

# Studies on Functional Polycyclosiloxanes with Dynamic Covalent Bonds

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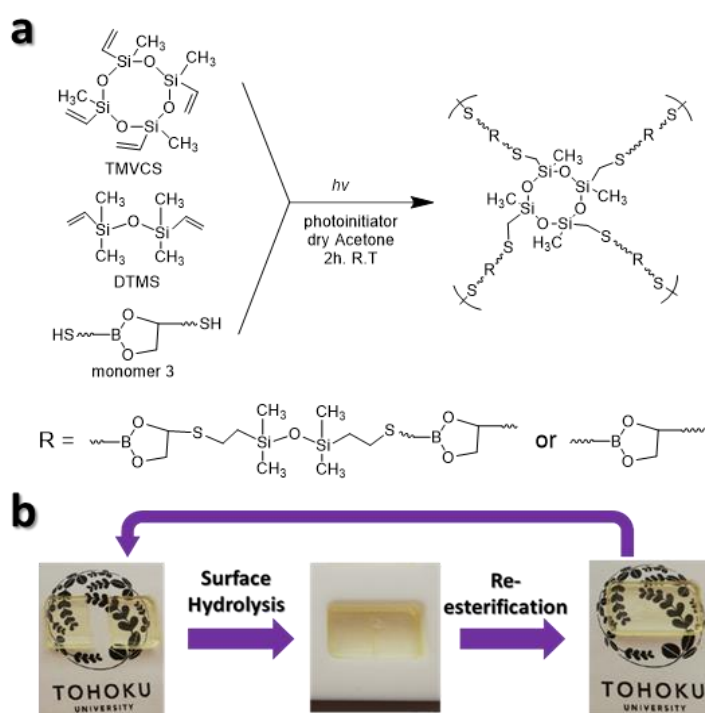
## 論文内容要約

Organic-inorganic hybrid materials are defined as materials consisting of both organic and inorganic components in the sub-millimeter and nanometer size. Such materials are promising for high-performance applications because their properties do not simply result from the sum of the individual components but also from their synergetic effects. Among them, polysiloxanes with the repeating unit ( $R_2SiO$ ) such as poly(dimethylsiloxane) (PDMS) combining inorganic Si-O bonds and organic R components in the macromolecular structures were demonstrated with excellent thermal resistance, optical transmittance, bio-compatibility and flexibility for applications in contact lenses, soft electronics, elastomers, etc. Industrial synthesis of PDMS started from hydrolysis polymerization of dimethyldichlorosilane, which generated terminal silanol groups for network formation. In this process, further functionalization of PDMS is limited because the reactive groups for further functionalization is nonprogrammable and randomly introduced. Our group has succeeded in developing linear polysiloxane polymers (pCS) starting from four-functional 1,3,5,7-tetramethylcyclotetrasiloxane (TMCS) and two-functional 1,3-divinyltetramethylsiloxane (DTMS) at a mixing ratio of 1:1, which have two remaining reactive  $-Si-H$  groups in each repeating unit for further functionalization. In particular, transparent networked pCSs and catechol containing pCSs have been developed for creating transparent, flexible, and thermal resistant materials, adhesive thin films, and so on. On the other hand, dynamic bonds, which respond to pH, temperature, molecular interaction, UV, etc. are interesting for novel materials design with stimuli-responsiveness and unique properties. There are two kinds of dynamic bonds: covalent dynamic bond such as boronic acid interactions and catechol-metal interactions and non-covalent dynamic bond such as multiple hydrogen bonds of 2-ureido-4[1H]-pyrimidinone (UPy). Of the two dynamic bonds, the covalent dynamic bond is stronger and more stable than the non-covalent dynamic bond.

In this thesis, novel functional polycyclosiloxanes bearing dynamic covalent bonds (boronic acid and catechol) were synthesized and characterized. The polycyclosiloxanes can form ultrathin films for metal ion sensing and nanoparticle adsorption, respectively (**Chapter 2** and **Chapter 4**). It is indicated that rational polymer structure design introduced the amphiphilicity to functional polycyclosiloxanes, which endowed them good film formation properties using dip-coating method. Moreover, networked polycyclosiloxanes containing boronic acids as dynamic crosslinkers were also synthesized for



