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# Reactive ladder-like poly(p-decyl anilino)silsesquioxane for functional material's precursor: Synthesis, characterization and functionalization

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#### ABSTRACT

A well-defined polysilsesquioxane with reactive Si–N bonds, poly(p-decyl anilino)silsesquioxane (PASQ), was successfully prepared using supramolecular template polymerization. The monomers 1,3-bis-(p-decyl anilino)-1,1,3,3-tetrachloro-disiloxanes first self-assembled into ladder superstructures (LSs) primarily through the synergistic interactions of hydrogen bonding and the van der Waals interactions, and then polymerized by adding water and triethylamine to produce a well-defined PASQ. The LSs was fully characterized using vapor pressure osmometry (VPO), UV–vis spectroscopy and X-ray diffraction (XRD). NMR and XRD measurements revealed that the PASQ was a ladder polymer. The reactivity of PASQ was confirmed by its Si–N bond reacting with trimethylsilanol to form a ladder-like trimethylsiloxysilicate (LMQ). The ladder structure of LMQ was also thoroughly characterized, which further verified the ladder structural regularity of PASQ.

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#### 1. Introduction

Considerable attention has been devoted to the preparation of organic/inorganic hybrid polymers, such as polymers based on silsesquioxanes, because of their unique and attractive properties [1– 4]. Ladder polysilsesquioxanes, which are hybrid materials with an inorganic double-chained backbone, have attracted considerable interest because of their excellent thermo-resistant and mechanical properties [5–7]. However, some common factors that affect the regularity of the ladder are still difficult to control when synthesizing ladder polysilsesquioxanes. For instance, the unavoidable use of multi-functional monomers may result in irregular cross-linking and other side reactions [8]. Supramolecular template polymerization is an effective method for synthesizing all types of polymers with designed structures [9-12]. Based on the supramolecular template polymerization technique, we proposed the 'supramolecular architecture-directed stepwise coupling/polymerization' (SCP) method for the synthesis of ladder polysilsesquioxanes [13]. Currently, a series of ladder organo-bridged polysiloxanes and ladder polysilsesquioxanes have been successfully obtained using SCP [14-16]. In addition, these ladder polysiloxanes and polysilsesquioxanes contain many types of organic ladder rungs, such as light-emitting 9,10-diphenylanthryl [17] or organic side groups such as phenyl-Br [18], -CH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>3</sub> [19], -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OC<sub>6</sub> H<sub>4</sub>NO<sub>2</sub> [20] and –CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>(CHCH<sub>2</sub>O) [21].

Much attention should be devoted to the reactive ladder polysiloxanes because they are important precursors for the functional ladder polymers that have special properties. Among the typical reactive groups mentioned above, phenyl-Br and -CH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>3</sub> groups can react through the functional groups of the C-Br and C=O bonds, respectively, which results in the formation of Si-Cbased hybrid ladder polysiloxanes with low thermo-stability, as previously reported [22-26]. Recently, we reported the synthesis of reactive ladder polyhydrosilsesquioxane, which can be converted to many types of functional ladder polysiloxanes primarily with the use of hydrosilylation reactions. However, as a precursor for functional ladder polymers, polyhydrosilsesquioxane has some limitations: its synthesis is relatively complicated, resulting in a low yield [27]; the very high reactivity of the Si-H bond makes it difficult to store; and the inorganic nature results in extremely poor solubility in organic solvents. Therefore, the pursuit of new reactive ladder polysiloxanes that can act as an effective macromolecular intermediate for introducing the polysiloxane-double-chain structure is of importance.

To the best our knowledge, ladder polysilsesquioxanes containing Si—N containing side groups have not currently been reported. Based on silazane chemistry, the Si—N bond also has varied reactivity, such as hydrolysis, varied substitution reactions, oxidation, etc.; moreover, it is easier to control the reactivity of the Si—N bond than the Si—H bond. Furthermore, the organic group bonded to the N-atom can not only supply supramolecular interactions to result in an easier synthesis but also provide better product solubility than the ladder polysilsesquioxanes containing Si—H bonds.

