博士論文

Dynamic Features of Network Polymers with Vicinal-Diols

(ビシナルジオールを有するネットワークポリマーの動的特性)

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Chapter 1. Introduction

Vicinal-diol, that is two hydroxyl groups bonded to neighboring carbon atoms (1,2-relationship), can be found in various biomolecules such as nucleic acids, polysaccharides, or polyphenols. Hydrogen bonds (H-bonds) between molecules via mono hydroxyl group are generally weak with a binding strength of ~20 kJ/mol, whereas when it comes to vicinal structure or multi-ol structure, they exhibit characteristic interactions that cannot be achieved between mono hydroxyl group containing molecules. For example, glucose units in cellulose tightly interact with each other by multiple H-bonds (intra- or intermolecular) that results in the formation of linear and flat structure of particular strength. Furthermore, vicinal-diol containing molecules have abilities to form highly pH-dependent dynamic covalent bonds with metals or boronic acids.[1] Due to these fascinating physical and chemical interactions of vicinal-diol moieties, tremendous biomimetic polymers bearing vicinal-diol structure have been reported which exhibit dynamic features such as self-healing, selective sensing, and gelation properties. However, most of the previous studies are limited to mechanically soft hydrogels presumably due to the inherent hydrophilic nature of dynamic vicinal-diol moieties. In addition, the dynamics of small molecules is hardly kept when they are embedded in polymers because the properties of the polymers are largely influenced by the macromolecular scale factors such as mobility or entanglement of the polymer chain.

The aim of the doctoral thesis is the application of vicinal-diol chemistry to bulk polymers to inducing characteristic dynamic features with mechanical robustness. The thesis consists of two main chapters. In chapter 2, the author reports water-triggered dynamic bulk polymers by adopting a dynamic reaction between vicinal-diols and boronic acids. The polymers showed two interesting features which are shown in sections 2.1 and 2.2, respectively. Chapter 3 introduces the new design strategy for the preparation of dynamically crosslinked rubber via solely H-bonds between vicinal-diol groups.

Chapter 2. Water-triggered Dynamic Polymers

The reversibility in esterification between vicinal-diols and boronic acids has been intensively utilized in biomedical and material applications.[2] Generally, the thermodynamics of the reaction is susceptible to pH in water. Under high pH conditions, the boronate-esters are readily formed through esterification between vicinal-diols and highly reactive boronate-acid intermediates having tetrahedral boron center (Fig. 1a, dotted box). Moreover, the reaction between boronate-acids and vicinal-diols exhibits high reversibility with the higher rate of bond formation over hydrolysis under wet conditions.

To introduce the water-triggered dynamic behavior to bulk polymers, the author designed boronate-esters bearing B−N dative bonds which are hydrophobic but have highly water-sensitive dynamicity. As shown in Fig. 1b, as a hydrophobic polymer containing vicinal-diol, a catechol-functionalized polymer **P1** was first prepared and then **P1** was crosslinked with *p*-phenyldiboronic acid in the presence of triethylamine (TEA) as a Lewis base. TEA facilitates the formation of boronate-esters by increasing the reactive boronate-acid

intermediates in organic solvent instead of pH control in water. The network polymers having two different crosslinking densities were prepared; **P2-LC** with the lower crosslink density (60% of diol moieties are crosslinked with boronic acids, assuming the crosslinking reaction proceeds quantitatively) and **P2-HC** with the higher crosslink density (fully crosslinked, assuming quantitative reaction).
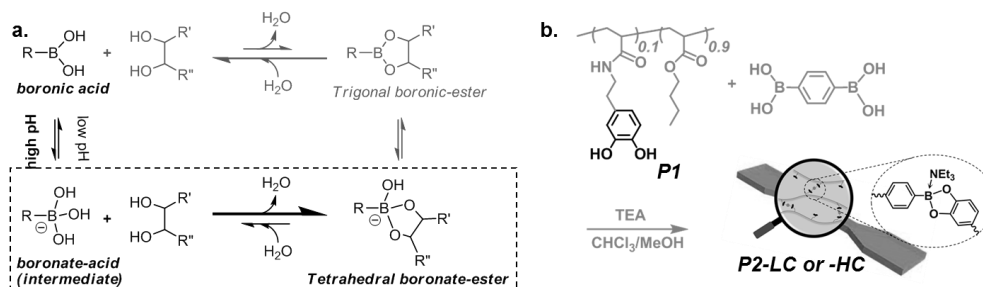

Figure 1. (a) Thermodynamic equilibrium between a boronic acid and its ester derivatives. (b) Preparation of network polymers containing tetrahedral boronate-ester bonds.

