How do polymer chains with different topologies crawl through a cylindrical pore under an elongation flow?

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Abstract

For a linear chain, we have, for the first time, observed the discontinuous first-order coil-to-stretch transition; namely, it can pass through a pore much smaller than its unperturbed size only when the flow rate is higher than a critical value ($q_{c,\text{linear}}$) that is independent of the chain length as predicted, but varies with the pore size ($D$), very different from the prediction. Such a discrepancy is attributed to an improper assumption that each sub-chain (blob) inside the pore is a non-draining hard sphere under a flow. For a star-like chain, we have also, for the first time, revealed that for a given arm length ($L_A$), $q_{c,\text{star}}$ dramatically increases with the arm number ($f$); but is nearly independent on $L_A$ for a given $f$, which is also contradictory to the prediction made by de Gennes and Brochard-Wyart. Therefore, we have to revise their theory in the region $f_{\text{in}} < f_{\text{out}}$, where $f_{\text{in}}$ and $f_{\text{out}}$ are the numbers of arms inside and outside the pore, respectively; and also accounted for the effective length of each blob [6]. Further, for a hyperbranched chain, we have experimentally unearthed that $q_{c,b}$ depends on the polymerization degree of the entire chain and subchain ($N_t$ and $N_b$) as $q_{c,b} \sim N_t^\gamma N_b^\phi$, where $\gamma$ and $\phi$ are 1.0 and -0.4, much different from the predicted values, which is attributed to the compression of the hyperbranched chain inside the pore and also to different chain conformations when the relative ratio of $N_b$ and $D$ changes for different subchain lengths. After quantitatively understanding how polymer chains with different topologies crawl through a pore, we are now able to cleanly separate them by using their topology instead of size. Finally, we have established a unified description of the critical flow rate for polymer chains with different topologies. During this study, we have developed a novel method to prepare “defect-free” hyperbranched chains; and obtained a number of classic scaling laws for hyperbranched chains, e.g., their average radius ($\langle R \rangle$) is scaled to both $N_t$ and $N_b$ as $\langle R \rangle \sim N_t^{\alpha} N_b^{\beta}$, where $\alpha = 0.46$ and $\beta = 0.11$ for average radius of gyration ($\langle R_g \rangle$); and $\alpha = 0.48$ and $\beta = 0.09$ for the average hydrodynamic radius ($\langle R_h \rangle$), fairly close to the previously predicted 1/2 and 1/10; and the intrinsic viscosity ($[\eta]$) is scaled to both $N_t$ and $N_b$ as $[\eta] = K_\eta N_t^{\nu} N_b^{\mu}$ with $\nu = 0.39$ and $\mu = 0.31$. We also speculate why protein and RNA are linear, not an accident!

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