Structure-mechanical property relationship in highly homogeneous polymer networks

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Crosslinked polymers, such as rubber and gel, are conventionally fabricated via a random crosslinking reaction, which inevitably lead to various inhomogeneities in the polymer network structure, deteriorating the performance of the material (Fig. 1a). A promising way to precisely control the network structure is the *module-assembly* strategy, in which the network is constructed by end-linking of monodisperse star-shaped prepolymers (Fig. 1b) [1]. In this talk, I will introduce my recent studies on the structure-property relationship of precisely controlled polymer networks.

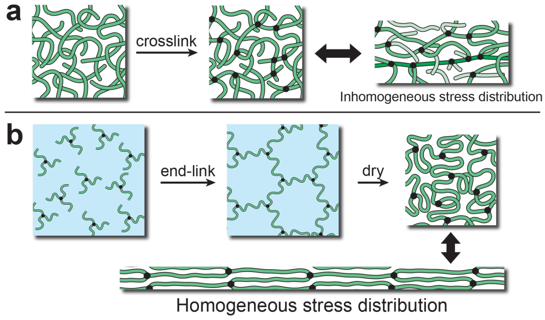

Fig. 1. (a) Conventional and (b) homogeneous elastomers.

Firstly, I synthesized and characterized a polyacrylate-based module-assembled elastomer [2]. Poly(*n*-butyl acrylate) (PBA), an amorphous polymer with a low glass transition temperature, was chosen as the main polymer component. A four-arm star PBA was synthesized by controlled radical polymerization, and the star PBA was end-linked in solution and the solvent was removed to obtain a PBA elastomer. The elastomer, which supposedly had a highly homogeneous network structure, was relatively weak, with the ultimate strength of ca. 0.17 MPa. This rather unexpected (and disappointing) result motivated me to further explore different main chain structures to achieve good mechanical properties of module-assembled elastomers.

Next, I developed a module-assembled elastomer consisting of bottlebrush (BB) polymers [3]. The backbone chain of BB polymers adopts a stretched conformation due to densely grafted long side chains. I hypothesized that this rigid conformation could lead to high elasticity. The module-assembled BB elastomer showed strain-stiffening at relatively small strains. The in situ small-angle X-ray scattering (SAXS) during tensile testing revealed that the preferential orientation of the rigid main chain was synchronized with the strain-stiffening behavior. However, the strength of the homogeneous BB elastomer was very low (~0.02 MPa).

Then, I constructed a module-assembled elastomer from an amorphous aliphatic polyester (poly(4-methyl-ε-caprolactone), PMCL), instead of polyacrylates with a relatively bulky side group [4]. Much different from the previous examples, the PMCL module-assembled elastomer showed high tensile strength (~25 MPa) and stretchability (strain at break ~ 1800%). Moreover, it exhibited an unusually large strain-stiffening capability, which has not been reached by any other soft materials known to date. From the in situ SAXS and wide-angle X-ray scattering (WAXS) during tensile testing, it was found that the unusual strain-stiffening and high strength was caused by the strain-induced ordering of the PMCL chains under an extreme strain. In the presentation, I will discuss about the above topics in more details.

References

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