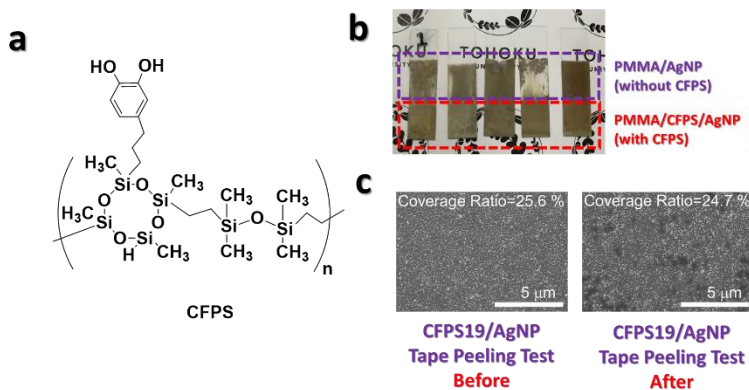
self-healing due to its dynamic characteristics. The synthesis of monomers and the final networked polymers was done through an efficient thiol-ene click reaction because radical-based thiol-ene processes have many advantages, for example, 1) simple photo-reaction systems, 2) ambient atmosphere and room temperature reaction conditions, 3) high potential for bulk polymerization and 4) fast reaction rate. First, a new dithiol monomer containing boronic acid groups was synthesized. Its dynamic characteristics were confirmed through comparing its NMR spectra with and without water addition in the NMR solvents. The networked dynamic pCSs were synthesized through a photo-catalyzed thiol-ene reaction of the dithiol monomer and a mixture of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMVCS) and 1,3-divinyltetramethylsiloxane (DTMS) (**Fig. 3(a)**). During the reaction, the molar ratio of thiol groups to vinyl groups was kept at 1:1. Varying the TMVCS:DTMS ratio, crosslinked samples were modified with different mechanical strengths. The networked structures were confirmed using NMR and FT-IR measurements. The optical transmittance was also investigated with UV-vis measurement. Interestingly, all the crosslinked polycyclosiloxanes exhibited self-healing properties (**Fig. 3(b)**). The self-healing rate can be adjusted through water addition to the healing parts. Strain-stress curves were also measured before and after healing, which indicated the highly efficient self-healing properties. The self-healable materials are promising to be applied as artificial skin, smart coating material, ion and sugar sensing, etc.



**Fig. 3.** (a) Synthetic route of the boronic acid-functionalized networked polycyclosiloxanes and (b) photographs of its self-healing properties.

In **Chapter 4**, polycyclosiloxanes containing catechol groups were studied because catechol groups have outstandingly strong, reversible, and pH-dependent adsorption onto inorganic surfaces (metals and metal oxides) as well as hard metal ions in solution. Considering the backbone flexibility and hydrophobicity of polycyclosiloxane, in our previous report pendent catechol groups were introduced into pCS to develop a catechol-functionalized linear polycyclosiloxane (CFPS, **Fig. 4(a)**) as a versatile platform for nanoparticle anchors. It was found that CFPS provided exceptional adhesion property that was able to anchor silver nanoparticles (AgNPs) to prepare a CFPS/AgNPs hybrid nanoassembly film for applications to surface enhanced Raman scattering (SERS) sensing. However, the investigation on the adhesion properties of CFPS was only focused on a

catechol substitution ratio of 88%. Comprehensive understanding and systematic studies on the adhesion behavior and properties were not constructed as a function of the substitution ratio of catechol in the polycyclosiloxane. In this chapter, a series of CFPS polymers was synthesized with different catechol substitution ratios (CFPS $x$ ,  $x$  is the percentage number of the substituted catechol,  $x=19, 38, 57, 76, 89$ ) through controlling the feeding ratio of the remaining  $\text{-Si-H}$  groups to the catechol containing monomer. Dip-coating films of each CFPS were prepared on Si and plastic substrates. Surface morphologies and surface free energy were also investigated. AgNPs adsorption ability and CFPS/AgNPs nanoassembly films strength were investigated in detail using scanning electron microscopy (SEM) and a tape peeling test (Figs. 4(b-c)). The nanoparticle coverage was easily tuned by the catechol substitution ratio, which is generally difficult using traditional methods. Moreover, the tape-peeling test proved that the adhesion was sufficiently strong even for CFPS19/AgNP.



**Fig. 4.** (a) Chemical structure of catechol-functionalized linear polycyclosiloxane, (b) photographs of the nanoassembly films. The upper part is PMMA/AgNP nanoassemblies (bare PMMA substrate) and the bottom part is PMMA/CFPS/AgNP nanoassemblies (from left: CFPS89, CFPS76, CFPS57, CFPS38, CFPS19) and (c) SEM images of the CFPS19/AgNP nanoassemblies on Si substrates before (left) and after (right) tape peeling test.