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Therefore, ladder polysilsesquioxanes containing Si—N bonds may be a better precursor for providing a versatile method for producing ladder polysiloxanes containing various functional groups. In this paper, we report the synthesis of ladder-like poly(p-decyl anilino)silsesquioxane (PASQ) using the SCP method (Scheme 1A). The regularity and reactivity of PASQ were also confirmed.

#### 2. Experimental

#### 2.1. Materials

Hexachlorodisiloxane was purchased from Gelest (Morrisville, United States). Trimethylchlorosilane and trimethylsilanol were purchased from Aldrich. 4-decyl aniline was purchased from Alfa Aesar. Toluene, 1,4-dioxane and triethylamine (TEA) were distilled over a sodium benzophenone complex. Acetone was distilled over potassium carbonate.

#### 2.2. Characterization

Infrared Spectrometry (IR) spectra were recorded using a Bruker Tensor 27 spectrophotometer between 400 and 4000  $\rm cm^{-1}$  (KBr) at

25 °C. Solution <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were performed on a Bruker AV-400 FT-NMR spectrometer at room temperature. Solution and solid-state <sup>29</sup>Si NMR measurements were performed on Bruker AV-300 and Bruker AV III-400 NMR instruments, respectively. XPS data were collected using an ESCA-Lab220i-XL electron spectrometer from VG Scientific with 300 W Al K $\alpha$  radiation. The base pressure was approximately  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Elemental analysis was performed on a Heraeus CHN-RAPID/DATEL System (Germany). X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2400 diffractometer with Cu Ka radiation at a scanning rate of 5° min<sup>-1</sup>. VPO analyses were conducted in dry toluene at 40 °C on a Knauner VPO instrument (Germany) at 20% relative humidity. UV-vis spectra were obtained on a Shimadzu UVvis spectrometer model UV-1601PC. Gel permeation chromatography (GPC) measurements were performed using a Waters chromatograph connected to a Water 410 differential refractometer with THF as an eluent. Thermogravimetric analyses (TGA) were performed on a SDT Q600; the sample was heated from 30 °C to 1000 °C at a rate of 10 °C min<sup>-1</sup> in a dynamic nitrogen atmosphere with a flow rate of 100 mL min<sup>-1</sup>.



Scheme 1. Synthetic route for PASQ and LMQ.

#### 2.3. Synthesis of ladder poly(p-decyl anilino)silsesquioxanes (PASQ)

A mixture of 4-decyl aniline (4.66 g, 20 mmol), triethylamine (2.02 g, 20 mmol) and anhydrous toluene (100 mL) was added dropwise into a three-necked flask containing anhydrous toluene (50 mL) and hexachlorodisiloxane (2.84 g, 10 mmol) under an argon atmosphere over 12 h at room temperature. After continuous stirring for an additional 2 h, a mixture of toluene (50 mL), 1,4-dioxane (100 mL), water (0.36 g, 20 mmol) and triethylamine (6.06 g, 60 mmol) was added drop-wise over 12 h at room temperature. The mixture was then heated to 45 °C for 6 h. To end-cap the terminal Si-OH group, Me<sub>3</sub>SiCl (0.5 mL) in toluene (20 mL) was added slowly over the course of 2 h at 45 °C. First, 1,4-dioxane and partial toluene were removed by distillation. Triethylamine hydrochloride was then removed by filtration under argon. Finally, anhydrous acetone was added to the remaining solution to precipitate a white solid (4.88 g). The yield was 86%. IR (KBr, thin film, cm<sup>-1</sup>): 3372 (--NH), 2921, 2854 (--CH<sub>3</sub>CH<sub>2</sub>--), 1617 (--Ph), 1514 (Si-N), 1200-1000 (Si-O-Si). <sup>1</sup>H NMR (400 MHz, d<sub>4</sub>-o-dichlorobenzene, δ, ppm): 6.91 (4H, Ar-H), 6.52 (4H, Ar-H), 3.53 (2H, --NH), 2.47 (4H, CH<sub>2</sub>), 1.53 (4H, CH<sub>2</sub>), 1.25-1.20 (28H, CH<sub>2</sub>), 0.86 (6H, CH<sub>3</sub>), 0.22 (3H, Si-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, d<sub>4</sub>-o-dichlorobenzene, δ, ppm): 143.9 (Ar–C), 133.2 (Ar–C), 129.4 (Ar–C), 114.9 (Ar-C), 35.1 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 1.2 (Si-CH<sub>3</sub>). Solid <sup>29</sup>Si NMR (100 HMz, δ, ppm) 13.7  $(-O-SiMe_3)$ , -99.5  $(-Si(NH)O_{3/2})$ . Anal. found for  $C_{12}H_{36}Si_4O_2$ (C<sub>32</sub>H<sub>52</sub>N<sub>2</sub>Si<sub>2</sub>O<sub>3</sub>)<sub>n</sub>: C 34.05, H 9.11, N 4.81.

