Supramolecular architecture-directed synthesis of a reactive and purely inorganic ladder polyhydrosilsesquioxane†

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A reactive and purely inorganic high Mw perfect ladder polyhydrosilsesquioxane (H-LPSQ) was first prepared under the direction of two imperative supramolecular architectures: ladder superstructure (H-LS) and donor–acceptor complex (DAC).

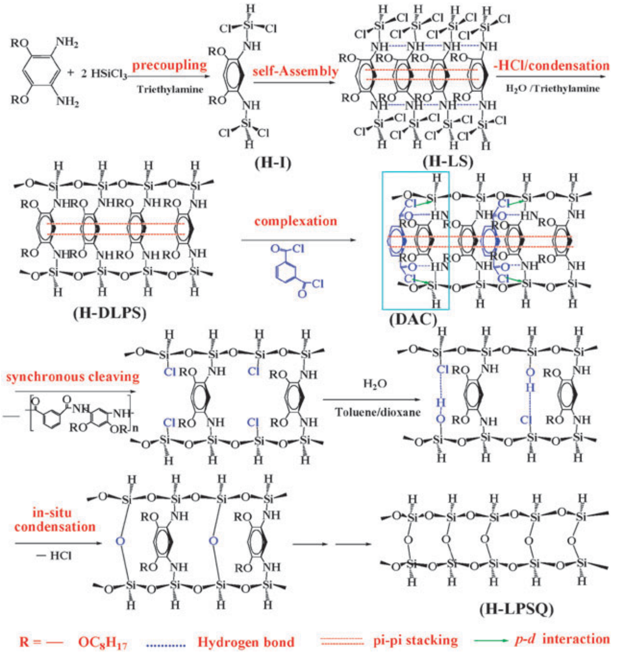
Ladder polymers are of special importance as advanced materials due to their superior thermo-resistance and mechanical strength.[1] Recently, many studies have focused on high molecular weight (Mw) ladder organo-grafted polysilsesquioxanes (**R-LPSQ**s) for their unique hybrid double chain structures.[2–4] However, it is very difficult to obtain well ordered high Mw **R-LPSQ**s from a trifunctional monomer ($RSiCl_3$) due to the formation of undesirable branched or cross-linked products. In 1960, Brown *et al.*[5] first reported a high Mw ladder polyphenylsilsesquioxane (**Ph-LPSQ**). Nevertheless, its structure was refuted later by Frey *et al.*[6] Brook[4] pointed out that the high Mw ladder polysilsesquioxanes reported are generally random networks, but the ladder structure may be obtained under certain controlled conditions.

Ladder polyhydrosilsesquioxane (**H-LPSQ**) is not only an important material with good dielectric behavior,[7] but also an indispensable precursor for a variety of functional ladder polymers with photoelectric and liquid-crystalline properties. Therefore, synthesis of perfect, high Mw **H-LPSQ** is of particular significance in both theoretical and practical respects.

Supramolecular template polymerization is an effective method to synthesize all kinds of polymers with designed structures.[8,9] To synthesize perfect **R-LPSQ**s, Zhang *et al.* proposed a supramolecular template strategy named "supramolecular architecture-directed stepwise coupling and polymerization",[10] by which a series of well-defined organo-bridged ladder polysiloxanes (**R-OLPS**s) and **R-LPSQ**s[11,12] have been prepared. Especially, a perfect ladder polysilsesquioxane with a special triphenylene side group which has strong π-stacking and enhanced stereo-selective effects was synthesized for the first time.[13] However, this approach is invalid for the synthesis of **H-LPSQ**. Furthermore, in comparison with the synthesis of **R-LPSQ**s, it is more difficult to synthesize **H-LPSQ** for the following reasons: (1) Si–H is highly reactive and unstable; (2) **H-LPSQ** is purely inorganic and has extremely low solubility in almost all kinds of solvents; (3) There is no π–π stacking interaction or utilizable stereo-effect.

