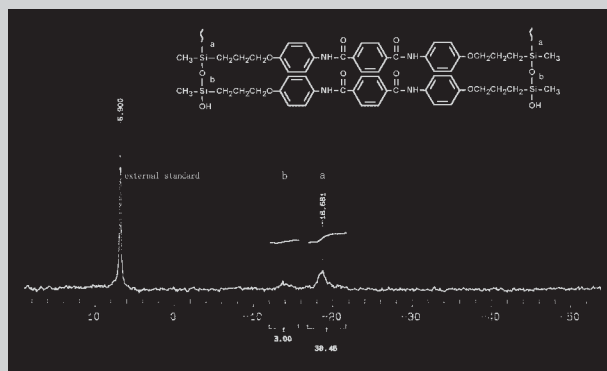**Full Paper:** A novel stereo-regular organo-bridged ladder-like polymethylsiloxane (**LPMS**) was synthesized by a stepwise coupling polymerization on the basis of an amido H-bonding-assisted self-assembling template. The monomer *N,N′*-bis{4-[3-(diethoxymethylsilyl)propoxy]-phenyl}ter-ephthalamide (**M**), prepared by hydrosilylation reaction at high temperature, was hydrolyzed in a dilute solution at a low temperature to form a ladder-like supramolecular intermedi-ate through amido H-bonding interactions, which was further condensed to form the polymer **LPMS**. A combination of techniques including ^{1}H NMR, ^{29}Si NMR, and FT-IR spec-troscopies X-ray diffraction (XRD), and differential scanning calorimetry (DSC) were used to characterize the titled polymer **LPMS**, and the results indicate that the polymer possesses an ordered ladder-like structure.

^{29}Si NMR spectrum of the polymer **LPMS**.

Hydrogen-Bonding-Directed Template Synthesis of Novel Stereo-Regular Organo-Bridged Ladder-Like Polymethylsiloxane

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Introduction

Ladder-like polysiloxane has attracted much attention from chemists around the world for many years because of its unique double-chain structure, good film-forming ability, excellent thermal stability, and ideal mechanical properties. In general, ladder-like polysiloxanes are divided into two categories: oxygen-bridged polysiloxane (i.e., polysilses-quioxane) and organo-bridged polysiloxane. Brown et al.[1] first reported the synthesis of soluble ladder-like poly-phenylsilsesquioxane (Ph-T) via "equilibration polymer-ization" in 1960. However, its structure was disputed eleven years later by Frye and Klosowski[2] because of the presence of many defects such as branches and cyclics in the polymer. They pointed out that Ph-T is not really a ladder-like polymer, but is actually a "partially opened polycyclic cage". A probable reason is that the reaction intermediate (phenylsilanetriol) and its derivatives pro-duced in the synthetic process may form some randomly

interlaced aggregates rather than ladder-like ones because of the absence of template assistance. On the other hand, in comparison with the polysilsesquioxane, the organo-bridg-ed polysiloxane usually possesses better compatibility with commercial polymers and improved mechanical properties, and thus has more potential applications. In fact, as early as 1960, Andrianov et al.[3] attempted to synthesize 1,4-phenylene-bridged polymethylsiloxane, but unfortunately obtained insoluble cross-linked gels because of similar reasons to Brown et al. The intermediate, *Si,Si′*-dimethyl-benzenebissilane-1,4-diol, forms interlaced aggregates instead of ladder-like ones and results in gelation because the reaction temperature used ($\approx$100 °C) is so high that the template effect ($\pi-\pi$ interactions) are entirely destroyed. It is obvious that multifunctional monomers (e.g., phenylsilane-triol) are usually prone to forming irregular cross-linked polymers. Only with strong template interactions can the silanols be aligned to form ordered ladder-like structures, and only then can the ladder-like polysiloxanes be obtained.

In recent years, the synthesis of microstructure-controlled polymers through weak interactions (such as H-bonding, $\pi-\pi$ interactions, etc.) based on templated self-assembly has greatly intensified. For example, Harata et al.[4] first synthesized a polymeric hollow nanotube of cyclodextrins by linking neighboring cyclodextrins pre-threaded with a poly(ethene glycol) chain through H-bonding and van der Waals interactions. Stupp et al.[5] reported the synthesis of two-dimensional polymers based on homochiral and $\pi-\pi$ overlapping interactions. Enlightened by these studies, our group developed a novel H-bonding templating method called stepwise coupling polymerization (SCP) to synthesize ladder-like polysiloxanes.[6] It involves preaminolysis of trichlorosilane with p-phenylenediamine to form ladder-like H-bonding-assembled intermediates, followed by hydrolysis and a polycondensation process. By this method, a series of ladder-like polysilsesquioxanes $(RSiO_{3/2})_n$ (R = alkyl, aryl, allyl, vinyl, amino, and so on) have been synthesized.[7] Recently, we also prepared a series of ladder-like organo-bridged polysiloxanes including phenylene-bridged polysiloxane and its mesomorphic polymers,[8,9] and diphenyl ether-bridged polysiloxane as well as aryl ester-bridged ladder-like polysiloxane via $\pi-\pi$ interaction templated synthesis[10,11] However, the structural regularity of these polymers is still limited because of the weak template effect caused by the fragile Si–N linkage and weak H-bonding of N–H···N between phenylenediamine molecules in the former case or the weak $\pi-\pi$ template interactions in the latter. Obviously, efficient templates with stronger secondary interactions are highly desired for preparing structurally well-controlled ladder-like polysiloxanes.