#### 2.4. Synthesis of ladder-like trimethylsiloxysilicate (LMQ)

PASQ (2.84 g, 5 mmol of repeating unit), toluene (100 mL), and trimethylsilanol (1.8 g, 20 mmol) were placed into a three-necked flask equipped with a reflux condenser and a magnetic stir bar under argon. The reaction was continued for 48 h at 50 °C. Finally, methanol (100 mL) was added and the targeted product, LMQ (1.30 g), was precipitated from the solution. The yield was 93%. IR (KBr, thin film, cm<sup>-1</sup>): 2959 (–CH<sub>3</sub>), 1260, 849, 759 (Si–CH<sub>3</sub>), 1190–1000 (Si–O–Si). <sup>1</sup>H NMR (400 MHz, *d*<sub>8</sub>-THF, δ, ppm): 0.85 (Si–CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 1.56 (Si–CH<sub>3</sub>). Solid <sup>29</sup>Si NMR (100 MHz, δ, ppm): 13.3 (–O–SiMe<sub>3</sub>), –106.6 (–SiO<sub>4/2</sub>). Anal. found for C<sub>12</sub>H<sub>36</sub>Si<sub>4</sub>O<sub>2</sub> (C<sub>6</sub>H<sub>18</sub>Si<sub>4</sub>O<sub>5</sub>)<sub>n</sub>: C 24.85, H 6.01.

#### 3. Results and discussion

#### 3.1. Formation and characterization of the ladder suprastructures (LSs)

As shown in Scheme 1A, 1,3-bis-(p-decyl anilino)-1,1,3,3-tetrachloro-disiloxane (BATD) was synthesized through the dehydrochlorination of hexachlorodisiloxane and 4-decyl aniline with triethylamine (TEA) as a catalyst and acid-absorbent. Two equivalents of 4-decyl aniline were added dropwise into hexacholorodisiloxane at room temperature. The structure of BATD was confirmed using <sup>29</sup>Si NMR, which gives a resonance at  $\delta$ –52.6 ppm that indicates that there was only one type of Si-atom, namely (–NH)Si(O)Cl<sub>2</sub> (Fig. 1), without Si(O)Cl<sub>3</sub>, (–NH)<sub>2</sub>Si(O)Cl and (–NH)<sub>3</sub>Si(O). Because the Si–Cl and Si–NH bonds are both moisture sensitive, both TEA and toluene were dried over a sodium benzophenone complex before use. The system must remain anhydrous and anaerobic throughout the reaction process. The resulting BATD was not separated, but was preserved in the solution to continue the following reaction.

In solution, BATD was observed to be able to spontaneously assemble into the ladder superstructure (LS) primarily through the synergistic interactions of  $N-H\cdots N$  hydrogen bonding and the van der Waals interaction among the octyl groups (Scheme



Fig. 1. Solution <sup>29</sup>Si NMR spectrum of BATD and solid-state <sup>29</sup>Si NMR spectra of PASQ and LMQ.