Here, we report a supramolecular architecture-directed approach to the perfect **H-LPSQ** as shown in Scheme 1. It includes two steps: (A) precoupling and ladder superstructure (**H-LS**) directed synthesis of sacrificial 4,6-bis(octyloxy)benzene-1,3-diamine-bridged ladder polyhydrosiloxanes (**H-DLPS**); (B) a donor–acceptor complex (**DAC**)-based synchronous cleavage of the bridge and *in situ* condensation. 4,6-Bis(octyloxy)-benzene-1,3-diamine was intentionally chosen as the precoupling agent because the octyloxy-substitutions are necessary to increase the solubility of the series precursors. Consequently, high molecular weight **H-DLPS** and **H-LPSQ** can be obtained. The two imperative supramolecular architectures, **H-LS** and **DAC**, determine the ladder regularity of **H-LPSQ**, and the careful control of the reaction conditions plays an important role in preserving the reactive Si–H groups.

Bailey[1] has proposed that the most desirable type of reaction for the formation of a perfect ladder is the one in which both sides of the ladder are formed simultaneously.



Scheme 1 Synthetic route to **H-LPSQ**.

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In this work, $HSiCl_3$ was transferred into a ladder precursor (**H-I**) by precoupling reaction under −15 °C. Noteworthily, **H-I**s can be self-assembled into perfect ladder superstructure (**H-LS**) so as to achieve the synchronous growth of the ladder. The sacrificial perfect **H-DLPS** is then synthesized *via* stoichiometric hydrolysis-dehydrochlorination condensation reaction of **H-LS**.

In order to obtain perfect **H-LPSQ** from **H-DLPS**, "synchronous cleavage" of the bridge and *in situ* condensation is essential. Conventional acid or base catalyzed hydrolysis can't realize the "synchronous cleavage of the bridge". It has been reported that Si–N can be cleaved and transferred into Si–Cl by acid chloride through a nucleophilic addition-elimination mechanism.[14] To achieve "synchronous cleavage", isophthalyl dichloride (IPC) was selected as the cleaving agent. It is proposed that when IPC is added into **H-DLPS**, it can form a donor–acceptor complex (DAC) with the bridge by a synergy of hydrogen bonding between carbonyl and amino groups, benzene ring π-stacking and dπ–pπ interaction of the p-electrons of Cl and the d-orbital of Si. The Cl-atom of IPC then links to the Si-atom, and breaks the Si–N bonds of the bridge and further transfers them into two Si–Cl bonds. The formation of DAC ensures the synchronous breakage of the two Si–N bonds on the same bridge, so that Si–O–Si can be formed *in situ* by hydrolysis and dehydrochlorination condensation of the two new Si–Cl. In addition, IPC is added in a batch manner so that the double-chain of **H-DLPS** maintains a ladder structure and the *in situ* condensation can carry through most effectively.

To verify the reaction process, the formation of **H-LS** has to be confirmed first. The concentration dependent UV spectra of **H-I** show that when the concentration of **H-I** increases, a new absorbance peak appears at 390 nm and the absorbance peak at 307 nm shifts to 310 nm. It indicates that **H-I** molecules can be self-assembled to give π–π and hydrogen-bonded adducts, **H-LS** (see Fig. S1 in the ESI†). Table 1 shows the characterization data of **H-LS**. As a supramolecular assembly by π-stacking aided hydrogen-bonding, XRD analysis presents two characteristic diffraction peaks corresponding to ladder width and thickness respectively[5] (see Fig. S2 in the ESI†). The apparent degree of polymerization (DP) was determined at 40 °C by vapor pressure osmometry (VPO) in toluene. It indicates that **H-LS** possesses *ca.* 14 repeat units of **H-I**. The ^{29}Si NMR spectrum of **H-I** gives only one sharp peak at $\delta = -22.2$ ppm with baseline-width (Δ) as small as *ca.* 1 ppm (Fig. 1A-a) suggesting that **H-LS** consists of a very regular ladder structure rather than randomly interlaced or branched structures.

Table 1 Characterization data of **H-LS**; **H-DLPS**; **H-LPSQ** and **Ch-LPSQ**

Sample	DP[a] or Mw	W/T [d] by XRD (nm)	δ/Δ by ^{29}Si NMR[e]
H-LS	14[b]	0.82/0.40	−22.2/1
H-DLPS	135 230[c]	0.94/0.40	−19.7/1
H-LPSQ	84 370[c]	0.45/0.40	—
Ch-LPSQ	109 824[c]	0.72/0.41	−22.6/1

[a] Degree of polymerization. [b] Determined by vapor pressure osmometry. [c] Determined by laser light scattering. [d] W = the ladder width and T = the ladder thickness. [e] δ/Δ = chemical shift and baseline-width.

