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Template of Concerted CT and H-Bonding Interactions-Directed Synthesis of a Highly Soluble and Perfect Organo-Bridged Ladder Polymethylsiloxane

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ABSTRACT: The highly soluble, perfect 2,5-dipropyl (alternate hydro- and benzo-) quinone-bridged ladder poly(methylsiloxane) (abbreviated as **L**) with molecular weight $M_n = 1.9 \times 10^4$ was successfully synthesized for the first time through the supramolecular ladder assembly template (**L′**) formed via the concerted effect of charge transfer (**CT**) interaction of quinone−hydroquinone (abbreviated as **Q−HQ−CT**) and silanol's H-bonding one of the hydrolates of monomers, 2,5-di[(3-dihydroxymethylsilyl)propyl]hydroquinone (**M$_1$′**) and 2,5-di[(3-dihydroxymethylsilyl)propyl]benzoquinone (**M$_2$′**). The presence of perfect ladder structures of polymer **L**, in particular, ladder assembly **L′** very susceptible to ambient environment were well confirmed by the following data: (1) XRD analysis shows that **L** demonstrates two diffraction peaks representing the characteristic ladder width $d_1 = 11.78$ Å and the ladder thickness $d_2 = 4.91$ Å respectively, which are approximately consistent with the molecular simulation-based width $d_1' = 12.40$ Å and thickness $d_2' = 5.40$ Å. Similarly, solution XRD shows that **L′** also demonstrates the two peaks representing the width $d_1 = 11.05$ Å and the thickness $d_2 = 4.61$ Å, respectively, suggesting the presence of ladder structure of **L′**. (2) ^{29}Si NMR measurement gives the sharp peak with extremely small half peak width, $W_{hp} < 1$ ppm, of the moiety [$=SiO_{2/2}-$] for either **L** or **L′**. (3) UV spectroscopy displays a new set of "red-shift" absorption peaks which are generated by **CT** interaction between **M$_1$′** and **M$_2$′** of **L′**. Moreover, there is the significant similarity of the peak fashions of **L** and **L′**. Meanwhile, fluorescence spectroscopy (FS) analysis shows emission peaks of **L** and **L′** are very alike. These results demonstrate that **L′** also has ladder structure. (4) In a series of control experiments, addition of H bond or **CTC**-blocking reagent (urea or **HQ**) to the solution of **L′** led to destruction of **L′** and great changes of the spectra of XRD, ^{29}Si NMR, UV, and FS. (5) As circumstantial evidence, DSC measurement gives a very high glass transition temperature ($T_g = 137$ °C), further indicating that **L** has a rigid rodlike skeleton without noticeable branches.

Introduction

Ladder polysiloxanes (**LPS**) including both oxygen-bridged ladder polysilsesquioxanes (**LPSQ**) and organo-bridged ladder polysiloxanes (**OLPS**) are very important organic/inorganic hybrid materials[1] because of their excellent physical and chemical properties rendered by their unique double-stranded structure. As early as 1960, Brown et al.[2] first reported the synthesis of a soluble, high molecular weight (M_w) ladder poly(phenylsilsesquioxane) (**Ph−LPSQ**) by "equilibration thermal polymerization". It made a great worldwide stir because they used a trifunctional monomer to obtain such a ladder polymer. Unfortunately, the genuineness of the very "first" ladder **Ph−LPSQ** was denied by Frye et al.[3] in 1971. Until today, despite a great effort in controlling the reaction conditions and kinetics, the synthesis of **LPSQ** with any single uniform structure still remains a great challenge to polymer chemists.

On the other hand, Adrianov et al.[4] also in 1960 attempted to prepare 1,4-phenylene-bridged poly(methylsiloxane) (**Ph−OLPS**), but obtained only some insoluble gel. Likewise, Oikawa et al.[5] mentioned **Ph−OLPS** with an ideal ladder structure in 1990, but they did not give any convincing characterization data. Obviously, a major reason for all of the aforementioned failures is the lack of any effective ladder template so that the multifunctional monomers or their derivatives typically arrange in a randomly interlaced manner, unavoidably leading to branched polymers.

As Bailey[6] clearly pointed out, the most desirable type of reaction for the formation of a perfect ladder is one in which both sides of the ladder are either formed simultaneously or no reaction occurs. If the reaction is at all reversible, it is desirable that both sides of the ladder structure are broken at the same time. So, it is necessary to precisely arrange the multifunctional monomers or derived intermediates into a desired supramolecular ladder assembly before the polycondensation occurs. Accordingly, we put forward a supramolecular template strategy to realize Bailey's statement, by which, indeed, a series of **OLPS**s have been successfully prepared in recent years. The first $\pi-\pi$ stacking self-assembling template-directed synthesis of 4,4′-phenylene ether-bridged poly(vinylsiloxane)[7] was reported earlier. However, since the $\pi-\pi$ interaction is comparatively weak, the stereoregularity of the **OLPS**s is not very high, as implied by the $W_{hp} \sim 2$ ppm for the moiety [$=SiO_{2/2}-$] in

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the ^{29}Si NMR spectrum. To align the monomeric molecules or derived intermediates in a real ladder fashion and consequently increase stereoregularity of **OLPS**, we then utilized a phenol H-bonding template to prepare 2,5-dipropylhydroquinone poly(methylsiloxane).[8] As expected, the W_{hp} of the polymer was reduced to 1 ppm. Most recently, a series of highly ordered **OLPS**s using the aryl amido H-bonding as the template was synthesized.[9−13] Because the amido H-bonding is generally much stronger compared with the $\pi-\pi$ stacking or phenol H-bonding interactions, these polymers exhibit a much narrower W_{hp} < 0.6 ppm, indicating a perfect ladder stereoregularity. Regrettably, these aryl amide-bridged **OLPS**s have such low solubility that their applications are greatly limited.

