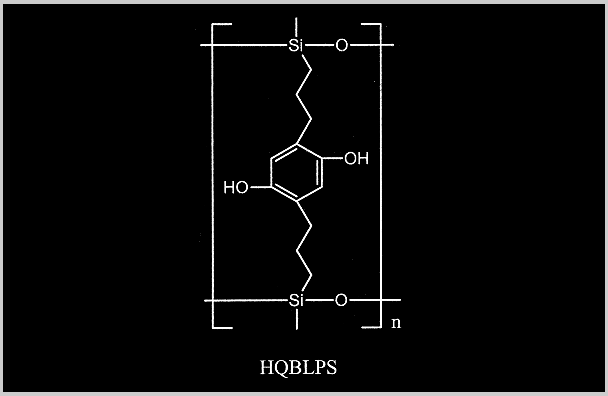
Communication: A novel 2,5-dipropylhydroquinone-bridged ladder-like polymethylsiloxane (HQBLPS) was successfully synthesized by means of a hydroquinone H-bonding self-assembling template in three main steps, including hydrosilylation coupling, hydrolysis and polycondensation. It is essential to strictly control the reaction conditions to bring the H-bonding template into full play throughout the whole synthetic process. The factors affecting stereoregularity and molecular weight of the HQBLPS are discussed.



Synthesis of a Novel 2,5-Dipropylhydroquinone-Bridged Ladder-Like Polymethylsiloxane Using a Hydroquinone H-Bonding Self-Assembling Template

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Introduction

Since Brown et al. reported the first ladder-like polyphenylsilsesquioxane in 1960,[1] this class of ladder-like polysiloxanes (LPS) has attracted world-wide attention, although Frye et al. queried the ladder-like structure.[2] Many efforts were focused on modifying the side chains to prepare a number of ladder-like polysilsesquioxanes with various inert or reactive groups via the Brown's *equilibration polymerization*[3] or the *stepwise coupling polymerization* put forward by our group.[4] Meanwhile, it can be anticipated that organo-bridged ladder-like polysiloxanes (OBLPSs) will have more potential applications than the siloxane-bridged polysiloxanes because the OBLPS microstructure and properties are relatively easy to control. As early as in the 1960s, Andrianov et al. tried to synthesize 1,4-phenylene-bridged LPSs, but only obtained oil-like oligomers or crosslinked gels instead of the desired ladder-like polymers[5] due to the deficiency of an effective template during the polymerization process. Encouragingly, a series of well-defined polymers including an organic nanotube polymer,[6] two-dimensional polymers,[7] etc. have been successfully prepared so far using the template technology. OBLPSs may thus be prepared by means of supramolecular template-aided synthesis. In fact, our group had already tried to prepare OBLPSs via π-π stacking and gained some positive results.[8] However, this π-π stacking interaction is relatively weak and resulted in low stereoregularities of the OBLPSs. Contrarily, H-bonding is a highly directional, medium-strength, reversible interaction. It is regarded as a favorite intermolecular force in self-assembling systems. In this article, we report the synthesis of a novel HQBLPS directed by hydroquinone H-bonding self-assembly.

Experimental Part

Materials

All the reagents and solvents were commercially available and of analytical grade. 3,4-Dihydropyran (DHP) was pur-

