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# **‘In-Chain’ and ‘Side-Chain’ Modified Poly(silphenylenesiloxane)s as High Temperature Polymers**

Yang Liu

Supervisor: Professor Dr. Yusuke Kawakami  
School of Materials Science, JAIST

## **Abstract**

High temperature polymers are greatly used in many applications, especially in modern technologies such as advanced aerospace and microelectronics. In conventional technologies, various halogen, nitrogen or phosphorus containing polymers are usually used as high temperature polymers, but the emission of toxic and corrosive gases during the thermal decomposition is still a serious drawback. It is known that siloxane polymers possess excellent thermal and oxidative stability and relative free of hazardous gas emission. Recent interests of high temperature polymer have been focused on siloxane-containing polymers.

In this dissertation, synthesis and characterization of novel high temperature polymers from modified poly(silphenylenesiloxane)s and evaluation of their thermal stabilities have been described. For achieving the purpose of this study, two approaches have been employed in the synthesis of modified silphenylenesiloxane polymers, one is so-called ‘in-chain modification’, and the other is ‘side-chain modification’.

In-chain modified poly(silphenylenesiloxane)s, poly[ {(oxy-dimethylsilylene)(1,4-phenylene)(dimethylsilylene)}-*ran*-(oxydimethylsilylene)(1,3-phenylene)(dimethylsilylene)]], were prepared from bis(silyl)benzene (**BSB**) isomers, 1,4-bis(dimethylsilyl)benzene and 1,3-bis(dimethylsilyl)benzene, with water in various ratios by cross-dehydrocoupling polymerization in the presence of  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ . Each isomer showed almost equal reactivity in the polymerization, but cyclic dimer was formed in the polymerization involving *m*-**BSB**, resulting in lower yield and low molecular weight of the formed polymers. Except the polymer prepared from pure *p*-**BSB** is crystalline, all polymers containing *m*-phenylene partially or totally in the backbone are amorphous polymers, and have lower  $T_g$  ranging from  $-33^\circ\text{C}$  to  $-49^\circ\text{C}$ . All silphenylenesiloxane polymers are thermally stable to temperatures about  $400^\circ\text{C}$ . Thus, these polymers, especially polymers containing *m*-silphenylene groups, show great promise as high-temperature siloxane elastomers.

Side-chain modification was firstly performed in the synthesis of poly(silphenylenesiloxane)s containing hydride or vinyl functional side groups. Modified polymers containing function side groups were successfully synthesized by the deaminative polycondensation of hydride or vinyl substituted 1,4-bis(aminosilyl)benzene with 1,4-bis(hydroxydimethylsilyl)benzene and hydroxy terminated silphenylenesiloxane prepolymer. Except for a random copolymer, they all have alternating structures and show low  $T_g$ s ranging from  $-23^\circ\text{C}$  to  $-40^\circ\text{C}$ . Introducing hydride and vinyl substituents, especially the vinyl functions, remarkably improves the thermal stability of the polymer. All polymers are considered having potential for using as high-temperature elastomers. Furthermore, the functional polymers also open an interesting field of chemical modification of poly(silphenylenesiloxane)s. A primary study was carried out on the further chemical modification of the silicon hydride functionalized polymer by hydrosilylation reaction with allyl glycidyl ether, and the vinyl functionalized polymer by hydroboration and oxidation. These modifications gave new silphenylenesiloxane polymers with epoxy and alcohol side functions, which are also considered to have attractive potential applications.

Because significant effect on enhancement of thermal stability was given by vinyl substituent, a series of poly(silphenylenesiloxane)s with high content of vinyl side-substituents were synthesized, in which the vinyl-content varies from 25% to 100%. DSC measurement revealed they are amorphous polymers and show their  $T_g$  at relatively low temperature ranging from  $-32^\circ\text{C}$  to  $-52^\circ\text{C}$ . Dynamic and isothermal TG analyses indicate that they all possess greatly improved thermal stability up to  $500^\circ\text{C}$  and have ultra high char yields in both inert and oxidative condition. Among them, the most thermally stable poly(tetravinyl-*p*-silphenylenesiloxane), fully vinyl-substituted, remained 90% char when heated to  $1000^\circ\text{C}$  and almost did not lose its weight (just 0.5% weight loss) during a period of 5 hours at  $400^\circ\text{C}$  in nitrogen. Poly(silphenylenesiloxane)s containing high content of vinyl substituted should be excellent high-temperature polymers and have potentials in application as heat-resistant or flame-retardant materials.

Therefore, novel silphenylenesiloxane polymers synthesized from the ideas of ‘in-chain’ and ‘side-chain’ modification have shown satisfactory performance on the thermal stability. Furthermore, polymers containing vinyl side functions, besides high temperature vulcanizable, can also be chemically cured by such as hydrosilylation addition to give the polymers new functionality or develop to cross-linked networks. The cross-link density may also be controlled over a broad range depending on the ratio of the cross-linker to vinyl groups. Thus, high temperature materials can be obtained with properties ranging from a slightly cross-linked elastomer to a highly cross-linked resin structure. Prospective research is worthwhile to investigate the chemical and thermal cure of those vinyl-containing polymers, and the thermal and mechanical properties of the cured materials.