2-1. Autonomous Self-healing Polymers with the Assistance of Atmospheric Moisture

As a water resource, it would be very attractive to use atmospheric moisture as a stimulus for dynamic polymers. If moisture can induce a dynamicity of boronate-esters in bulk polymers, **P2-LC** is expected to show characteristic dynamic property such as autonomous self-healing under ambient conditions. The term autonomous here means that healing does not need any other human interventions.

First, to examine whether **P2-LC** is kept crosslinked under both dry and humid conditions, the structure of boron atoms in dried and moistened **P2-LCs** were evaluated by solid state ^{11}B NMR spectroscopy and attenuated total reflectance-Fourier transform-infrared spectrometry (ATR-FTIR). As shown in Fig. 2a, both dried and moistened **P2-LCs** have clear peaks at around 8.4 ppm, which are consistent with a tetrahedral structure of boron with a B−N dative bond. In addition, a broad peak around 24 ppm which corresponds to free boronic acids was not prominent. Therefore, the author confirmed that the boronate-esters had high hydrolytic stability in bulk **P2-LC** even under humid conditions.

Next, water-induced dynamicity of **P2-LC** was confirmed by self-healing tests under three different humidity conditions (75%, 55% and 30% relative humidity, RH). The samples which were stored under each humidity condition were cut, reattached, and then placed under each RH condition for healing. After 3 days, the samples being healed under 55% and 75% RH exhibited remarkable healing efficiency (Fig. 2b), whereas no self-healing was observed under 30% RH condition. The results indicate that tiny amounts of water molecules in moistened polymer induced the dynamicity of the boronate-esters that contributes to self-healing ability under 55% and 75% RH.

The stress-adaptability was evaluated by cyclic tensile tests. When **P2-LC** was unloaded after elongation of 60% under a dry condition (30% RH), the polymer recovered its original dimension with residual strain of 2% (Fig. 2c). In contrast, under a humid condition (55% RH), lower recovery was observed with residual strain of 6%. The results imply that **P2-LC** is elastic under dry condition, whereas it becomes more malleable by moistening under a more humid condition.

Based on the water-induced malleability, the author examined reprocessability of **P2-LC**. Finely cut **P2-LC** was first saturated at 75% RH, and then pressed at room temperature. As shown in Figure 2d, the

reprocessed sample was fully reshaped with well recovered mechanical properties. In contrast, when the sample was reprocessed without moistening, it showed rough surfaces and severely deteriorated mechanical properties. Interestingly, when dried **P2-LC** was pressed at slightly increased temperature (60 °C), it was also fully recycled. The author expects that this dual-stimuli responsiveness of the boronate-ester is due to the presence of water-responsive B−O bonds and heat-responsive B−N bonds (Fig. 2e).
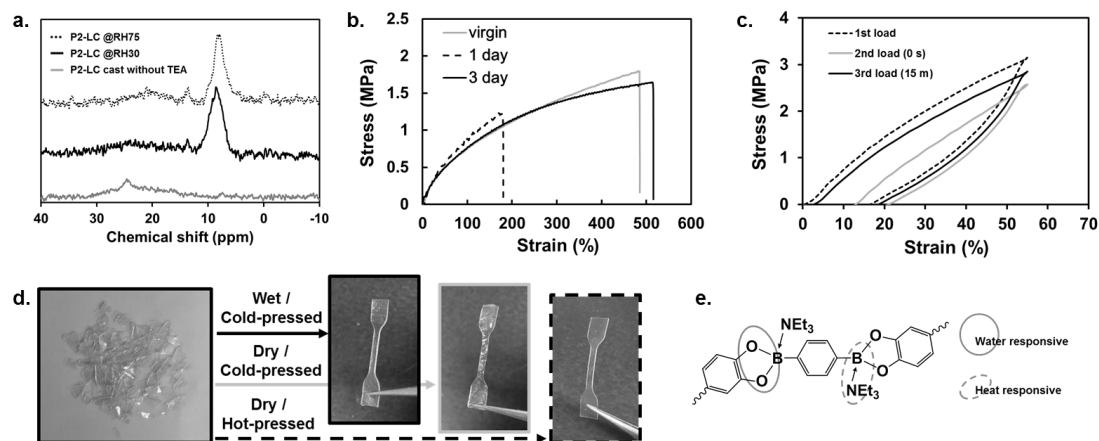

