

## H-bonding assisted template synthesis of a novel ladder-like organo-bridged polymethylsiloxane

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### Abstract

A novel soluble aryl amide-bridged ladder-like polymethylsiloxane (ALPS) was synthesized via a stepwise coupling polymerization by means of H-bonding self-assembling template. The new monomer *N,N'*-di(4-methyldiethoxyl-phenyl)-terephthaloyl amide, prepared by dehydrocoupling reaction of *N,N'*-di(4-hydroxy-phenyl)-terephthaloyl amide with methyldiethoxysilane, was hydrolyzed in a dilute solution at low temperature to form a proposed ladder-like supramolecular intermediate through amido H-bonding interaction, which was further condensed to form polymer ALPS using dibutyltindilaurate as catalyst. A combination of techniques including <sup>1</sup>H NMR, <sup>29</sup>Si NMR, FTIR, X-ray diffraction (XRD), DSC, and light scattering were used to characterize the titled polymer ALPS. The results indicate the polymer ALPS possesses an ordered ladder-like architecture.

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**Keywords:** H-bonding assembly; Template synthesis; Ladder-like polymers

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### 1. Introduction

The preparation of one or two dimensional organosilicon polymers with well-controlled architectures is a great challenge in organosilicon polymer chemistry. Historically, the first ladder-like polysilsesquioxane, a polyphenylsilsesquioxane (Ph-T) for being specific, was reported by Brown et al. in 1960 [1]. Its ladder-like structure, however, was disputed eleven years later by Frye and Klosowski because of the presence of many defects such as branches and cyclics in the polymer [2]. They concluded from their study that the so called ‘Ph-T’ is actually ‘partially opened polycyclic cages’. It was believed that the reactive intermediate (phenylsilanetriol) produced in the early synthetic process forms some randomly interlaced aggregates rather than ordered ladder-like ones due to the absence of template assistance.

In comparison with polysilsesquioxane, the organo-bridged ladder-like polysiloxanes are relatively easier to make, and their properties (such as chemical affinity, solubility and compatibility with other commercial polymers) can be controlled and fine tuned by varying the bridge moieties with different functional groups. In fact, as early as in 1960, Andrianov et al. [3] have attempted to synthesize 1,4-phenylene-bridged polymethylsiloxane, but only obtained some insoluble gels instead of the desired ladder-like polymers because the reaction temperature (~100 °C) used is so high that the π–π interaction template between bridged phenylene groups are entirely destroyed.

Template synthesis of microstructure-controlled polymers through weak interactions (e.g., H-bonding, π–π interaction and van der Waals force) has recently attracted much attention. Harata et al. [4] synthesized a polymeric hollow nanotube of cyclodextrins by linking neighboring cyclodextrins pre-threaded with poly(ethene glycol) (PEG) chain through H-bonding and van der Waals interactions. Stupp et al. [5] reported the synthesis of two-dimensional planar polymers based on homochiral and π–π overlap

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interactions. Moreau et al. [6] prepared a long-range ordered lamellar hybrid silica by amido H-bonding self-assembly.

In this context, we further developed a H-bonding tempting strategy called stepwise coupling polymerization (SCP) [7] to prepare ladder-like polysiloxanes. The pre-aminolysis method, one kind of SCP, involves a coupling reaction of trichlorosilane with 1,4-phenylenediamine to form coupled intermediates, capable of auto-association to ladder-like superstructure through N–H···N hydrogen bonding, followed by hydrolysis and polycondensation process [8]. By this method, a series of ladder-like polysilsesquioxanes ( $RSiO_{3/2}$ )<sub>n</sub> (R = alkyl, aryl, allyl and so on) have been synthesized [9–11]. Though these materials possess numerous interesting properties, their structural imperfection and irregularity have been noticed due to the weak template effect of phenylenediamine caused by fragile amino H-bonding (N–H···N). To improve the template effect, we recently designed a template agent, *N,N'*-diallyl-[4,4'-oxybis(benzyl amide)], to prepare ladder-like polysiloxanes [12]. Through strong amido H-bonding (N–H···O=C) of the template, we successfully synthesized a highly ordered ladder-like polysiloxane, whose regular structures were fully examined and confirmed by a series of techniques including <sup>1</sup>H NMR, <sup>29</sup>Si NMR, FTIR, XRD, DSC, static and dynamic light scattering, and viscosimetry.