1A). The apparent degree of polymerization (DP) of LS formed in 0.1 mol/L toluene/dioxane (1/1 mL/mL) was determined by vapor pressure osmometry (VPO) and was approximately 7. UV detection was used to monitor the LS formation process (Fig. 2). In a toluene/ dioxane (1/1 mL/mL) mixture, as the monomer concentration increases, the absorbance peak assigned to phenyl groups displays a remarkable red shift from 284 nm to 298 nm, which can be attributed to the energy reduction induced by the intermolecular N-H...N hydrogen bonding. X-ray diffraction (XRD) is an effective method to characterize the ordered structures, and it has been successfully applied to characterize the ladder structure in the literature [13]. To maintain the well-organized molecular arrangement in the solution, we used a freeze-drying method for preparing the LS samples for XRD characterization. As shown in Fig. 3, the XRD patterns of the LS sample from the toluene/dioxane solution (0.1 mol/L) exhibit two characteristic peaks at approximately 3.2° (2.76 nm) and  $19.9^{\circ}(0.44 \text{ nm}) 2\theta$ . Based on the literature [13], these peaks represent the ladder width and the ladder thickness. When the temperature was increased to 80 °C. the intensity of the two peaks decreased remarkably. The higher temperature apparently destroyed the weak molecular interactions, resulting in the collapse



Fig. 2. UV spectra of LSs.



Fig. 3. XRD patterns of LMQ, PASQ, LS, and LS at 80 °C; schematic diagrams of LMQ and PASQ with three repeating units.

of the LS. This phenomenon confirmed that the LS should indeed be a supramolecular aggregate. Combining these results, it can be deduced that BATD actually self-assembled into regular LSs rather than the randomly interlaced or branched structures.

### 3.2. Synthesis and characterization of ladder poly(p-decyl anilino)silsesquioxanes (PASQ)

The obtained highly regular LSs are critical for producing the well-defined ladder PASQ. The LSs performed as a reaction template for directing the hydrolysis and condensation polymerization of BATD into PASO. Here, although BATD has four functional groups, it actually behaves like a di-functional monomer due to the confinement of the supramolecular ladder structure. As described above, LSs are based on dynamic, non-covalent interactions. Therefore, to ensure that the LSs remained undestroyed and directed the entire PASQ polymerization process, it is necessary to control the rigorous reaction conditions. For example, the reaction temperature was maintained below 50 °C, the optimal solvent system was a toluene/dioxane mixture with low polarity and low electron-donating ability [28], a low monomer concentration  $(\sim 0.1 \text{ mol/L})$  was used, etc. In addition, the half-quantity hydrolysis of the Si-Cl bonds in BATD and the following dehydrochlorination condensation was used rather than the total-amount hydrolysis and dehydration condensation to reduce the use of the polar mixture solvent [15]. Because the Si-Cl bond is quite reactive and the dehydration condensation occurs as soon as Si-OH bonds form, controlled amounts of water were added dropwise to avoid some side reactions, such as gelation. TEA was used as a catalyst and HCl-adsorbent to avoid the undesired cleavage of the Si-N bonds. At the end of the polymerization, trimethylchlorosilane was used to end-cap the Si-OH bonds to avoid defects of the end chain.

After polymerization, the obtained PASQ was purified by precipitation in anhydrous acetone, and then dried in a vacuum oven at room temperature. PASQ was readily soluble in common organic solvents such as toluene, chloroform, and THF. Furthermore, thin films of PASQ were found to be easily fabricated by casting and spin-coating from solution. The VPO measurement provides a  $DP \sim 21$  for PASQ, which is larger than  $DP \sim 7$  of the dynamic supramolecular polymer LSs. From Scheme 1A, the LSs with the

lower *DP* may first transform into oligomers with Si—OH and Si—Cl end groups, which further grow into the higher molecular weight PASQs by dehydrochlorination. Obviously, the *DP* data should be affected by the monomer concentration, the reaction time and other reaction conditions. In addition, the number-average molecular weight ( $M_n$ ) of PASQ is determined to be 13.2 kDa with PDI = 1.46 by GPC in THF with polystyrene as standards, implying that the *DP* is ~23 (Fig. 4). The nitrogen content determined from elemental analysis is 4.81 wt.%, from which the *DP* could be calculated to be ~20. The *DP* values calculated from the three measurements for PASQ and in good agreement with each other.

