

博士論文

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)

黄 鑫

Chapter 1. Introduction

Loosely crosslinked polymer networks including gels and elastomers comprise 3-dimensionally crosslinked polymer chains. They have a wide range of applications in various fields such as tissue engineering, electronics, automotive industry, and 3D printing. It is important to enhance mechanical properties of polymer networks for higher application requirements. However, there is a trade-off between stiffness and stretchability in mechanical properties of covalently crosslinked networks. One of the most promising ways to solve this trade-off, i.e., to achieve both high stiffness and stretchability simultaneously, is introduction of dynamic bonds to the polymer network. Dynamic bonds have lower bond energy than covalent bonds and undergo reversible association and dissociation. The representative examples of dynamic bonds are hydrogen bonds, metal-ligand interactions, ionic interactions, host-guest interactions, and π - π interactions. They can increase the rigidity, stretchability, and toughness of polymer networks by acting as additional transient crosslinks that prevent stress concentration during deformation.^[1,2] However, the relationship between the molecular characteristics of dynamic bonds and the macroscopic mechanical properties of the polymer network has not been established. Although many studies have utilized various dynamic bonds to enhance mechanical properties, they adopted different polymer backbones and network structures, which makes it difficult to extract only the effect of different dynamic bonds on mechanical properties. Moreover, almost all the polymer networks with dynamic bonds have been formed either by the random copolymerization of monomers and crosslinkers or by the random crosslinking of polymer chains, which unavoidably brings the structural defects into the network. These defects often have negative influences on the properties of polymer networks. They may also introduce undesired complexity to the system because the defects may disturb the effect of dynamic bonds. In addition, the random polymer network is difficult to be interpreted by theoretical models.

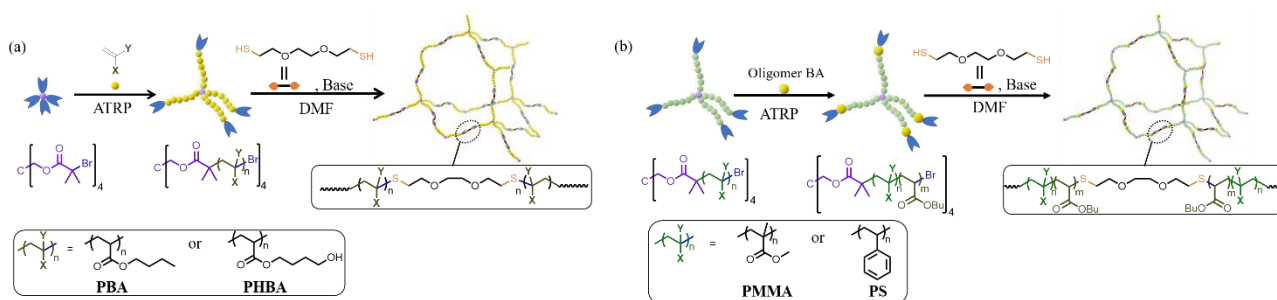
The aim of this doctoral thesis is to reveal the relationship between the molecular characteristics of dynamic bonds and the mechanical properties and establish the design principle for enhancing mechanical reliability of polymer networks. To solve the aforementioned problems, I introduce different hydrogen bonds into a nearly ideal polymer network with the identical network structure. As the most reliable method to construct ideal networks, the end-linking of monodisperse star polymers is used.^[3] As the dynamic bond, hydrogen bonds are chosen among various kinds of interactions because their bond energies can be widely and easily tuned by the molecular design. This thesis consists of four chapters. Chapter 1 introduces the general background, motivation, and objective of this study. In chapter 2, I develop a simple and versatile method to construct functional nearly ideal polymer networks, aiming to establish the experimental basis to introduce dynamic bonds into nearly ideal polymer networks. In chapter 3, I utilize the method developed in chapter 2 to investigate the influence of different hydrogen bonds on the mechanical properties of the polymer networks with nearly ideal network structure. Chapter 4 is for the conclusion and future perspectives.

