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Communications to the Editor

Hydrosilylation Polymerization of Double-Decker-Shaped Silsesquioxane Having Hydrosilane with Diynes

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Introduction. Organic–inorganic hybrid materials have attracted much attention because they offer the opportunity to develop high-performance materials that combine many desirable properties of conventional organic and inorganic components such as thermal stability, solubility, and processability. Particularly, polyhedral oligomeric silsesquioxane (POSS) is an interesting class of inorganic component. It has a nanometer-sized silica-like cage structure and can be functionalized with a wide variety of organic groups.[1] Use of POSS derivatives as a monomer has demonstrated to be an efficient method for nanocomposite materials design[2] as well as for side chains[3] or end groups[4] in hybrid polymers. The incorporation of POSS into some polymers have led to enhancement in the physical properties such as thermal and mechanical stability,[3c,h,l,m] flammability,[3e] oxidative resistance,[3i] and low dielectric constant.[3a,b]

Although numerous POSS-based materials have been prepared, few papers have reported the synthesis of soluble polymers with POSS in the main chain.[5] In step polymerization system, it is necessary for the monomer to have precisely two functional groups to obtain linear high molecular weight polymers. Since it is difficult to introduce only two functional groups to POSS, polymerization from POSS monomer predominantly generates insoluble cross-linked polymers.[2] Among them, Tanaka et al. reported soluble polymers with high thermal stability via hydrosilylation polymerization of octakis(hydrosilsesquioxane) (T_8^H) with diynes.[5c] However, the polymer has an ill-defined structure containing multiple brancheds due to use of octafunctional T_8^H monomer.

In a previous paper, we reported the synthesis of a novel POSS, double-decker-shaped silsesquioxane (DDSQ).[6] Since the DDSQ possess precisely two reactive hydrosilane groups, it should make linear hybrid polymers. Here we present the synthesis of linear polymers from hydrosilylation polymerization of DDSQ with diynes.

Results and Discussion. We initially studied the reaction of DDSQ with 2 equiv of diphenylacetylene to investigate whether model compound **1** was formed quantitatively (Scheme 1). 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. The GPC of the products exhibited predominantly one peak (Figure 1). After separation by preparative GPC, the fraction proved to be compound **1**, meaning that almost no side reactions occurred, such as the further hydrosilylation of the resulting double bond.

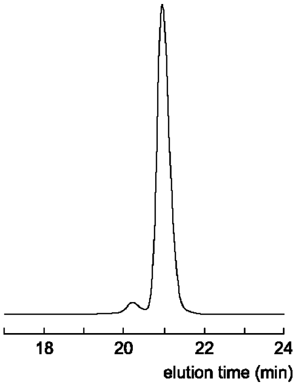

Figure 1. GPC of the products of the model reaction.

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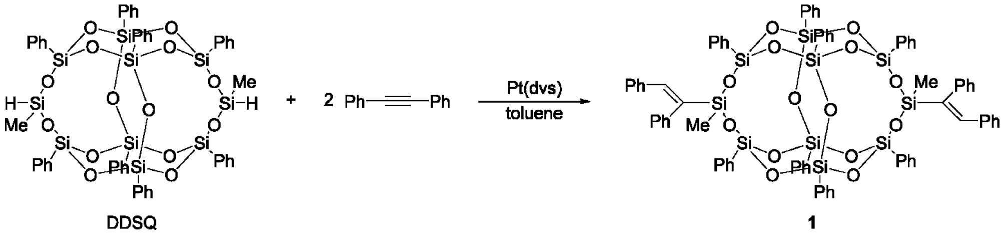
Scheme 1



