Technical Summary for

Towards Quantitatively Predicting the Properties of Gels and Elastomers

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Polymer networks are critical to the modern society. Applications of polymer networks, in the forms of gels and elastomers, are prevalent throughout everyday life. However, while polymer networks had been studied extensively over the past few decades, most theoretical efforts were focused on model polymer networks with idealized regular topology, e.g., lattices. While these studies have provided important insights into the physics of polymer networks, the neglection of variation in network topology can significantly undermine the predictive power of existing theories because real polymer networks rarely constitute such regular connectivity. To provide accurate predictions, the role of irregularities in network topology must be considered. Therefore, this thesis investigates the formation of topological defects in polymer networks and how they impact the mechanical properties and the sol-gel transition of end-linked networks.

The first part of this thesis focuses on the topology of end-linked networks and the formation of topological defects. Herein, rate theories and kinetic Monte Carlo simulations are developed to simulate the gelation between two multi-arm macromonomers through end-linking. It is shown that even with a precursor geometry that eliminates the formation of primary loops, or self-loops that connect network junctions to themselves, polymer networks still invariably possess higher order cyclic defects that involve two or more network junctions. Furthermore, it is found that the cyclic topologies of networks synthesized from end-linking multi-arm polymer precursors, or A_f+B_f networks, are characterized by the same universal function that determines the cyclic topologies of A_2+B_f networks, or networks that are formed by crosslinking bifunctional polymer precursors with multi-functional crosslinkers. In both cases, the formation of loops and cyclic defects is solely determined by the product of precursor concentration and the volume pervaded by the polymer precursors, a dimensionless parameter that characterizes the ratio between the intermolecular and intramolecular length scales.

The second part of this thesis focuses on quantifying the impacts of topological defects on the mechanical properties of polymer networks. First, the assumptions of classical linear elasticity theories are revisited. Starting by introducing a single defective site into an otherwise ideal lattice network, the impacts of topological defects are studied through perturbation, and close form expressions for the effects of isolated dangling ends and loops are derived in the context of phantom network theory. It is found that in this infinite dilution limit, all loops of order three or larger do not exhibit any net impact on network elasticity. Next, the perturbative treatment is extended in a manner analogous to the Virial expansion to consider the correlated effects of multiple adjacent defects. Notably, the Virial coefficients between most types of

defects vanish, and the linear theory is exact in the absence of fused loops. Lastly, beyond the perturbative approximation, a new non-mean-field network theory is developed for networks with abundant defects. Overall, the results of the new elasticity theories show good quantitative agreement with the moduli of loopy gels. Furthermore, comparisons to experimental data also reveal that cyclic defects may introduce changes to the conformations of network strands. Since this factor directly impacts the modulus and swelling of a network, this finding motivates further studies on the role of topological defects in the spatial arrangement of network strands. Beyond linear mechanics, the underlying assumptions of the fracture theory of Lake and Thomas have also been revisited. Here, Lake-Thomas theory's sharp crack plane assumption is revised to reflect experimental observations that the rupture of network strands does not only occur within a microscopically thin region. In this work, instead of assuming that crack propagates by tearing all network strands across the crack plane, crack propagation is assumed to take place through the sequential tearing of micro-networks at the tip of the crack. This new assumption allows networks with weak defective strands to crack much earlier than networks without such weak bonds. It is shown that with this revision, tearing energy data of loopy networks can be quantitatively explained, thereby providing insights into the molecular details of fracture mechanics.

The final part of this thesis investigates the impacts of looping reactions on the sol-gel transition. During the crosslinking of telechelic polymer chains into a network, the system undergoes a competition between bridging and looping reactions. Since looping events do not contribute to the growth in molecular weight, they severely influence the kinetics of the emergence of the giant component (i.e., the gel). In this part, a kinetic Monte Carlo simulation is used to investigate the mechanism by which loops delay the onset of gelation, as well as the impact of looping events on the criticality of the sol-gel transition. Overall, it is found that a purely topological kinetic model can provide accurate predictions on the gel point suppression across many systems, revealing that factors such as packing effects and excluded volume interactions play secondary roles in sol-gel transition. Furthermore, it is found that loops introduce inhomogeneous rates of bond formation that render the percolation model not directly applicable to the real gelation process. As a result, when looping events are introduced, the criticality of the sol-gel transition can be significantly impacted, demonstrated by a change in the apparent percolation critical exponents. For loopy networks, a family of previously unreported criticality classes are discovered.

In summary, this work provides a comprehensive study on how topological defects impact the properties of polymer networks. Through developing new theories, classical assumptions have been revisited and physical insights into the molecular details of defective networks have been established. Meanwhile, with the improved accuracy, the models presented in this work can also contribute to the development of new gels and elastomers in the future.