Chapter 2. Formation of Nearly Ideal Polymer Networks by a Simple and Versatile Method

The defects induced by random crosslinking are summarized into two categories, namely spatial defects (i.e., the inhomogeneous spatial distributions of polymer chains) and topological defects including nonuniform

chain length between neighboring crosslinks, dangling chains, and loops. Ideal networks are free of such defects. They have a constant functionality of the crosslink points, consist of elastic chains with an identical length, and are macroscopically and microscopically homogeneous in terms of spatial distribution of polymer chains.^[4] Although it is impossible to perfectly satisfy all of these conditions because of intrinsic polydispersity of polymer chains and incomplete reaction, nearly ideal networks, which are close to these ideal conditions, can be realized. Several studies have reported that nearly ideal networks can be synthesized by end-linking of monodisperse star polymers of poly(ethylene glycol) (PEG)^[3], poly(acrylic acid)^[5], and poly(*N*-isopropylacrylamide)^[6]. However, the reported synthetic methods still possess some of the following problems. 1) The method needs complicated end-group modifications after polymerization. 2) The conversion of end-linking reaction is low, which causes the topological defects. 3) The reaction rate of end-linking is uncontrollable, which leads to the spatial defects. Spatial defects are generated if the end-linking reaction is so fast that the gelation threshold is reached before the polymer chains are homogeneously distributed. 4) The synthesized polymer networks are hard to be modified. The aim of this chapter is to develop a simple, efficient, and controllable method to form modifiable nearly ideal polymer networks to solve the above problems. The method will enable us to conveniently introduce hydrogen bonding functional groups in the nearly ideal polymer networks.

I designed a method involving only two steps, namely controlled polymerization and end-linking. The synthetic strategy used in this study is shown in **Scheme 1a**. A monodisperse star polymer with alky bromide end groups was first obtained by atom transfer radical polymerization (ATRP) of a vinyl monomer using a tetra-functional initiator. Subsequently, the bromide end-groups of the star polymer were directly reacted with a dithiol linker in the existence of a base via S_N2 nucleophilic substitution reaction to form a network. The excess base and its bromide salt produced by the reaction can be removed by immersing formed polymer networks in excess polar solvents. Poly(*n*-butyl acrylate) (PBA) was first used as a representative vinyl polymer. ¹H NMR and size exclusion chromatography (SEC) indicated the formation of monodisperse star polymer. The star-PBA gel could be formed in several minutes after mixing polymer, dithiol linkers, and base solutions as shown in **Figure 1a**.



Scheme 1. (a) Preparation of star-PBA and star-PHBA gels by combining ATRP and thiol-bromide reaction. (b) Preparation of star-PMMA-oBA and star-PS-oBA gels by modification with BA oligomers at chain ends followed by the thiol-bromide reaction.

The gelation process and final elasticity of the star-PBA system were examined by a rheological measurement. **Figure 1b** shows the time evolution of the storage G' and loss G'' moduli after the addition of

dithiol linkers and bases. Initially, G' is lower than G'' , which indicates that the sample is in the liquid state. Then G' exceeds G'' after 6 min, clearly indicating the transition from a viscoelastic liquid to a viscoelastic solid (i.e., to a gel). G' approaches a constant value with time and the value after 17 h (orange line in **Figure 1b**) is close to the theoretical elastic modulus G_{theo} estimated from the phantom network model without defects or entanglements. This result strongly indicates that the star-PBA gel is nearly free of topological defects. The end-group reaction conversion p was estimated to be 92% based on the observed G' using the phantom network model and tree-like approximation, which was comparable to the reported conversion of 80–90% for the star polymer-based network of PEG with similar M_n .^[7] Small-angle X-ray scattering (SAXS) data for the star-PBA gel also suggested the low level of spatial inhomogeneity.

Gelation time has a considerable impact on the formation of defects in the polymer network. In this study, gelation time can be controlled via the strength and/or amount of the base. **Table 1** lists the gelation time with different kinds and amounts of bases. Stronger base (higher pK_a) and/or a larger amount of base relative to thiol groups leads to shorter gelation time. The observed gelation times, which range widely from seconds to days, demonstrate that the reaction rate in this method is controllable.

To further investigate the thiol-bromide reaction conversion between the polymer and dithiol linker, linear-PBA having alkyl bromide end group was conjugated with dithiol linker utilizing the same procedure applied in the gelation experiment with star-PBA. **Figure 1c** and **d** show SEC traces and ¹H NMR spectra of linear-PBA before and after conjugation with dithiol linker in the presence of base.

