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# Supramolecular Template-Directed Synthesis of Soluble Quadruple-Chain Ladder Polyphenylsiloxane (Ph-QCLP) with High Molecular Weight

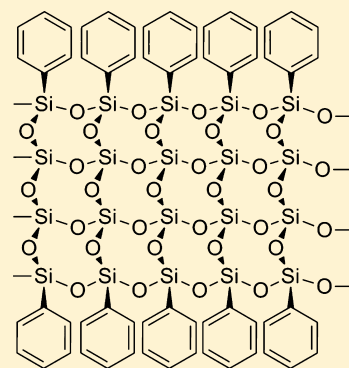
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**ABSTRACT:** Quadruple-chain ladder polyphenylsiloxane (Ph-QCLP) was synthesized by a supramolecular template-directed stepwise coupling and polymerization method including three steps: (1) Multifunctional ladder monomer **M**<sub>2</sub> with four Si–Cl, four Si–OMe, and four Si–N groups was designed and synthesized by precoupling reaction. In solution **M**<sub>2</sub>s spontaneously self-assembled to be ladder superstructure (LS) by synergy of the hydrogen bonding and the  $\pi$ – $\pi$  stacking interactions. Directed by LS template in a neutral condition that guaranteed the Si–OMe and Si–N groups were left undestroyed, **M**<sub>2</sub>s underwent controlled hydrolysis of Si–Cl groups and dehydrochlorination polymerization to be 1,3-di(3-aminophenylamino)-tetramethoxyl-disiloxane-bridged ladder polyphenylsiloxanes (DCLP). (2) A precursor, bis-*m*-phenylenediamine-bridged quadruple-chain ladder polyphenylsiloxanes (QCLP), was synthesized via the controlled hydrolysis of Si–OMe groups of DCLP followed by confined dehydration polymerization in an alkaline condition which guaranteed the Si–N groups were still undestroyed. (3) The target Ph-QCLP was obtained through synchronous bridge-cleavage and in situ condensation of QCLP. The whole reaction process was well monitored by a concerted combination of FTIR, <sup>1</sup>H NMR, X-ray diffraction (XRD), and <sup>29</sup>Si NMR measurements. In particular, <sup>29</sup>Si NMR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) results confirmed that Ph-QCLP possessed well-defined quadruple-chain ladder structure and extremely high thermo-stability.

**KEYWORDS:** quadruple-chain ladder polymer, polysiloxanes, self-assembly, supramolecular structures



## INTRODUCTION

Due to the unique hybrid structure of inorganic double-chain siloxane backbone and organic ladder-rungs or side groups, ladder polysiloxanes possess excellent thermal stability and good mechanical performance and consequently have attracted considerable attention<sup>1</sup> since 1960.<sup>2,3</sup> Just as Brook cited, the high molecular weight (MW) polysilsesquioxane materials are generally random networks.<sup>4</sup> Theoretically, the most desirable pattern of reaction for the formation of a perfect ladder is one in which both sides of the ladder form simultaneously.<sup>5</sup> Accordingly, we proposed a supramolecular template strategy by which a series of well-defined organo-bridged ladder polysiloxanes (R-OLPSs)<sup>6</sup> and ladder polysilsesquioxanes (R-LPSQs)<sup>7</sup> have been prepared. The first perfect ladder poly(triphenylene-terminated-alkyl) silsesquioxane was synthesized by the supramolecular approach based-on the synergy of  $\pi$ – $\pi$  stacking and H-bonding.<sup>7a</sup> Then, we developed a more universal supramolecular architecture-directed approach to the perfect ladder polyhydrosilsesquioxane (H-LPSQ).<sup>7b</sup> It includes two steps: (A) precoupling and ladder superstructure directed synthesis of a sacrificial phenylenediamine-bridged ladder polyhydrosiloxane (H-DLPS) and (B) a donor–acceptor complex (DAC)-induced synchronous cleavage of the organo-bridge and in situ condensation. Afterward, as an

extension of this approach, a well-defined triple-chain ladder polyphenylsiloxane (Ph-TCLP) was successfully synthesized in a similar manner.<sup>8</sup> In this paper, we further expand this approach to prepare a soluble quadruple-chain ladder polyphenylsiloxane (Ph-QCLP) which is of particular structural significance and broad application perspectives such as high-temperature-resistant materials. Due to the special inorganic grating-like skeleton and peripheral organic groups, Ph-QCLP can give superior physical and chemical properties to common polymers. Moreover, the preparation of quadruple-chain polymer can enrich the polymer chemistry, nanochemistry, and other related fields.

