Polymer Bulletin 46, 15–21 (2001)

Polymer Bulletin

Synthesis and characterization of liquid-crystalline silsesquioxanes

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Received: 7 December 2000/Accepted: 29 December 2000

Summary

Liquid-crystalline (LQ) silsesquioxanes having various mesogenic moieties were synthesized by hydrosilylation reaction of octa(hydridosilsesquioxane) and terminal alkenes with mesogenic groups using hexachloroplatinic acid as a catalyst. The obtained LC silsesquioxanes were characterized by FT-IR, ^{1}H- , ^{29}Si-NMR. From the results of differential scanning calorimetry (DSC) and optical polarizing microscopy, their liquid crystallinities of nematic phase were found to be much more stable than those of the corresponding mesogenic compounds due to the effect of the inorganic part which is polyhedral hydridosiloxane core. It was also found that the thermal stabilities of LC silsesquioxanes were improved after hydrosilylation reaction through a thermogravimetric analysis (TGA).

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) combining unique hybrid (inorganic-organic) chemical compositions with nano-sized cage structures have long been important and interesting class of materials because of their unusual structures involving several rings connected together in a finite three dimensional molecular skeleton (1-5). Especially, since they show considerable potentials for use as a low dielectric material as well as applications in modeling of silica surfaces and interfaces, they have recently received much attention (6-8). POSS, e.g. $(RSiO_{15})_8$, where R can be a various number of functional groups, offer the opportunity to develop a wide range of hybrid materials with diverse properties. Laine et al. proposed POSS with polymerizable groups and polymerized them to produce hybrid materials having the crosslinked density or degree of polymerization which can be excellently controlled (9, 10). Feher and coworkers have developed a new strategy for preparing functionalized POSS from fully-condensed frameworks using various methods like base or acid catalyzed cleavage (11, 12). So far these well-defined functionalized POSS have been prepared by the hydrosilylation reaction of terminal olefins with octa(hydridosilsesquioxane) or direct hydrolytic condensation reaction of silane-bearing compounds (13-15). However, the clear explanation on the mechanism of direct hydrolytic condensation reaction has not been explored yet.

We, therefore, have recently studied on POSS having various organic groups made by a set of synthetic methods, as described above. Using these

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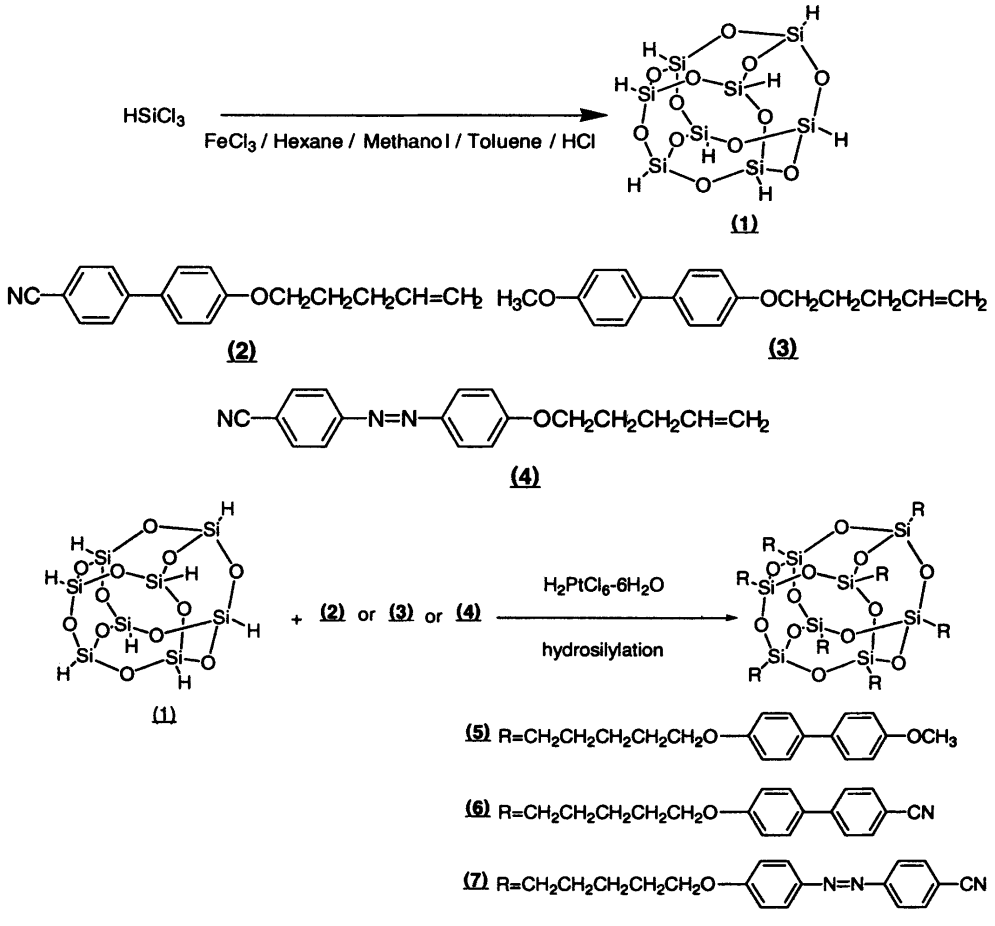
functionalized POSS and organic polymers, homogeneous hybrid materials were obtained by utilizing physical interactions, i.e. hydrogen or aromatic interaction (16, 17). The obtained hybrid materials could be reversibly dissolved in solvents and cast again without any separation. Thus, POSS-based hybrids may provide potential of organic/inorganic hybrid materials having remarkable mechanical properties and high thermal stability. In this paper, we describe the synthesis of POSS with different kinds of mesogenic units by hydrosilylation reaction and also examine LC behavior, thermal properties, and their solubilities.