Figure 1c reveals the disappearance of the original linear-PBA peak and appearance of a new peak whose apparent peak molecular weight was almost twice as high as that of the original peak while keeping the low polydispersity. The conversion of thiol-bromide reaction was estimated to be 93% by SEC, indicating the

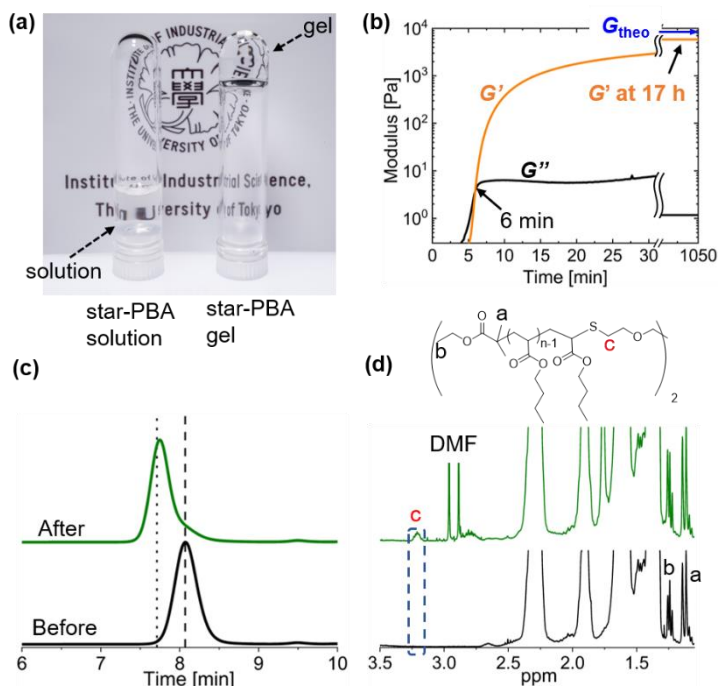


Figure 1. (a) Photograph of the tilting-tube test for the star-PBA solution and the gel. (b) Time evolution of G' and G'' for the star-PBA solution during gelation. The final G' after 17 h and the theoretical modulus (G_{theo}) are indicated by orange line and blue horizontal arrow, respectively. (c) SEC traces and (d) ¹H NMR spectra in CDCl_3 for linear-PBA before and after the thiol-bromide reaction.

Table 1. Gelation times of star-PBA solutions with different kinds and amounts of bases.

Base ^[a]	pK_a ^[b]	[Base]/[SH]	Gel Time
DBU	24.33	1.2	< 30 s
		2	< 10 s
TMG	23.30	1.2	≈ 30 s
		1.2	30 min
MPDA	20.04	2.4	6 min
		5	4 min
		1.2	—
DIPEA	18.90	10	1 d
		30	3 h

[a] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TMG = tetramethylguanidine, MPDA = *N*-methylpropane-1,3-diamine, DIPEA = *N,N*-diisopropylethylamine. [b] The pK_a of the base in acetonitrile was taken from the literature.^[8]

almost quantitative end-linking reaction. The ^1H NMR spectra (**Figure 1d**) of the linear-PBA before and after the thiol-bromide reaction indicate the emergence of the methylene proton derived from thioether (peak c). The reaction conversion of 84% was calculated by integrating peak c against peaks a and b (assigned to initiator residue), which also proved the high conversion of thiol-bromide reaction between PBA and dithiol linker. The stability of the ester groups of PBA against strong bases was also confirmed by mixing star-PBA with large amount of base (45 times) used in thiol-bromide reaction overnight. ^1H NMR and SEC confirmed no degradation reactions such as hydrolysis.