It is well known that the amido H-bonding (N–H···O=C) existing in natural peptide, protein, or synthetic polyamide is very strong and stable. For example, poly(terephthaloyl p-phenylenediamine) can form lyotropic liquid crystals in concentrated sulfuric acid or N-methylpyrrolidone (NMP), and can be further spun into high-strength fibers (Kevlar). Many 1-, 2- and 3-dimensional supramolecular arrays aggregated through amido H-bonds have been reported.[12] Herein, we report the design and preparation of a new template, N,N'-bis(4-allyloxyphenyl)terephthalamide (**T**), which possesses much stronger intermolecular amido H-bonding than our earlier templates, and its use as a powerful template to synthesize regular ladder-like organo-bridged polysiloxanes.

Experimental Part

Materials

All the reagents and solvents were commercially available and of analytical grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone. Methyldiethoxysilane and N-methylpyrrolidone were dried with zeolite overnight and distilled

twice prior to use. The catalyst, dicyclopentadienylplatinum dichloride (Cp_2PtCl_2), was prepared according to a literature method.[13] Other reagents were used as received.

Techniques

The X-ray diffraction (XRD) analysis was recorded on a Rigaku D/MAX 2400 diffractometer. ^1H NMR and ^{29}Si NMR analyses were carried out on a Varian Unity 200 (U.S.A.) operating at 200 MHz, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. Chemical shifts (δ) were reported in ppm, referenced to tetramethylsilane (TMS, 0 ppm) as an internal standard for ^1H NMR measurements, and to hexamethyldisiloxane (MM, 6.9 ppm) as an external standard for ^{29}Si NMR measurements. Chromium acetylacetonate was used as a relaxation reagent for ^{29}Si NMR analyses. The FT-IR measurement was performed with a Perking Elmer 80 spectrometer. Differential scanning calorimetry (DSC) analysis was performed on a Mettler Toledo Star-822 differential scanning calorimeter. Mass spectrometry (MS) measurements were carried out on a BIFLEX III MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometer (Bruker Analytical System, Inc) utilizing a 5-chlorosalicylic acid matrix which contains sodium ions. Elemental analysis was performed with a Heraeus CHN-RAPID DATEL System, Inc (West Germany). The molecular weight was determined by light scattering (LS) methods using a DLS-700 (Otsuka Electronic Co. Ltd.) apparatus equipped with a He–Ne laser source (10 mW, $\lambda = 632.8$ nm). The details of the light scattering instrumentation were described elsewhere.[14] All samples were carefully fractionated by precipitation of the polymer from an NMP solution with methanol, and further purified by reprecipitation from dimethyl sulfoxide solution with methanol in order that the molecular weight distribution was narrowly dispersed. Dusts and other impurities were removed by pressure filtration (Millipore 0.2-μm microfilter). Measurements of differential refractive index increment (dn/dc) were made with a RM-102 (Otsuka Electronic Co. Ltd.) differential refractometer operating at a wavelength of $\lambda = 632.8$ nm. A value of dn/d$c = 0.086$ was determined.

Synthesis of Template Agent
N,N'-Bis(4-allyloxyphenyl)terephthalamide (**T**)