Figure 2. (a) Solid-state ^{11}B NMR spectra of **P2-LC**. Dotted line: moistened sample at 75% RH; Black line: dried sample at 30% RH; and Gray line: mixture of **P1** and *p*-phenyldiboronic acid. (b) Stress–strain curves of **P2-LC** healed at 75% RH. (c) Loading–unloading cycles under dry conditions with **P2-LC**. (d) Dual-stimuli responsive reprocessabilities of **P2-LC**. The finely cut dry films were recycled in three ways. Black arrow: the cut film was moistened at 75% RH, and then pressed at 20 MPa for 2 h at 25 °C; Gray arrow: the dry cut film was pressed at 20 MPa at 25 °C for 2 h; and Dotted arrow: the dry cut film was hot-pressed at 10 MPa for 30 min at 60 °C. (e) Two reactive bonds of the boronate-esters bearing B−N dative bonds.

2-2. Non-Swellable Self-healing Polymer under Submerged Conditions

Recently, water-triggered dynamic coordination between metals and vicinal-diols has been incorporated into bulk polymers for underwater self-healing.[3] The polymers showed excellent healing ability, but under submerged conditions, they exhibited severe water absorption. Compared to those dynamic metal-diol complexes, the tetrahedral boronate-ester bearing B−N bond is expected to have different nature with less electrostatic interactions due to electrically neutral and sterically bulk structure. Therefore, the author examined underwater properties (e.g. swelling and healing behavior) of **P2-HC**. As a reference sample with a metal-diol complex as a dynamic bond, the network polymer containing the Ca^{2+}-diol complex **P3** was prepared by replacing *p*-phenyldiboronic acid with $CaCl_2$ in the preparation of **P2-HC**.

First, the water absorption behavior was confirmed under water and seawater conditions. As shown in Fig. 3a, **P2-HC** showed almost 6 times and 10 times lower water absorption compared to **P3** in water and seawater, respectively. Notably, **P2-HC** swelled only up to ~2 wt% in seawater condition. The results of water contact angle measurements clearly supported the difference between the two polymers. **P2-HC** showed hydrophobic characteristic with the contact angle of 103°, and this value was almost the same as non-crosslinked polymer **P1**. In contrast, the value of **P3** was 88°, indicating hydrophilic nature. In order to obtain insight into the difference in the water affinity, the morphology of the two polymers was visualized by atomic-force microscopy (AFM) and transmission electron microscopy (TEM, **Fig. 3b**). Interestingly, **P3** showed phase-separated morphology and the size of granular domains was ~100 nm. As the domains appeared darker than

the matrix in the TEM image, they had higher electron density, presumably due to the concentrated Ca^{2+}-diol complexes by electrostatic interactions. In sharp contrast, notable phase-separation was not observed in the images of **P2-HC**. The results indicate that the boronate-esters bearing B−N bond were well dispersed in a polymer matrix. It can be inferred that the botonate-esters were almost isolated from each other due to electrically neutral and sterically bulk bond

Figure 3. (a) Swelling ratio of **P2-HC** and **P3** under submerged conditions. (b) TEM images of **P2-HC** and **P3**. The scale bars represent 500 nm. (c) Self-healed **P2-HC** under submerged conditions for 3 days. (d) Photographs of the tensile test of **P2-HC** after 3 days of healing in seawater.

structure. Therefore, the author concluded that the water affinity of the network polymers was affected not only by the hydrophobicity of polymer chains but also by their mesoscopic morphologies which could be controlled by electrical nature of crosslinkers.

Self-healing tests were conducted under submerged conditions. **P2-HC** showed quantitative healing ability in both water and seawater conditions (Fig. 3c and 3d), whereas **P3** did not show effective healing behavior. In **P2-HC**, uniformly distributed and highly dynamic boronate-esters would lead to efficient reconstruction of damaged network structure. In the case of **P3**, however, efficient network reconstruction would be difficult because individual metal-diol complexes clustered together, resulting in poor healing behavior.