To inspect the applicability of this method to other vinyl polymers, poly(4-hydroxybutyl acrylate) (PHBA), poly(methyl methacrylate) (PMMA), and polystyrene (PS) gels were synthesized. PHBA was chosen because it had hydroxy side groups that would enable further functionalization, while PMMA and PS were selected as representative examples of general vinyl polymers. The star-PHBA gel (**Figure 2b**) was constructed by the same method as star-PBA gel (**Scheme 1a**). However, the star-PMMA and star-PS did not form gel with this method because the steric hindrance originated from the bulky groups adjacent to alky bromide end-groups prevented the $\text{S}_{\text{N}}2$ nucleophilic substitution. Therefore, the method was slightly modified as shown in **Scheme 1b**. The BA oligomer (oBA) was attached to each chain end of star-PMMA and star-PS to form star-PMMA-oBA and star-PS-oBA, which were then reacted with dithiol linkers to construct polymer networks in the presence of base. The appearances of star-PMMA-oBA and star-PS-oBA gel are shown in **Figure 2d and f**, suggesting the successful gelation. This method easily transforms various vinyl polymers into nearly ideal polymer networks by taking advantage of the generality of ATRP and highly efficient thiol-bromide end-linking reaction.

Chapter 3. Effect of Dynamic Bonds on the Mechanical Properties of Polymer Networks

Dynamic bonds have been commonly introduced into the polymer networks with randomly crosslinked structures to enhance the mechanical performance. Randomly crosslinked polymer networks with and without dynamic bonds or with different ratio/kinds of dynamic bonds have been compared to indicate that the mechanical properties were enhanced after introduction of dynamic bonds.^[2,9] However, it is difficult to directly reveal the influence of dynamic bonds because the defects induced by the random crosslinking also affect the influences of dynamic bonds. Moreover, to the best of my knowledge, there are no studies concentrating on the effect of various kinds of dynamic bonds on the mechanical properties in the same polymer network systematically. The aim of this chapter is to develop a systematical understanding in the relationship between the molecular characteristics of dynamic bonds and mechanical properties.

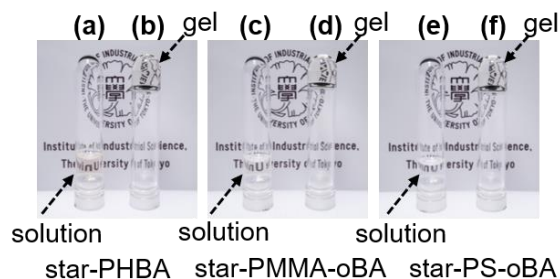
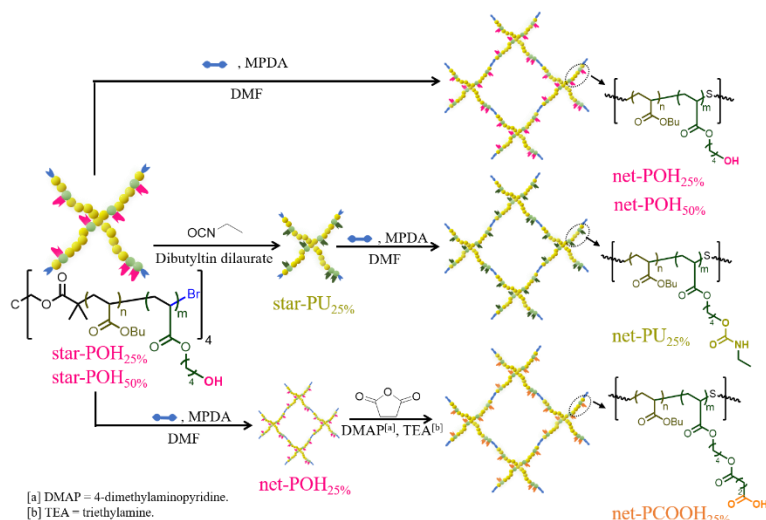


Figure 2. Photographs of star-PHBA solutions (a) before and (b) after gelation, star-PMMA-oBA solutions (c) before and (d) after gelation, and star-PS-oBA solutions (e) before and (f) after gelation.