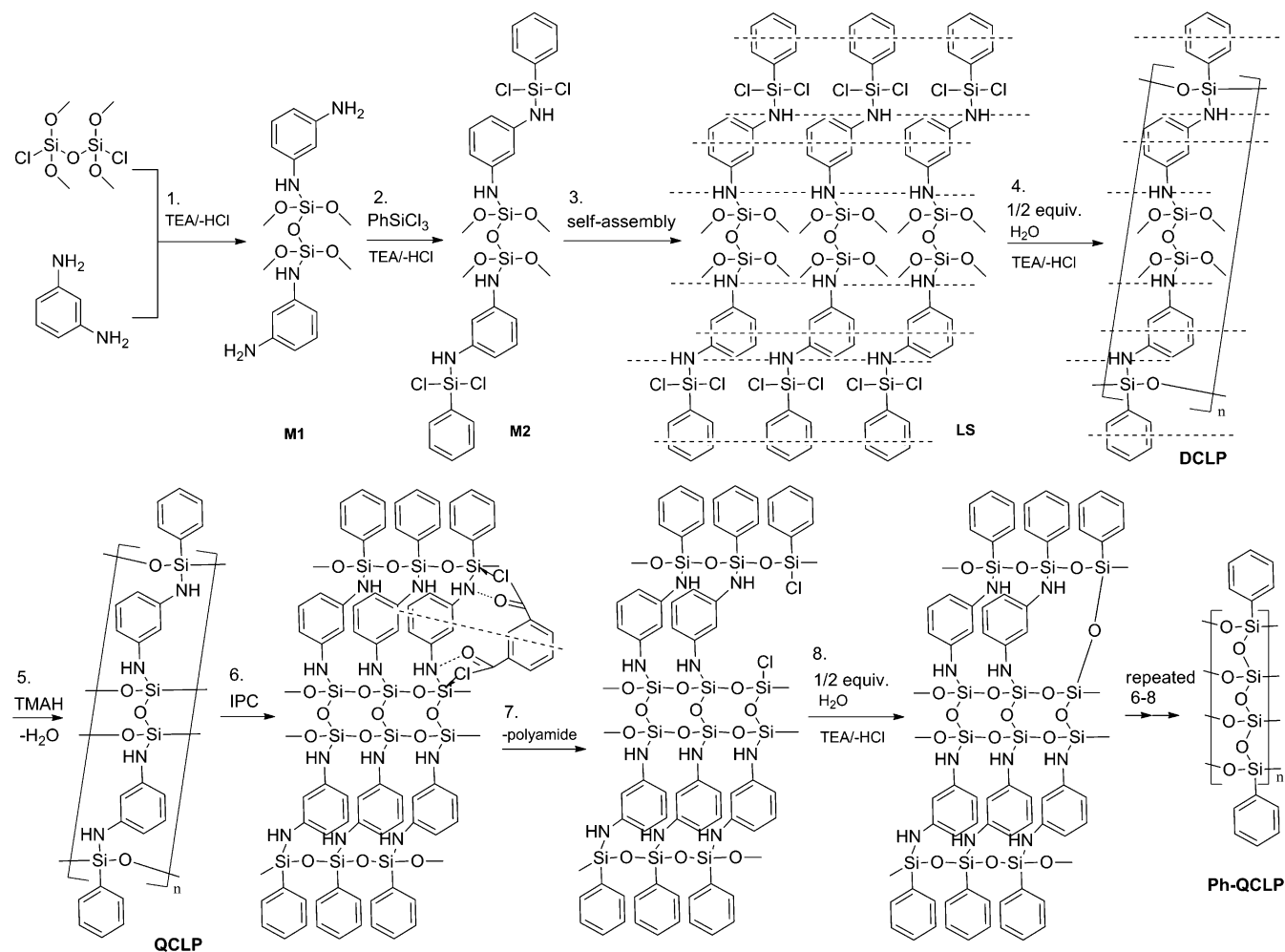
However, there is also a tremendous challenge in preparing Ph-QCLP because the higher probability of irregular cross-linking and other side reactions resulted from the unavoidable use of the multifunctional monomers. So, to obtain well-defined Ph-QCLP, it is essential to strictly carry out the step-by-step reactions of different functional groups during the whole polymerization process; otherwise, there might be mostly irregular gels and other undesirable byproduct.

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Scheme 1. Synthetic Route of Ph-QCLP



Herein we report a three-step synthesis method to prepare the well-defined **Ph-QCLP** as shown in Scheme 1: (a) Via a synergy of hydrogen bonding and  $\pi$ - $\pi$  stacking organo-bridged ladder units **M2s** self-assemble to stable regular ladder-superstructures (**LSs**), which are used as both the polymer precursors and the reaction template to form a regular organo-bridged double chain ladder polysiloxane (**DCLP**) through the controlled hydrolysis and dehydrochlorination condensation of the most active Si-Cl groups. (b) By careful hydrolysis and condensation of the moderate active Si-OMe groups in alkaline condition, **DCLP** further converts to be organo-bridged quadruple-chain ladder polyphenylsiloxanes (**QCLP**). (c) Through synchronous *m*-phenylenediamine bridge cleavage induced by isophthaloyl chloride (IPC) and in situ dehydrochlorination condensation, **QCLP** converts to the target **Ph-QCLP**.

## EXPERIMENTAL SECTION

**Materials and Measurements.** Tetramethyl orthosilicate, silicon tetrachloride, phenyltrichlorosilane, and  $\text{Me}_4\text{NOH}$  (TMAH) were purchased from Alfa Aesar and used as received. *m*-Phenylenediamine and isophthaloyl chloride were purchased from Alfa Aesar and recrystallized from alcohol and dichloromethane, respectively. Toluene, dioxane, and triethylamine were distilled over sodium benzophenone complex. Water was deionized. IR measurement was performed with a Perkin-Elmer 80 spectrometer, and the sample solution was dropped on a KBr flake and dried before testing. Solution

$^1\text{H}$  NMR and  $^{29}\text{Si}$  NMR measurements were carried out on Bruker AV-400 and Bruker AV-300 NMR instruments, respectively, using TMS as reference at room temperature. X-ray diffraction (XRD) analysis was recorded on a Rigaku D/MAX 2400 diffractometer. VPO analyses were measured in dry toluene at 40 °C on a Knauner VPO instrument (Germany) at 20% relative humidity. Differential scanning calorimetry (DSC) investigations were carried out on a Mettler Toledo Star 822 differential scanning calorimeter with heating rate 10 °C  $\text{min}^{-1}$  in nitrogen atmosphere. Thermogravimetric analyses (TGA) was made using a 7 Series thermal analysis system (Perkin-Elmer). The sample was heated from 40 to 700 °C at a rate of 10 °C  $\text{min}^{-1}$  in a dynamic nitrogen atmosphere with a flow rate of 70 mL  $\text{min}^{-1}$ .