Scheme 2

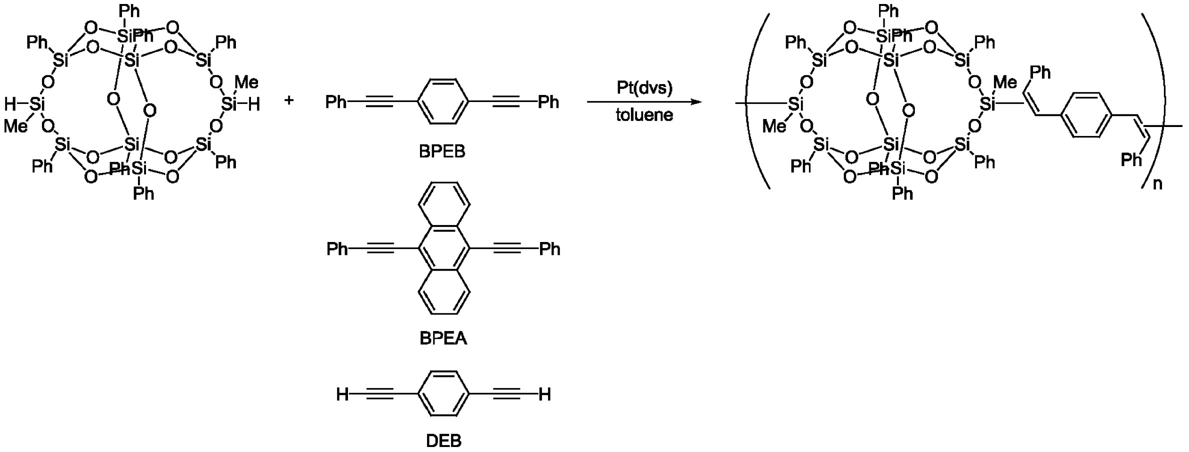


Table 1. Polymerization of DDSQ with Diynes by Hydrosilylation Reaction

polymer	feed ratio of DDSQ (DDSQ/diyne)	diyne	yield (%)[b]	M_n[c]	M_w/M_n[c]	T_d[d]	T_g[e]
P1	1	BPEB	97	29100	4.1	518	153
P2	1.2		97	14600	2.9	489	156
P3	1	BPEA	90	11900	4.9	301	
P4	1	DEB	insoluble				

[a] Polymerization conditions: 1 mmol of diyne in 2 mL of toluene with 0.2 mol % of Pt(dvs). [b] After reprecipitation into MeOH. [c] Determined by GPC with polystyrene standard. [d] TGA, 10 °C/min in N_2. [e] DSC, second heating, 10 °C/min in N_2.

Based on the model reaction, the hydrosilylation polymerization of DDSQ with diynes was performed under the same conditions (Scheme 2). The results of the polymerization and thermal properties are summarized in Table 1. The polymerization of DDSQ with 1,4-bis(phenylethynyl)benzene (BPEB) gave a high molecular weight polymer (**P1**) with $M_n = 29\,100$. The molecular weights obtained by GPC are only rough estimations because the polymers are considerably more rigid than polystyrene. The chemical structures were characterized by NMR and IR spectra. In the ^{1}H NMR spectrum of **P1**, the DDSQ methyl group signal was observed between 0.22 and 0.38 ppm, and the vinyl, phenyl, and phenylene group signals were observed between 6.41 and 7.59 ppm. In the ^{13}C NMR spectrum, the methyl group signal was well resolved at −1.21 ppm. However, the signals for vinyl, phenyl, and phenylene groups were unresolvable between 125 and 142 ppm. The complexity of the signals is caused because main chain is composed of α and β addition units or cis and trans arrangements. Moreover, there is no indication of single carbon−carbon bond in the ^{13}C NMR spectrum, indicating that hydrosilylation had only taken place at the triple bond of the starting diyne, and subsequent hydrosilylation of the resultant double bond did not occur. The ^{29}Si NMR spectrum showed three signals reflecting chemical structure (Figure 2). Comparing the spectrum of **P1** with DDSQ, the signal at −32.60 ppm of $SiHMeO_2$ of DDSQ disappeared completely, and a new signal at −34.13 ppm of $SiCMeO_2$ was observed.

To obtain thermally stable cross-linked polymer, the polymerization of 1.2 equiv of DDSQ with BPEB was attempted. However, compared to **P1**, lower molecular weight polymer (**P2**) with $M_n = 14\,600$ was generated. In the ^{13}C NMR spectrum, no signal due to a single carbon−carbon bond was detected. These results indicate that the reactivity between a double bond in the main chain and hydrosilane of DDSQ is very low, and cross-linked polymer is not obtained by the hydrosilylation.

The polymerization of DDSQ with 9,10-bis(phenylethynyl)-anthracene (BPEA) afforded a moderate molecular weight polymer (**P3**) with $M_n = 11\,900$. On the other hand, the polymerization of DDSQ with diethynylbenzene (DEB) gave an insoluble polymer (**P4**) after reacting for 30 min. In this case, it is considered that since the steric hindrance of a double bond formed by polymerization is less than that of BPEB, the hydrosilylation of the double bond in main chain with the hydrosilane of DDSQ proceeded to give cross-linked polymer.