Experimental Section

General Procedure

^{1}H NMR spectra were recorded using a 270MHz JEOL-JNM-GX270 NMR spectrometer. UV absorption spectra were obtained from a JASCO V-530 spectrophotometer. FT-IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. The thermal behavior was examined by DSC and TGA (Seiko Instruments Inc., Shimadzu DT-30) under a nitrogen and air atmosphere, respectively. The birefringent textures of LC silsesquioxanes were observed by a polarizing microscope (Nikon Type-120) equipped with a hot stage.



Scheme 1

Materials

4,4-Dihydroxybiphenyl and 4-cyano-4-hydroxybiphenyl were recrystallized from methanol. 1,2-Dichloroethane was distilled from magnesium sulfate under nitrogen. Acetone was distilled from potassium carbonate under nitrogen. Ethanol was distilled from calcium hydride. Toluene and methanol were distilled from sodium metal and magnesium methoxide, respectively. Other solvents and reagents were commercially supplied and used without further purification.

Synthesis of octa(hydridosilsesquioxane) and mesogenic compounds

Octa(hydridosilsesquioxane) (**1**) was synthesized in 16% yield by the hydrolytic condensation reaction of trichlorosilane, according to the procedure reported before (18). Three kinds of terminal alkenes with mesogenic moieties (**2**, **3**, **4**) were prepared according to a literature procedure (19, 20).