The synthetic route to template agent **T** is shown in Scheme 1. To a 250-ml flask were added 5.4 ml (40 mmol) of triethylamine, 100 ml of THF, and 4.36 g (40 mmol) of p-aminophenol. CHCl$_3$ (50 ml) containing 4.06 g (20 mmol) of terephthaloyl dichloride was added dropwise into the flask with vigorous stirring. The reaction mixture was filtered to remove THF and CHCl$_3$. The filter cake was washed with a large amount of water and recrystallized from DMSO to get 6.23 g of intermediate (N,N'-bis(4-hydroxyphenyl)terephthalamide). A mixture of 3.48 g (10 mmol) of the intermediate, 100 ml of absolute methanol, 2.0 ml (22 mmol) of allyl bromide, and 6.07 g (22 mmol) of potassium carbonate was refluxed for 12 h with vigorous stirring. Water was then added to dissolve the inorganic salts. The mixture was filtered and the filter cake was recrystallized from DMSO twice to obtain white crystals of
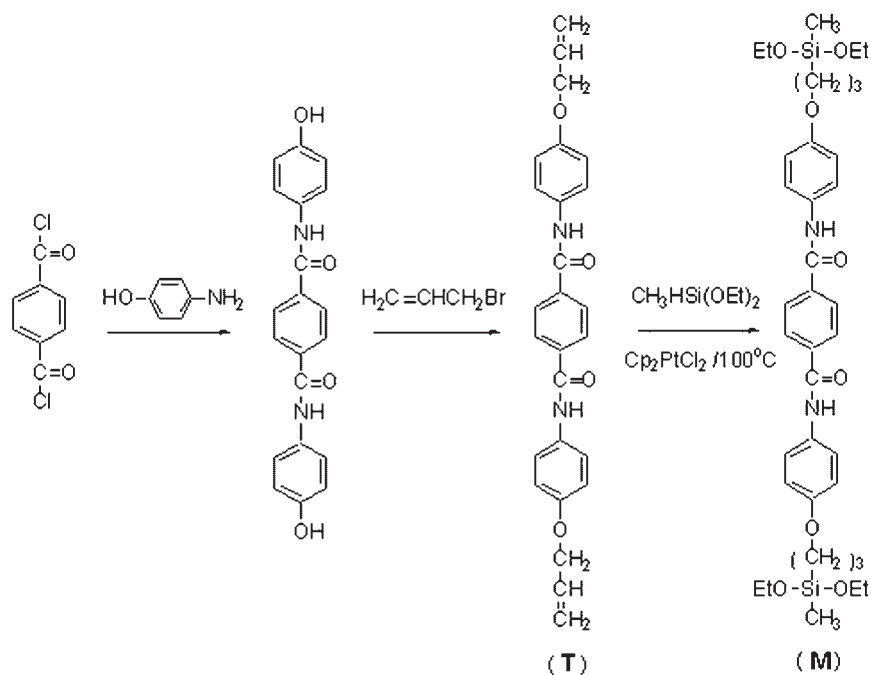
Scheme 1.   Synthetic route to the template agent **T** and monomer **M**.

N,N'-bis(4-allyloxyphenyl)terephthalamide (**T**) in 72% yield. Melting point: 347.6 °C.

^{1}H NMR (DMSO-d_6): $\delta = 10.28$ (s, 2H, N$\underline{H}$), 8.06 (s, 4H, NHCOC$_6\underline{H}_4$CONH), 6.94, 7.68 (d, d, 4H, 4H, C$_6\underline{H}_4$OH, $J = 2.8$ Hz), 6.03 (m, 2H, CH$_2$=C$\underline{H}$), 5.22 (q, 4H, C$\underline{H}_2$=CH), 4.55 (d, 4H, OC$\underline{H}_2$).

FT-IR (KBr): 3 318 (s, vN–H), 1 640 (vs, vC=O), 1 597 (vC=C$_{arom}$), 1 247 (s, vC–O–C$_6$H$_4$), 818 cm^{-1} (γC–H$_{arom}$).

Synthesis of Monomer N,N′-Bis{4-[3-(diethoxymethylsilyl) Propoxy]-Phenyl}terephthalamide (M)

To a 100-ml Schlenk flask were added 4.28 g (10 mmol) of templating agent **T** and 5 mg of catalyst Cp$_2$PtCl$_2$. The reaction system was evacuated and refilled with argon three times. Under the argon atmosphere, 100 ml of NMP was injected into the flask through a syringe. After **T** was dissolved completely, 3.4 ml (22 mmol) of methyldiethoxysilane was also injected into the system. The reaction solution was stirred at 100 °C

for 24 h. Then after NMP and residual methyldiethoxysilane were distilled out under reduced pressure, a white waxy solid of monomer **M** was obtained in 97% yield. The detailed characterization data for monomer **M** are given in Table 1.

Synthesis of {N,N′-Bis[4-propyloxylphenyl]terephthalamide}-Bridged Ladder-Like Polymethylsiloxane (LPMS)

Monomer **M** (3.5 g, 5 mmol) was dissolved in 25 ml of NMP. A mixed solution of 0.45 ml (25 mmol) of water and 25 ml of NMP was added dropwise into the monomer solution in an ice-water bath. The reaction mixture was stirred at room temperature for several hours and was gradually warmed to 50 °C for another 12 h. Three drops of concentrated H$_2$SO$_4$ were then added to the mixture to catalyze the condensation reaction. The system was stirred at 50 °C for 100 h and continuously evacuated (by vacuum) to remove any water produced from the condensation reaction. Occasionally, small amounts of gel

Table 1.   Characterization data of monomer **M**.

Item of characterization	Results
Appearance	white or yellowish waxy solid
Solubility	soluble in polar solvents such as DMSO, NMP, etc.
FT-IR (KBr)	3 313(s, vN–H), 2 973 (vCH$_3$), 1 640(vs, vC=O), 1 598 (vC=C$_{arom}$), 1 248 (s, vC–O–C$_6$H$_4$), 1 107, 1 079 (vSi–OEt), 951 (vSi–C), 824 cm^{-1} (γC–H$_{arom}$)
^{1}H NMR (DMSO-d_6)	$\delta = 10.28$ (s, 2H, NH), 8.05 (s, 4H, NHCOC$_6\underline{H}_4$CONH), 6.88, 7.64 (d, d, 4H, 4H, C$_6\underline{H}_4$OH, $J = 2.7$ Hz), 3.93 (t, 4H, C$_6$H$_4$OC$\underline{H}_2$), 3.75 (q, 8H, OC$\underline{H}_2$CH$_3$), 1.75 (m, 4H, SiCH$_2$C$\underline{H}_2$), 1.14 (t, 12H, OCH$_2$C$\underline{H}_3$), 0.68 (t, 4H, SiC$\underline{H}_2$), 0.09 (s, 6H, SiC$\underline{H}_3$)
^{29}Si NMR (DMSO-d_6)	$\delta = -4.694$, CH$_3$(OEt)$_2\underline{Si}$CH$_2$
MALDI-TOF	C$_{36}$H$_{52}$N$_2$O$_8$Si$_2$ (M$^+$): Calcd. 696.3; Found [M+Na]$^+$, 719.2
Elemental analysis	C$_{36}$H$_{52}$N$_2$O$_8$Si$_2$ (696.3): Calcd. C 62.04, H 7.52, N 4.02; Found C 61.89, H 7.24, N 4.15