Three kinds of hydrogen bonding functional groups were introduced into the nearly ideal networks. Here, hydrogen bonds are chosen among various dynamic bonds because it is easy to tune their bond energies in a wide range via the molecular design. Then mechanical properties of these polymer networks as well as those without dynamic bonds were measured. **Scheme 2** shows the synthetic route of this study. Random star copolymer of *n*-butyl acrylate (BA) and functionalized acrylate was first synthesized by ATRP followed by deprotection to yield random star copolymer with hydroxy (OH) groups, which was further reacted with dithiol linker to form a network with OH groups. The networks with urethane (U) and carboxylic acid (COOH) groups were respectively formed by the post-polymerization modifications of the star copolymer with OH groups followed by thiol-bromide reaction and post-gelation modification of polymer network with OH groups. The mole percentage of repeat units with functional groups *x* in each copolymer is indicated as the subscript “*x*%”. The star random copolymers with each functional group were named as star-POH_{25%}, star-PU_{25%}, star-PCOOH_{25%}, and star-POH_{50%}. The networks of these prepolymers were named as net-POH_{25%}, net-PU_{25%}, net-PCOOH_{25%}, and net-POH_{50%}. The nearly ideal network of star-PBA (net-PBA) was constructed by the method shown in **Scheme 1a** and the random network of BA (*r*-net-PBA) was synthesized by free radical copolymerization of BA and a diacrylate crosslinker. After construction of polymer networks, they were all dried to form elastomers for further measurements. The star prepolymers were all characterized by ¹H NMR and SEC to confirm the synthesis of designed monodisperse random star copolymers. The polymer networks were characterized by attenuated total reflection infrared (ATR-IR) spectroscopy to reveal the existence of functional groups and hydrogen bonds. The



Scheme 2. Preparation of polymers networks with nearly ideal network structure and various hydrogen bonding groups including hydroxy, carboxylic acid, and urethane.

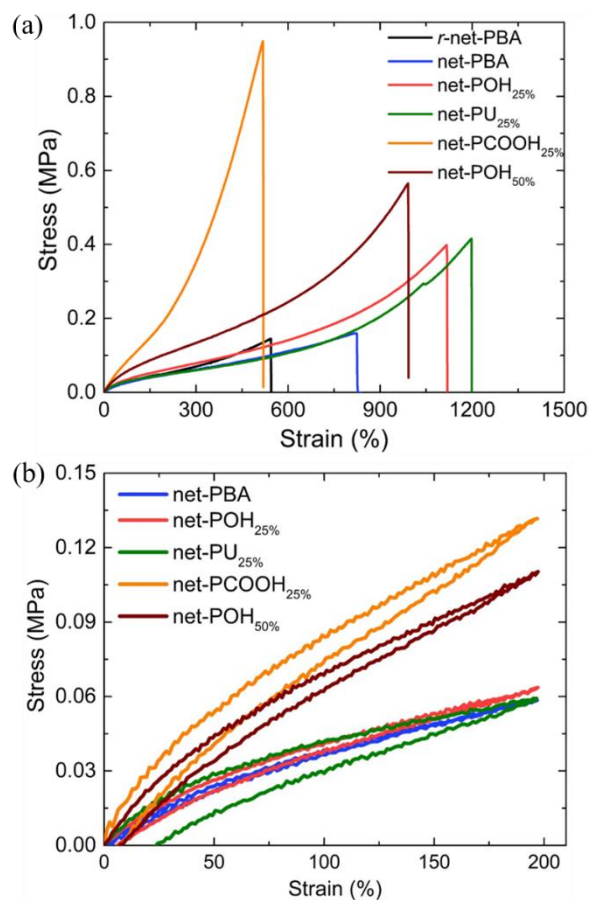


Figure 3. (a) Stress-strain curves and (b) cyclic tests of the elastomers *r*-net-PBA, net-PBA, net-POH_{25%}, net-PU_{25%}, net-PCOOH_{25%}, and net-POH_{50%}. strain rate: 0.076 s⁻¹.

characterization methods ranged from macroscopic to microscopic scales, from mechanical properties of polymer networks, to linear viscoelasticity of polymer chains, and finally to the binding energies of hydrogen bonds.