In this paper, we report the design and synthesis of a new template agent, *N,N'*-di(4-hydroxy-phenyl)-terephthaloyl amide (T), which also possesses very strong amido H-bonding template to prepare regular amide-bridged ladder-like polymethylsiloxane (ALPS). A variety of characterization methods including <sup>1</sup>H NMR, <sup>29</sup>Si NMR, FTIR, XRD, DSC, and light scattering were combined to verify the ordered ladder-like structure of polymer ALPS.

## 2. Experimental

### 2.1. Materials

All the reagents and solvents were commercially available and of analytical grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone. Methyl-diethoxysilane, dimethylsulfoxide (DMSO) and *N*-methyl-pyrrolidone (NMP) were dried with zeolite overnight and distilled twice prior to use. The catalyst, dicyclopentadienyldichloroplatinum ( $Cp_2PtCl_2$ ), was prepared according to a literature method [13]. Other reagents were used as received.

### 2.2. Techniques

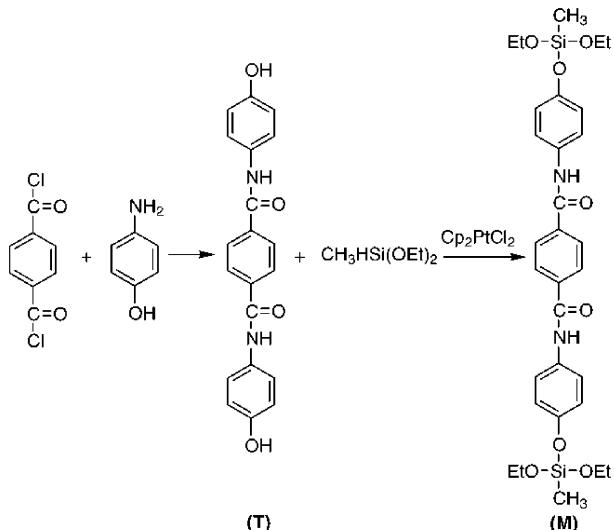
The XRD analysis was recorded on a Rigaku D/MAX 2400 diffractometer. <sup>1</sup>H NMR measurements and <sup>29</sup>Si NMR measurements were carried out on Varian Unity 200 and JNH-FX100 (JBOX) NMR instruments respectively, using

deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) as solvent. Chemical shifts ( $\delta$ ) were reported in ppm, referenced to tetramethylsilane (TMS, external standard, 0 ppm) for <sup>1</sup>H NMR and hexamethyldisiloxane (MM, external standard, 6.9 ppm) for <sup>29</sup>Si NMR. Chromium (III) acetylacetone was used as a relaxation agent for <sup>29</sup>Si NMR measurement. The FTIR measurement was performed with a Perking Elmer 80 spectrometer. Differential scanning calorimetry (DSC) experiment was performed on a Mettler Toledo Star-822 differential scanning calorimeter at a heating rate of 20 °C/min. The molecular weight was determined by light scattering (LS) method using a DLS-700 (Otsuka Electronic Co. Ltd.) apparatus equipped with He–Ne laser source (10 mW,  $\lambda = 632.8$  nm). Element analysis was carried out with a Heraeus CHN-RAPID DATEL system instrument.

### 2.3. Synthesis

#### 2.3.1. Synthesis of template agent *N,N'*-di(4-hydroxy-phenyl)-terephthaloyl amide (T)

The synthetic route to template agent T was shown in Scheme 1. 4.36 g of *p*-aminophenol (40 mmol) and 4.04 g of triethylamine (40 mmol) were dissolved in 100 ml of THF. Terephthaloyl chloride (4.06 g, 20 mmol, dissolved in 50 ml THF) was added dropwise into the *p*-aminophenol solution under vigorous stirring. The reaction mixture was stirred at room temperature for 4 h, and then filtered to remove THF. The filter cake was washed with large amount of acetone and water to get a brown solid, which was recrystallized twice from DMSO to get white crystals of T in 70% yield. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  in ppm): 10.25 (s, 2H, –NH), 9.22 (b, 2H, –OH), 8.11 (s, 4H, NHCO–C<sub>6</sub>H<sub>4</sub>–CONH), 6.78, 7.73 (d, d, 4H, 4H, –C<sub>6</sub>H<sub>4</sub>–OH). FTIR (cm<sup>−1</sup>): 3500–3210 (broad,  $\nu$  O–H), 3332 (strong,  $\nu$  N–H), 1643 (strong,  $\nu$  C=O), 1601 (median,  $\nu$  C=C<sub>arom</sub>), 1250 (strong,  $\nu$  O–C<sub>6</sub>H<sub>4</sub>), 671 (median,  $\gamma$  N–H). Elemental Anal.