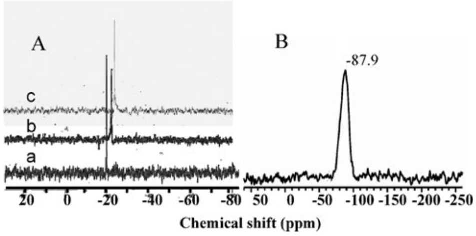

Fig. 1 A. ^{29}Si NMR spectra of (a) Ladder superstructure (**H-LS**); (b) **H-DLPS**; (c) **Ch-LPSQ**; B. Solid state CP/MAS ^{29}Si NMR of **H-LPSQ**.

Similarly, the sacrificial **H-DLPS** was also confirmed to be the perfect ladder polymer. (Table 1, Fig. 1A-b and Fig. S2 in the ESI†). Moreover, a high glass transition temperature T_g (67.6 °C) is attributed to great restriction of the internal rotation of the double main chain for a highly rigid ladder structure (see Fig. S3 in the ESI†).

The formation of a stable donor–acceptor complex (**DAC**) of IPC with **H-DLPS** also needs to be confirmed, which is critical for the "synchronous cleavage". As shown in Fig. 2, when IPC and **H-DLPS** were mixed with equal molar amounts of IPC/the bridge, a low-energy absorbance at 386 nm emerged, which is different from the characteristic peaks of IPC and **H-DLPS**. This suggests the formation of DAC adducts.

To further confirm that IPC could realize "synchronous cleavage of the bridge", a model compound containing a Si–H group, *N*,*N*′-bis(dimethylsilyl)-4,6-bis(octyloxy)benzene-1,3-diamine, was synthesized. Then IPC was added stepwise to break the bridge of the model compound. ^{29}Si NMR measurement was conducted to monitor the kinetic process during the reaction (Fig. 3). When the model compound was mixed with IPC in a molar ratio of 3 : 2, there were two peaks at $\delta = -15.8$ and $\delta = 12.5$ ppm respectively (Fig. 3b), indicating existence of two kinds of silicon skeletons. The peak at $\delta = -15.8$ ppm is assigned to the organo-bridged model compound, and the peak at $\delta = 12.5$ ppm is assigned to dimethylchlorosilane derived from the break of bridge on the model compound by IPC. It suggests that the two Si–N bonds at the same bridge should be broken simultaneously, or a third peak should appear. While the model compound and IPC were mixed in a 1 : 1 molar ratio, only one peak of $\delta = 12.5$ ppm was observed (Fig. 3c), indicating that it reacted with IPC completely and only dimethylchlorosilane could be detected.

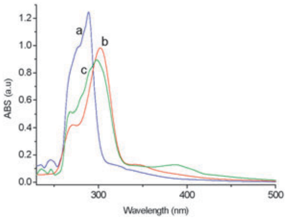

Fig. 2 UV spectra of (a) IPC; (b) **H-DLPS**; (c) **H-DLPS** and IPC (IPC and the bridge of **H-DLPS** are in equal molar amounts).

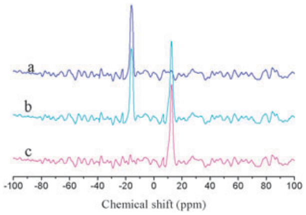

Fig. 3 ^{29}Si NMR spectra of (a) model monomer; (b) model compound and IPC (3 : 2) and (c) model compound and IPC (1 : 1).

In addition, it can be deduced that the Si–H groups are inert to IPC under the reaction conditions.