**Synthesis of Hexamethoxydisiloxane.** A mixture of 25 mL of methanol, 1 mL of water, and 0.5 mL of 1 M HCl was added dropwise under stirring to a 100 mL flask containing 76.11 g of tetramethyl orthosilicate (0.5 mol) and 25 mL of methanol at room temperature over a period of 3 h. After further stirring for 24 h, methanol was removed by rotary evaporation, and the residue mixture was subjected to distillation to afford pure product as a colorless oil. bp, ~135 °C. Yield, 43%.  $^{29}\text{Si}$  NMR (59.6 MHz):  $\delta = -86.24$  ppm.

**Synthesis of 1,3-Dichloro-tetramethoxy-disiloxane.** A mixture of 25.8 g of hexamethoxydisiloxane (0.1 mol) and 11.4 g of silicon tetrachloride (0.07 mol) was added into an autoclave and heated to 200 °C for 2 h. After that, the mixture was fine distilled to collect a colorless, liquid product (bp, ~115 °C, 62.6 g, 56%).  $^{29}\text{Si}$  NMR (59.6 MHz):  $\delta = -76.3$  ppm.

**Synthesis of 1,3-Di(3-aminophenylamino)-tetramethoxy-disiloxane (M1).** A mixture of 2.67 g of 1,3-dichloro-tetramethoxy-disiloxane (10 mmol), 20 mL of dioxane, and 20 mL of toluene was

added dropwise into a three-necked 250 mL flask containing 2.16 g of *m*-phenylenediamine (20 mmol), 3 mL of triethylamine, 60 mL of dioxane, and 40 mL of toluene over 4 h at 0 °C. After further stirring for 4 h, 50 mL of hexane was added to precipitate 1.85 g of white solid. Yield: 45%. IR (KBr): 3000–3600 (–NH<sub>2</sub>, –NH), 3048, 1607 (–Ph), 2964, 2847 (–CH<sub>3</sub>), 1497 (–Si–N), 1196, 1075 cm<sup>–1</sup> (Si–OCH<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 6.63 (dd, 2H, ph–H), 5.77 (m, 6H, ph–H), 4.62 (s, 4H, –NH<sub>2</sub>), 4.08 (s, 2H, –NH), 3.60 (s, 12H, –OCH<sub>3</sub>) ppm. <sup>29</sup>Si NMR (59.6 MHz) δ = –74.9 ppm.

**Synthesis of 1,3-Di(3-aminophenylamino)-tetramethoxyl-disiloxane-Bridged Ladder Polyphenylsiloxanes (DCLP).** A total of 4.23 g of PhSiCl<sub>3</sub> (20 mmol) was added into a three-necked 250 mL flask containing 4.10 g of **M1** (10 mmol), 80 mL of dioxane, 60 mL of toluene, and 20 mL of triethylamine at 0 °C. After stirring for 24 h, the reaction was warmed up to room temperature (rt), and then a mixture of 0.72 g of water, 20 mL of dioxane, and 20 mL of toluene was dropwise added into the system over 6 h. Then, the mixture was heated to 40 °C for another 24 h. To end-cap the terminal Si–OH groups, Me<sub>3</sub>SiCl (0.2 mL) was added slowly over 6 h at 40 °C. The solution was condensed to about 30 mL, and then 30 mL of hexane was added to afford 3.82 g white solid. Yield, 63%. IR (KBr): 3000–3600 (–NH), 3048, 1604 (–Ph), 2964, 2857 (–CH<sub>3</sub>), 1499 (–Si–N), 1196 (Si–OCH<sub>3</sub>), 1430, 1263 (Si–Ph), 1000–1100 cm<sup>–1</sup> (Si–O–Si). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 6.3–8.0 (br, 18H, ph–H), 4.13 (s, 2H, –NH–), 3.62 (s, 12H, –OCH<sub>3</sub>) ppm. <sup>29</sup>Si NMR (59.6 MHz) δ = –23.0, –71.9 ppm.