would appear during the condensation process, which were removed by filtering. Methanol (10 ml) was then added dropwise into the filtrate and a white deposit slowly appeared, which was collected and dried in a vacuum oven below 50 °C for 72 h to finally obtain the product, polymer **LPMS**, as a white solid in 66% yield.

Results and Discussion

### Molecular Design of the Template Agent **T**

It is noteworthy that in the synthesis of polymer **LPMS** by stepwise coupling polymerization (SCP), as shown in Scheme 2, the key point is how to bring the template effect of **T** into full play. The first step in the SCP process is the hydrolysis of monomer **M**, prepared by the hydrosilylation reaction of template **T** with methyldiethoxysilane, to form intermediate **1**. The intermediate molecules may self-assemble side by side through the interaction of amido H-bonding (C=O···N–H) and silanol H-bonding (H···O–H) of the **T**-bridged spacer to form an ordered ladder-like aligned array **2**. Then, via a dehydration condensation reaction, an oligomer is formed and further condensed into an ordered ladder-like polymethylsiloxane (**LPMS**). Apparently, the formation of highly regulated polymer **LPMS** requires an efficient template effect of the bridging **T** units. The stronger the H-bonding between the intermediates, the more regular a structure the polymer has. In addition, to make the neighboring intermediate stand side by side, it is necessary

to link the two Si atoms with a stiff bridging unit rather than a flexible one. Accordingly, the use of *N,N′*-bis(4-allyl-oxyphenyl)terephthalamide, a stiff and rigid aryl amide molecule with very strong intermolecular amido H-bonding (C=O···N–H), would allow the formation of highly regular ladder-like organo-bridged polymethylsiloxane polymers.

Synthesis and Characterization of the Monomer **M**

Monomer **M** was synthesized via the hydrosilylation reaction of template **T** with methyldiethoxysilane. It is known that amido groups can retard the hydrosilylation reaction because of the slight poisoning of Cp_2PtCl_2 catalyst via coordination.[15] Thus the hydrosilylation reaction should be conducted at higher temperature (100 °C) to destroy this coordination, and consequently the monomer **M** can be obtained in a very high yield (97%).