It is noteworthy that as early as the 1960s, **CT** interaction between an electron deficient unit (acceptor) and an election rich one (donor) has been widely applied as an efficient template in self-assembling synthesis.[14] Especially, quinone-hydroquinone (abbreviated as **Q−HQ**) was used to form a charge-transfer complex (**CTC**),[15,16] in which **Q** and **HQ** groups alternately stand face to face in either crystal state of **CTC**[17] or even in solution.[18,19] In light of these informative works, we tried to exploit such efficient intermolecular forces of the $\pi-\pi$ stacking and the H-bonding interactions as template for preparing the perfect **OLPS**. According to Kakudo,[20] the H-bonding between terminal silanol groups can form a square-planar configuration. Therefore, ladder assembly **L′** formed via a concerted effect between **CT** and silanol's H-bonding interaction can efficiently control the synthetic mechanism of polymer **L**.

In this paper, we report the synthesis of **L** through ladder assembly **L′** formed by the synergy between the **Q−HQ−CT** and H-bonding interactions of α,*ω*-tetrahydroxysilanes, $\mathbf{M_1'}$ and $\mathbf{M_2'}$. Ladder assembly **L′** and polymer **L** not only have perfect ladder structure with a narrow W_{hp} < 1 ppm in ^{29}Si NMR spectra but also exhibit very high solubility in common solvents. Therefore, it well enables investigation of special properties and exploring applications of such a new kind of **O−LPS**.

Experimental Section

Materials. All the reagents and solvents were commercially available and of analytical grade. Methyldichlorosilane, *N*-methylpyrrolidone (**NMP**), Tetrahydrofuran (THF) and tetramethylammonium hydroxide (**TMAH**) were purchased from Beijing Chemical Factory. 3,4-Dihydropyran (**DHP**) was purchased from Across Company. The THF and NMP were distilled from sodium-benzophenone prior to use. Dicyclopentadienylplatinum dichloride (Cp_2PtCl_2), was prepared according to the literature.[21]

Techniques. FT-IR spectra were recorded on a Perkin-Elmer 80 spectrometer using KBr pellets. ^{1}H NMR and ^{29}Si NMR spectra were obtained on a JWH−FXIOO (FT; 800 MHz, ^{1}H; 119 MHz, ^{29}Si) spectrometer using $CDCl_3$ as solvent. UV−vis spectra were gained on an UV-1601 PC spectrometer. The FS determination was performed with F-4500 FL spectrophotometer. Mass spectrometry (MS) measurements were carried out on a high-resolution AEI MS-50 spectrometer using electron impact (EI) technique. Differential scanning calorimetry (DSC) measurement was conducted on a Perkin-Elmer DSC-7 differential scanning calorimeter. The solid and solution X-ray diffraction (XRD) analyses were measured on a Rigakn D/MAX 2400 X-ray diffractometer. Molecular weight was determined by vapor pressure osmometry (VPO) method in THF at room temperature on a Knauer VPO instrument (Germany).

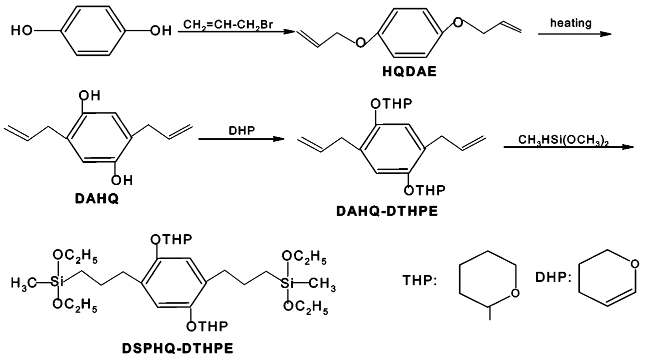
1. Monomer Synthesis. 1.1. 2,5-Di[3-(diethoxymethylsilyl)propyl]hydroquinone ($\mathbf{M_1}$). See Scheme 1 for the synthetic route.

1.2. 2,5-Di[3-(diethoxymethylsilyl)propyl]benzoquinone ($\mathbf{M_2}$). See Scheme 1 for the synthetic route.

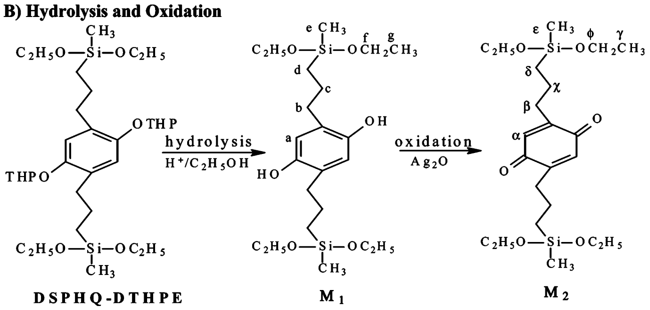
Synthesis of Diallylhydroquinone—Ditetrahydropyranyl Ether (DAHQ—DTHPE). Hydroquinone diallyl ether (**HQDAE**) and 2,5-diallylhydroquinone (**DAHQ**) were prepared according to the literature.[22] **DAHQ−DTHPE** was prepared as follows: A solution of 3,4-dihydropyran (**DHP**) (17 mL, 60 mmol) and **DAHQ** (10.0 g, 53 mmol) in CH_2Cl_2 (150 mL) containing two drops of hydrochloric acid (36.5 wt %) were stirred at 25 °C for 24 h. The mixture was then washed with 1 N aqueous NaOH to remove unprotected phenol. After removing solvent volatiles under reduced pressure, the residue was recrystallized with CH_3OH to give 15.0 g (78.0%) of white solid (mp: 76.5 °C), **DAHQ−DTHPE** as white solid (mp: 76.5 °C).