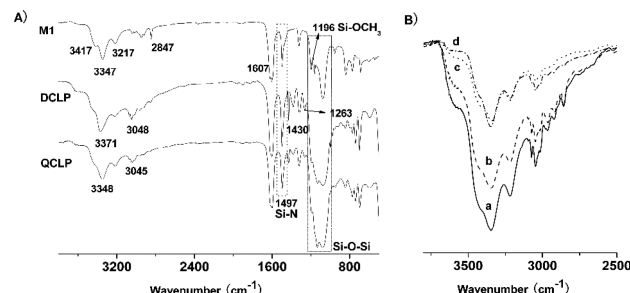
**Synthesis of Bis-*m*-phenylenediamine-Bridged Quadruple-Chain Ladder Polyphenylsiloxane (QCLP).** A mixture of three drops of Me<sub>4</sub>NOH, 30 mL of dioxane, and 0.72 g of H<sub>2</sub>O was added dropwise into a three-necked 250 mL flask containing 6.06 g of **DCLP** (10 mmol), 50 mL of dioxane, and 30 mL of methanol over 4 h at rt. After stirring for 24 h, the mixture was heated to 50 °C for another 72 h. In the reaction process water was removed by distillation under pressure. Finally, 30 mL of hexane was added to precipitate 3.82 g of white solid. Yield: 74%. IR (KBr): 3000–3600 (–NH), 3045, 1600 (–Ph), 1497 (–Si–N), 1430, 1260 (Si–Ph), 1000–1100 cm<sup>–1</sup> (Si–O–Si). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 6.5–8.0 (br, 18H, ph–H), 4.10 (s, 4H, –NH) ppm. <sup>29</sup>Si NMR (59.6 MHz): δ = –22.8, –80.0 ppm.

**Synthesis of the Target Quadruple-Chain Ladder Polyphenylsilsesquioxane (Ph-QCLP).** A total of 5.14 g (10 mmol of repeating unit) of **QCLP**, 80 mL of dioxane, and 60 mL of toluene were placed in a 250 mL three-necked flask equipped with a reflux condenser and a magnetic stir bar. Under argon purge, 1.32 g (6.67 mmol, 2/3 equivalent of **QCLP**) of IPC, and 20 mL of *N,N*-dimethylacetamide (DMA) were added drop-by-drop over 2 h at rt. The reaction was continued for another 10 h. Then, 0.12 g (6.67 mmol, 2/3 equivalent of **QCLP**) of water, 1.34 g (13.34 mmol, 4/3 equivalent of **QCLP**) of Et<sub>3</sub>N, and 10 mL of DMA were dropwise added into the solution over 2 h at rt. The reaction was continued for additional 10 h at 40 °C. The above-mentioned procedure was repeated twice with total reaction time of 72 h. After that, 50 mL of toluene and 5 mL of water were added, and the DMA/water phase was washed with toluene. The toluene phase was collected, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then condensed to 20 mL. At last, 15 mL of hexane was added, and a white solid immediately emerged, which was dried in a vacuum oven at 40 °C for 24 h to afford 1.25 g of desired **Ph-QCLP**. Yield, 33%. IR (KBr): 3074, 1595 (–Ph), 1431, 1260 (Si–Ph), 1000–1100 cm<sup>–1</sup> (Si–O–Si). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 6.5–8.0 (br, ph–H) ppm. <sup>29</sup>Si NMR (59.6 MHz): δ = –80.5, –112.0 ppm.

## RESULTS AND DISCUSSION

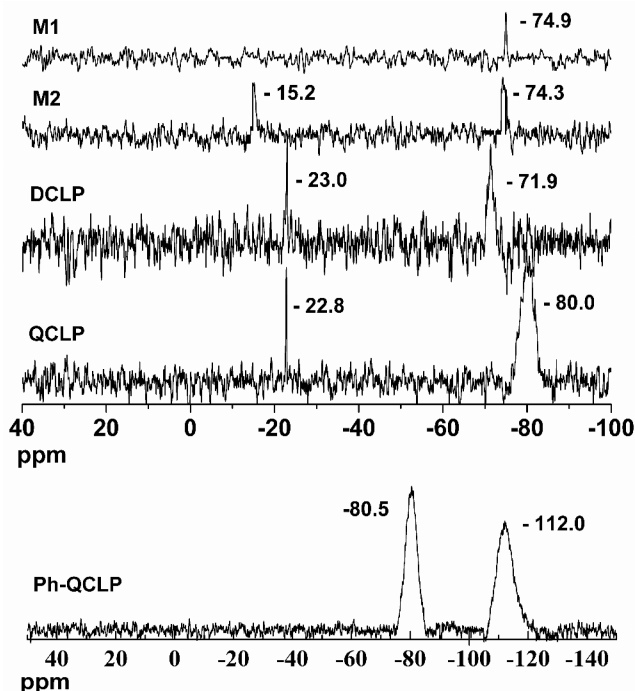
**Synthesis of DCLP.** **M1** was prepared by condensation of 1,3-dichloro-tetramethoxyl-disiloxane with *m*-phenylenediamine as shown in Scheme 1. To prevent the undesirable hydrolysis of the Si–OMe group, slightly excessive Et<sub>3</sub>N was used as HCl-absorbent, and the reaction temperature was kept at low temperature (0 °C). This reaction was monitored by the

appearance of an IR peak around 1497 cm<sup>–1</sup> ascribed to the Si–N bond (Figure 1). Due to the high air sensitivity of Si–N, –NH<sub>2</sub>, and Si–OMe groups, **M1** was used as soon as prepared.



**Figure 1.** IR spectra of (A) **M1**, **DCLP**, and **QCLP**; (B) hydrolysis–condensation progress of **DCLP** to **QCLP** with Me<sub>4</sub>NOH as catalyst, (a) 6 h, (b) 24 h, (c) 48 h, and (d) 72 h.