Generally, the regularity of ladder-like polysiloxanes is strongly affected by the purity of monomers and the reaction conditions. The purer the monomer, the more regular a structure the polysiloxane has. It can be seen from the ^{1}H NMR spectrum of monomer **M** (Figure 1) that the hydro-silylation of **T** with methyldiethoxysilane leads to the selective formation of a β-adduct. No α-adduct is formed, possibly because of the use of the polar solvent NMP and the much higher steric hindrance of $CH_3Si(OEt)_2^-$ in the formation of α-adduct than β-adduct.[16] It can also be concluded from ^{29}Si NMR measurements (Table 1) that
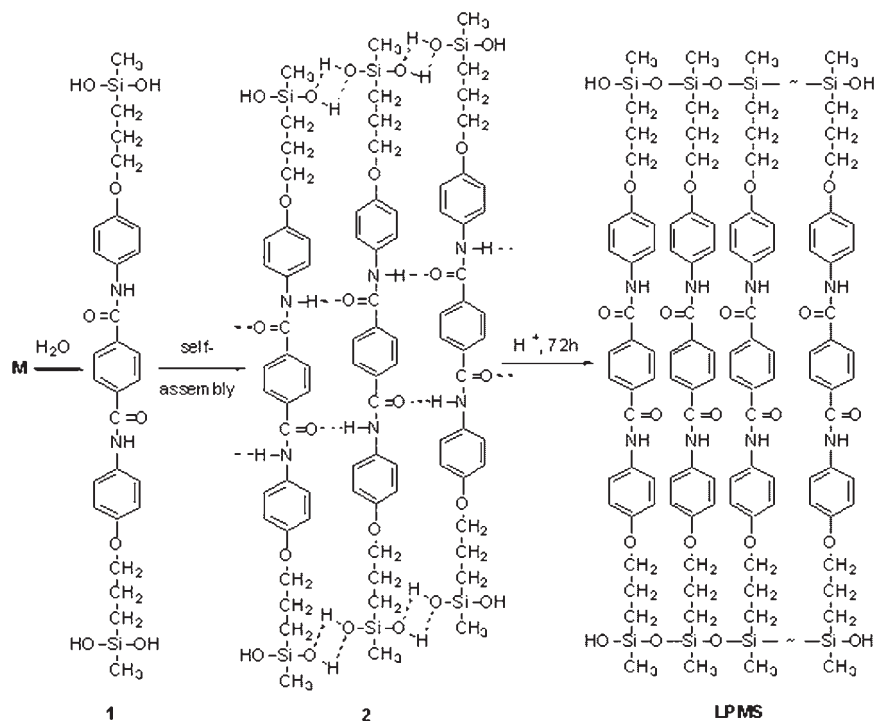
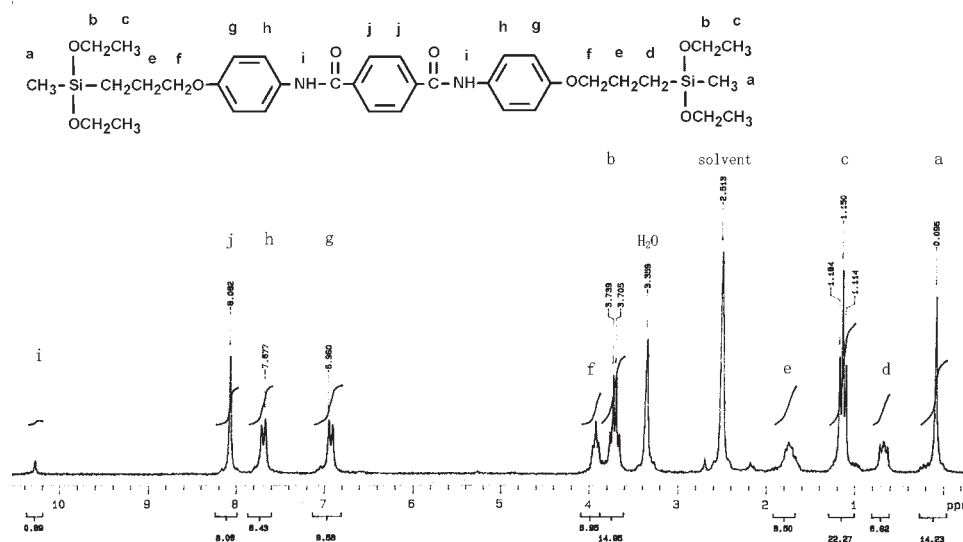Scheme 2. A proposed mechanism for the synthesis of polymer **LPMS**.

Figure 1. ^{1}H NMR spectrum of the monomer **M**.

except for the β-adduct $CH_3(OEt)_2\underline{Si}CH_2CH_2^-$ ($\delta = -4.694$ ppm), no α-adduct or any other impurities are produced in the hydrosilylation reaction. Similar conclusions can also be obtained from the FT-IR spectrum, MALDI-TOF measurementm and elemental analysis of monomer **M** (Table 1). In summary, it is demonstrated by the ^{1}H NMR, ^{29}Si NMR, FT-IR, MALDI-TOF, and elemental analyses that the monomer **M** prepared by the hydrosilylation reaction is the expected pure compound.

Synthesis of the Titled Polymer **LPMS**

A proposed mechanism for the formation of polymer **LPMS** is shown in Scheme 2. It should be emphasized that it is most important to ensure the H-bonding template is brought into full play throughout the synthetic process. Thus, in the first step, water was added very slowly at a low temperature to gradually hydrolyze the monomer **M**, resulting in the formation of intermediate **1**. The silanols ($\equiv$Si–OH) of intermediate **1** could form stable square-planar H-bonded arrays suggested by Kakudo and co-workers.[17] Thus, under the strong H-bonding interactions of C=O···H–N and O–H···O, a speculative extended-ladder-like H-bonded supramolecular aggregate **2** may form from the tetrasilanol **1**. The ladder-like aggregate **2** was then gradually condensed using concentrated H_2SO_4 as catalyst to form a ladder-like oligomer, which was further condensed to the ladder-like polymer **LPMS**. The polymer solution was treated with methanol as precipitating agent to obtain a yellow solid polymer, which was redissolved in DMSO and further purified by reprecipitation with methanol to obtain a white or yellowish polymer **LPMS**. Some reaction conditions affecting the regularity of polymer **LPMS** are discussed below.

Effect of Temperature on the Synthesis of Polymer **LPMS**

It is found that the regularity of polysiloxanes is strongly affected by the reaction temperature. If the hydrolysis is carried out at a high temperature ($T > 60$ °C) or water is added too rapidly, a lot of insoluble gels immediately emerge. The reason for this is that H-bonding interactions are broken at high temperature, resulting in the destruction of the ladder-like aggregate and the formation of irregular interlaced tetrasilanols. The latter are rapidly and randomly condensed at high temperature to produce insoluble three-dimensional network gels. Apparently, insoluble gels will also be generated if the condensation is conducted at too high a temperature for the same reason. Therefore, it is necessary to strictly control the reaction temperature to guarantee the H-bonding template effect throughout the whole synthetic process.