Scheme 1.

Calcd for  $C_{20}H_{16}N_2O_4$ : C, 68.96; H, 4.63; N, 8.04. Found: C, 68.78; H, 4.77; N, 8.12.

### 2.3.2. Synthesis of $N,N'$ -di(4-methyldiethoxysiloxyphenyl)-terephthaloyl amide monomer (M)

Referring to a literature [14], methyldicholosilane ( $CH_3HSiCl_2$ ) and ethyl alcohol (molar ratio = 1:2) were simultaneously added dropwise into boiling petroleum ether (30–60 °C). The mixture was stirred under refluxing for 2 h and then fractionally distilled to collect methyldiethoxysilane ( $CH_3HSi(OEt)_2$ ) at 102–103 °C in 82% yield. According to the synthetic route to monomer M (shown in Scheme 1), 3.5 g of crystals of T (10 mmol) and 5 mg of  $Cp_2PtCl_2$  were added to a 100 ml Schlenk flask. The system was evacuated and charged with dry argon three times. Then 100 ml of NMP and 4 ml of  $CH_3HSi(OEt)_2$  (25 mmol) were injected into the flask. The mixture was stirred at 100 °C for 48 h. After removing the solvent and residual  $CH_3HSi(OEt)_2$  by vacuum distillation, a white waxy solid M was obtained in 93% yield. Characterization data for M are listed in Table 1.

### 2.3.3. Synthesis of amide-bridged ladder-like polymethylsiloxane (ALPS)

3.05 g of monomer M (5 mmol) was dissolved in 50 ml of NMP, and 0.36 g of water (diluted with 10 ml THF) was added dropwise into the monomer solution at 0 °C under stirring. The system was stirred at room temperature for an additional 24 h to complete the hydrolysis reaction. Then, the hydrolytic product was mixed with 50 ml of NMP containing 3.05 g (5 mmol) of monomer M, and followed by an addition of two drops of dibutyltindilaurate to catalyze the dealcoholizing condensation reaction. The reaction mixture was further stirred at 50 °C for 72 h under reduced pressure to distil off the alcohol released. Finally, 40 ml of

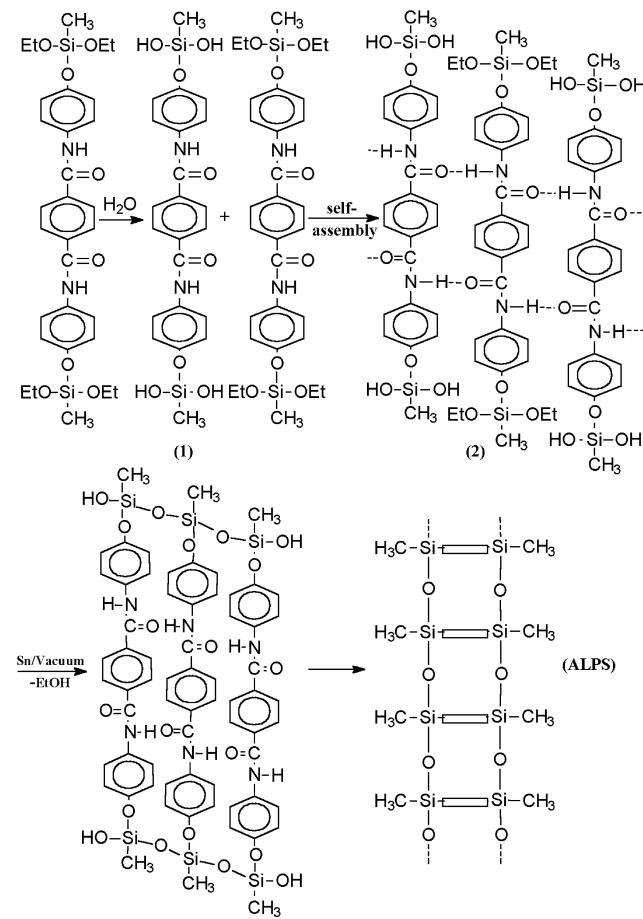
methanol was added dropwise into the mixture and some precipitates gradually emerged. The precipitates were collected and dried in a vacuum oven at 40 °C for 48 h to give the polymer ALPS as a yellowish solid in 71% yield. Elemental Anal. Calcd for  $(C_{22}H_{20}N_2O_6Si_2)_n$ : C, 56.88%; H, 4.34%; N, 6.03%; Si, 12.09%. Found: C, 56.79%; H, 4.31%; N, 5.97%; Si, 12.13%.