**M2** was synthesized through dehydrochlorination reaction of **M1** and PhSiCl<sub>3</sub> with Et<sub>3</sub>N as catalyst at 0 °C. Because of the highly reactive Si–Cl<sub>s</sub>, it is fairly difficult to isolate the pure **M2** for characterization. Even so, chemical shift variation in <sup>29</sup>Si NMR spectra between **M1** (–74.9 ppm) and **M2** (–15.2, –74.3 ppm) still clearly indicated the complete transition of **M1** to **M2** though there was a peak broadening possibly arising from minor hydrolysis of Si–Cl<sub>s</sub> groups (Figure 2).

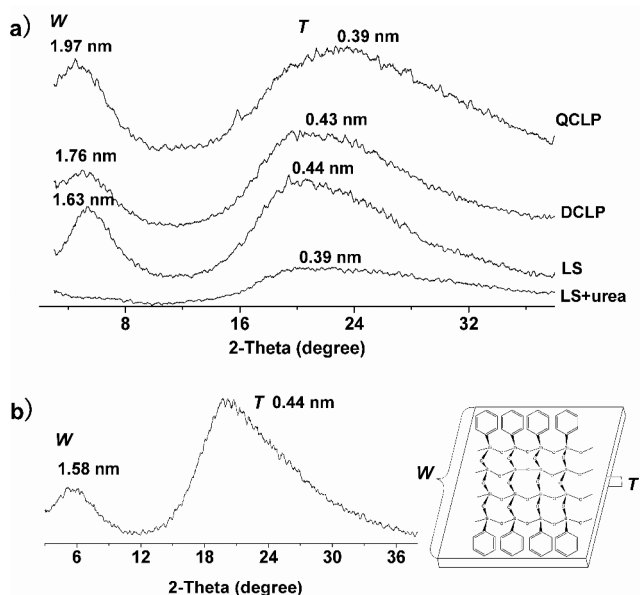


**Figure 2.** <sup>29</sup>Si NMR spectra of **M1**, **M2**, **DCLP**, **QCLP**, and **Ph-QCLP**.

In toluene/dioxane (v/v = 1/1) solution, **M2** was found to be able to spontaneously assemble into a regular ladder superstructure (**LS**) via presumably synergistic interactions of N–H···N hydrogen-bonding and benzene ring  $\pi$ – $\pi$  stacking. The apparent degree of polymerization (**DP**) of **LS** (0.1 mol/L toluene solution of **M2**) was determined by vapor pressure osmometry (VPO) to be about 6. It is noteworthy that the MW determination was not performed by the usual gel permeation



chromatography (GPC) because GPC is calibrated by ball-like polystyrene as standard but ladder polymers such as **DCLP** are rigid bar-like molecules. XRD analysis is an effective method to characterize ordered structures, and it was successfully applied to characterize ladder structure in literature.<sup>6,7</sup> In order to maintain the original molecular arrangement in solution, we used a freezing-dry method to prepare the low air-stable **LS** samples. As shown in Figure 3, the XRD profile of the **LS**

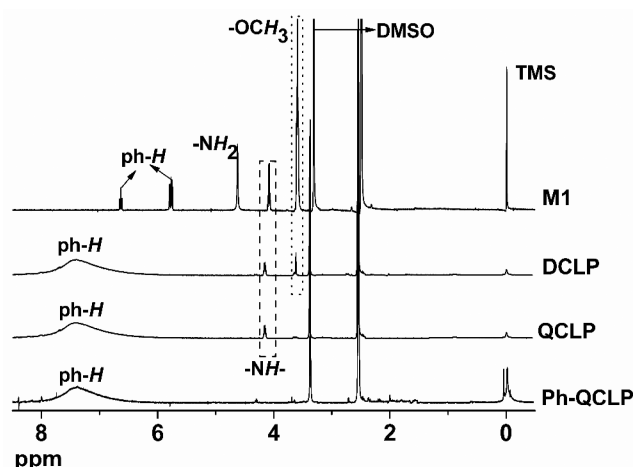


**Figure 3.** (a) XRD profiles of **LS** (namely the assembly of **M2**), **LS** + urea, **DCLP**, and **QCLP**; (b) XRD profile of **Ph-QCLP** and schematic diagram of **Ph-QCLP** with four repeat units.

sample shows two characteristic peaks with  $2\theta$  around  $5.42^\circ$  and  $20.02^\circ$  ( $d = 1.63$  and  $0.44$  nm), which respectively corresponded to ladder width (**W**) and ladder thickness (**T**). It was found that the addition of urea, an H-bonding blocking agent, led to remarkable reduction of the intensity of the **W** peak, implying that H-bonded **LS** was seriously destroyed. This result fully suggested the supramolecular feature of **LS**.

Directed by the **LS** template, **M2s** carried out the confined polymerization to be regular **DCLP** with high MW. Since the weak noncovalent interactions are extremely susceptible to external conditions, for example, temperature, the polarity, and electro-donating ability of the solvents,<sup>9</sup> careful precautions were taken to avoid breaking **LS** during the polymerization and thus ensure the formation of high-ordered **DCLP** instead of branched or cross-linked products. After several trials, the proper reaction conditions were selected: toluene/dioxane ( $v/v = 1/1$ ) mixture with low polarity and low electro-donating ability, below  $50^\circ\text{C}$ , stoichiometric hydrolysis-dehydrochlorination condensation, and  $\text{Et}_3\text{N}$  catalyst. At the end of polymerization,  $\text{Me}_3\text{SiCl}$  was used to end-cap **Si-OHs** to obtain stable **DCLP** with  $\text{DP} \sim 107$ .