Effect of Catalyst on the Synthesis of Polymer **LPMS**

It is well known that the polycondensation reaction of silanols can be promoted in the presence of acid or base as catalyst. To prevent amide groups from decomposition, and H-bondings from being broken by base, sulfuric acid is preferred. Moreover, the acidic catalyst has a stronger condensing ability than the basic one for the silanols having electro-donating groups. Since the polycondensation reaction is a balance between monomer and polymer, the side-product of the condensation reaction, water, must be removed timely from the reaction system in order to obtain high molecular weight polymer. Therefore, the reaction mixture was continuously stirred and evaporated under reduced pressure to increase the molecular weight of polymer **LPMS**.

Effect of Medium Polarity on the Synthesis of Polymer **LPMS**

To maintain a good H-bonding templated effect, a non-polar solvent is usually recommended for the reaction. However, these solvents normally have a very poor solvating power for the reactive intermediates and the final polymer **LPMS**. Therefore, a suitable solvent needs to have a good balance between polarity and solvency. Here, a polar aprotic solvent *N*-methylpyrrolidone (NMP) was chosen based on the above-mentioned considerations, even though the **LPMS** would be yellowed because of the slight oxygenation of the NMP in atmosphere.

Characterization of the Polymer **LPMS**

A variety of characterization techniques including ^{1}H NMR, ^{29}Si NMR, and FT-IR spectrometries, XRD, LS, and DSC were used for the structural determination of polymer **LPMS**.

As shown in the ^{1}H NMR spectrum of polymer **LPMS** (Figure 2), No peak assignable to an –OCH$_2$CH$_3$ group ($\delta = 3.75, 1.14$) is observed, suggesting that the monomer **M** has been completely hydrolyzed. The widened hump-like peaks of the aromatic hydrogens and other groups, arising from the high viscosity of the **LPMS** in deuterated DMSO, implies that the monomer has been condensed into a relatively high molecular weight polymer. Unfortunately, the coupling constants are not observed because of the limit of the NMR instrument used.

It can be seen from the FT-IR spectrum of polymer **LPMS** (Figure 3) that, instead of two absorption peaks (1 107 and 1 079 cm^{-1}) assigned to the vibration of Si–OEt (Table 1), a very strong and broad adsorption between 1 010

and 1 180 cm^{-1}, corresponding to the stretching vibration of Si–O–Si, is observed indicating that the monomer has been hydrolyzed and condensed into a high molecular weight polymer containing Si–O–Si bonds.

It is well known that ^{29}Si NMR spectroscopy is one of the most powerful tools to characterize the structure of organosilicon polymers. Generally, there are three groups (D^0, D^1, and D^2) of distinct peaks for silicon atoms with different degrees of condensation in the ^{29}Si NMR spectrum.[18] A D^0 peak represents an uncondensed silicon atom with two hydroxyl groups =Si(OH)$_2$. A D^1 peak represents a partially condensed silicon atom with one siloxane bond and one hydroxyl substituent =Si(–O–)OH. A D^2 peak represents a fully condensed silicon atom with two siloxane bonds =Si(–O–)$_2$. It is shown in Figure 4 that there are two kinds of silicon atom (D^1 and D^2) in the polymer **LPMS**. The first peak (D^1) at $\delta = -13.88$ ppm is assigned to the terminal silicon atom of a ladder-like chain (CH$_3$)(–CH$_2$)SiOH(–O–). Another major resonance (D^2) at $\delta = -18.681$ ppm represents the internal silicon atoms CH$_3$(–CH$_2$)Si(–O–)$_2$ located at the backbone of the polymer **LPMS**. No monomer silicon atoms [=Si(OEt)$_2$] or D^0 peaks [=Si(OH)$_2$] are found in the spectrum. This result is consistent with the expected ladder-like structure of **LPMS** and also indicates that the monomer **M** is fully hydrolyzed and condensed into a high molecular weight polymer. It is noteworthy that according to Mabry and Weber,[19] a chiral center can cause a ^{29}Si NMR signal to split, which means that different stereo-configurations can result in a splitting or widening of a resonance peak. Similarly, several different stereo-configurations (*cis*-isotactic or *cis*-syndiotactic and so on) perhaps coexist in the titled ladder-like polymer **LPMS**, which is probably the main reason for the signal widening of the major D^2 peak at $\delta = -18.681$ ppm.
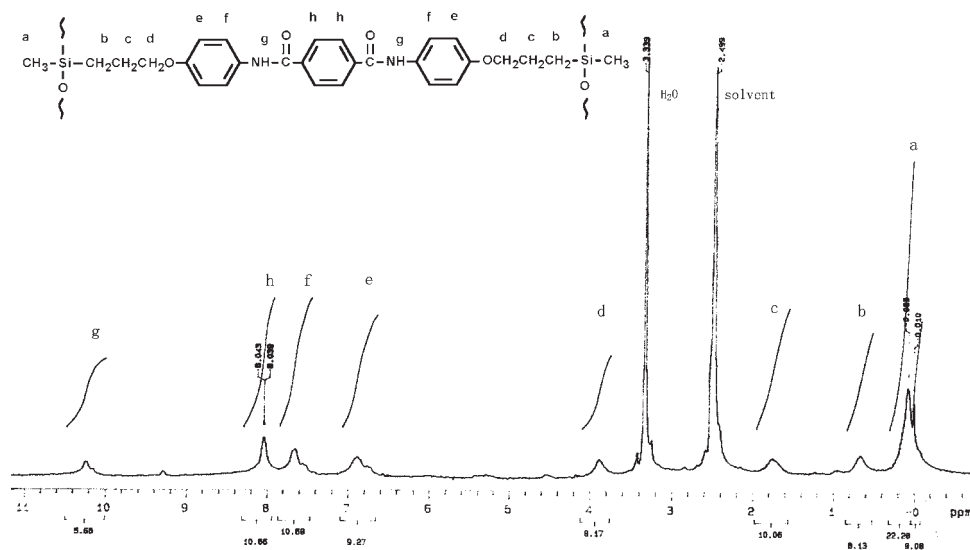