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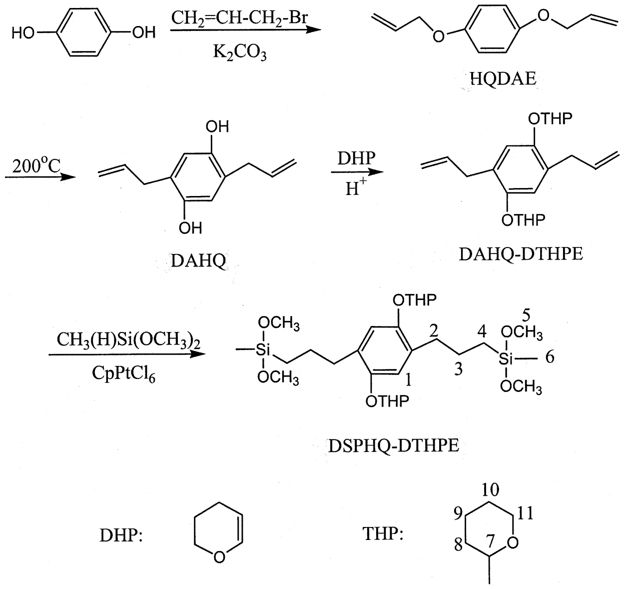
chased from Acros Company. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone. Dicyclopentadienylplatinum dichloride (Cp_2PtCl_2)[9] used as the hydrosilylation catalyst and pyridinium *p*-toluenesulfonate (PPTS)[10] used as the catalyst for protecting the phenol moieties were prepared according to procedures described in the literature.

Analytical Techniques

FT-IR spectra were recorded on a Bruker EQUINOX55 spectrometer. ^1H and ^{29}Si NMR spectra were obtained on a JNH-FX100 (JBOX) 300 MHz NMR spectrometer. Mass spectrometry (MS) measurements were carried out on an AEI MS-50 high resolution spectrometer using electron impact (EI). Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo Star-822 calorimeter at a heating rate of 20 °C/min. X-ray diffraction (XRD) analysis was measured on a Rigaku D/MAX 2400. Vapor pressure osmometry (VPO) measurements were carried out in THF at room temperature on a Knauer VPO instrument.

Synthesis of Monomer 2,5-Di[3-(dimethoxymethylsilyl)-propyl]hydroquinone Ditetrahydropyranyl Ether (DSPHQ-DTHPE)

The synthetic route toward DSPHQ-DTHPE is shown in Scheme 1. Hydroquinone diallyl ether (HQDAE) and 2,5-diallylhydroquinone (DAHQ) were prepared according to literature procedures.[11] DAHQ ditetrahydropyranyl ether (DAHQ-DTHPE) was prepared by protecting phenols with DHP: A solution of DAHQ (5.7 g, 30 mmol) and DHP (7.88 ml, 90 mmol) in CH_2Cl_2 (200 ml) containing catalyst PPTS (1.5 g, 6 mmol) was stirred for 8 h at 25 °C. The solution was then washed with 1 N aqueous NaOH to remove PPTS and unprotected phenol. After removal of the solvent, the residue was recrystallized from CH_3OH, giving 8.13 g (76%) of white crystals; m.p. 79.3 °C.



Scheme 1. Synthetic route toward monomer DSPHQ-DTHPE.

Monomer DSPHQ-DTHPE was prepared in a hydrosilylation reaction: A solution containing a trace of Cp_2PtCl_2, DAHQ-DTHPE (3.58 g, 0.01 mol), $CH_3HSi(OCH_3)_2$[12] (3.18 g, 0.03 mol) and 30 ml THF was stirred at 40 °C under argon for 36 h. After the volatile components were removed in vacuo, the DSPHQ-DTHPE was obtained in 98% yield as a colorless oil.

FT-IR (KBr): 1502 (Ph), 1086 (Si—O—C), 1258, 1411 cm^{-1} ($Si—CH_3$).

^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.88$ (s, 2H, H^1), 5.30 (m, 2H, H^7), 3.55–3.92 (m, 4H, H^{11}), 3.50 (s, 12H, H^5), 2.60 (m, 4H, H^2), 1.59–1.86 (m, 16H, H^3, H^8, H^9, H^{10}), 0.70 (m, 4H, H^4), 0.11 (s, 6H, H^6) (see Scheme 1 for proton assignments).

^{29}Si NMR (60 MHz, $CDCl_3$): $\delta = -3.8$.

MS (70 eV): *m/z = 572* (M^+).