**DCLP** was a white solid and was dissolved in toluene, dioxane, and other common organic solvents. Compared with the IR spectrum of **M1**, besides the absorbance peaks of  $-\text{NH}$  ( $3370\text{ cm}^{-1}$ ),  $\text{Si-N}$  ( $1497\text{ cm}^{-1}$ ),  $-\text{Ph}$  ( $3048, 1600\text{ cm}^{-1}$ ), and  $\text{Si-OCH}_3$  ( $1196\text{ cm}^{-1}$ ), there were new absorptions characteristic of  $\text{Si-Ph}$  ( $1430, 1263\text{ cm}^{-1}$ ) and  $\text{Si-O-Si}$  ( $1000\text{--}1100\text{ cm}^{-1}$ ) in the IR spectrum of **DCLP** (Figure 1). Also, as shown in Figure 4, the  $^1\text{H}$  NMR resonance of  $-\text{NH}_2$  disappears and



**Figure 4.**  $^1\text{H}$  NMR spectra of **M1**, **DCLP**, **QCLP**, and **Ph-QCLP**.

the **Ph-H** resonances broaden from **M1** to **DCLP**, which just resulted from the polymerization reaction. Meanwhile, the resonance peaks of  $-\text{NH}$  and  $-\text{OCH}_3$  still existed and were unchanged, suggesting they were preserved well in the polymerization and post-treatment process. The ladder structure of **DCLP** was also verified by XRD with two distinct peaks around  $2\theta = 5.02^\circ$  and  $20.68^\circ$  (Figure 3). The corresponding spacing ( $d$ ),  $1.76$  and  $0.43$  nm, respectively represented **W** (the intramolecular chain-to chain distance of the polymer) and **T** (the thickness of the macromolecular chain).<sup>6,7</sup> This result was consistent with the predicted values ( $1.90$  and  $0.39$  nm) based on molecular simulation calculation (by Materials Studio). Note that these values were close to those of **LS** samples, suggesting that **LS** was indeed the precursor of ladder polymer **DCLP**. On the other hand, the  $^{29}\text{Si}$  NMR spectrum of **DCLP** in Figure 2 shows two resonances with the chemical shift  $\delta$  around  $-23.0$  (half-height width  $\Delta_{1/2} < 1$  ppm) and  $-71.9$  ppm ( $\Delta_{1/2} \sim 2$  ppm), ascribed to the repeating moieties  $\text{Ph-Si}(\text{NH})\text{O}_{2/2}$  and  $\text{Si}(\text{NH})(\text{OMe})_2\text{O}_{2/2}$ , respectively. It is known that in solution  $^{29}\text{Si}$  NMR, the narrower the resonance peak of the silicon atoms, the higher the ladder regularity of polysiloxane.<sup>6,7</sup> So, the relative low  $\Delta_{1/2}$  suggested that **DCLP** possessed pretty good ladder regularity. Combining XRD and  $^{29}\text{Si}$  NMR results, it could be deduced that **DCLP** consisted of regular ladder structures, instead of randomly interlaced or branched structures. Note that the  $\text{Si-N}$  bond had relatively high reactivity, so **DCLP** needed to be purified and stored in an environment free of acid and water to keep its high regularity for following use.

**Synthesis of QCLP.** **QCLP** was prepared through hydrolysis and condensation of  $\text{Si-OMe}$  groups located at the ladder-rungs of **DCLP**. In this conversion, the choice of catalyst system was essential due to the existing of reactive  $\text{Si-N}$  bonds.  $\text{Et}_3\text{N}$  was first selected as catalyst because the  $\text{Si-N}$  bond was inert to it. However, the hydrolysis and condensation reaction was too slow under this condition. Then  $\text{CH}_3\text{COOH}$  was used as alternate, but  $\text{Si-Ns}$  were liable to cleave. Eventually the  $\text{Me}_4\text{NOH}/\text{CH}_3\text{OH}$  system was chosen owing to its moderate basicity, which could ensure the hydrolysis-condensation of  $\text{Si-OMes}$  without undesirable destruction of  $\text{Si-N}$  bonds. This assumption was corroborated by IR detection (Figure 1). As reaction proceeded, characteristic absorptions of  $\text{Si-OMe}$  ( $2964, 2857\text{ cm}^{-1}$ ) and  $\text{Si-OH}$  ( $\sim 3300\text{ cm}^{-1}$ ) gradually weakened, but that of  $\text{Si-N}$  ( $1497$

$\text{cm}^{-1}$ ) remained unchanged. Moreover, the disappearance of  $-\text{OCH}_3$  resonance in  $^1\text{H}$  NMR reflected the complete hydrolysis–condensation of Si–OMes into Si–O–Si bonds (Figure 4). **QCLP** was a pale yellow solid and also dissolved in toluene, dioxane, and other common solvents. **DP** of **QCLP** determined by VPO was about 98, approximately consistent with 107 of **DCLP**. The little variation of **DPs** supported the proposed reaction mechanism, that is, there was only intramolecular reaction but no additional chain extension from the capped **DCLP** to **QCLP**.