Figure 2. ^{1}H NMR spectrum of the polymer **LPMS**.
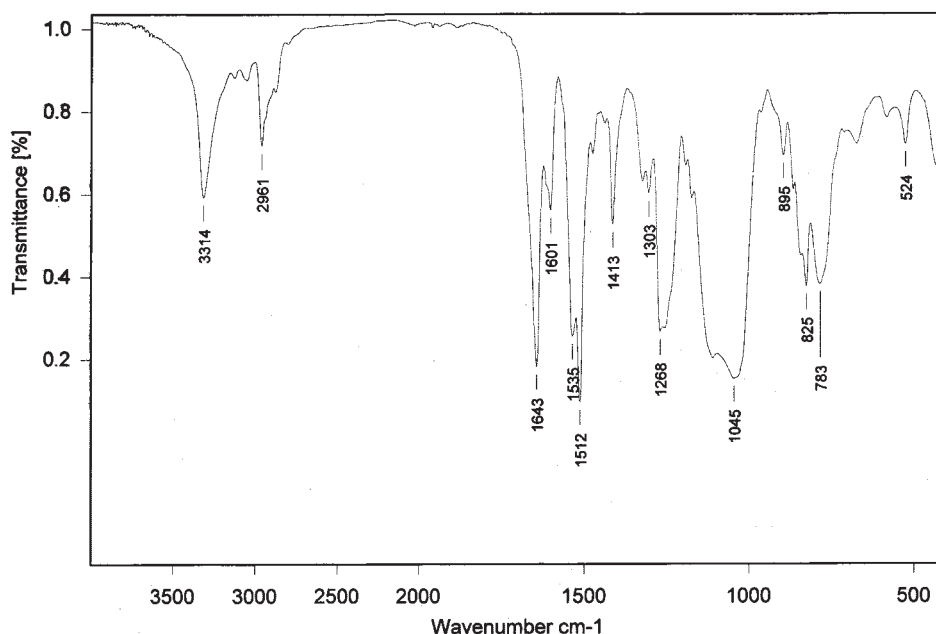
Figure 3. FT-IR spectrum of the polymer **LPMS**.

There are two distinct peaks in the XRD spectrum of polymer **LPMS** as shown in Figure 5. Referring to Brown et al.[1], Andrianov et al.[3], and Shi et al.[20], the first peak ($2\theta_1 = 3.36°$, $d_1 = 2.62$ nm) representing the intramolecular chain-to-chain distance (2.60 nm, simulated by Alchemy 2000) of **LPMS** is narrow and sharp, implying that the polymer has a relatively rigid skeleton and possesses a highly regular structure. The second diffusing peak ($2\theta_2 \approx 19.6°$, $d_2 = 0.45$ nm) is more complicated and possibly stands for the thickness of the macromolecular chain or the intermolecular space between polymer chains.