Synthesis of Polymer HQBLPS

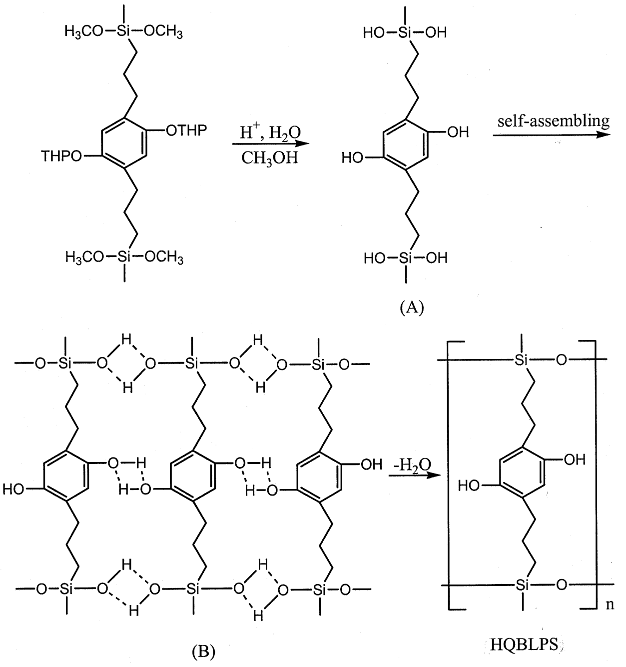
A mixture of 50 ml acetone, 10 ml methanol and 1 ml of a 10% aqueous HCl solution was added dropwise into a flask containing DSPHQ-DTHPE (5.70 g, 0.01 mol), 60 ml toluene and 10 ml diethylene glycol dimethyl ether (DEGDE) at 0 °C over 4 h. The solution was kept at room temperature for 10 h with stirring. Acetone and methanol were then removed and a drop of H_2SO_4 was added. Polycondensation was carried out at 40 °C in vacuo, and the water was removed by azeotropic distillation for 4 d during which about 30 ml of dry toluene were added in batches. After adding 30 ml of DEGDE, the system was concentrated to about 15 ml. After the dropwise addition of about 15 ml of H_2O, some precipitates appeared gradually, which were dried at 50 °C for 10 h, giving HQBLPS as a brown solid in 75% yield. The brown color arose from residual amounts of the Pt catalyst of hydrosilylation reaction.

Results and Discussion

Synthesis of Polymer HQBLPS

As the catalyst for the hydrosilylation reaction is also capable of catalyzing the silylation of phenolic oxygen atoms,[13] the phenol moieties had to be protected in advance. Many methods have been used for the protection of phenol moieties.[14] Here, DHP was chosen because it effectively protects phenols and can be readily removed under very mild conditions.[10,15] Monomer DSPHQ-DTHPE was thus successfully synthesized by the hydrosilylation reaction.

A proposed mechanism for the formation of HQBLPS is shown in Scheme 2. In the hydrolysis step, $Si—OCH_3$ groups were hydrolyzed to silanol groups (Si—OH) and the protective tetrahydropyranyl groups (THP) were eliminated in diluted solution, simultaneously resulting in the formation of intermediate tetrasilanol **A**, whose Si-OH groups can form stable square-planar H-bonds as suggested by Kakudo.[16] After acetone and methanol were slowly evaporated below 50 °C, a pre-organized ladder-like H-bonded aggregate **B** gradually formed via H-bonding interactions between the phenol groups or Si—OH



Scheme 2. Proposed synthetic route toward polymer HQBLPS.

groups themselves. Finally, aggregate **B** was further condensed to HQBLPS.