The mechanical properties of polymer networks were characterized by uniaxial tensile tests. The stress-strain curves of elastomers are shown in **Figure 3a**. net-PBA shows higher strain at break (ϵ_{\max}) with similar Young's modulus (E_Y , small strain behavior of polymer networks) to *r*-net-PBA, indicating that the existence of defects leads to more stress concentration. The networks with hydrogen bonds, net-POH_{25%}, net-PU_{25%}, and net-PCOOH_{25%}, show higher E_Y than net-PBA. net-POH_{25%} and net-PU_{25%} show higher ϵ_{\max} , but that of net-PCOOH_{25%} is lower, compared with net-PBA. These results suggest that net-POH_{25%} and net-PU_{25%} are stiffer and more stretchable than net-PBA, breaking the trade-off between stiffness and stretchability. This is due to the increase of apparent crosslink density and prevention of stress concentration by the hydrogen bonds. The net-COOH_{25%} is rigid with high stiffness but low stretchability. Compared to net-POH_{25%}, net-POH_{50%} shows higher E_Y with similar ϵ_{\max} , suggesting the formation of more crosslinks by hydrogen bonds. The cyclic tests of polymer networks were carried out to estimate the recovery process of polymer networks. The hysteresis loop (shown in **Figure 3b**) becomes larger after introduction of hydrogen bonds, suggesting that the hydrogen bonds dissipated the energy during stretching. net-POH_{25%} and net-PU_{25%} have similar E_Y value and loading curve, but exhibit distinct unloading curve, indicating that they have different recovery rates.

In order to estimate the effects of hydrogen bonds on the mobility of polymer chains (small strain behavior), linear viscoelasticity of uncrosslinked polymer chains were characterized by rheological measurements. It is reported that the entanglement molecular weight of PBA is 28 kg/mol,^[10] which is larger than the molecular weight of a one-arm of studied star polymers. Thus, the studied polymers are all unentangled. The rheological behavior of star-PBA is first taken as an example (**Figure 4**). The master curves of storage (G') and loss modulus (G'') were constructed based on the time-temperature superposition principle (symbols in **Figure 4a**). The Rouse model, which predicts the linear response of unentangled polymer melts, is used to fit with the experimental data (solid lines in **Figure 4a**). The friction coefficient (ζ) of polymer

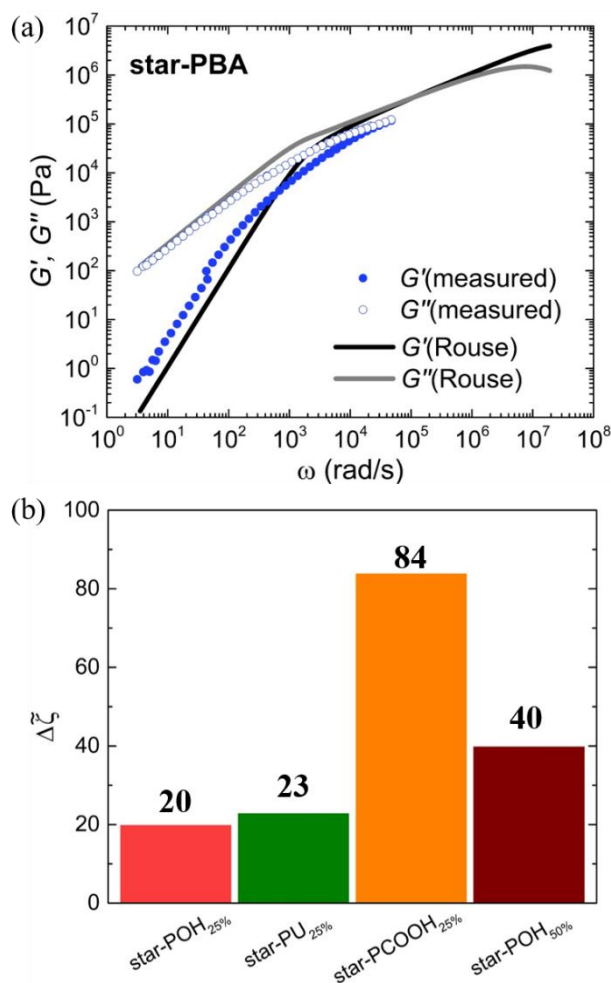


Figure 4. (a) Storage and loss modulus master curves of star-PBA. (b) Relative increment of friction coefficient of star polymers relative to star-PBA.

chains was extracted by fitting, which reflects the difficulty of polymer motion. The increment of friction coefficient of star polymers from that of PBA, ζ_{PBA} , was used as the measure: $\Delta\tilde{\zeta} = (\zeta - \zeta_{PBA})/\zeta_{PBA}$, which are shown in **Figure 4b**. The $\Delta\tilde{\zeta}$ increases after introduction of hydrogen bonds, suggesting that the formation of hydrogen bonds reduces the mobilities of polymers. The enhancement by different groups is in the order of $\text{OH} \sim \text{U} < \text{COOH}$, which suggest the strength of hydrogen bonds increases from OH and U to COOH groups. The higher amount of OH groups also has a larger effect.

