

## Preparation and Properties of Hyperbranched Polymers

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### Introduction

Hyperbranched polymers have been paid attention because of their unique structure. They have characteristic points such as low viscosity, low density, amorphous nature, and high solubility in organic solvents. Especially, they have many terminals whose number is the same of that of repeating units as far as they are synthesized from AB<sub>2</sub> type monomers. These characteristics of the hyperbranched polymers make them new functionalized polymers. We have reported synthesis and properties of hyperbranched polymers as well as dendrimers. A large part of these dendritic polymers consisted of aromatic condensation polymers such as aromatic polyamides [1], polyimides [2], and polybenzoxazoles [3]. On the other hand, we presented some examples of siloxane containing dendrimers [4] and hyperbranched polymers [5]. Polysiloxanes have unique properties such as low T<sub>g</sub>, high decomposition temperature, water repulsion, and good dielectric property. They are widely fabricated from liquid (oil)

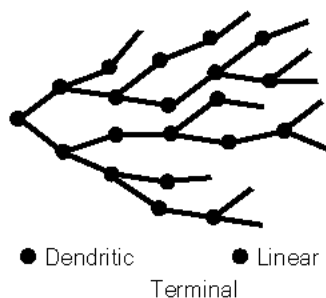
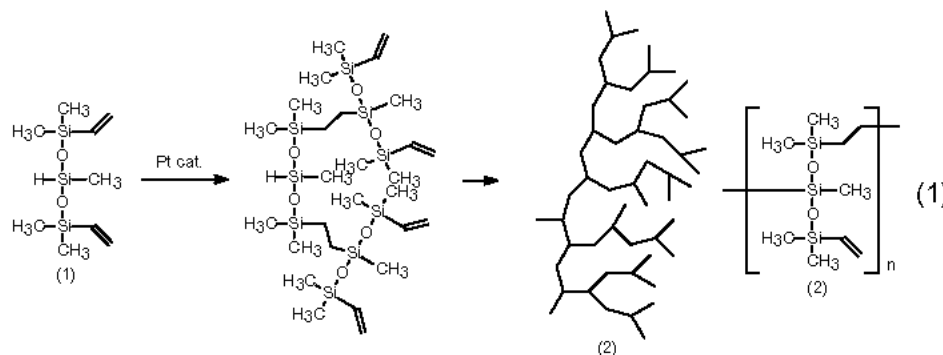
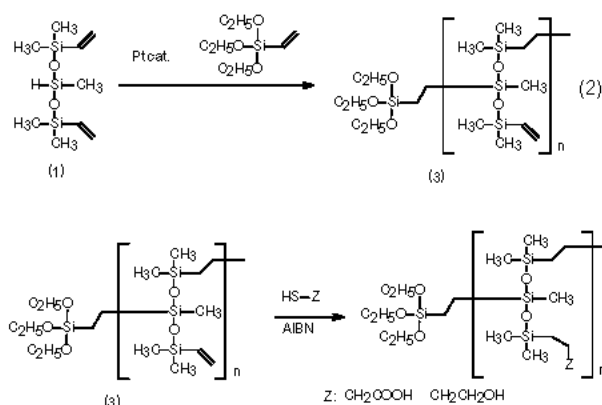


Fig. 1. Hyperbranched polymers



to solid (resin) by changing the extent of crosslinking. The dendritic



polysiloxanes seems to be highly functionalized facinated macromolecules. In this paper, preparation and properties of hyperbranched siloxysilanes are mainly described.

### Preparation of Hyperbranched polysiloxysilanes (HBPS)

Hyperbranched polysiloxysilanes (HBPS) are easily synthesized as shown in eq. 1, and have the similar structure to hyperbranched polysiloxanes. HBPS (2) with a vinyl terminal was synthesized starting from AB<sub>2</sub> monomer (1) possessing one Si-H and two vinyl functional groups. The polymerization was carried out through the hydrosilylation reaction in the presence of platinum catalysts.[6] The polymer was growing by the connection of silicon atom and a carbon of the vinyl group. HBPS (2) was colorless liquid having the molecular weight of ca. 6000. The terminal vinyl group of (2) can be converted to various functional groups as shown in Scheme 1. Especially, HBPS possessing carboxylic acid functional group was soluble in basic aqueous solution. It seemed to form a micelle with hydrophobic branching polysiloxysilane unit and hydrophilic carboxylic acid.