It is well known that glass transition temperatures (T_g) can be used to evaluate the flexibility of macromolecular chains. In contrast to the common flexible single-chained polymethylsiloxane which has a very low T_g (e.g., the T_g of poly(dimethylsiloxane) is below $-100\,°C$), the T_g of polymer **LPMS** is as high as $280.7\,°C$ (Figure 6), clearly suggesting that the polymer **LPMS** has a relatively stiff backbone. A possible explanation for this discrepancy is that polymer **LPMS** has a unique double-chain structure and rigid ladder-rungs with strong H-bonding interactions, which remarkably restricts the internal rotation of the
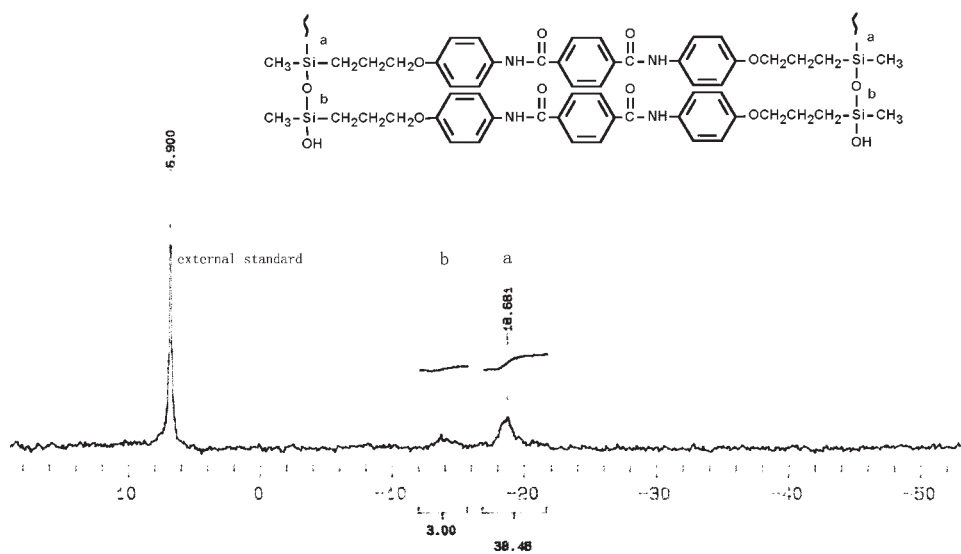
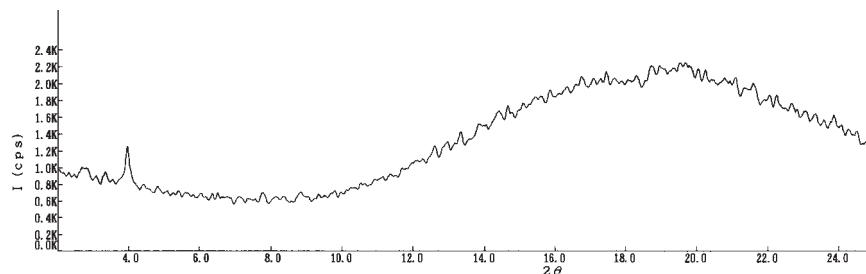

Figure 4. ^{29}Si NMR spectrum of the polymer **LPMS**.
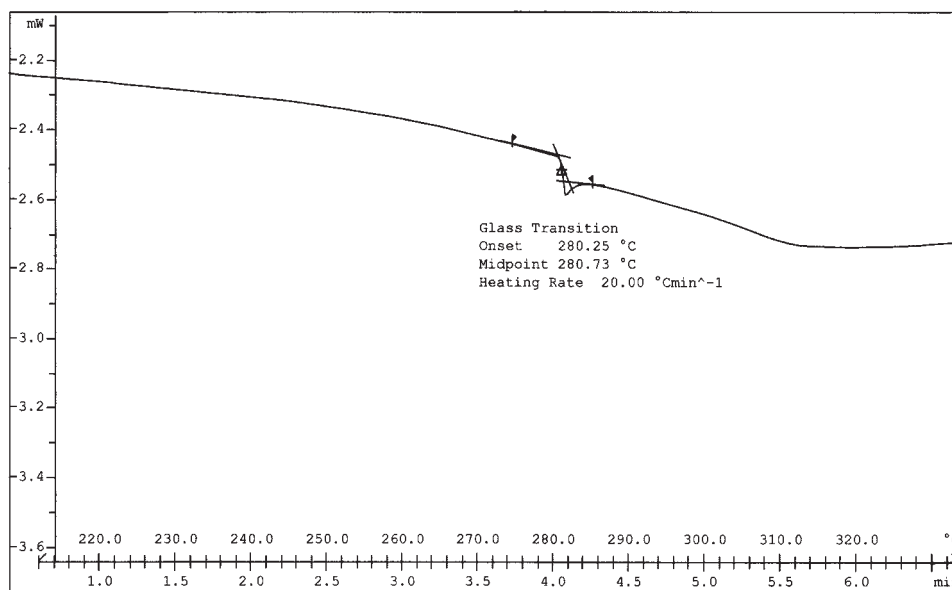
Figure 5.   XRD pattern of the polymer **LPMS**.

Figure 6.   DSC curve of the polymer **LMPS**.

Si–O–Si bonds and the segment mobility of polymer **LPMS**.

The molecular weight of polymer **LPMS** was measured by light scattering instead of gel permeation chromatography (GPC) since GPC measurements are based on the size exclusion principle usually using single-chained polystyrene as a standard, a poor reference for polymer **LPMS** which possess a semi-rigid double-chain structure. The weight-averaged molecular weight ($\overline{M}_w$) of polymer **LPMS** is 2.1×10^5 g·mol^{-1} with a polydispersity index (calculated by Judith's method[21]) of about 1.27.

Conclusion

A novel soluble, high-molecular-weight organo-bridged ladder-like polymethylsiloxane (**LPMS**), was prepared by a H-bonding-based self-assembly template through a stepwise coupling reaction. The polymer was characterized by a combination of FT-IR, ^{1}H NMR, and ^{29}Si NMR spectroscopies, XRD, LS, and DSC. The results show that the polymer possesses a semi-rigid, highly ordered ladder-like structure. This H-bonding-assisted synthetic method is likely used to prepare other kinds of ladder-like polysiloxanes.

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