## 3. Results and discussion

It is noteworthy that in the synthesis of ALPS the essential point is how to bring the template effect of  $T, N,N'$ -di(4-hydroxy-phenyl)-terephthaloyl amide, into full play. Some relevant factors are discussed below.

### 3.1. Molecular design of templating agent T

A proposed mechanism for the formation of the polymer ALPS is shown in Scheme 2. The first step is the hydrolytical reaction of monomer M to form intermediate (1). The intermediate molecules and monomer M may be self-assembled side by side through the interaction of amido H-bonding ( $N-H \cdots O=C$ ) to form ordered ladder-like alignment (2), from which an oligomer was formed via



Scheme 2.

Table 1  
Characterization data of monomer M

Item	Data
Appearance	White waxy solid
Solubility	Soluble in DMSO, NMP etc.
FTIR (KBr, $cm^{-1}$ )	3318, 2962, 1640, 1597, 1514, 1255, 1107, 1078, 951, 879, 794
$^1H$ NMR ( $\delta$ in ppm)	9.0 (s, 2H, $NH$ ); 8.04 (s, 4H, $-COCH_2CO-$ ); 7.78, 6.70 (d, 4H, 4H, $-OC_6H_4NH-$ ); 3.8 (q, 8H, $OCH_2CH_3$ ); 1.1 (t, 12H, $OCH_2CH_3$ ); 0.09 (S, 6H, $SiCH_3$ ) –40, $CH_3(OEt)_2SiOC_6H_4$
$^{29}Si$ NMR ( $\delta$ in ppm)	No diffraction peaks
X-ray diffraction	Calcd for $C_{30}H_{40}N_2O_8Si_2$ : C, 58.80; H, 6.58; N, 4.57. Found: C, 57.97; H, 6.46; N, 4.72
Element analysis	

the dealcoholysis reaction. The oligomer was further condensed to form the ordered ladder-like ALPS. Apparently, the formation of a regular ladder-like structure requires efficient template effect of the T. The stronger the H-bonding, the higher the structure regularity of the polymer has. Accordingly, the use of *N,N'*-di(4-hydroxyphenyl)-terephthaloyl amide as a templating agent, a molecule with a very strong intermolecular H-bonding (N–H···O=C), would allow the formation of highly regular ladder-like organo-bridged polymethylsiloxane polymers.

### 3.2. Optimizing the preparation of monomer M

In our previous work, either hydrosilylation reaction or Grignard reaction was introduced to synthesize the monomer [15,16]. To obtain an effective templating for making highly regular ladder-like polysiloxane, it is necessary to link the two Si-atoms with a stiff bridging group, free of flexible spacers. As a result, the hydrosilylation of an alkene, which leads to the formation of a flexible spacer (–CH<sub>2</sub>–CH<sub>2</sub>–) between Si-atom and the bridging group, is avoided as a route to synthesize the monomer; neither is the reaction of silane with Grignard reagents due to its low reaction yield (<50%). Instead, a novel method, namely dehydrocoupling, was employed to prepare the *N,N'*-di(4-methyldiethoxysiloxy-phenyl)-terephthaloyl amide monomer (Scheme 1). Recently the dehydrocoupling reaction of phenols with silane has been widely and extensively studied by Li and Kawakami [17] in the polycondensation of  $\alpha,\omega$ -dihydrosilanes with diols. Several catalysts including tri(diphenylideneacetone) dipalladium Pd<sub>2</sub>(dba)<sub>3</sub> and RhCl(PPh<sub>3</sub>)<sub>3</sub> etc. have been used to promote the reaction in their study. Interestingly, we found that Cp<sub>2</sub>PtCl<sub>2</sub>, a common catalyst for the hydrosilylation of alkenes, can also catalyze the dehydrocoupling reaction cleanly and efficiently even at a high temperature (100 °C) and yield monomer M in a very high yield (93%).