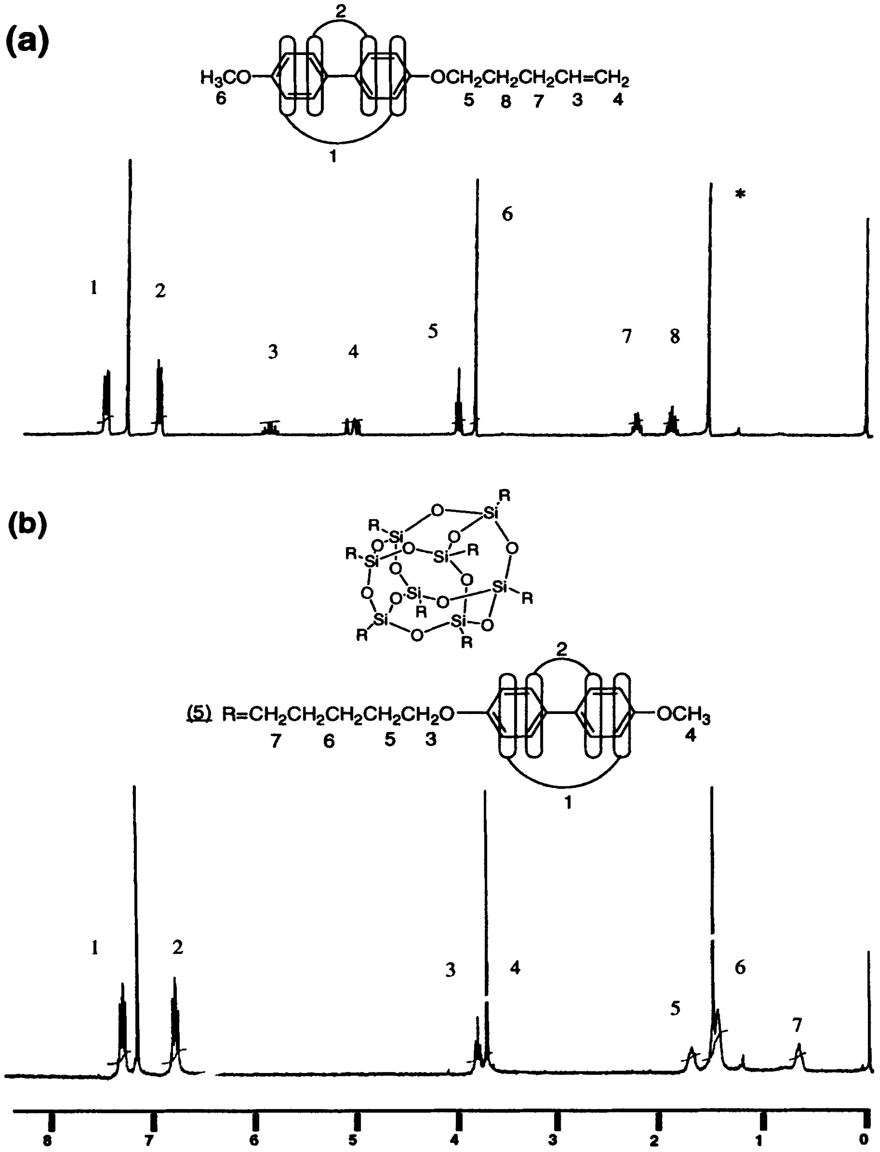


Figure 1. ^1H NMR spectra of (a) Vinyl-OCH_3 and (b) Cubic-OCH_3. Asterisk shows the peak due to water.

Synthesis of LC silsesquioxanes

Synthesis of Octa(5-(4-methoxybiphenyloxy)pentyl)-octasilsesquioxane (Cubic-OCH_3) (**5**). Hydridosilsesquioxane (**1**) (0.3 g, 0.71 mmol) was dissolved in distilled 1,2-dichloroethane (20 ml). The mixture was stirred, and 5-(4-methoxybiphenyloxy)-1-pentene (1.8 g, 7.1 mmol) and 2.78 mM 1,2-dimethoxyethane solution of $H_2PtCl_6 \cdot 6\ H_2O$ were added. The reaction mixture was refluxed for 24h under nitrogen. The white precipitate appeared when the solution was cooled down to the room temperature. The white crude product was recrystallized from 1,2-dichloroethane (1.2 g, 66%), mp 215°C. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 4H), 6.9 (m, 4H), 3.9 (t, 2H), 3.8 (s, 3H), 1.8 (m, 2H), 1.4-1.6 (m, 4H), 0.7 (m, 2H), ^{29}Si NMR ($CDCl_3$): - 66.6.

Synthesis of Octa(5-(4-cyanobiphenyloxy)pentyl)-octasilsesquioxane (Cubic-CN) (**6**). (**6**) was synthesized by the same method as the above procedures except that the product was isolated by precipitation in methanol. Yield was 52%, mp 140°C. ^{1}H NMR ($CDCl_3$): δ 7.65 (m, 4H), 7.45 (m, 2H), 6.93 (m, 2H), 3.9 (t, 3H), 1.7 (m, 2H), 1.3-1.6 (m, 4H), 0.7 (m, 2H), ^{29}Si NMR ($CDCl_3$): -66.7.

Synthesis of Octa(5-(4-benzonitrileazophenyloxy)pentyl)-octasilsesquioxane (Cubic-AZO) (**7**). (**7**) was prepared by the same procedure of making (**6**). Yield as 50%, mp 173°C. ^{1}H NMR ($CDCl_3$): δ 7.92 (m, 4H), 7.76 (m, 2H), 6.97 (m, 2H), 3.96(t, 3H), 1.74 (m, 2H), 1.3-1.6 (m, 4H), 0.72 (m, 2H), ^{29}Si NMR ($CDCl_3$): -66.7.