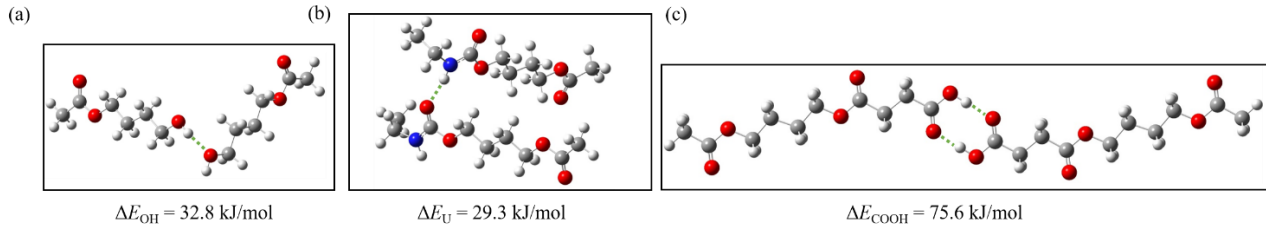


Figure 5. Stable dimers formed by hydrogen bonds between two (a) OH, (b) U, and (c) COOH groups. Red, gray, blue, and white colored balls represent oxygen, carbon, nitrogen, and hydrogen atoms, respectively.

The binding energies of the hydrogen bonds between the functional groups, OH, U, and COOH groups, were quantified by the DFT calculation. The model compounds were taken from the corresponding polymers, whose stable conformers were determined by the DFT optimization. Then the possible hydrogen bonded dimers were constructed and optimized. Hydrogen bonds formed by the dimerization of functional groups (OH, U, and COOH) and the dimerization of the functional group and the ester were considered, whose binding energies were compared to find out the most stable dimer, representing the strength of hydrogen bonds in the star polymers or polymer networks. **Figure 5** shows the optimized arrangements of the most stable dimers and their corresponding binding energies (ΔE_{stable}). ΔE_{stable} of OH and U are comparable, but COOH possesses the higher energy compared with the other two because it comprises two hydrogen bonds and a highly electron deficient proton in O-H which is a good hydrogen bond donor.