Table 1 shows thermal properties of HBPS having various terminal groups. In general, glass transition temperatures (T<sub>g</sub>) of dendritic macromolecules significantly depended on the terminal groups. For instance, in the present case, hydroxyl group made T<sub>g</sub> higher compared with other less polar functional groups. This phenomenon can be explained by interaction between HBPS molecules because of hydrogen bond. The decomposition temperature also depended on the terminal groups. Hydroxyl group is easily decomposed compared with vinyl and epoxy functional groups.

Table 1. Thermal Properties of HBPS

| Sample <sup>a)</sup> | T <sub>g</sub> (°C) <sup>b)</sup> | T <sub>dl0</sub> (°C) |
|----------------------|-----------------------------------|-----------------------|
| Vinyl                | -97                               | 500                   |
| Hydroxyl             | -36                               | 360                   |
| Epoxy                | -81                               | 440                   |

- a) Samples are indicated as the terminal functional group  
b) Measured by DSC with heating rate of 10 °Cmin<sup>-1</sup> under nitrogen  
c) Measured by TGA with heating rate of 10 °Cmin<sup>-1</sup> under nitrogen

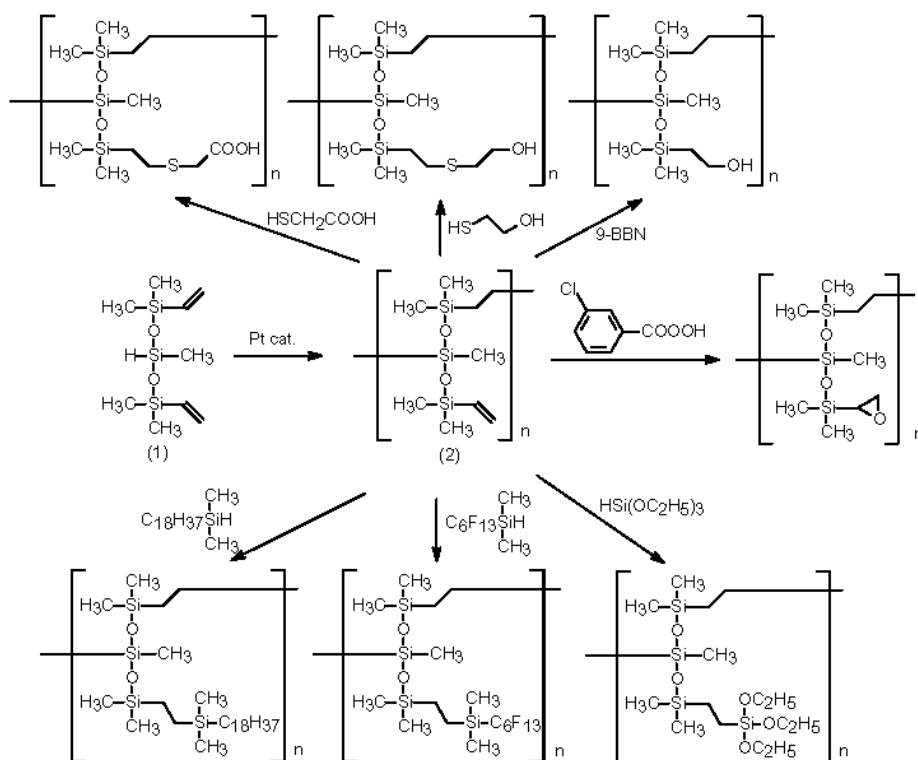
### Affinity of HBPS against Inorganic Surface

It was interesting that HBPS had strong affinity to inorganic surface such as glass and silica gel. For instance, epoxy group terminated HBPS act as a good dispersion reagent for inorganic particles. When particle (100 nm) of barium titanate oxide was dispersed in hexane, the particle precipitated easily. On the other hand, if small amount of HBPS was added to the solution, dispersion could be kept over 24 h. Furthermore, triethoxysilyl group was introduced at the focal point of HBPS to increase ability for adhesion to the inorganic surface. This is a technique to control the molecular weight by adding mono-vinyl functionalized reagent to the polymerization system. (Eq. 2) The terminal vinyl functional group of HBPS (3) was further converted to carboxylic acid and alcohol functional groups by radical addition reaction of thiols. To immobilize these HBPSs to a silicon wafer surface, the silicon wafer that was washed by the mixture of sulfuric acid and hydrogen peroxide aqueous solution was