### 3.3. Controlling the synthesis of polymer ALPS

Reaction conditions affecting the properties of polymer ALPS are discussed below:

#### 3.3.1. Effect of temperature on the regularity of polymer ALPS

In the first hydrolysis step, it was found that many insoluble three-dimensional network gels would be formed immediately if the hydrolysis was carried out at high temperature or water was added too rapidly. The reason is that while H-bonding is weakened at high temperature, the hydrolysate (tetrasilanol) was promptly produced, which leads to destruction of the ladder-like alignment and rapid formation of irregular interlaced tetrasilanol. The latter are randomly condensed to produce insoluble network gels. Therefore, the hydrolysis reaction of monomer M should be conducted very slowly at low temperature (0 °C) in diluted

solution. And for the same reason, the condensation reaction temperature is confined to not more than 50 °C.

#### 3.3.2. Effect of catalyst on molecular weight of polymer ALPS

It is known that both acids and bases can promote the condensation of silanols. However, the SiOPh bond in monomer M, which is hydrolytically unstable in the presence of acids, and the low reactivity of the silanols bearing electron-donating groups (e.g., methyl) in the presence of bases [18] prevent both acids and bases from being used as catalysts in the current system. A new catalyst, dibutyltindilaurate, was chosen to promote the dealcoholizing condensation reaction. As a result, the SiOPh bond is preserved during the polycondensation process, which can be proved from the forementioned elemental analysis results of polymer ALPS. Since the polycondensation reaction is a balance process between monomer and polymer, the side-product (alcohol) must be removed timely from reaction system in order to obtain a high molecular weight polymer. So the reaction mixture was continuously stirred and evaporated under reduced pressure to increase the molecular weight of polymer ALPS.

#### 3.3.3. Effect of medium polarity on the regularity of polymer ALPS

To maintain a good H-bonding templated effect, non-polar or low-polar solvent is typically recommended in the hydrolysis and condensation reaction. However, these solvents normally have a very poor solvating power for the reaction intermediates and the final polymer. Therefore, a suitable solvent needs to have a balance between the polarity and solvating power. Here a polar aprotic solvent *N*-methylpyrrolidone (NMP) was chosen based on these factors, though the ALPS would be yellowed due to the slight oxygenation of the NMP in atmosphere.

### 3.4. Characterization of polymer ALPS

A variety of characterization techniques including <sup>1</sup>H NMR, <sup>29</sup>Si NMR, FTIR, XRD, DSC, LS and elementary analysis were used for the structural characterization of polymer ALPS.

As shown in the FTIR spectrum of polymer ALPS (Fig. 1), instead of two absorption peaks (1107 cm<sup>-1</sup>, 1078 cm<sup>-1</sup>) of monomer M (Table 1), a very strong and broad adsorption at 1099.54 cm<sup>-1</sup> corresponding to the stretching vibration of SiOSi linkage was observed, indicating that the monomer M has been completely condensed to polymer containing SiOSi bonds. It was noteworthy that no distinct peaks for the terminal hydroxyl were found in the spectrum. This is mainly caused by the low content of terminal hydroxyl in the polymer and the strong vibration peak of N–H (3306.92 cm<sup>-1</sup>) which covers up the vibration peak of O–H.