Scheme 1. Synthetic Route to Monomers $\mathbf{M_1}$ and $\mathbf{M_2}$

A) Hydrosilation and protection of phenol



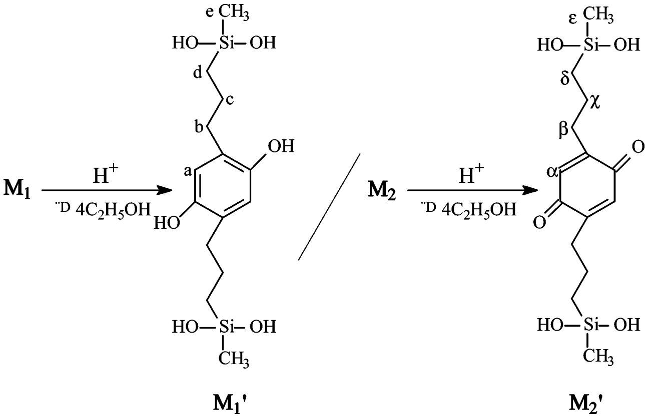
B) Hydrolysis and Oxidation



Synthesis of 2,5-Di[3-(diethoxymethylsilyl)propyl]hydroquinone Ditetrahydropyranyl Ether (DSPHQ—DTHPE). DSPHQ−DTHPE was prepared by hydrosilylation reaction of **DAHQ−DTHPE** with $CH_3HSi(OC_2H_5)_2$ in the presence of Cp_2PtCl_2 catalyst. A 100 mL flask containing **DAHQ−DTHPE** (3.6 g, 0.01 mol) and a trace of Cp_2PtCl_2 was purged with dry argon three times. $CH_3HSi(OC_2H_5)_2$ (3.18 g, 0.03 mol), obtained by the ethanolysis of CH_3HSiCl_2, and 30 mL of THF were injected into the flask. The mixture was stirred at 40 °C under argon for 36 h to yield 6.1 g (97%) of a transparent, colorless and oily **DSPHQ−DTHPE**.

Synthesis of Monomers, $\mathbf{M_1}$ and $\mathbf{M_2}$. First, acidified petroleum ether was prepared by passing dry HCl, which was produced by the interaction of concentrated sulfuric acid with sodium chloride, into freshly distilled petroleum ether. The acidified petroleum ether (2 mL) was then mixed with **DSPHQ−DTHPE** (2.0 g) and anhydrous ethanol (70 mL). The mixture was stirred under argon for 1 h. The solution was then washed with 1 N aqueous $NaHCO_3$ to about pH = 5−6. After removing the volatiles, the residue was purified by passing silicon gel-filled column using the ethanol as eluent. Next, 0.64 g (44%) of $\mathbf{M_1}$ was obtained as colorless oil. After that, 0.34 g of $\mathbf{M_1}$ was dissolved in 100 mL of *N*-methylpyrrolidone (**NMP**). Then 1.5 g of anhydrous Na_2SO_4 and 1.3 g of Ag_2O was added. The mixture was stirred at room temperature, and then was filtered to remove the Na_2SO_4. The filtrate was further distilled in a vacuum to remove **NMP**, yielding a residue, which was also purified by silicon gel-filled column using the ethanol as eluent. Finally, 0.28 g (82%) of $\mathbf{M_2}$ was obtained as brownish oil.

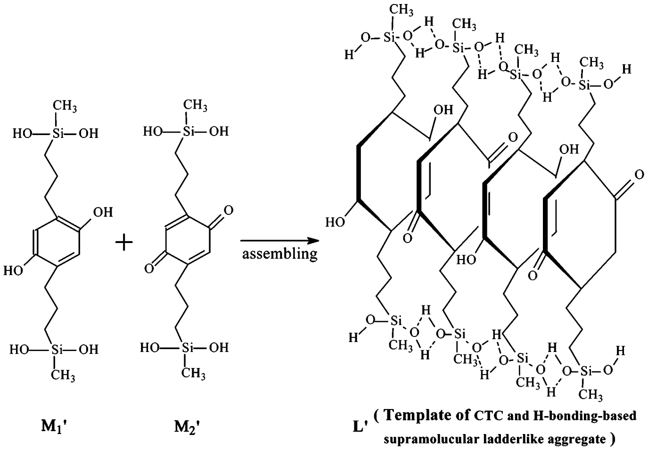
2. Synthesis of Polymer L. 2.1. Hydrolysis of $\mathbf{M_1}$ and $\mathbf{M_2}$. (a) First, 0.25 g (0.50 mmol) of $\mathbf{M_1}$ was put into a 100 mL of flask, into which 10 mL of THF, 30 mL of acetone, and 1.0 mL of 1 M hydrochloric acid were added dropwise at 0 °C over 3 h. Then the solution was stirred for 15 h at 40 °C. After most of acetone and



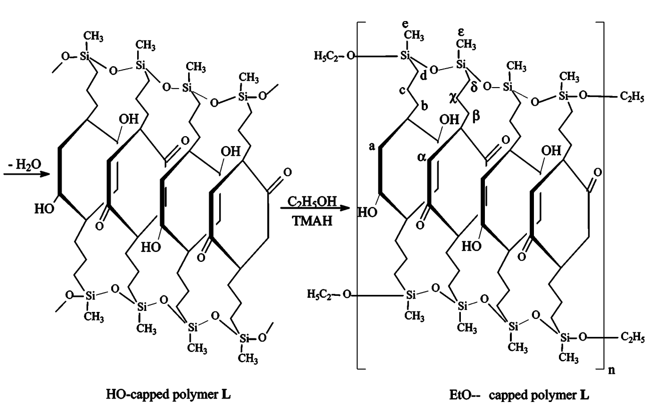
the C_2H_5OH released were removed, the left solution of $\mathbf{M_1}'$ was kept at 50 °C for the next reaction without further purification.