The structure of PASQ was characterized using IR and NMR. The IR characterization supported the assumption that the Si—N bonds are intact because of the immediate absorption of released HCl by TEA. As shown in Fig. 5, there are absorption bonds for –NH (~3372), CH<sub>3</sub>–CH<sub>2</sub>– (2921, 2854), –Si–N (~1514), –Ph (~1617) and Si–O–Si (1200–1000 cm<sup>-1</sup>); however, there are no absorption bonds for Si–OH and –NH<sub>2</sub>, which indicates that the breaking of Si–N bond is prevented. In Fig. 6A, the <sup>1</sup>H NMR spectrum of PASQ shows the resonances of hydrogen corresponding to Si–CH<sub>3</sub> ( $\delta$  0.22), –C<sub>10</sub>H<sub>21</sub> ( $\delta$  0.86, 1.20, 1.25, 1.53, 2.46), –NH– ( $\delta$  3.53) and



Fig. 4. GPC curves of PASQ and LMQ.

Ar—H ( $\delta$  6.53, 6.92 ppm). In addition, from the integral ratio of –CH<sub>3</sub> and Si–CH<sub>3</sub>, *DP* could also be calculated to be 28. In Fig. 6B, the <sup>13</sup>C NMR spectrum of PASQ exhibits the resonances of carbon corresponding to Si–CH<sub>3</sub> ( $\delta$  3.9), –C<sub>10</sub>H<sub>21</sub> ( $\delta$  14.0–35.8) and Ar–C ( $\delta$  115, 129.1, 129.4, 143 ppm). For <sup>29</sup>Si NMR, because the resonances of (–NH)SiO<sub>3/2</sub> may overlap with the glass peak, solid <sup>29</sup>Si NMR was used to characterize PASQ. As shown in Fig. 1, there are two peaks with  $\delta$  13.7 and –99.5 ppm, which could be attributed to end groups of –O–SiMe<sub>3</sub> and the repeating units of –Si(NH)O<sub>3/2</sub>, respectively.

After the polymerization has completed, the ladder structure is chemically fixed. The ladder structure of PASQ was also characterized using XRD (Fig. 3). PASQ displays two distinct peaks at approximately  $2.76^{\circ}$  (3.17 nm) and  $19.9^{\circ}$  (0.44 nm)  $2\theta$ . According to a previous report [13], the former peak represents the intramolecular chain-to-chain distance (i.e., the width of the ladder) in the polymer, and the latter is the thickness of the macromolecular chain. These data are very close to the predicted values (3.00 nm and 0.43 nm) based on molecular simulation calculations (using Materials Studio). In addition, note that there was also a small difference between the ladder width of the LS (2.76 nm) with the predicted values of the PASQs. Considering the flexibility of  $-C_{10}H_{21}$ and the sensitivity of LS to the environment, this small difference was easily understood. Therefore, the consistent ladder width of the LS and the LPASQ implied that the former was the precursor of the latter, which also confirmed the supramolecular template polymerization mechanism.

## 3.3. Synthesis and characterization of ladder-like trimethylsiloxysilicate (LMQ)

MQ silicone resin consists of mono-functional units  $(R_3SiO_{1/2})$ and tetra-functional units  $(SiO_{4/2})$ . Because of its excellent properties, such as high hardness, antifriction and radiation resistance, it has been widely used in adhesives, paints, personal care products and other fields [29–32]. However, the synthesis mechanism for MQ is still not clear, and neither its synthesis process nor structure is controllable [33,34]. It is well known that Si—N and Si—OH bonds could react to form Si—O—Si bonds. To further confirm the ladder structure of PASQ and to determine the reactivity of its Si—N groups, Me<sub>3</sub>SiOH was used and reacted with PASQ to form ladderlike trimethylsiloxysilicate (LMQ), as shown in Scheme 1B.

LMQ is easily prepared from PASQ and trimethylsilanol under 50 °C for 48 h. The conversion of PASQ into LMQ was well monitored using IR, NMR and X-ray photoelectron spectroscopy (XPS).



Fig. 5. IR spectra of PASQ and LMQ.



Fig. 6. (A) <sup>1</sup>H NMR and (B) <sup>13</sup>C NMR spectra of PASQ and LMQ.