No peak assignable to OCH<sub>2</sub>CH<sub>3</sub> group was observed in

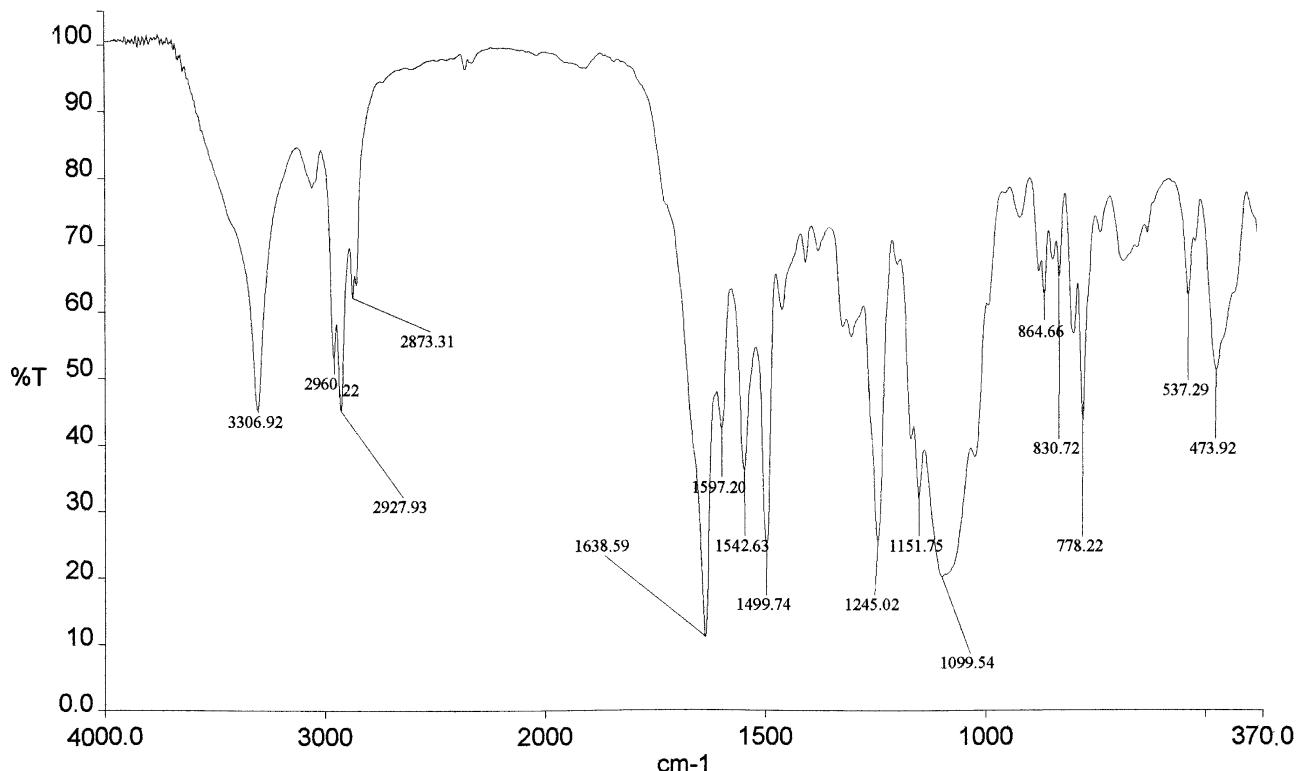
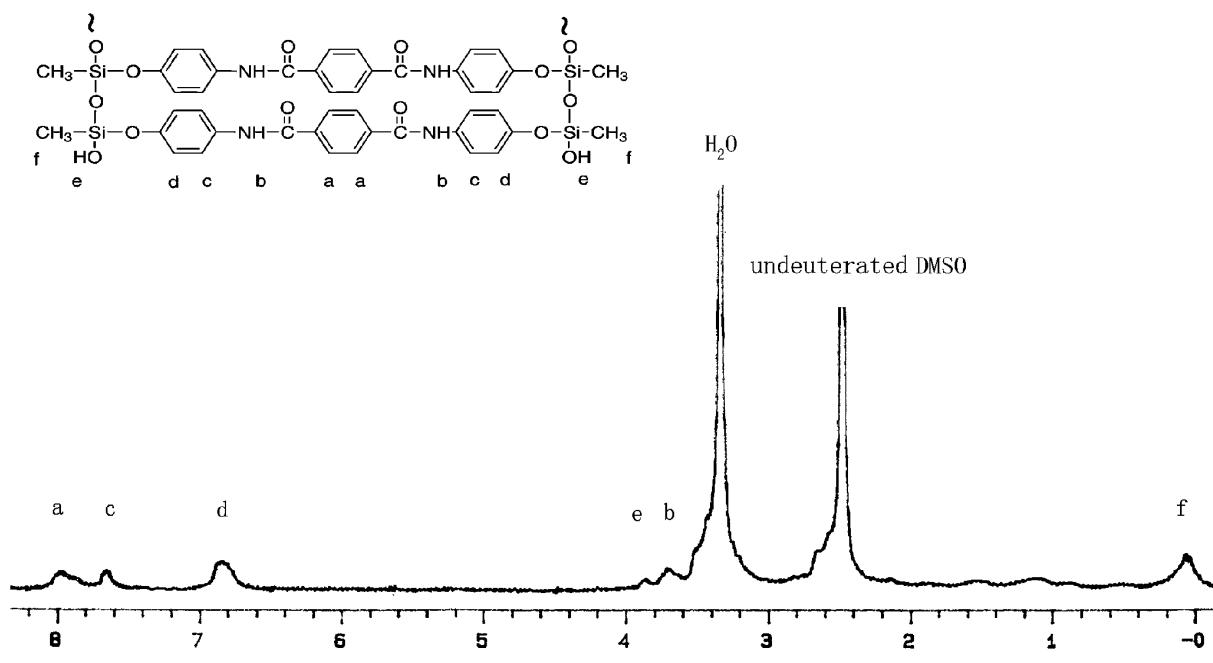