The synchronous cleavage of the bridge results in two Si–Cl groups forming simultaneously. If one of them is hydrolyzed into Si–OH, it would immediately and conveniently react with the other Si–Cl in the presence of triethylamine, which is both catalyst and HCl absorbent, to generate a $\equiv$Si–O–Si$\equiv$ bond. Finally, all the bridges of **H-DLPS** are ruptured and converted to Si–O–Si bonds. The Mw of the **H-LPSQ** is 84 370 determined by laser light scattering. In the meantime, an aromatic polyamide was produced and detected as by-product.[15]

Complete conversion of **H-DLPS** to the perfect ladder **H-LPSQ** was also confirmed by elemental analysis, which shows that **H-LPSQ** contains no nitrogen or carbon elements but Si, O and H atoms. The distinguishable absorption of a Si–H stretching vibration at 2251 cm^{-1} in the IR spectrum of **H-LPSQ** suggests Si–H groups should be well preserved (see Fig. S6 in the ESI†). The XRD profile of **H-LPSQ** also gives two distinct peaks that corresponding to the ladder width and thickness respectively (see Fig. S4 in the ESI†). Although solution ^{29}Si NMR is efficient for confirming the ladder regularity, it can't be used for **H-LPSQ** because of its extremely low solubility (<5 wt%) in organic solvents. Hence, solid-state ^{29}Si NMR was adopted. As a result, a single peak at $\delta = -87.9$ ppm was observed in the solid-state ^{29}Si NMR spectrum (Fig. 1B). It indicates that all the Si atoms are in very similar microenvironments, namely regular ladder skeletons.

For further confirmation of the perfection of **H-LPSQ** and reactivity of its Si–H groups, a solubility-increasing cyclohexyl group was introduced into the **H-LPSQ**'s backbone by the hydrosilylation of cyclohexylene catalyzed by Cp_2PtCl_2. The resultant ladder polycyclohexylsilsesquioxane (**Ch-LPSQ**) also gives two distinct peaks in the XRD spectrum corresponding to the ladder width and thickness, respectively. (see Fig. S4 in the ESI†). Moreover, as shown in Fig. 1A-c, the ^{29}Si NMR spectrum of **Ch-LPSQ** shows exceedingly sharp peak at $\delta = -22.6$ ppm with Δ of $\sim$1 ppm, indicating that all the Si atoms exist in almost the same chemical environment and the ladder possesses perfect tacticity. In contrast to the general silsesquioxane (-$SiO_{3/2}$) with chemical shift $\delta = -70 \sim -80$ ppm in the ^{29}Si NMR spectrum, the perfect **Ch-LPSQ** gives the -$SiO_{3/2}$ characteristic $\delta = -22.6$ ppm with a remarkably down-field shift of $\sim$60 ppm. Furthermore, the δ value of perfect **Ch-LPSQ** is independent of the solvent's polarity (acetone, toluene). These results indicate that ladder **Ch-LPSQ** tends to form a helical structure in solution, which may be formed by strong intra-molecular dipole–dipole interactions of the $\equiv$Si–O–Si$\equiv$ linkages. The Si–O–Si units with 50% ionic character preferably attract each other.[16] The helical structure enhances the de-shielding effect along the parallel direction of the tightly stacked helical polymer chains, and results in the remarkable shift.[17] In addition, **Ch-LPSQ** shows a high T_g (143.8 °C) that is contributed by the highly regular rigid ladder structure (see Fig. S5 in the ESI†). Because the conversion of **H-LPSQ** to **Ch-LPSQ** doesn't involve any breaking of the ladder chains of **H-LPSQ**, the perfection of **Ch-LPSQ** represents the perfection of **H-LPSQ**. The successful preparation of **Ch-LPSQ** also verifies the high reactivity of the Si–H groups on **H-LPSQ**.

In conclusion, a reactive and perfect, purely inorganic high Mw ladder polyhydrosilsesquioxane (**H-LPSQ**) has been prepared successfully. It includes ladder superstructure (**H-LS**)-directed synthesis of sacrificial 4,6-bis(octyloxy)-benzene-1,3-diamine-bridged ladder polysiloxanes **H-DLPS** and then supramolecular complex (**DAC**)-based synchronous cleavage and *in situ* condensation. The two important supramolecular architectures (**H-LS** and **DAC**) and the ladder polymers (**H-DLPS**, **H-LPSQ** and **Ch-LPSQ**) have been well characterized. Perfect **Ch-LPSQ** was obtained from **H-LPSQ**, which further verifies the structural perfection and the possible functionality of **H-LPSQ**.

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