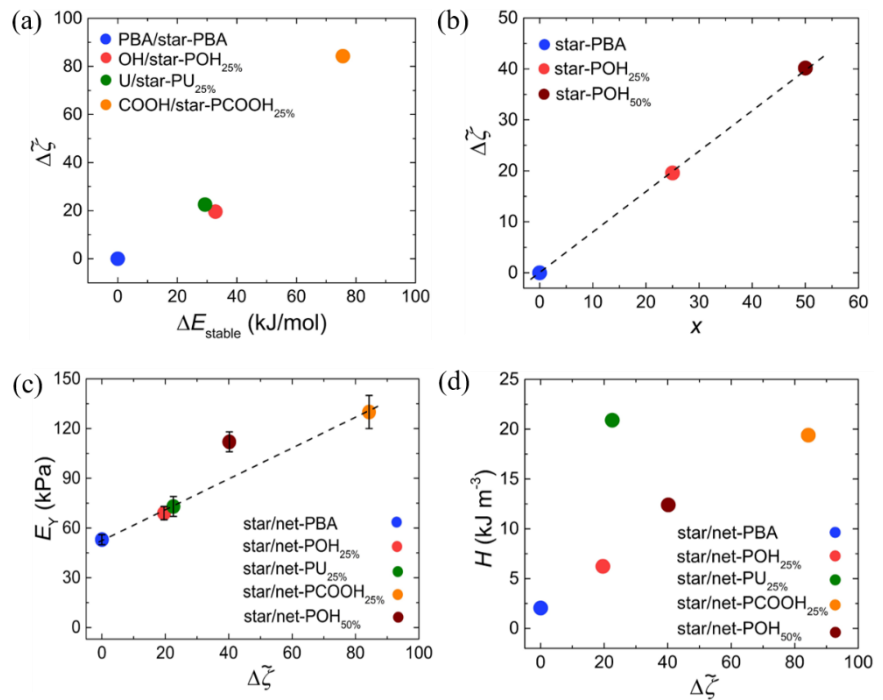


Figure 6. Relationship between the parameters. (a) ΔE_{stable} of hydrogen bonds and $\Delta\tilde{\zeta}$ of star polymers. The hydrogen bond energy in the PBA is assumed to be zero. (b) x of hydroxy groups and $\Delta\tilde{\zeta}$ of star polymers. (c) $\Delta\tilde{\zeta}$ of star polymers and E_{γ} of polymer networks. (d) $\Delta\tilde{\zeta}$ of star polymers and H of polymer networks.

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After characterization of macroscopic mechanical properties of polymer networks, friction coefficient of polymer chains, and microscopic binding energies of hydrogen bonds, the relationship among them were revealed. **Figure 6a** shows the relationship between ΔE_{stable} and $\Delta\tilde{\zeta}$. The OH and U have similar ΔE_{stable} and $\Delta\tilde{\zeta}$ while those of COOH are much higher. This indicates that ΔE_{stable} and $\Delta\tilde{\zeta}$ are positively correlated, i.e., the binding energy determines the friction coefficient of the polymer chains. **Figure 6b** shows the mole ratio of hydroxy groups (x) versus $\Delta\tilde{\zeta}$. Changing x by two times increases $\Delta\tilde{\zeta}$ by two times, which suggests the proportionality between the hydrogen bond density and the friction coefficient of polymer chains. **Figure 6c** shows the $\Delta\tilde{\zeta}$ of polymer chains versus the Young's modulus (E_Y) of polymer networks. Their relationship is almost linear except for the star-POH_{50%}/net-POH_{50%}, which indicates that the difficulty of polymer motion determines the stiffness of the polymer networks. However, the star-POH_{50%}/net-POH_{50%} appears above the linear relationship for $x = 25$ series, indicating that the amount of hydrogen bonds has a more significant effect on the stiffness of polymer networks than on the friction coefficient of polymer chains. **Figure 6d** shows the $\Delta\tilde{\zeta}$ of polymer chains versus hysteresis area (H) of corresponding polymer networks, which shows a positive correlation except for star-PU_{25%}/net-PU_{25%}. The different behavior of star-PU_{25%}/net-PU_{25%} from others indicates that recovery process should be related not only to the thermodynamic properties (ΔE_{stable}) but also the kinetic factor (association/dissociation rate) of hydrogen bonds, which should depend on the chemical structures of hydrogen bonding groups. In summary, it was found that the thermodynamic properties of hydrogen bonds affected the difficulty of polymer motion and further influenced the stiffness of the polymer networks. The stretchability was also related to the thermodynamic properties of hydrogen bonds. The recovery process was dependent not only on the thermodynamic properties but also on the kinetic properties of the hydrogen bonds.

Chapter 4. General Conclusion and Future Perspectives

The study on the influence of hydrogen bonds on the mechanical properties of nearly ideal functionalized polymer networks was divided into two steps. First, I discovered that the combination of controlled polymerization and subsequent end-linking reaction provided a simple and versatile method to construct nearly ideal polymer networks with various repeat unit structures. Second, I found out that the small strain behaviors including polymer mobility and stiffness of polymer network were closely related to the thermodynamic properties of hydrogen bonds, namely ΔE and amount of hydrogen bonds, which also affected the stretchability of polymer networks. The recovery rates of polymer networks were affected by the thermodynamic and kinetic properties, namely association rates of hydrogen bonds, which was related to the chemical structures of hydrogen bonding groups. In addition, the introduction of hydrogen bonds with moderate strength and amount could effectively break the trade-off between stiffness and stretchability.

The developed method to construct nearly ideal polymer networks can be used to explore the fundamental aspects of polymer networks with theoretical model and expand the applications of the nearly ideal polymer networks. The systematic knowledge on the relationship between molecular design of dynamic bonds and

mechanical properties of polymer networks can help us to obtain the polymer networks with required mechanical properties through the introduction of specifically designed dynamic bonds.

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