Results and Discussion

The synthetic route of LC silsesquioxanes (LC-Cubes) is shown in Scheme 1. LC-Cubes were synthesized by the hydrosilylation reaction of octa(hydridosilsesquioxane) (**1**) and terminal alkenes with mesogenic groups (**2, 3, 4**) using hexachloroplatinic acid as a catalyst. Figure 1 shows ^{1}H NMR spectra of Cubic-OCH_3 and 5-(4-methoxybiphenyloxy)-1-pentene. The peak of C=C double bond in the terminal alkene disappeared completely at 5.9 and 5.1 ppm, whereas a new broad peak of methylene groups adjacent to Si atom of cube core and the peaks of methoxy biphenyl showed up at 0.7, 7.4, and 6.9 ppm, respectively.

Table 1. Phase transition temperatures of mesogenic compounds and LC-Cubes

Samples	Phase transition temperature/℃	
	Thermal transition[a]	Tm[b]
Vinyl-OCH_3	i 109 n 102 k	123
Vinyl-CN	i 65 n 48 k	87
Vinyl-AZO	i 113 n 101 k	124
Cube-OCH_3	k 166 n 215 i	215
Cube-CN	k 70 n 139 i	139
Cube-AZO	k 140 n 173 i	173

[a]Observed by optical polarizing microscope. [b]Melting temperature was detected by DSC thermogram.

Relative integration ratio between the characteristic peaks matched well with the structure of Cubic-OCH_3 as we expected. Also, ^{29}Si NMR spectra (-66.6) and UV spectrum (absorption at 296 nm) indicated that mesogenic moieties were precisely introduced to the eight hydro groups of cube through the hydrosilylation reaction. It was found that the solubility of the obtained LC-Cubes is dependent on the nature of mesogenic moieties on the cube core. Cubic-CN is soluble in $CHCl_3$, benzene, THF and toluene, while Cubic-AZO and Cubic-OCH_3 have a solubility in $CHCl_3$, THF and only hot $CHCl_3$, respectively.

The LC behavior of the prepared mesogenic compounds and LC-Cubes was investigated by means of DSC and optical polarizing microscopy. The phase transition temperatures are summarized in Table 1. Mesogenic compounds and LC-Cubes showed the monotropic behaviors in LC phase appeared as a nematic phase on the cooling cycle and heating cycle, respectively. This result is nearly consistent with that observed by DSC. The LC temperature ranges of LC-Cubes became wider than those of corresponding mesogenic compounds. This may be ascribed to the increase of local concentration of LC moieties as the mesogenic compounds were introduced to the eight hydro groups of silsesquioxane.

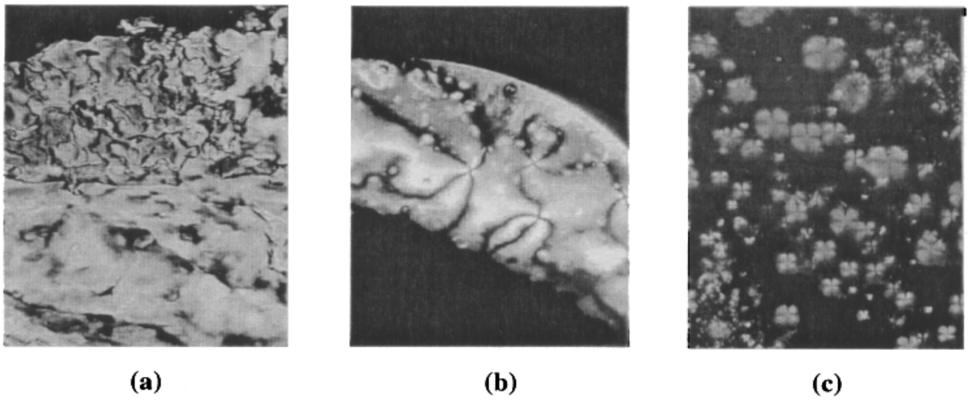

(a) (b) (c)

Figure 2. Optical polarizing micrographs of vinyl mesogenic compounds during a cooling cycle: (a) (× 500), Vinyl-OCH_3 at 109℃ ; (b) (× 500), Vinyl-CN at 64℃ ; (c) (× 200), Vinyl-AZO at 110℃ .

