Hydrosilylation Polymerization of Cage Silsesquioxane Having Hydrosilane with Divinyl or Diyne Derivertives

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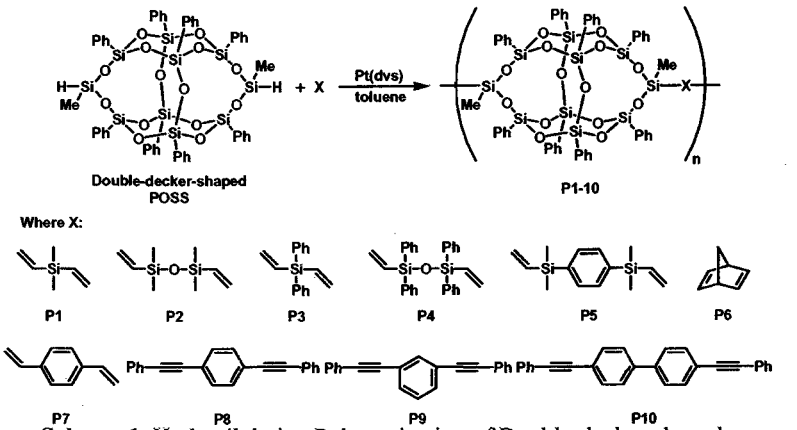
[Introduction] Polyhedral oligomeric silsesquioxane (POSS) molecules have attracted increasing attention, because they have nanometer-sized silica-like cage structure and can be functionalized with a wide variety of organic groups. The incorporation of POSS into some polymers has led to enhancement in the physical properties such as thermal and mechanical stability, oxidative resistance, and low dielectric constant. Since it is difficult to introduce only two functional groups to POSS, polymerization from POSS monomer predominantly generates insoluble cross-linked polymers. To improve their poor solubility, we have synthesized novel linear organic-inorganic hybrid polymers from hydrosilylation polymerization of double-decker-shaped POSS having hydrosilane with divinyl or diyne derivertives.

[Result and Discussion] To determine the polymerization condition of POSS with acetylene derivertives, we initially studied the model reaction of double-decker-shaped POSS with 2 equivalent of diphenylacetylene. The model reaction was carried out in the presence of 0.2 mol % of Karstedt's catalyst (Pt(dvs)) in toluene at 100 °C for 24 h., and the POSS reacted with two diphenylacethlenes was formed quantitatively. The GPC chromatogram of the product exhibited predominantly one peak with no peak. The result indicates that almost no side reactions were occurred, such as the further hydrosilylation of the resulting double bond. Based on the model reaction, the hydrosilylation polymerization of double-decker-shaped POSS with divinyl or diyne derivertives was performed under the same conditions (Scheme 1). The chemical structures of **P1-10** were determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectra. The molecular weights of **P1-10** were measured by GPC, and all polymers showed high molecular weight (M_n > 10,000). Thermal behaviors were characterized by DSC, and TGA measurement, and **P1-10** showed high decomposition temperature (425-518 °C). In particular, **P8-10** exhibit relatively high grass transition temperature (137-184 °C). The solubility of **P1-10** was tested in several common organic solvents and **P1-10** readily soluble in toluene, tetrahydrofuran and chloroform and so on. Transparent films were prepared by solvent casting and spin coating and have low dielectric constants about 2.6.



Scheme 1. Hydrosilylation Polymerization of Double-decker-shaped POSS with Divinyl or Diyne Derivertives

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