(b) First, 0.23 g (0.5 mmol) of $\mathbf{M_2}$ was put into a 100 mL of flask, into which 10 mL of THF, 30 mL of acetone and 1.0 mL of 1 M hydrochloric acid were added dropwise at 0 °C over 3 h. Then the solution was stirred for 15 h at 40 °C. After most of acetone and the byproduct C_2H_5OH were removed, the left solution of $\mathbf{M_2}'$ as the hydrolyzed product of $\mathbf{M_2}$ was kept as well at 50 °C for the next reaction without further purification.

2.2. Formation of Ladder Assembly L′ Based on the synergy of Q—HQ—CT and H-Bonding Interactions.



2.3. Dehydration Polycondensation of L′ and EtO-Capping.



A solution of equimolar $\mathbf{M_1}'$ (0.25 g, 0.5 mmol, in 10 mL of THF) and $\mathbf{M_2}'$ (0.23 g, 0.5 mmol, in 10 mL of THF) was concentrated to about 10 mL. After dropwise addition of 15 mL of H_2O, a precipitate appeared gradually, which was collected and dried in a vacuum oven for 12 h. Then the precipitate and 30 mL of xylene and 60 mL of absolute alcohol were mixed in a 250 mL flask, into which several drops of 0.1 M aqueous solution of **TMAH** and a few grains of dry zeolite was added. After the mixture was heated at refluxing temperature for 4 h, the ethanol and water released was azeotropically distilled off slowly until the temperature reached 130 °C. The reaction system was refluxed for another 5 h until all the catalyst **TMAH** was completely decomposed. Then the solution was concentrated to about 30 mL. After filtration, the filtrate was finally concentrated in a vacuum to obtain 0.34 g (70%) of brown solid **L**.

Results and Discussion

1. Synthesis and Characterization of Monomers $\mathbf{M_1}$ and $\mathbf{M_2}$. Monomers, $\mathbf{M_1}$ and $\mathbf{M_2}$, and their hydrolytes, $\mathbf{M_1}'$and $\mathbf{M_2}'$ were designed and synthesized with a view to prepare the ladder polymer **L**. $\mathbf{M_1}$ was synthesized by the hydrolysis of **DSPHQ−DTHPE**. At first, **DHP** was used as an effective protective agent for phenolic hydroxy group, and then was readily removed under so diluted acidic condition as to decrease cleavage of the hydrolyzable Si−OEt bonds of **DSPHQ−DTHPE**. The reason for low yield of $\mathbf{M_1}$ is that when the phenolic ether group of **DSPHQ−DTHPE** is hydrolyzed a part of silyl ether groups $\mathbf{M_1}$ is simultaneously hydrolyzed to silanol, which is unavoidably subject to further condensation to form siloxane bonds.

The preparation of $\mathbf{M_2}$ is similar to that of $\mathbf{M_1}$. It should be noted that no cross condensation between Si−OH and phenolic hydroxyl groups was observed during the synthesis of the monomer $\mathbf{M_1}'$ and $\mathbf{M_2}'$ because Si−OH group cannot react with acidic phenol's hydroxyl group in the condition used.

The characterization data of $\mathbf{M_1}$ and $\mathbf{M_2}$ are listed in Tables 1 and 2.

2. Synthesis of Polymer L. 2.1. Concerning How to Bring Ladder Template L′ into Full Play throughout the Polycondensation Process. The synergy between the **Q-HQ-CT** and silanol's H-bonding interactions can make the hydrolytes, $\mathbf{M_1}'$ and $\mathbf{M_2}'$, spontaneously arranged into **L′** without the necessity of imposing other additional confined geometry. Noteworthily, both **CT** and H-bonding interactions are comparatively weak compared with the covalent bond and they are thus strongly affected by the following factors: reaction temperature, electronic property of the solvent, and hydrolysis rate.

A. Reaction Temperature. In general, the reaction temperature has to be kept under 60 °C, otherwise the intermediates, $\mathbf{M_1}'$ and $\mathbf{M_2}'$, would easily gel because the weak interactions-based supramolecular ladder assembly **L′** would be destroyed at higher temperature.

B. Electronic Property of the Solvents. Generally, use of any strong electron-accepting or -donating solvents should be avoided since they would form some new kind of **CTC** with the hydrolytes, $\mathbf{M_1}'$ or $\mathbf{M_2}'$, resulting in destruction of **L′**.

C. Hydrolysis Rate. The hydrolysis rate must be controlled strictly. If water adds too fast, highly branched polymers would be produced immediately due to rapid random condensation. Thus, the hydrolysis reaction must be carried out by slowly feeding water into a dilute solution of monomers at a lower temperature ($<$60 °C).

2.2. Removal of Water. Since the polycondensation reaction in the presence of trace of hydrochloric acid is an equilibrium process, the water released as the condensation byproduct must be removed timely to obtain a high molecular weight polymer.

