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Preparation, Characterization, Surface Modification and Applications of Siloxane Polymers

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Abstract
This dissertation describes research carried out in the area of siloxane polymers, which refers to a group of polymers based on alternating silicon-oxygen backbones. The inexpensive starting materials and extraordinary thermal, mechanical and optical properties make siloxane polymers promising materials in a lot of applications, such as lithography,

optical devices, self-healing materials and ion conducting membranes.

Four projects are described after the introduction section. In the first project, extremely crosslinked silicone networks with novel structure are prepared by hydrosilylation of two tetra-functional cyclic monomers, 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasilxane (D_4^V). By introducing cyclic structures into the network and increasing the crosslink density, the thermal stability is improved, the Young's modulus and hardness of these siloxane networks are also be enhanced. In addition, some traditional properties of PDMS have been reserved, such as UV transparency, low surface tension and being reaction injection moldable.

The second project involves using the extremely crosslinked silicone network from the first project as a replica material for both nanoimprint lithography (NIL) and capillary force lithography (CFL). Because the advantageous properties of D_4^H-D_4^V networks meet all the requirements of NIL and CFL, such as UV transparency for photo nanoimprint lithography, thermal stability for high printing temperatures, high modulus for high printing pressures, low surface energy for easy demolding and molecular smoothness for achieving small scale features, this material was tested to fabricate sub-25 nm scale patterns from blu-ray discs and sub-9 nm scale patterns from anodized aluminum templates.

The third chapter describes a study on thermal reconstruction of oxygen plasma-treated poly(dimethylsiloxane) networks with controlled crosslink density. Instead of using a commercial product, e.g. Dow Corning Sylgard 184, pure silicone networks were prepared by hydrosilylation of various monomers and/or precursors. The relationship of reconstruction rate versus crosslink density is described.

The fourth project involves in surface modification of extremely crosslinked silicones using a chemical method. A stable hydrophilic surface was prepared by peroxide oxidation. After incorporating silanol groups on the surface, subsequent modifications with various reactive silanes were conducted and control of surface properties was demonstrated. The hydrophilic surfaces show similar reactivity to that of oxidized silicon wafers.

The last chapter describes a "living" siloxane network which has been used as a self-healing material. Through ring opening polymerization of octamethylcyclotetrasiloxane (D_4) and bis (heptamethylcyclotetrasiloxanyl)-ethane (bis-D_4) in the presence of a quaternary ammonium catalyst, "living" siloxane networks with controlled crosslink density were prepared. Based on the equilibrium of cyclic and linear species, the "living" networks exhibit "self-healing" abilities and can be "reshaped" via chemical stress relaxation upon application of external mechanical stress.