The hydroquinone H-bonding template obviously plays a key role in constructing the desired ladder-like structure. For this reason, special emphasis should be put on the following three factors: (i) *Concentration.* In order to bring the template effect of the phenol groups into full play, it is extremely important that all THP protecting groups are completely removed before silanol condensation occurs. The hydrolysis reaction of monomer DSPHQ-DTHPE thus must be carried out in very dilute solution to avoid silanol condensation without the hydroquinone H-bonding template. Besides, water must be added very slowly. (ii) *Medium.* H-bond interactions are generally decreased with increasing polarity of the media. However, thanks to the insolubility of intermediate **A** in nonpolar toluene, a suitable amount of polar DEGDME was added, although it may slightly weaken the template effect. (iii) *Catalyst.* Both acid and base can be used to catalyze the silanol condensation. In the present case, only acid (here: H_2SO_4) can be used, as the phenol groups could react with bases, resulting in the invalidity of the template effect. (iv) *Condensation temperature.* It is well known that H-bonding interactions become very weak at high temperature ($T > 50\,^\circ C$). If the temperature is too low, on the other hand, polycondensation reaction will proceed too slowly. So the temperature should be controlled in the range 30–50 °C.

In addition, in order to increase the molecular weight of HQBLPS, azeotropic distillation with toluene under reduced pressure was employed to remove any water just formed during polycondensation.

Characterization of Polymer HQBLPS

As shown in Table 1, a combination of FT-IR, ^1H and ^{29}Si NMR spectroscopy, XRD, DSC and VPO was used for the structural characterization of HQBLPS.

In the FT-IR spectrum, characteristic absorption bands of HQBLPS are observed at 1074 cm^{-1} (Si—O—Si), 1509 cm^{-1} ($—C_6H_2—$), 1423, 1259 cm^{-1} ($Si—CH_3$) and 3402 cm^{-1} (—OH). The ^1H NMR spectrum proves that the signals for THP and $Si—OCH_3$ groups disappeared. According to the ^{29}Si NMR spectrum (Figure 1), three types of Si atoms are present in the polymer. The major peak centered at $\delta = -21$ ppm and split into a doublet represents fully condensed Si atoms ($=Si^1(—O—)_2$) on the ladder-like skeleton. According to Mabry,[17] a chiral center can cause the splitting of a ^{29}Si NMR signal, which means that different stereo-configurations cause this splitting. Similarly, several different stereo-configurations (cis-isotactic, cis-syndiotactic, etc.) may coexist in ladder-like polymers, which probably is the main reason for the ^{29}Si NMR signal splitting. The minor peak at $\delta = -13$ ppm could be assigned to

Table 1. Characterization data of polymer HQBLPS.

Method	HQBLPS
Appearance	brown solid
Solubility	soluble in THF, acetone, ethanol, etc.
FT-IR (cm^{-1})	3402 (—OH), 1509 (Ph), 1423, 1259 ($Si—CH_3$), 1074 (Si—O—Si)
^1H NMR (δ, acetone-d_6)	6.58 ($—C_6H_2—$, 2H), 2.60 ($—C_6H_2—CH_2—$, 4H), 1.83 ($Si—CH_2—CH_2—$, 4H), 0.63 ($Si—CH_2—$, 4H); 0.08 ($Si—CH_3$, 6H)
^{29}Si NMR (δ, acetone-d_6)	–20 to –22 (major, $=Si^1(—O—)_2$), –13 (minor, $=Si^2(—OH)—O—$), –9 (minor, $=Si^3(OH)_2$)
δ (Å, XRD)	8.5, 4.9
T_g (°C, DSC)	84
$\bar{M}_n$ (Dalton, VPO)	11700
n (repeating units)	38