2.3. End-Capping Reaction. To stabilize the silanol-terminaed polymer **L** the end-capping reaction with ethanol was carried out according to our previous work.[23] An effective transient catalyst, tetrmethylammonium hydroxide (**TMAH),** is applied for the dehydration/ethanolysis reaction between ethanol and the terminated Si−OH groups, resulting in a completely ethoxy-capped **L** of high storing-stability at room temperature

Table 1. Characterization Data of Monomer M_1

characterization item	result
appearance	colorless oil
solubility	highly soluble in ordinary solvents, such as: $CHCl_3$, THF
anal. found (calcd)	C, 57.1 (57.6); H, 10.2 (9.2); O, 21.1 (20.9)
MS (EI)	458.7 (*m*/z of molecular cation)
FT-IR (cm^{-1}) (KBr)	3431 (w, $-OH$); 1261 and 1419 (s, $Si-CH_3$); 1498 (s, Ph), 1078 (s, $Si-OEt$)
^1H NMR (δ in ppm)	6.90 (s, 2H, H^a); 2.60 (m, 4H, H^b); 1.6 (m, 4H, H^c); 0.7(m, 4H, H^d); 0.1 (s, 6H, H^e); 3.5 (m, 8H, H^f; 1.1 (m, 12H, H^g)
^{29}Si NMR (δ in ppm)	-3.6 (s, $CH_3\,(Et_2O)_2\mathit{Si}O_{2/2}$)

Table 2. Characterization Data of Monomer M_2

characterization item	result
appearance	brownish oil
solubility	highly soluble in ordinary solvents such as $CHCl_3$, THF,
elemental analysis (found/calcd)	C: 57.2% (57.8%), H: 9.2% (8.3%), O: 21.1% (21.0%)
MS (EI)	456.6 (*m*/z of molecular cation)
FT-IR (cm^{-1}) (KBr)	1651 (s, $C{=}O$); 1261 and 1420 (s, $Si-CH_3$); 1499 (s, Ph); 1078 (s, $Si-O-Si$).
^1H NMR (δ ppm)	7.3 (s, 2H, H^{α}); 2.6 (m, 4H, H^{β}; 1.6 (m, 4H, H^{χ}); 0.7 (m, 4H, H^{δ}; 0.1 (s, 6H, H^{ϵ}); 3.5 (m, 8H, H^{ϕ}); 1.1 (m, 12H, H^{γ})
^{29}Si NMR (δ ppm)	-3.7 (s, $CH_3\,(Et_2O)_2\mathit{Si}O_{2/2}$)

Table 3. Characterization Data of Polymer L

characterization items	results
appearance	brown solid
solubility	soluble in low polar solvents such as THF and toluene
M_n (Da, by VPO)	19 770
FT-IR (cm^{-1}) (KBr)	3431 cm^{-1} (w. unassociated $-OH$ group of HQ);1651 (s, $C{=}O$), 1261,1419 (s, $Si-CH_3$), 1498 (m, Ph), 1078 (s, $Si-O-Si$), 3500$-$3600 (w, $Si-OH$)
^1H NMR (δ in ppm)	7.3 (m, H^{α}); 6.6(m, H^a); 2.62 ($H^{b\beta}$), 1.70 ($4H^{c\chi}$), 0.63 (m, $H^{d\delta}$), 0.08 (m, $H^{e\epsilon}$)
solid ^{29}Si NMR (δ in ppm)	-17.5 minor peak, $=Si\,(OH)\text{-}O_{1/2}$-; -22.5, major peak, $=Si\,O_{\,2/2\,-}$ with $W_{hp} < 1$ ppm
powder XRD (found/calcd, *d* in Å)	$d_1 = 23.5/20$ for the ladder width of **L**; $d_2 = 10.5/9.0$ for the ladder thickness of **L**
DSC (T_g/°C)	137

and meanwhile **TMAH** can be thoroughly removed because it would decompose almost quantitatively at ca. 130 °C into gaseous trimethylamine and methanol.

3. Characterization of Polymer L

The characterizing data for polymer **L** are given in Table 3.

The M_w of **L** was measured by vapor pressure osmometer (VPO) method instead of common gel permeation chromatography (GPC) because **L** is a stiff double chain molecule meanwhile calibration for GPC generally utilizes polystyrene as the reference standard, which is a flexible linear polymer and adopts a coil conformation in the solution. In addition, it is also not recommended to use light scattering method to investigate the solution properties of **L** because the dark color of **L** can absorb the laser light (wavelength $\lambda = 330$ nm) used and emit a new undesirable fluorescent light to interfere with the measuring accuracy. Hence, instead, the VPO method is utilized to measure the M_w of **L**.

As shown in Table 3, the FT-IR spectrum of polymer **L** demonstrates characteristic absorption peaks of the unassociated $-OH$ group of **HQ**: $C{=}O$; $Si-CH_3$; Ph; $Si-O-Si$; trace $Si-OH$ groups.

With reference to literature,[2,24] a ladder polysiloxane, despite a short segment, demonstrates two typical characteristic diffraction peaks in XRD patterns: one represents intramolecular chain-to-chain distance corresponding to the width (d_1) of the ladder polysiloxane molecule and another one the ladder thickness (d_2). As shown in Figure 2, the polymer **L** indeed demonstrates two distinct peaks: the ladder width d_1 (11.78Å) and the ladder thickness d_2 (4.91Å), which have decent coincidence with the calculated dimension $d_1' = 12.4$Å and $d_2' = 5.4$ Å based on Alchemy 2000 V 1.0 as simulation software.