The XRD profile of **QCLP** film also gave two peaks: the diffraction peak around  $4.48^\circ$  ( $d = 1.97$  nm) originated from the intramolecular chain-to-chain distance of the quadruple-chain polymer and the diffusion peak around  $22.70^\circ$  ( $d = 0.39$  nm) arising from the stack of macromolecular chains (Figure 3). These data were also in accordance with the simulated dimensions ( $d = 1.94$  and  $0.39$  nm) (by Materials Studio). For  $^{29}\text{Si}$  NMR, **QCLP** similarly showed two characteristic peaks,  $\delta$ -22.8 ppm ( $\Delta_{1/2} < 1$  ppm,  $\text{Ph-Si}(\text{NH})\text{O}_{2/2}$ ) and  $-80.0$  ppm ( $\Delta_{1/2} \sim 5$  ppm,  $-(\text{NH})\text{SiO}_{3/2}$ ) (Figure 2). Compared to **DCLP**, there was no variation of  $\text{Ph-Si}(\text{NH})\text{O}_{2/2}$  resonance while the change of  $-\text{SiOMe}$  to  $\text{Si-O-Si}$  resulted in a resonance upfield-shift ( $-71.9 \rightarrow -80.0$  ppm) with the increase of  $\Delta_{1/2}$  ( $2 \rightarrow 5$  ppm). The latter phenomenon displayed that the polymer regularity was lowered, which might be caused by some defects derived from incomplete hydrolysis and condensation of minor Si–OMes. Even so, these characterizing results still confirmed the relatively regular quadruple-chain structure of **QCLP**. Similarly, to prevent the undesired cleavage of Si–N bonds, **QCLP** should be stored without base and water.

**Synthesis and Characterization of Ph-QCLP.** After successful synthesis of **QCLP**, the next step was how to convert it into the target **Ph-QCLP**. The diaminophenylene bridges that hold ladder structure should be removed simultaneously and Si–O–Si bridges should form immediately afterward to avoid defects. In our past report on preparing the perfect **H-LPSQ**, **IPC** was successfully used to solve this problem.<sup>7c,10</sup> Accordingly, here **IPC** was also chosen as diaminophenylene-bridge-cleaving agent. As shown in Scheme 1, one **IPC** could initially form a donor–acceptor complex (**DAC**) with a diaminophenylene bridge through a synergy of  $\text{C}=\text{O} \cdots \text{HN}$  hydrogen bonding, benzene rings  $\pi$ – $\pi$  stacking, and  $\pi$ -type back-bonding interactions of lone paired  $p$ -electrons of Cl-atoms with the low-lying  $\sigma^*$  orbital of Si-atoms. Then the bridge was synchronously broken to be two Si–Cl groups with polyaramide as a byproduct.<sup>11</sup> The two new-born Si–Cl bonds then underwent stoichiometric hydrolysis to be a Si–OH and a Si–Cl group. The existing of  $\text{Et}_3\text{N}$  quickly catalyzed the in situ dehydrochlorination condensation of Si–OH and Si–Cl linked by  $\text{O-H} \cdots \text{Cl}$  hydrogen bonding to be a Si–O–Si bridge.

Because there was a difference between the distance of two Si atoms in  $\equiv\text{Si}-m\text{-PDA}-\text{Si}\equiv$  ( $\sim 0.6$  nm) and in  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  ( $\sim 0.3$  nm) according to the molecular simulation, in the dehydrochlorination condensation the 12-membered macrocyclic intermediate might bring the ladder chain a slight nonplanar distortion. To minimize the local distortion and thus maintain the overall integrity of ladder structure, a step-by-step conversion method was employed. Both bridge-cleaving agent and water were added in a batch manner. Each time stoichiometric **IPC** was first dropwise added as dilute solution and after it reacted completely, the corresponding water solution was slowly dropped into the reaction system. This

procedure was repeated at least three times with total reaction time of about 72 h below  $50^\circ\text{C}$ . Therefore, in every moment of the whole process, there were a few bridges cleaved, the local distortion was limited, and high regular ladder structure of the whole main chain was not destroyed. Meanwhile, the rigorously controlled amount of **IPC** or water, as well as the low macromolecular concentration, also effectively prevented mismatch between different macromolecular chains. In brief, the above reaction conditions worked well to control the regularity of resulting **Ph-QCLP** as discussed later.

IR was applied to monitor the reaction progress (Figure 5). The gradual decrease and final disappearance of Si–N

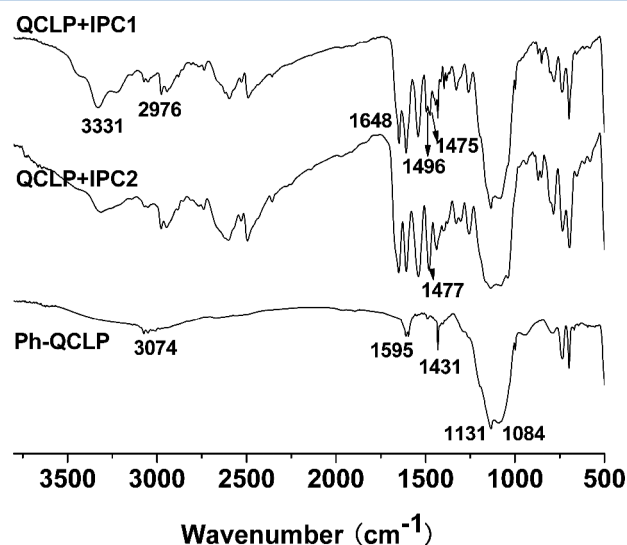


Figure 5. IR spectra of **QCLP** to **Ph-QCLP**.

