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Study on Triblock Copolymers: From Relaxation Dynamics of Solution to Toughening Mechanism of Physical Double Network Hydrogels
(トリブロック共重合体に関する研究: 溶液緩和のダイナミクスからダブルネットワーク物理ゲルの高靱性化原理まで)

This work aims to get a better understanding of the structure and underlying toughening mechanism of tough and self-recoverable hydrogels. For this purpose, we chose the tough and self-recoverable hydrogels based on self-assembly of ABA type triblock copolymer as a model system, and used NMR, rheology and time-resolved SAXS as detection technique. The effects of molecular parameters (including chain length of A or B block and triblock copolymer concentration) and external parameters (including temperature and) on preparation process, self-assembly structure, and structure-property relationship of gels were systemically studied. The main results and conclusions of this thesis are summarized as follows:

- 1). Relaxation dynamic of precursor solutions. The effects of temperature and polymer concentration on relaxation dynamics of precursor solution was studied by combining temperature-sweep rheological measurement and NMR. Our results suggest that this system obeys time-temperature superposition (TTSP) and time-concentration superposition (TCSP) quite well, and shows a sol-gel transition by decreasing temperature. This allow us to separate the activation energy of micelle relaxation from chain friction of entanglements. We found that the activation energy of micelle relaxation, originating from endblock chain pullout from micelle, is independent of the polymer concentration. While the sol-gel transition temperature increases with polymer concentration, which could be explained as a preferred intermolecular association between endblock chains at high concentration.
- 2). Contribution of physical crosslinks and trapped entanglements in B gels. The individual contributions to the effective network from trapped chain entanglements and crosslinks in a physical triblock copolymer gels were successfully estimated by probing the modulus at uncrosslinked state (solution) and crosslinked state (B gel). The entanglements G_N in uncrosslinked solution were probed by TTSP. The trapped entanglements G_e was calculated by G_N normalized by swelling ratio from the solution to B gel. the contribution from crosslinks was calculated by subtracting the contribution of G_e from G , the total modulus of B gel. The ϕ_P dependence of G_e and G_c obeys power law with exponents of 2.5 and 1.0. The experimental exponent is perfectly conformed to the theoretical predictions, confirmed that our method is an effective method to separate the entanglements from crosslinks in physical hydrogels. It should be open the new door for designing new materials from theoretical viewpoint.
- 3). Structure evolution of B gels. In the gel (named as B gel), with increasing concentration, the elastic modulus originated from number of elastically active chains firstly increase followed by a plateau. In addition, structure evolution was also observed in small angle X scattering (SAXS). Based on micro SAXS and macro mechanical property, we concluded that

the dangling chain which has no contribution, is dominant at low concentration; while at high concentration, the bridged micelles is dominant.

4). Toughening mechanism of B-DN gels. Based on results from a combination of in-situ small-angle X-ray scattering and customized tensile device, the structure evolution during deformation was revealed, which suggests that the high toughness of self-recoverable B-DN gels is a synergistic effect of multiscale energy dissipation. In initial small strain region, the breaking and reforming of hydrogen bonding in chain scale dissipates energy, resulting in 100% self-recovery; In the middle strain region, the chain pullout of endblock from the micelles and debris reorganization of 1st network for forming cluster dissipate energy; In the large strain region, microvoids form, which also dissipate energy.

5). Creation of tough and self-recoverable B-DN thin gel membrane. Benefiting from the thoroughly understanding of chain structure and self-assembly structure in gelation process and final gels, for the first time, we successfully prepared thin (10-100 μm) but ultra-tough and 100% recoverable hydrogel membranes with high water content. Those membranes exhibit high pH sensitivity, excellent mechanical properties (even superior to those of various biological membranes), biocompatibility, and postoperative anti-adhesive property, foreshadowing their potential use as substitutes for biological membranes or postoperative anti-adhesive membrane.