

## 論文の内容の要旨

論文題目 Synthesis and Property of Functionalized Polymer Networks  
with Nearly Ideal Structure

(理想に近い構造を有する機能性ポリマーネットワークの合成と物性)

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Polymer networks involving gels and elastomers consist of three-dimensionally crosslinked polymer chains with many applications in our daily life. To satisfy increasing application needs, it is important to heighten the mechanical properties of polymer networks. One of the most effective ways is incorporation of the dynamic bonds into the polymer networks. Dynamic bonds possess lower bond energy than covalent bonds, which can reversibly associate and dissociate during stretch, to enhance mechanical properties of polymer materials. However, the relationship between the choice of dynamic bonds and resulting mechanical properties of polymer networks is unclear. It comes from the following reasons. 1) Previous studies introduced various kinds of dynamic bonds into diverse polymer networks. 2) Polymer networks had defects induced by random crosslinking, which interfered the relationship between dynamic bonds and mechanical properties. 3) The random polymer network is hard to be explained by theoretical models. The objective of this doctoral thesis is to disclose the quantitative relationship between molecular characteristic of dynamic bonds and resultant mechanical properties and set up the design basis for improving mechanical reliability of polymer networks. In this study, I have synthesized modifiable nearly ideal polymer networks in a simple and

versatile manner and investigated the influence of different dynamic bonds on the mechanical properties of the polymer networks with nearly ideal network structures.

My doctoral thesis is divided into four chapters. The chapter 1 is the introduction of background, existing problems, and objective of my research. The topic of chapter 2 is construction of modifiable nearly ideal polymer networks in a simple and universal way, to introduce various dynamic bonds into nearly ideal polymer networks. The theme of chapter 3 is the research on the effect of different dynamic bonds on the mechanical properties of polymer networks with nearly ideal network structures by using the method developed in chapter 2. The chapter 4 is the conclusion and perspective of my study.

The topic of chapter 2 is the formation of modifiable nearly ideal polymer networks in a simple and versatile manner. Random crosslinking causes many defects, which are harmful for the properties of polymer networks. To avoid these defects and further clarify the relationship between dynamic bonds and mechanical properties of polymer networks, it is essential to construct polymer networks with nearly ideal structures and functionalizable ability. I developed a facile method to form nearly ideal polymer networks that requires only two steps, living polymerization and end-linking reaction of star polymers. The living polymerization ensures the almost uniform chain length between neighboring crosslinks. The quantitative end-linking of star polymers makes the networks without dangling chains. Both are beneficial for minimizing the topological defects. This method was applicable for several polymers including polyacrylates, polymethacrylate, and polystyrene to form nearly ideal polymer networks (gels). The poly(butyl acrylate) (PBA) is taken as an example for following discussion. The elasticity of the synthesized PBA network was close to the theoretical prediction without defects, indicating that the formation of polymer networks was practically free of topological defects. The end-linking reaction conversion for PBA network was estimated to be 92% and similar values were also achieved by polymer conjugation of linear-PBA chains. The gelation time was tunable by the strength and amount of bases used in the end-linking reaction, which is a

prerequisite to avoid the spatial defects. Small-angle X-ray scattering results of the PBA network indicated the low level of spatial defects. The proposed method easily converts several vinyl polymers into nearly ideal polymer networks via exploitation of living polymerization and highly effective end-linking reaction.

The theme of chapter 3 is the study on the influence of dynamic bonds on the mechanical properties of polymer networks. The relationship between different dynamic bonds and mechanical properties were examined in the nearly ideal and identical polymer networks, which was more systematical than previous studies utilizing diverse polymer networks. Hydrogen bonds were chosen among several dynamic bonds because their bond energies could be easily and widely varied. Different hydrogen bonding groups, hydroxyl, urethane, and carboxylic acid were randomly introduced into the nearly ideal polymer networks. The mechanical properties of polymer networks, mobility of uncrosslinked polymer chains, and hydrogen bond energies were characterized. The difficulty of polymer chains motion (friction coefficient of polymer chains) is positively correlated with the binding energies of hydrogen bonds and proportional to the amount of hydroxy groups. The stiffness of polymer networks (Young's modulus) has a linear relationship with the difficulty of polymer motion. The hysteresis area of polymer networks during cyclic tests shows a positive correlation with the difficulty of polymer motion except for the star polymer/polymer network having urethane. Therefore, the strength of hydrogen bonds affected the uncrosslinked polymer chains mobility and further influenced the rigidity of the polymer networks. In addition, the stretchability was also related to the strength of hydrogen bonds. The recovery ability of polymer networks was related not only to the strength of hydrogen bonds but also to the association/dissociation rate of hydrogen bonds.

Chapter 4 is the conclusion and perspective. First, I developed a novel and simple method to synthesize the miscellaneous kinds of nearly ideal polymer networks by combination of living polymerization and quantitative end-linking reaction. Second, I introduced several kinds of hydrogen bonds into the nearly ideal and same polymer networks. I found out that the small

strain characters, i.e., difficulty of polymer motion and rigidity of polymer networks, were closely related to the strength and amount of hydrogen bonds, which also influenced the stretchability of polymer networks. The recovery ability of polymer networks was affected by the strength and association/dissociation rate of hydrogen bonds, which was related to the chemical structures of hydrogen bonding groups.

The novel method developed in chapter 2, provides a general platform to construct the nearly ideal polymer networks, which will greatly contribute to the development of ideal polymer networks and exploring the fundamental aspects of polymer networks. The systematic understanding in the influence of hydrogen bonds on the mechanical properties in chapter 3 can provide a guidance for the development of tough polymer materials.