absorbance at  $1496\text{ cm}^{-1}$  represented the removal of the diaminophenylene bridge while the disappearance of Si–OH absorbance around  $3300\text{ cm}^{-1}$  stood for the completion of condensation. Furthermore, the extraction purification of product was also detected by IR, mainly according to the decrease of CONH absorbance at  $1648\text{ cm}^{-1}$ . In addition, the  $^1\text{H}$  NMR of the obtained product showed only a band from 6.5 to 8.0 ppm assigned to Ph–H, further proving the purity of **Ph-QCLP** (Figure 4). **Ph-QCLP** was a white solid and was dissolved in toluene, THF, and some other solvents. VPO determination gave **DP**  $\sim 103$  of **Ph-QCLP**, approximately close to  $\sim 98$  of **QCLP**. This result indicated that the quadruple-chain structure survived the “synchronous cleavage/in situ condensation” and there was not any intermolecular irregular chain extension or transfer.

The ladder structure of **Ph-QCLP** was also characterized by XRD. Two distinct peaks around  $5.60^\circ$  and  $20.18^\circ$  ( $d = 1.58$  and  $0.44$  nm) were observed (Figure 3). They respectively corresponded to **W** and **T**, consistent with the simulated dimensions ( $1.54$  and  $0.39$  nm) (by Materials Studio).  $^{29}\text{Si}$  NMR of **Ph-QCLP** showed two peaks,  $-80.5$  ppm ( $\Delta_{1/2} \sim 3$  ppm,  $\text{Ph-SiO}_{3/2}$ ) and  $-112.0$  ppm ( $\Delta_{1/2} \sim 4$  ppm,  $-\text{SiO}_{4/2}$ ) (Figure 2). The broadened resonance peaks indicated that the regularity of quadruple-chain polymer might slightly decrease in the bridge-conversion process. Due to the quite difficult control of the multifunctional reaction, this reduction could be acceptable and the above characteristic results along with the solubility in common solvent (such as toluene, THF) still

verified the relative regular quadruple-chain structure of Ph-QCLP.

The thermal properties of Ph-QCLP were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure 6). The decomposition temperature

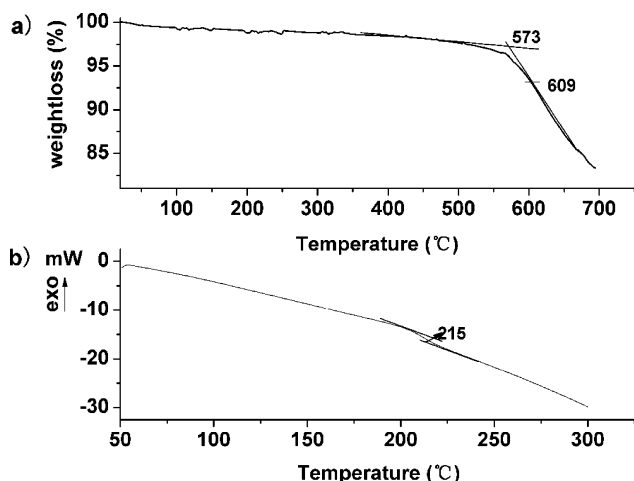


Figure 6. TGA (a) and DSC (b) curve of Ph-QCLP.

( $T_{\text{dec}}$ ) of Ph-QCLP was high up to 609 °C, and the temperature of weight loss of <20% is 700 °C. The glass transition temperature ( $T_g$ ) was 215 °C, higher than that of triple-chain ladder polyphenylsilsequioxane (158 °C).<sup>8</sup> It could be deduced that although there might be some structural defects due to the incomplete polymerization and conversion, Ph-QCLP still possessed high thermo-stability generated from its relatively regular quadruple-chain structure.

## CONCLUSIONS

The soluble well-defined quadruple-chain ladder polyphenylsiloxane, Ph-QCLP, with high MW was synthesized using the three-step supramolecular template method. Directed by regular ladder superstructure LS based on a synergy of hydrogen bonding and  $\pi$ - $\pi$  stacking, the precursors, DCLP and QCLP, were prepared in succession. Finally, through the “synchronous cleavage/in situ condensation”, the target Ph-QCLP was obtained. In the whole synthetic route the supramolecular interactions played important roles. The target Ph-QCLP was characterized by the following facts: (1) IR showed that the Si-Cl, Si-OMe, and CONH absorbance completely disappeared; (2) XRD showed two distinct peaks respectively corresponding to W and T, which were consistent with the simulated dimensions; (3) the  $^1\text{H}$  NMR showed only a band from 6.5 to 8.0 ppm assigned to Ph-H; (4)  $^{29}\text{Si}$  NMR showed two peaks at -80.5 ppm (Ph-SiO<sub>3/2</sub> moiety) and -112.0 ppm (SiO<sub>4/2</sub> moiety) with almost equal integral area, suggesting that Ph-QCLP should consist of SiO<sub>3/2</sub> and SiO<sub>4/2</sub> moieties in equimolar ratio; and (5) unusual  $T_{\text{dec}}$  of as high as 609 °C and  $T_g$  of as high as 215 °C are remarkably superior to common high temperature-resistant polymers. The relatively regular grating-like structure of Ph-QCLP gives it potential application for special thermo-stable hybrid polymer materials.

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## Notes

The authors declare no competing financial interest.

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