Chapter 3. Dynamic Rubber via Solely Hydrogen-bond between Vicinal-diols

The author has discovered that it was possible to introduce rubber-like properties to linear polybutadiene by introducing vicinal-diol moieties, even though they are merely aliphatic alcohols (Fig. 4). Remarkably, **P4** exhibited

Figure 4. Synthetic scheme of polymer **P4**.

robust mechanical properties even without permanent crosslinks or additives. It has also been shown to have excellent dynamic features such as self-healing (quantitative healing at room-temperature in 3 d) and self-recovery (85% of hysteresis recovery) (Fig. 5a and 5b). These dynamic properties imply that **P4** is networked through dynamic crosslinks consisting of vicinal-diols. The results of differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS) revealed that **P4** was amorphous and did not have significant self-assembled structure. Therefore, the dynamic crosslinker would possibly be a dimer between two vicinal-diols, which was hard to be considered as a strong interaction.

To study the origin of the interaction between vicinal-diols, energy calculations of (*R,R*)-2,3-butanediol as a model compound were carried out with DFT(B3LYP)/6-311G** level. At the monomer level, the the two
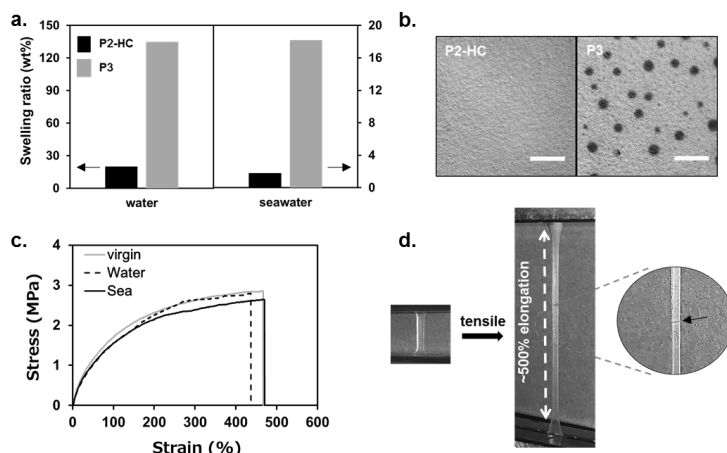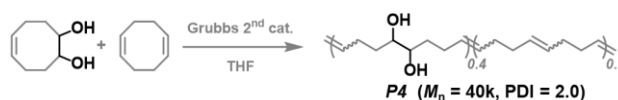
most relevant conformers were characterized by the O-C-C-O dihedral angle in the different two *gauche* orientations (named as G and G', Fig.5c). The higher stability of the two *gauche* conformers over a *trans* conformer is explained by the presence of intramolecular H-bond in vicinal-diol structures. The energy barrier between the two *gauche* conformers was calculated to be 21 kJ/mol. Interestingly, when the bulkiness around the vicinal-diol increased by replacing 2,3-butanediol to 3,4-hexanediol, the barrier was found to decrease to 13 kJ/mol. This low barrier implies that these conformers are free to interconvert at room temperature. Next, the energy calculations were performed for the dimers of GG, G'G' and GG'. As a result, various dimer modes through four H-bonds were identified, and the binding energy was revealed to be 45 ~ 60 kJ/mol (Fig. 5d). The results of DFT calculation are interesting because the interaction between two vicinal-diols involving four H-bonds was favorable in terms of both enthalpy (strong H-bonds) and entropy (various modes).
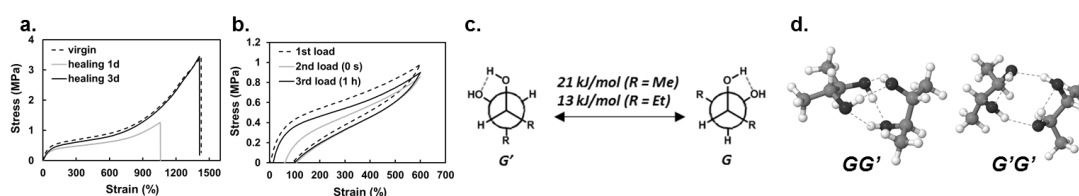

Figure 5. (a) Stress–strain curves of **P4** healed at room temperature for 1~3 days. (b) Loading–unloading cycles of **P4**. (c) Newman projections for the two relevant conformers of model compounds and energy barrier. (d) Various dimer modes with a binding energy of 45~60 kJ/mol.