The IR spectrum of LMO exhibits absorption bands for Si-CH<sub>3</sub>  $(\sim 2959, 1260, 849, 759)$  and Si-O-Si  $(1190-1000 \text{ cm}^{-1})$  groups (Fig. 5). Compared to the IR spectrum of PASO, the absorption bands for NH ( $\sim$ 3372), -Si-N ( $\sim$ 1514) and -Ph ( $\sim$ 1617 cm<sup>-1</sup>) are absent, indicating the complete cleavage of the Si-NH- side groups. The <sup>1</sup>H NMR spectrum of LMQ only presents a peak at  $\delta$ 0.1 ppm assigned to Si-CH<sub>3</sub>, whereas the <sup>13</sup>C NMR spectrum of LMQ also only presents a peak at  $\delta$  1.56 ppm assigned to Si–CH<sub>3</sub>, further indicating the disappearance of the Si-NH- side groups (Fig. 6). The solid-state <sup>29</sup>Si NMR spectrum of LMQ, shown in Fig. 1, exhibits two resonances at approximately  $\delta$  13.3 and -106.6 ppm, which are ascribed to -O-SiMe<sub>3</sub> and -SiO<sub>4/2</sub>, respectively. The disappearance of the peak at  $\delta$  –99.5 ppm was ascribed to -Si(NH)O<sub>3/2</sub>, and the remarkable increase of the resonance integral ratio of the end groups to the repeating units distinctly indicates the conversion from the Si-N-based side groups to the Si-O-Si-based side groups. In the XPS spectrum of LMQ, the disappearance of the peak assigned to the N1s electrons also implies the complete removal of the *p*-decyl anilino groups (Fig. 7).

The *DP* of LMQ determined by VPO is approximately 22, which is very close to the *DP* ~ 20 of PASQ. The GPC curve of LMQ exhibits a peak with  $M_n \sim 6680$ , and thus,  $DP \sim 23$  (Fig. 4). Meanwhile, the elemental analysis presents a carbon content of 24.85 wt.%, from which *DP* can be calculated to be ~23. Obviously, the *DP*s obtained using three methods are highly consistent and close to the *DP* of PASQ. The little variation of the *DP*s from PASQ to LMQ suggests that the reaction is just a conversion of the side groups without a change of the double-chain backbone.

The ladder structure of the final LMQ was also verified using XRD characterization (Fig. 3). The XRD pattern of LMQ shows two distinct peaks at approximately  $7.9^{\circ}$  and  $19.5^{\circ} 2\theta$ . The correspond-



Fig. 7. XPS spectra of PASQ and LMQ.



Fig. 8. TGA curve of LMQ.

ing spacing, 1.11 nm and 0.44 nm, represents the ladder width and ladder thickness. This result is consistent with the simulated dimensions (1.05 nm and 0.45 nm) using Materials Studio. We also investigated the thermal stability of LMQ using thermo-gravimetric analysis (TGA). As shown in Fig. 8, the decomposition temperature is approximately 510 °C and the ultimate weight loss is 33.8%, which is in agreement with the content of the organic groups in LMQ. The high thermal stability of LMQ also suggests its ordered ladder structure.

By combining all of the above characterization results, it can be concluded that the regular ladder-like LMQ was successfully prepared by the functionalization of PASO. Because the conversion does not involve any breaking of the main chain of PASO, the well-defined ladder structure of LMQ could reflect the ordered ladder structure of PASQ. The successful preparation of LMQ derived from PASQ may not only open a new way to synthesize MQ silicone resins but also suggests that PASQ is a promising precursor for preparing other hybrid materials with ladder polysiloxane structures.

#### 4. Conclusions

A soluble, reactive PASO was successfully prepared using a simple one-step polymerization. By fully taking advantage of the

intermolecular weak interactions, regular ladder superstructures were formed first, and then directed the synthesis of the well-defined PASQ. The ladder structures of the LSs and PASQ were thoroughly characterized. PASQ was converted to LMQ in high yield, which further demonstrated its ladder structure and reactivity. Because the Si–N bond can react with all types of functional groups, it is noteworthy that PASQ can be used as an effective macromonomer for preparing materials that have well-defined inorganic-organic hybrid structures.

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