



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

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今回、Chi Wu 先生の九州大学訪問の機会に講演会を企画しました。多数ご出席くださいますようお願い申し上げます。

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 ($q_{c,linear}$) 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), $q_{c,star}$ 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 $f_{in} < f_{out}$, where f_{in} and f_{out} are the numbers of arms inside and outside the pore, respectively; and also accounted for the effective length of each blob. 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 $q_{c,b} \sim N_t^\gamma N_b^\varphi$, where γ and φ are 1.0 and -0.4, much different from the predicted values, which is attributed to the compression of the hyper branched chain inside the pore and also to different chain confinements 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 hy[erbranched 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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