This characteristic H-bonds between vicinal-diols are expected to be very effective in exchanging between crosslinkers, which are important for dynamic properties of polymers. However, the question arise as to whether the binding energy of ca. 55 kJ/mol can account for the decent mechanical properties of **P4**. This question prompted the author to consider the viscoelastic properties of **P4** from the standpoint of time scale. For this purpose, the dynamic mechanical analysis (DMA) was carried out with varying temperature and frequency. The activation energy (E_a) and the relaxation time (τ) of **P4** were estimated to be ~153 kJ/mol and ~30 min, respectively, from the time-temperature superposition analysis and the resulting master curve (Fig. 6a). The values of E_a and τ can be regarded as the energy for slippage of the polymer chains and the lifetime of dynamic properties, respectively. So, what are the characteristics of a polymer with the relaxation time of several tens of minutes? In tensile tests (Fig. 5a and 5b), **P4** exhibited tough rubber-like mechanical properties, and the applied elongation rate in the test (0.1~0.2 s^{-1}) was only a few seconds on a time scale (5~10 seconds; reciprocal of the elongation rate). That is, in the time scale much shorter than the life time of dynamicity of **P4**, it is possible to regard **P4** as permanently crosslinked polymer. Conversely, if the stress applied on time scales sufficiently longer than τ of **P4**, the chain will slither through one another due to the dynamicity of crosslinks (Fig. 6b). In fact, when pulling **P4** at an extremely slow rate (~1.0×10^{-4} s^{-1}) whose time scale is longer than τ of **P4**, the polymer behaved like a viscoelastic material. The results suggest that if the relaxation time of polymers is on the several tens of minutes scale, the polymer can combine mechanical robustness and dynamic feartures in reasonable time scale.

The dynamic properties of low-molecular-weight polymers are mainly affected by crosslink density rather than the chain entanglement. Some previous papers reported self-healing of low-molecular-weight polymers
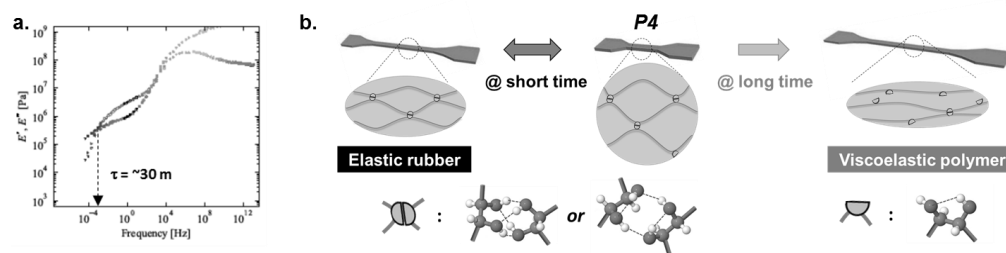
Figure 6. (a) Master curves of **P4**, prepared by the time-temperature superposition principle of storage modulus (E') and loss modulus (E") values obtained at 0.5, 1, 2, 5, 10 Hz in frequency with temperature range of −80 ~ 80 °C. Relaxation time (τ) of **P4** was estimated from the crossing point of the terminal slopes of E' and E". (b) **P4** exhibits an elastic or viscoelastic character according to the time scale at which stress is applied.

crosslinked by dense H-bonds.[4,5] In contrast, in the case of a high-molecular-weight polymer, the dynamic and mechanical properties are largely affected by chain entanglement, which makes it difficult to control the relaxation time of the polymer. For instance, when the crosslinking density by dynamic bonds is insufficient, the polymer flows (very short τ), while when it is too high, the mechanical strength is increased but the dynamic properties are lost (very long τ). Therefore, designing dynamic polymers with a high-molecular-weight chain with moderate relaxation time is very challenging. From this point of view, **P4** realized mechanically robust and highly dynamic properties by the combination of high-molecular-weight polymers with a low concentration of H-bonds. The author expects that moderate relaxation time in **P4** was obtained by applying strong and dynamic interactions of aliphatic vicinal-diols.

Chapter 4. Conclusion

Bulk polymers with vicinal-diol moieties exhibiting characteristic dynamic features were investigated by two different design strategies. First, by adopting "boronate-esters bearing B–N dative bonds" as dynamic crosslinks, the author developed water-triggered self-healing polymers which could be applied under various wet conditions. Next, the author demonstrated a tough and dynamic rubber with moderate relaxation time by using characteristic H-bonds between "aliphatic vicinal-diols". The author envisages that the results and the expected mechanisms of these works will provide a valuable strategy for the further development of dynamic bulk polymers.

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