The ^1H NMR spectrum of **L** shown in Figure 2 reveals that the signals for **THP** and $Si-OC_2H_5$ groups have completely disappeared by hydrolysis and the silanol group derived converted to $Si-O-Si$ bonds.

On the other hand, it is well-known that ^{29}Si NMR spectroscopy is a very powerful tool to judge the stereo-regularity of polysiloxane macromolecules. The higher the stereoregularity of ladder structure is, the sharper the peak of moiety $=SiO_{2/2}$ on the backbone is and thus the smaller the W_{hp} is. Generally, there are three types of distinct peaks for silicon atoms with different degree of condensation in the ^{29}Si NMR spectrum. The first peak represents a silicon atom of moiety [$=Si(OH)_2$]; the second represents a silicon atom of moiety [$=Si(OH)O_{1/2}$] and the third represents silicon atom of fully condensed moiety [$=SiO_{2/2}$]. As shown in Figure 3, the major peak **Si 1** centered at $\delta = -22.5$ ppm represents the third fully condensed moiety [$=SiO_{2/2}$] in the ladder skeleton. The minor peak **Si 2** at $\delta = -17.5$ ppm is assigned to terminal $=Si(OH)O_{1/2}$ functions, and there is not an additional peak ascribable to the moiety $=Si(OH)_2$. The peak area of **Si 1** is much bigger than **Si 2**, indicating that the most of Si atoms in polymer **L** exist as the fully condensed form of [$=SiO_{2/2}$]. Moreover, the half-peak width (W_{hp}) of peak **Si 1** is as narrow as <1 ppm. Thus, both the high peak intensity and the extremely narrow W_{hp} obviously confirm presence of the perfect ladder polymer skeleton.

The DSC curve of polymer **L** is shown in Figure 4. A distinct glass transition temperature (T_g) was observed at 137 °C. It is much higher than that of single-chain poly(dimethylsiloxane) ($T_g \approx -120$ °C). This result indicates that polymer **L** is a comparatively rigid macromolecular skeleton caused by the ladder structure with trace branches and the **CT** interactions between alternative **Q−HQ** moieties in polymer **L**.[25]

4. Confirming the Presence of Ladder Assembly L′. For comparison, some characterization data of **L** and **L′** and results of the control experiments are shown in Figures 1, 3, 5, and 6 and Table 4.

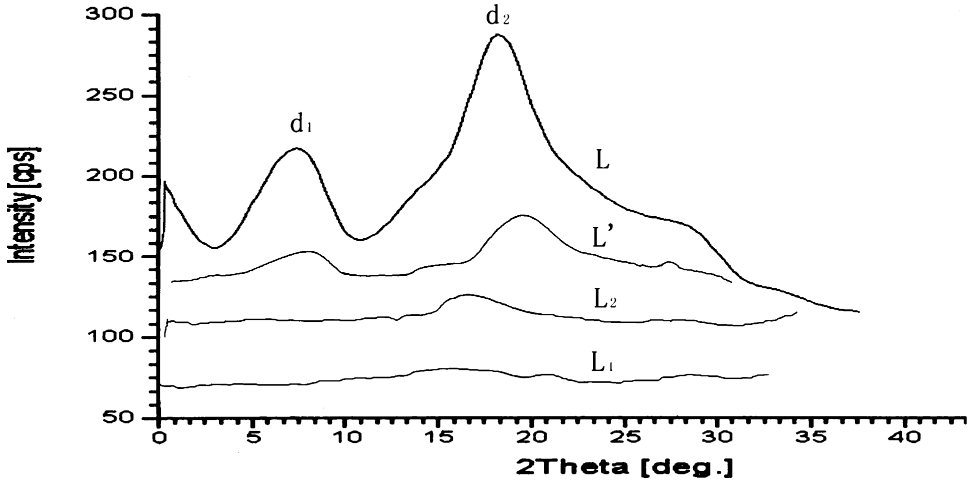


Figure 1. XRD patterns of polymer **L**, ladder assembly **L**′, and two comparative polymer samples: $\mathbf{L}_1$ obtained through **L**′ + H-bonding blocking agent urea and $\mathbf{L}_2$ obtained through **L**′+ **CTC**-blocking agent **HQ**.

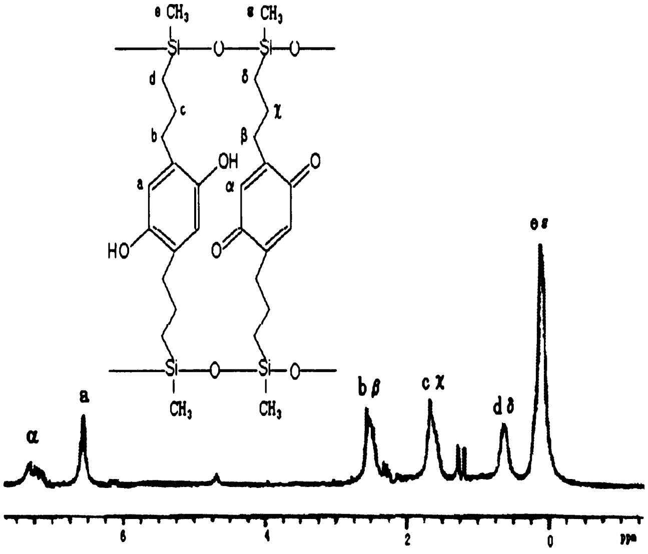


Figure 2. ^{1}H NMR spectrum of polymer **L**.

