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Crossover Behavior of Gas Transport in Polymer Melts: A Molecular Simulation Approach to the Robeson Plot KAI ZHANG, SANAT KUMAR, Columbia Univ — Efficient and selective transport of small gas molecules using lightweight and easily processable polymeric membranes is crucial in many clean energy technologies. For a pair of wanted (A) and unwanted (B) gases, the performance of membrane separation is characterized by the permeability of A (P_A) and the selectivity of A with respect to B (α_{AB} =P_A/P_B). Empirically, the so-called Robeson plot, i.e. the scatter plot of α_{AB} versus P_A, exhibits a tradeoff relation, whose upper bound sets the optimal membrane separation limit. Simple thermodynamic and kinetic argument like the Freeman theory predicts that the slope magnitude (λ) of the upper bound is purely determined by the molecular size ratio as λ =$(d_B/d_A)^2$-1. However, systematic studies of the Robeson plot on the molecular level and a quantitative understanding of the microscopic mechanisms that control the separation ability are still missing. We perform molecular dynamics simulation to calculate the permeability of model gas molecules in coarse-grained polymer melts, from which the corresponding Robeson plot is constructed. We observe a crossover behavior of gas transport as the gas size is tuned from below to above approximately twice the monomer size. The Freeman prediction is only valid in the large gas size limit. Further investigations on the gas dynamics show that its diffusion behavior changes from a geometric obstruction mechanism to an activated trap-and-jump process.

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