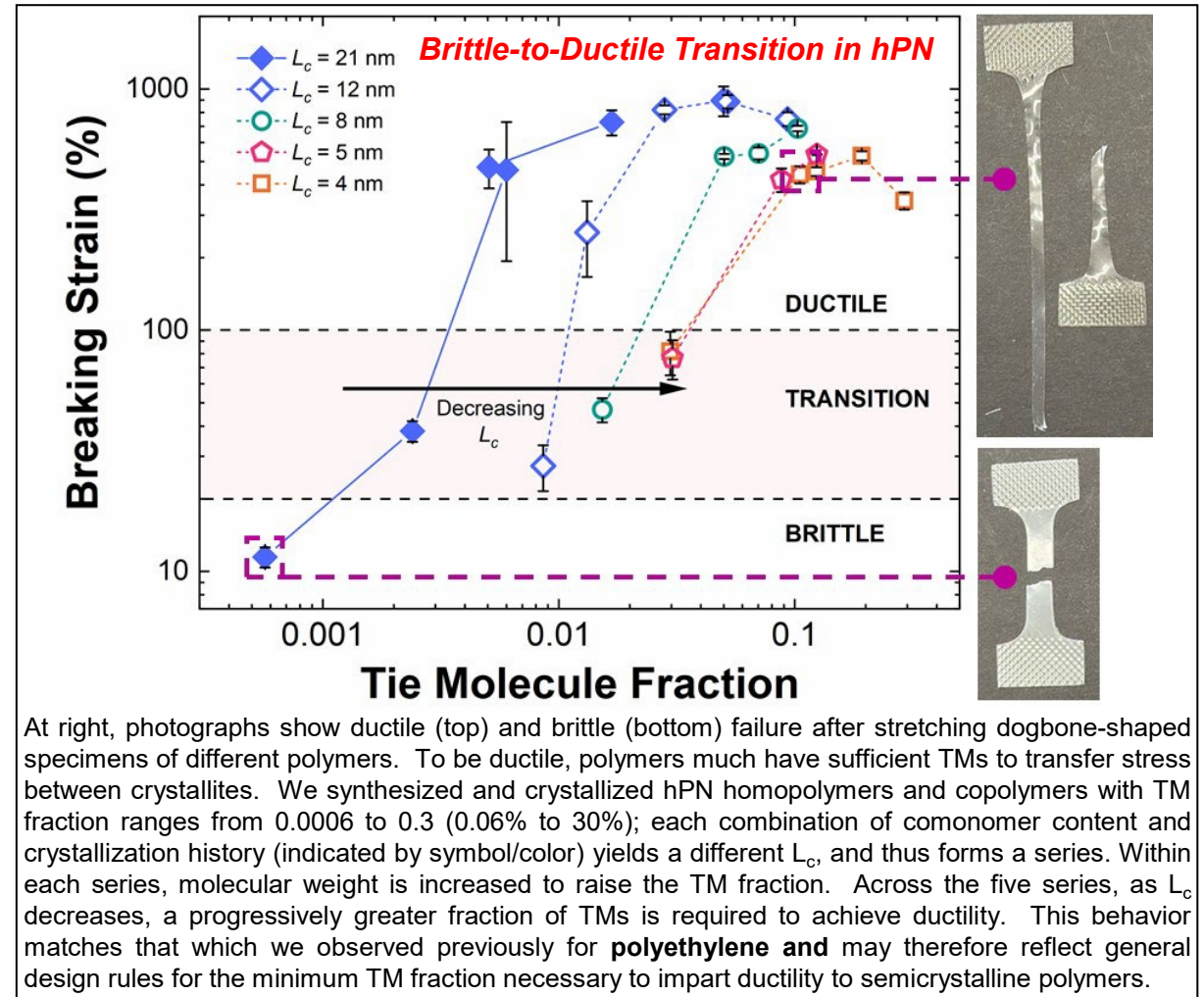


Richard A. Register, Princeton University

Semicrystalline polymers— such as polyethylene (PE) and polypropylene, the polymers produced in greatest volume worldwide— derive their toughness and ductility from *tie molecules* (TMs), polymer chains which span between crystallites. In the absence of TMs, semicrystalline polymers become brittle and unsuitable for most applications. A key question is “how many” TMs are needed for the polymer to exhibit ductility. In previous work under this award, we showed that in PE, the necessary fraction of TMs increased as the polymer crystallites became thinner. However, it was unclear whether this unexpected behavior was general or specific to PE, so we examined the brittle-to-ductile transition in a different semicrystalline polymer, hydrogenated polynorbornene (hPN), where we could finely tune the average crystallite thickness ( $L_c$ ) both by incorporating a comonomer along the polymer chain, and by varying the rate of cooling from the melt. As shown at right, the same trend is observed with hPN as with PE: more TMs are needed as  $L_c$  decreases, by a factor of 10 across the series. These findings are important for mechanical recycling of plastics, where cleavage of polymer chains (and hence of TMs) can occur during both environmental exposure and reprocessing; our relationships indicate the level of chain cleavage which can occur before the desirable properties of semicrystalline polymers are lost.



Richard A. Register, Princeton University

With COVID-19 restrictions on public gatherings lifted, we were grateful to be able to return to our active program of public science outreach this year, aiming to increase public appreciation of the unique behavior of polymers and their importance (and ubiquity) in modern life. Our group members were anchor participants in two events: off-campus at “Science Day / Día de la Ciencia” (Princeton Public Library) and on-campus at “Spring into Science” (Frick Atrium). Amongst the concepts demonstrated by our team were: swelling and deswelling of a superabsorbent polymer gel (crosslinked sodium polyacrylate); the elasticity of rubber and its ability to seal around punctures; the viscoelasticity of Silly Putty; the gelation of partially-hydrolyzed poly(vinylacetate) with borax (“making slime”); and the dramatic property changes which occur at the glass transition, as illustrated by damping behavior (“happy” and “sad” balls of two chemically different polymers—polychloroprene and polynorbornene—whose “demeanors” change when put on dry ice). Emphasizing the uniqueness and indispensability of polymers in daily life has never been more important than it is today.

Top figure caption: “Science Day / Día de la Ciencia” at the Princeton Public Library (November 5, 2022). PI (red shirt) illustrates polymer viscoelasticity with a ball of Silly Putty, to a rapt audience of primary schoolers. Other group members (to PI’s right) are demonstrating gelation, viscoelasticity, and the glass transition.

Bottom figure caption: “Spring into Science” in the Frick Atrium (Princeton University, April 22, 2023). On the right side of the demo table, from far right to left: group members demonstrate the glass transition, elasticity of rubbers, gelation, and swelling/deswelling. Photo taken by PI.