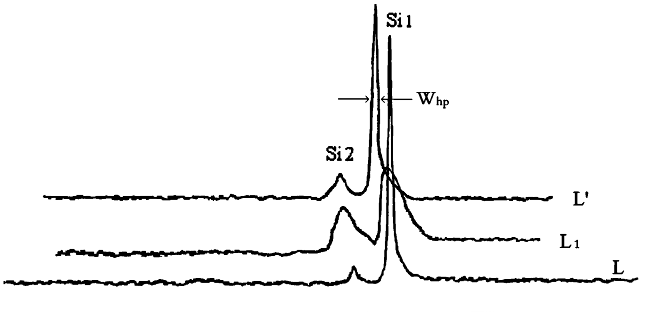


Figure 3. ^{29}Si NMR spectrum of polymer **L** (in solid state)**;** ladder assembly **L**′ and the comparative sample $\mathbf{L}_1$ (in solution) which was obtained through **L**′ + urea.

Because ladder assembly **L**′ is the most important proposal of the present work, its presence should be experimentally confirmed. However, considering that **L**′ is not as stable as the covalent ladder polymer **L**, therefore we characterized **L**′ by UV, FS, XRD, and ^{29}Si NMR in the solution state.

A. UV Investigation of Ladder Assembly L′. The intermediates $\mathbf{M}_1'$ and $\mathbf{M}_2'$, in solution can spontaneously form ladder assembly **L**′. This proposal is substantiated well by UV spectroscopy.

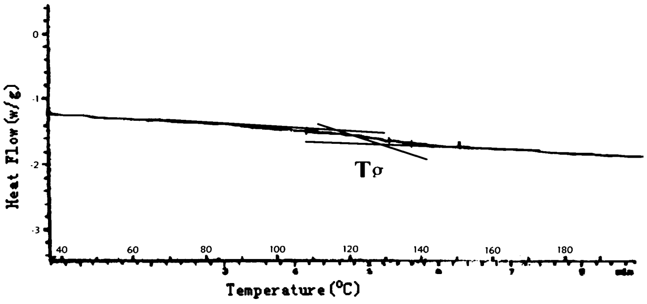


Figure 4. DSC curve of polymer **L**.

The **CT** interaction would take place in polymer **L** and ladder assembly **L**′. As shown in Figure 5, $\mathbf{M}_1'$ (curve a) and $\mathbf{M}_2'$ (curve b) display a strong absorption peak at 308 and 310 nm, respectively. When the two compounds are mixed at a 1:1 molar ratio, the mentioned-above two peaks are completely replaced by a new set of "red-shift" absorption peaks at 325 and 375 nm (curve c). This "red shift" takes place apparently due to **CT** interaction between $\mathbf{M}_1'$ and $\mathbf{M}_2'$ of **L**′,[25] suggesting groups **Q**s and **HQ**s of **L**′ are face to face aligned along the ladder architecture. As expected, curve d for polymer **L** also exhibits two similar "red-shift" absorption peaks at 327 and 380 nm like ladder assembly **L**′.

(Curve a stands for the spectrum of $\mathbf{M}_1'$; curve b for $\mathbf{M}_2'$; curve c for ladder assembly **L**′ and curve d for polymer **L**, respectively.)

As shown in Table 4, to investigate formation and function of ladder assembly **L**′, the above-mentioned two comparative samples: polymer $\mathbf{L}_1$ obtained through (**L**′ + urea) and polymer $\mathbf{L}_2$ obtained through (**L**′ + **HQ**), were examined. When urea or **HQ** is added into the **L**′ solution, the absorption peaks are shifted from 325/375 of **L**′ to 297/303 or 290/300 nm of unassociated $\mathbf{M}_1'$ and $\mathbf{M}_2'$ derived from **L**′, respectively, meaning destruction of **L**′.

B. Fluorescence Spectroscopy Investigation of Ladder Assembly L′. The fluorescence spectra of **L**′ and **L** are shown in Figure 6 using exciting light wavelength of 359 nm. The FS data indicate that the **L**′ and the **L** in solution has emitting peaks at 417 nm for **L**′ and 420 nm for **L**. The similar emitting behavior based on the curve shape and the maximum emission wavelength is observed.

Similarly, as shown in Figure 6 and Table 4, when urea or **HQ** is added into the **L**′ solution, the absorption peaks are shifted from 420/417 of **L**′ to 498/496 nm of unassociated $\mathbf{M}_1'$

Table 4. Comparison Data of Polymer L, Ladder Assembly L′, and Their Counterparts Prepared in Control Experiments

entry	ladder assembly **L′**	ladder polymer **L** prepd from **L′**	**L′** + urea	ladder polymer $\mathbf{L_1}$ prepd from **L′** + **urea**	**L′**+ HQ	ladder polymer $\mathbf{L_2}$ prepd from **L′**+ **HQ**
UV (nm)	325, 375	327, 380	297, 303	293, 303	290, 300	290, 300
FS (nm)	420	417	498		496	
XRD in soln (Å)	$d_1 = 11.05$	$d_1 = 11.78$		$d_1 = 0$		$d_1 = 0$
	$d_2 = 4.61$	$d_2 = 4.91$		$d_2 = 7.27$		$d_2 = 7.02$
^{29}Si NMR W_{hp} (ppm)	<1 ppm	<1 ppm		5.4 ppm		4.7 ppm

[a] Note: **L′** is the ladder assembly formed by Si−HQ + Si-Q (molar ration 1:1). **L** is obtained through ladder assembly **L′. $\mathbf{L_1}$** is obtained through **L′** + **urea**, and $\mathbf{L_2}$ is obtained through **L′** + **HQ**. Among them, urea is a H-bond blocking reagent and **HQ** is a **CT**-blocking one.

