f_{\text{out}}$) outside, where $f = f_{\text{in}} + f_{\text{out}}$. When $f_{\text{in}} \geq f_{\text{out}}$, we only need to consider those forwarded $f_{\text{in}}$ arms that occupied the pore. Each stretched arm acts as a tube with a diameter of $\xi_{\text{star}}$; namely, $D^2 = \xi_{\text{star}}^2 f_{\text{in}}$ so that $q_c/q_{c,\text{linear}} = f_{\text{in}}$. Similarly, when $f_{\text{in}} \leq f_{\text{out}}$, we have to consider those backwarded $f_{\text{out}}$ arms outside. In this case, the forwarded and stretched arms must be further stretched (i.e., with a higher flow rate) to generate a sufficient force to pull those outside arms into the pore. When they come into the pore, $D^2 = \xi_{\text{star}}^2 f_{\text{out}}$ so that $q_c/q_{c,\text{linear}} = f_{\text{out}}$. These two different cases can be summarized into one equation as

$$\frac{q_{c,\text{star}}}{q_{c,\text{linear}}} = \frac{f + |f - 2f_{\text{in}}|}{2} \tag{3}$$

Recent experimental results confirmed that for a given arm length ($L_A$), $q_{\text{star}}$ increases with $f$ but is nearly independent on $L_A$ [9], contradictory to the de Gennes' prediction, [2] in which the full extension of each pulled-in arm was assumed. Our derivation and experimental results reveal that such an assumption is not necessary and incorrect. It should be noted that we previously made one unfortunate mistake in *Polym Chem* **2011**, *2*, 1071 [9]; namely, the denominator in Eqs. (5b) and (6b) should be $f_{\text{out}}^2$ instead of $f_{\text{in}}^2$, which also affects fig. 6 there.

Transportation of a hyperbranched chain made of subchains with a uniform length ($l_b$) through a small pore is much more complicated, depending on whether $l_b$ is much larger or smaller than $\xi_{\text{branch}}$. In other words, when $l_b >> \xi_{\text{branch}}$, each blob contains a linear chain segment that is easily deformable (strong confinement); while $l_b << \xi_{\text{branch}}$, each blob itself contains a number of subchains, i.e., a hyperbranched and less-deformable chain segment (weak confinement). Previously, using the Flory scaling, de Gennes [2,3] deduced $q_{c,\text{branch}}$ for a hyperbranched chain in a good solvent and found that $q_{c,\text{branch}} \sim N_{t,\text{Kuhn}}^\gamma N_{b,\text{Kuhn}}^\varphi$, where $N_{t,\text{Kuhn}}$ and $N_{b,\text{Kuhn}}$ are numbers of Kuhn segments of the entire chain and the subchain; and $\gamma = 1/2$ and $2/3$; and $\varphi = -1/2$ and $2/15$, respectively, for strongly and weakly confined hyperbranched chains inside a cylindrical pore. Unfortunately, the prediction is partially incorrect because the barrier energy ($E_b$) of one layer (cross-section) of blobs was mistaken as $\sim k_B T$. Actually, $k_B T$ is the barrier energy for one blob. The barrier energy for one layer of blobs should be $k_B T$ multiplied by the number of blobs in one layer, i.e., $E_b = k_B T(D^2/\xi_{\text{branch}}^2)$. This explains why the correct exponent should be 2, as shown in Eq. (2), instead of 4 (Eq 30 of Ref 2).

As discussed above, each blob in the strong or weak confinement limits contains a linear or a hyperbranched chain segment with a maximum size of $D$. Assuming that each blob contains $n$ Kuhn segments and each Kuhn segment has a size of $a$, the volume fractions of the Kuhn segments inside each blob and inside the volume occupied by the entire confined and stretched chain should be identical, i.e., $a^3 n/\xi^3 = a^3 N_{t,\text{Kuhn}}/(D^2 L_o)$, for a uniform chain density, where $L_o$ is the optimal length of the entire chain stretched along the flow direction, i.e.,

$$\xi = \left(\frac{nD^2 L_o}{N_{t,\text{Kuhn}}}\right)^{\frac{1}{3}} \tag{4}$$

Let us first find $L_o$. After a chain is confined inside the pore and stretched to a length of $L$, its free energy ($F$) has an enthalpy term: $k_B T[N_{t,\text{Kuhn}}^2 a^3/(D^2 L)]$ and an entropy term: $k_B T(L/R_0)^2$, where $R_0$ is the unperturbed chain size. $L_o$ can be found from $dF/dL = 0$, i.e.,

$$L_o \cong a\left(\frac{N_{t,\text{Kuhn}} R_0}{D}\right)^{\frac{2}{3}} \tag{5}$$

Note that $R_0 = aN_{t,\text{Kuhn}}^{1/4} N_{b,\text{Kuhn}}^{1/4}$ and $aN_{t,\text{Kuhn}}^{1/2}$ for branched and linear chains, respectively. Actually, a linear chain can also be viewed as a special branched chain with one "branching" point, i.e., $N_{t,\text{Kuhn}} = N_{b,\text{Kuhn}}$; namely, we can also using $R_0 = aN_{t,\text{Kuhn}}^{1/4} N_{b,\text{Kuhn}}^{1/4}$ for a linear chain. It is also known that for a hyperbranched or a linear chain in good solvents, its root mean square radius of gyration $<R_g^2>^{1/2}$ is scaled to $N_{t,\text{Kuhn}}$ and $N_{b,\text{Kuhn}}$ as $aN_{t,\text{Kuhn}}^\alpha N_{\beta,\text{Kuhn}}^\beta$ with $\alpha = 1/2$ and $3/5$, and $\beta = 1/10$ and 0, respectively [12–15]. Similarly, we can also generally express the blob size ($\xi$) in good solvents as $\xi = aN_{t,\text{Kuhn}}^\alpha N_{\beta,\text{Kuhn}}^\beta$. A combination of Eqs. (2), (4) and (5) as well as two scaling equations of $R_0$ and $\xi$ results in