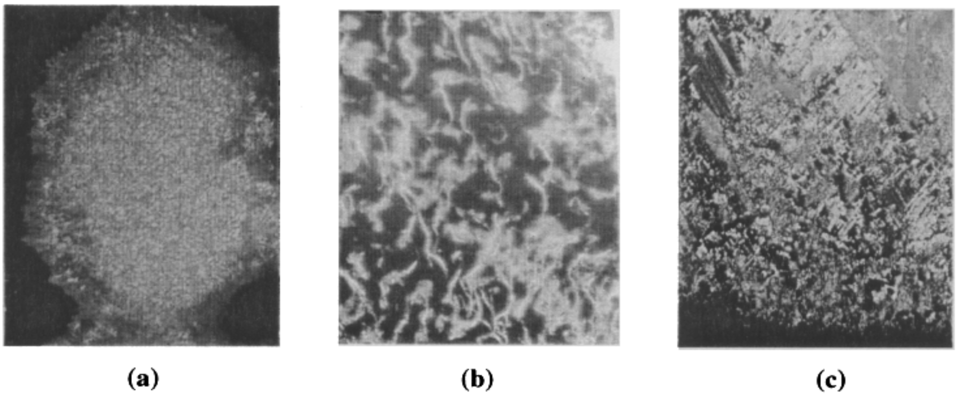

(a) (b) (c)

Figure 3. Optical polarizing micrographs of LC-Cubes during a heating cycle: (a) (× 500), Cube-OCH_3 at 200℃ ; (b) (× 100), Cube-CN at 111℃ ; (c) (× 200), Cube-AZO at 161℃

That is, the increase of local concentration caused by compact, fixed directionality of silsesquioxane makes it easier to reorient mesogenic moieties. It is also observed that the melting temperatures of LC-Cubes were increased as compared with those of mesogenic compounds. The obtained LC structures of mesogenic compounds and LC-Cubes had a typical nematic phase like thread-like and schlieren texture with disclinations as shown in Figures 2 and 3.

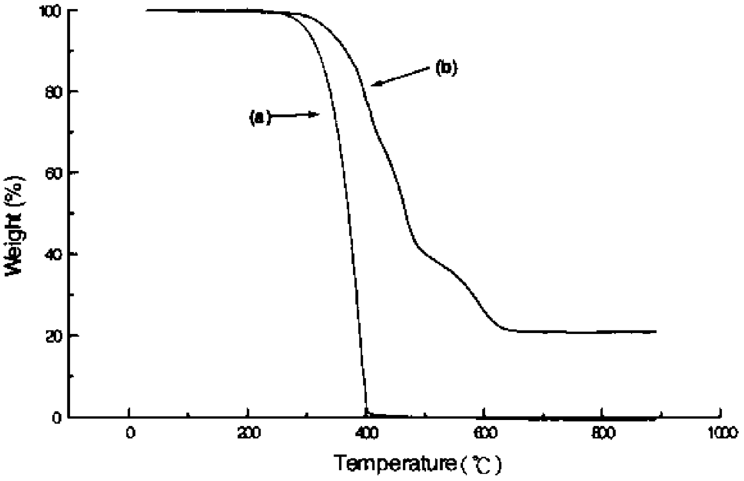


Figure 4. TGA thermograms of Vinyl-OCH_3 (a) and Cubic-OCH_3 (b) with a heating rate of 10℃ min^{-1}.

Figure 4 is representative TGA thermograms of mesogenic compounds and LC-Cubes. The temperatures of 10% decomposition of Cube-OCH_3 is much higher than that of Vinyl-OCH_3. It means that the rigid, hard inorganic core of silsesquioxane improved thermal stability of Cube-OCH_3. Cubic-CN and Cubic-AZO exhibited the same phenomenon, which is shown in Table 2.

Table 2. Thermal properties of mesogenic compounds and LC-Cubes[a]

Samples	Decomposition temperature (T_d)/℃			Residue at 900℃,%
	10%-loss	20%-loss	30%-loss	
Vinyl-CN	231	247	258	0
Cube-CN	389	416	434	22
Vinyl-AZO	240	255	264	0
Cube-AZO	367	427	537	23

[a] Determined from TGA curves by charring the samples up to 900℃ in air.

Conclusions

LC-Cubes having three kinds of mesogenic units were synthesized and examined by DSC, TGA, and optical polarizing microscopy. The liquid crystallinities of LC-Cubes show the nematic phase like thread-like and schlieren texture. LC-Cubes display very wide temperature range of nematic phase compared to mesogenic compounds due to the increase of local concentration derived from a spatially well-defined core of silsesquioxane. In addition, the obtained LC-cubes showed a good thermal stability.

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