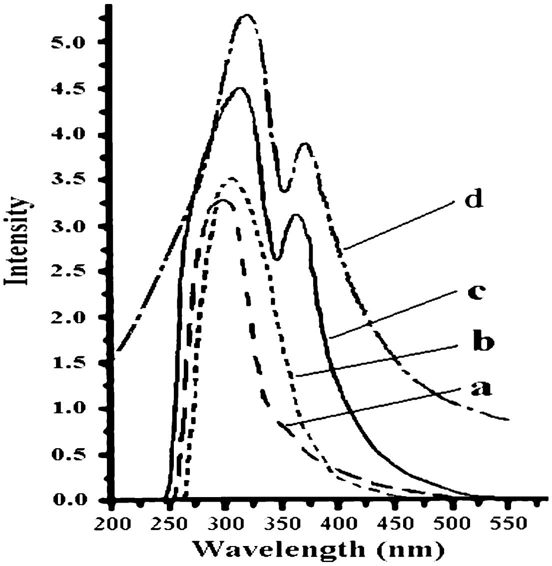


Figure 5. UV spectra of $\mathbf{M_1'}$, $\mathbf{M_2'}$ and a 1:1 molar ratio mixture of **L′**.

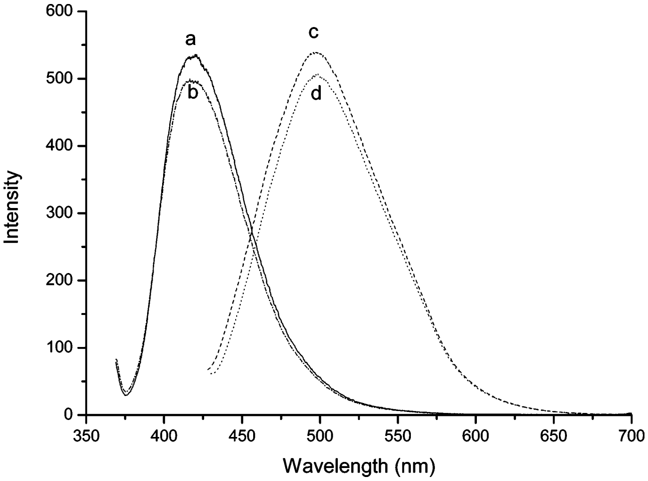


Figure 6. Fluorescence spectra: (a) ladder assembly **L′**; (b) polymer **L**; (c) **L′** + urea; (d) **L′**+ **HQ**.

and $\mathbf{M_2'}$ derived from **L′** respectively, meaning destruction of **L′**.

C. Solution XRD Investigation. The intermediates, $\mathbf{M_1'}$ and $\mathbf{M_2'}$, in solution can spontaneously form ladder assembly**.** This proposal were also substantiated well by solution XRD. The diffraction data indicate that **L′** gives two characteristic diffraction peaks ($d_1 = 11.05$ and $d_2 = 4.06$) which is similar to polymer **L**, suggesting that both **L′** and **L** have the similar ladder structure.

As shown in Figure 1 and Table 4, when urea is added into the solution of **L′**, as a result, polymer $\mathbf{L_1}$ only displays one peak ($d_2 = 7.27$). Similarly, when **HQ** is added into the solution of **L′**, polymer $\mathbf{L_2}$ also has only one peak ($d_2 = 7.02$). The absence of diffraction perks at small-angle region for the polymer $\mathbf{L_1}$ and $\mathbf{L_2}$ exhibits complete destruction of ladder assembly **L′**.

D. Si NMR Investigation. As shown in Figure 3 and Table 4, ^{29}Si NMR measurement demonstrate that assembly **L′** gives a sharp resonance absorption peak of the moiety [$=SiO_{2/2}-$] with W_{hp} <1 ppm, meaning either the **L′** or **L** has the perfect ladder structure. Besides, the above-mentioned two comparative samples, $\mathbf{L_1}$ obtained through (**L′** + urea**)** and $\mathbf{L_2}$ through (**L′** + **HQ**), were examined. $\mathbf{L_1}$ displays two peaks: one weak peak **Si 2** at $\delta = -15$ ppm is assigned to the moiety $=Si(OH)O_{1/2}$ and the strong main peak **Si 1** for the moiety $=SiO_{2/2}-$ on the ladder chain. The **Si 1** becomes much wider ($W_{hp} = 5.4$ ppm). Moreover, the area of the peak **Si 1** almost is equal to the area of the **Si 2** peak, meaning $\mathbf{L_1}$ has not been a ladder polymer. Likewise, polymer $\mathbf{L_2}$ is similar to $\mathbf{L_1}$.

From the control experiment we can clearly notice the important role of ladder assembly **L′**, through which the perfect ladder polymer **L** is successfully synthesized.

Conclusion

A novel highly soluble and perfect 2,5-dipropyl- (hydro- and benzo-) quinone-bridge ladder polysiloxane (**L**) was synthesized successfully by means of **CT** and H-bonding interaction-based self-assembling template **L′** between monomer hydrolytes, $\mathbf{M_1'}$ and $\mathbf{M_2'}$. The presence of polymer **L** and particularly, ladder assembly **L′** was well confirmed by a combination of VPO, FT-IR, UV, FS, solution XRD, and ^{1}H NMR, ^{29}Si NMR, and DSC. Both the polymer **L** and ladder assembly **L′** possess perfect ladder structures.

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