Table 2. Contact Angle of Hyperbranched Polysiloxysilanes treated Silicon Wafer

| Sample <sup>a)</sup> | Θ <sub>g</sub> (°) <sup>b)</sup> | Θ <sub>A</sub> (°) <sup>c)</sup> | Θ <sub>R</sub> (°) <sup>d)</sup> |
|----------------------|----------------------------------|----------------------------------|----------------------------------|
| Vinyl                | 105                              | 105                              | 33                               |
| Carboxyl             | 90                               | 83                               | 49                               |
| Hydroxyl             | 82                               | 110                              | 59                               |
| Silicon Wafe         | 32                               | 21                               | 29                               |

- a) Samples are indicated as the terminal functional group  
b) Static Contact Angel  
c) Advanced Contact Angle in Dynamic Contact Angel  
d) Reverse Contact Angle in Dynamic Contact Angel



Scheme 1. Functionalization of Terminal Vinyl Group

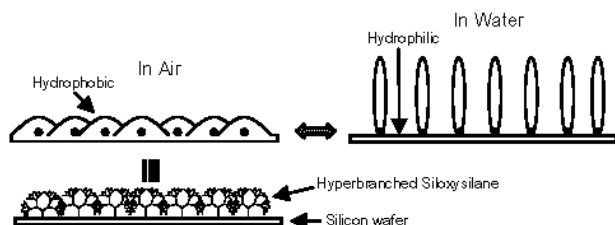
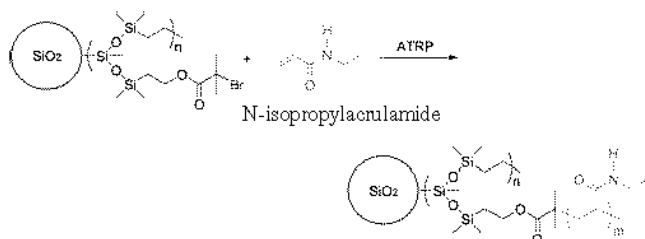


Fig. 2 Image of HBPSs in Air and Water

immersed in the toluene solution of HBPSs in the presence of catalytic amount of hydrochloric acid. Dynamic contact angles against water were measured for the HBPSs modified silicon wafers. Table 2 shows the results of the contact angles measurement. There are large different between the values of advanced and reduced contact angles in the present samples. This phenomenon may be explained as shown in Fig. 2. HBPSs were connected with the silicon wafer surface only at the focal point. In air, the silicon surface was covered with hydrophobic hyperbranched polymers, considering that  $T_g$ 's of HBPSs were much lower than the room temperature. On the other hand, as hyperbranched polymers expanded and swayed in water, the hydrophilic silicon surface came to be bare to water, and showed low contact angle.



Scheme 2. Immobilization of PIPAAm on Silica Bead

### Application of HBPS to Green Chromatography [7]

We also developed a method for immobilization of HBPS having the 2-bromoisobutyryl terminal group as a initiator for atom transfer radical polymerization (ATRP) on the silica surface to graft poly(N-isopropylacrylamide) (PIPAAm) as shown in Scheme 2. As PIPAAm has the lower critical solution temperature (LCST) at 32 °C, the silica surface was either hydrophilic or hydrophobic at lower or higher than LCST, respectively. The resulting PIPAAm modified silica was applied to a column packing material in temperature-responsive HPLC.

Because the silica surface changed hydrophilicity by changing column temperature, HPLC using the present bead is operated by gradation of temperature using only water as an eluent. Because any organic solvents are not necessary in this system, it is a clean chromatography system. Immobilization of HBPS with 2-bromoisobutyryl terminal group on the silica bead was conducted by mixing HBPS and silica bead in hexane. Atom transfer radical polymerization (ATRP) of PIPAAm in which HBPS on silica bead was the macroinitiator was carried out at room temperature in the presence of copper bromide and amine

catalyst. As shown in Fig.3, PIPAAm was successfully mobilized on the surface of the silica bead. The present PIPAAm mobilized silica bead was applied to HPLC column. It was found that two kinds of hydrophilic and hydrophobic steroids were separated using the column under temperature responsive system where only water was used as the eluent.

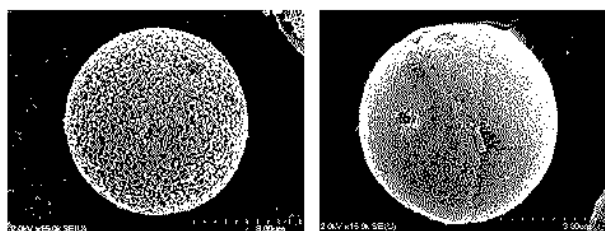


Fig. 3 Silica bead: Unmobilized (left), and mobilized with PIPAAm

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