$$\frac{q_{c,\text{branch}}}{q_{c,\text{linear}}} = \left(\frac{a}{D}\right)^{2(3-5\alpha)/3(3\alpha-1)} N_{t,\text{Kuhn}}^\gamma N_{b,\text{Kuhn}}^\varphi \tag{6a}$$

where

$$\gamma = \frac{\alpha}{3(3\alpha-1)} \quad \text{and} \quad \varphi = \frac{6\beta - \alpha}{3(3\alpha-1)} \tag{6b}$$

It should be noted that Eq. (6) generally covers different solvent qualities and confinements. In the weak confinement limit ($n >> N_{b,\text{Kuhn}}$), each blob contains a hyperbranched chain segment with $\alpha = 1/2$ and $\beta = 1/10$ in good solvents so that Eq. (6) becomes

$$\frac{q_{c,\text{branch}}}{q_{c,\text{linear}}} = \left(\frac{a}{D}\right)^{2/3} N_{t,\text{Kuhn}}^{\frac{1}{3}} N_{b,\text{Kuhn}}^{\frac{1}{15}} \quad or \quad \left(\frac{a}{D}\right)^{\frac{2}{3}} n_{\text{branch}}^{\frac{1}{3}} N_{b,\text{Kuhn}}^{\frac{6}{15}}$$
$$\times \text{(weak confinement)} \tag{7}$$

where $n_{\text{branch}}$ is defined as $N_{t,\text{Kuhn}}/N_{b,\text{Kuhn}}$, the number of branching points of a hyperbranched chain. While in the strong confinement limit ($n << N_{b,\text{Kuhn}}$), each blob contains a linear chain segment with $\alpha = 3/5$ and $\beta = 0$ in good solvents so that we have

$$\frac{q_{c,\text{branch}}}{q_{c,\text{linear}}} = \left(\frac{N_{t,\text{Kuhn}}}{N_{b,\text{Kuhn}}}\right)^{\frac{1}{4}} = n_{\text{branch}}^{\frac{1}{4}} \quad \text{(strong confinement)} \tag{8}$$

As expected, for linear chains, $N_{t,\text{Kuhn}} = N_{b,\text{Kuhn}}$, i.e., $n_{\text{branch}} = 1$ so that $q_{c,\text{branch}} = q_{c,\text{linear}}$. Note that Eq. (8) is identical to what de Gennes described after we correct the mistake, i.e., changing the exponent from 4 to 2 in Eq 30 of ref 2. However, our recent experimental results showed that the scaling components are different from those predicted in Eqs. (7) and (8). This is because when a hyperbranched chain is confined and squeezed inside a pore the scaling of its size and the number of Kuhn segments is not ½ but much smaller. This is not the point we like to discuss in this communication. The crossover between two different confinement limits occurs when the pore size reaches a critical value ($D^*$) at which sizes of the subchain and the pore become similar. Quantitatively, equalizing the right sides of Eqs. (7) and (8) leads to
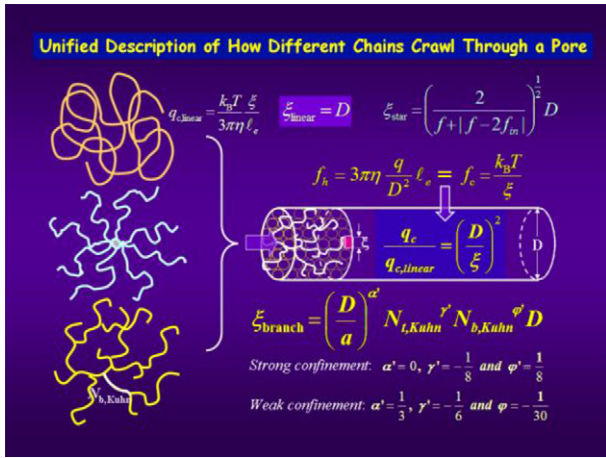
**Fig. 1.** Schematic of a polymer chain with different topologies confined inside a cylindrical pore and how blob size ($\xi$) varies with chain topology.

$$D^* = aN_{t,\text{Kuhn}}^{\frac{1}{8}} N_{b,\text{Kuhn}}^{\frac{19}{40}} \tag{9}$$

It is clear that $D^*$ weakly depends on the overall molar mass but more on the subchain length.

In summary, by assuming that a polymer chain confined inside a small cylindrical pore is divided into a number of "blobs" whose center of gravity is undergoing the Brownian motions under the thermal agitation, we have shown that it is necessary and sufficient to consider only confinement and hydrodynamic forces on a single blob. A direct balance between them leads to the critical (minimum) flow rate ($q_c$) to pull a chain through the pore without any priori

consideration of chain topology. Using such a simple approach, we have established a unified description of $q_c$, normalized by $q_{c,\text{linear}}$, as $q_c/q_{c,\text{linear}} = (D/\xi)^2$ for different chain topologies. The only thing left here is to deduce $\xi$ for each given chain topology. It should be noted that experimental results for linear, star and hyperbranched chains have been previously published and they support what we are discussing in this unified description [7–11,16]. Fig. 1 schematically summarizes our results for polymer chains with different topologies.

### Acknowledgment

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