The solubility of **P1** and **P2** was tested in several common organic solvents.[7] **P1** and **P2** were readily soluble in toluene, tetrahydrofuran, ethyl acetate, chloromethane, chloroform, *N*-methylpyrrolidone, *N*,*N*-dimethylacetamide, and *N*,*N*-dimethylformamide and insoluble in other solvents investigated. **P1** is also partially soluble in acetone and diethyl ether. **P1** could be cast into a transparent film.

The thermal properties of polymers **P1**−**P3** were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are shown in Table 1. **P1** and **P2** showed glass transition temperatures (T_g) at 152 and 156 °C, respectively, and no other transition temperatures were observed in the DSC curves. **P3** exhibited no thermal transition temperatures, indicating that the anthracene group increased the barrier of the longitudinal motion of the polymer chain. The TGA curve of **P1** showed an onset decomposition temperature (T_d) at 518 °C under nitrogen. The T_d of **P2** and **P3** was less

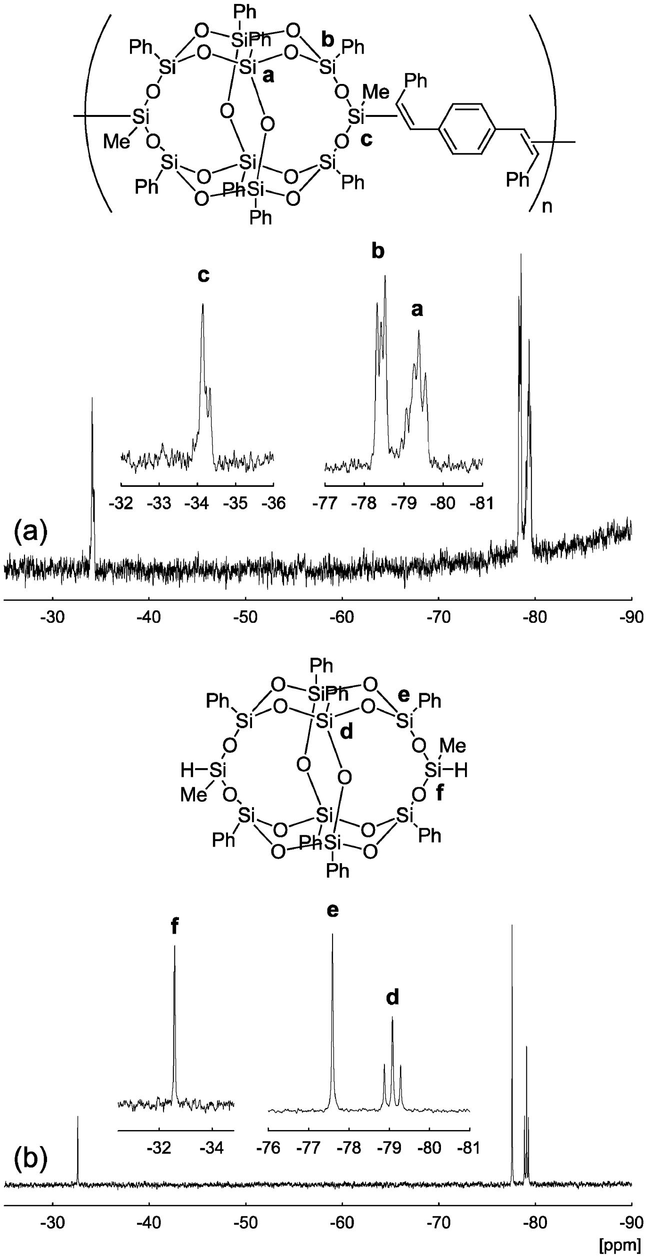


Figure 2. ^{29}Si NMR spectra of **P1** (a) and DDSQ (b).

than **P1**. The low molecular weight oligomers remained in the polymers may account for the rather low T_d.

In conclusion, new organic−inorganic hybrid polymers were prepared by the hydrosilylation polymerization of DDSQ with diynes. The polymerization proceeded without susequent hydrosilylation of the resultant double bond to give high molecular weight polymers. These polymers showed high thermal stability owing to main chain composed of DDSQ, double bond, and aromatic groups.

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Supporting Information Available: Experimental procedures and characterization data for DDSQ, **1**, **P1**, **P2**, and **P3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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