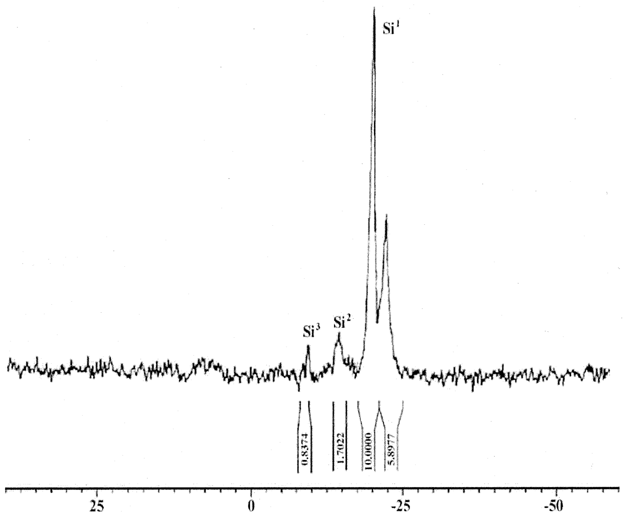


Figure 1. ^{29}Si NMR spectrum (60 MHz, acetone-d_6) of polymer HQBLPS.

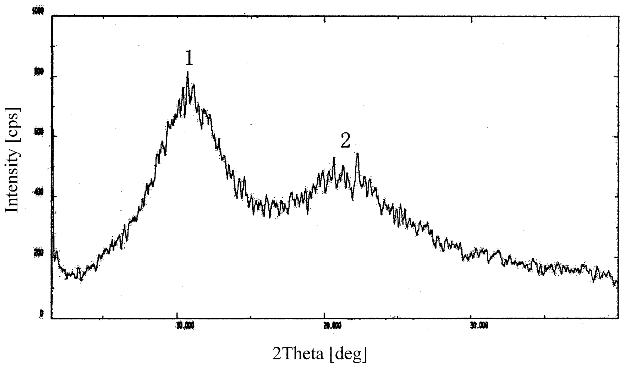


Figure 2. XRD pattern of polymer HQBLPS.

terminal silanol $=\mathrm{Si}^2(\mathrm{OH}){-}\mathrm{O}{-}$ rather than $\mathrm{Si}{-}\mathrm{OC}$ group. According to Noll,[18] we think that the condensation between acidic $\mathrm{Si}{-}\mathrm{OH}$ and $\mathrm{Ph}{-}\mathrm{OH}$ groups might be negligible, as the organosilanol groups in our system show great tendency to self-condense in the presence of H_2SO_4. This assignment is moreover consistent with the viewpoint of Williams,[19] who pointed out that the $=\mathrm{Si}(\mathrm{OH}){-}\mathrm{O}{-}$ chemical shift is $\delta = -13.9$ ppm when using acetone-d_6 as the solvent. The other minor peak at $d = -9$ ppm was attributed to terminal uncondensed silane-diol groups ($=\mathrm{Si}^3(\mathrm{OH})_2$) because two hydroxy groups lead to a downfield shift.

Figure 2 shows the XRD pattern of the polymer. According to the literature,[1, 20] the first halo appearing at 8.5 Å represents the intramolecular chain-to-chain distance in the ladder-like structure. However, this distance is shorter than that determined by molecular simulation (12.43 Å, using Chem 3D Ultra 6.0 software), which is probably due to the bending of the flexible $-(\mathrm{CH}_2)_3-$ chains of the organo-bridge. The second halo at 4.9 Å is more diffusing, which is regarded to be a result of the thickness of the ladder-like polymer.

The glass transition temperature (T_g) of ladder-like HQBLPS was determined by means of DSC to be 84 °C. It is much higher than that of single-chain polydimethylsiloxanes ($T_g \approx -120\,°\mathrm{C}$) thanks to its comparatively rigid ladder-like structure and to the H-bond interactions between the phenol-bridged groups.

HQBLPS is soluble in polar solvents due to its phenol and terminal silanol groups. The GPC method for determining the molecular weights of polymers is based on the volume-repulsion principle, using ball-like polystyrene as standards. As HQBLPS is a semi-rigid rod-like polymer, it is not suitable to determine its weight-average molecular weight ($\overline{M}_w$) by means of GPC. The number-average molecular weight ($\overline{M}_n$) of HQBLPS is about 11700 Dalton, as determined using the VPO method, which corresponds to about 38 repeating units.

Based on the characterization data detailed above, it is reasonable to conclude that HQBLPS possesses the expected ladder-like structure.

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