Fig. 1. FTIR spectrum of polymer ALPS.

the  $^1\text{H}$  NMR spectrum of polymer ALPS, which suggests that the monomer M has been fully condensed. However, as can be seen in Fig. 2, the resonance peak intensity of ALPS is much lower than that of water or undeuterated impurities in the solvent used ( $\text{DMSO-d}_6$ ), which is mainly caused by the poor solubility of ALPS in  $\text{DMSO-d}_6$  or any other deuterated solvents. The widened hump-like peaks of

aromatic hydrogen and other groups, arising from the high viscosity of ALPS in deuterated DMSO, imply that monomer M has been condensed to a relatively high molecular weight polymer. Unfortunately, the coupling constants were not observed due to the limit of the used NMR instrument. In addition, the appearance of aromatic hydrogen in the  $^1\text{H}$  NMR spectrum also indicates that the

Fig. 2.  $^1\text{H}$  NMR spectrum of polymer ALPS.

SiOPh bond is not cleaved during the polycondensation process.

Two peaks are demonstrated for the ladder-like polymer ALPS in the  $^{29}\text{Si}$  NMR (Fig. 3). It is noteworthy that, due to the poor solubility of ALPS in DMSO-d<sub>6</sub>, these two peaks are small and overlapped with the big resonance peak of the silicate-based NMR-tube. The first peak ( $\delta = -59$  ppm), which was usually designated as  $\alpha$ -peak, represents the terminal silicon atom  $\text{HOSi}(\text{Me})(\text{OPh})\text{O}^-$ . Another peak at  $\delta = -66$  ppm (usually designated as  $\beta$ -peak) represents the internal silicon atom in the backbone  $-\text{OSi}(\text{Me})(\text{OPh})\text{O}-$  [19]. This result shows that polymer ALPS mainly consists of the above two types of Si-atom without any other noticeable structural units, which is consistent with the expected ladder-like structure of ALPS. It is known that the regularity of ladder-like structure is directly relevant to the width of  $\beta$ -peak. The broader the  $\beta$ -peak, the lower regularity the polymer has. To emphasize the template effects, the widths at half height of the  $\beta$ -peak for the titled polymer ALPS and other ladder-like polysiloxanes are summarized in Table 2. As can be seen, the regularity of polymer ALPS is obviously improved owing to the strong template effect of *N,N'*-di(4-hydroxy-phenyl)-terephthaloyl amide. Nonetheless, the value for the width at half height of  $\beta$ -peak of polymer ALPS is still comparatively high (2.5–3.5 ppm) rather than a much lower value, which is probably contributed to the presence of structural irregularities (such as branches and local cyclic structures) and stereo-isomers (such as *cis*- or *trans*, isotactic or syndiotactic configura-

Table 2  
Comparison of  $^{29}\text{Si}$  NMR measurements of different polysiloxanes

Ladder-like polysiloxane	Width at half height of $\beta$ peak (ppm)
LPS prepared by Brown's method	5.0–7.0
LPS prepared by SCP using phenylenediamine as template	3.5–4.0
Titled polymer ALPS	2.5–3.5

tions) in the polymer ALPS, as found in some of the chiral organosilicon compounds [20].

The XRD pattern of polymer ALPS (Fig. 4) gives two hump-like peaks. Generally, crystalline polymers and oriented polymers give out sharp diffraction peaks, but amorphous polymers usually show no diffraction peaks in their XRD spectrum. The two hump-like diffraction peaks of amorphous ALPS indicate that the polymer possesses ladder-like structure but the structure is far from perfect. In addition, referring to Tang [12], Shi [21] and Liu [22], the first peak at 12.2 Å represents the intramolecular chain-to-chain distance of the ladder-like structure, which should be 20.3 Å according to the molecular simulation of polymer ALPS (simulated by Alchemy 2000). This large discrepancy is probably resulted from the inclined array of ladder rungs between double main chains. The second wide peak (4.9 Å) is possibly related to the thickness of the macromolecular chain. These results are in agreement with the proposed ladder-like structure for the polymer ALPS.

Glass transition temperature ( $T_g$ ) has normally been used

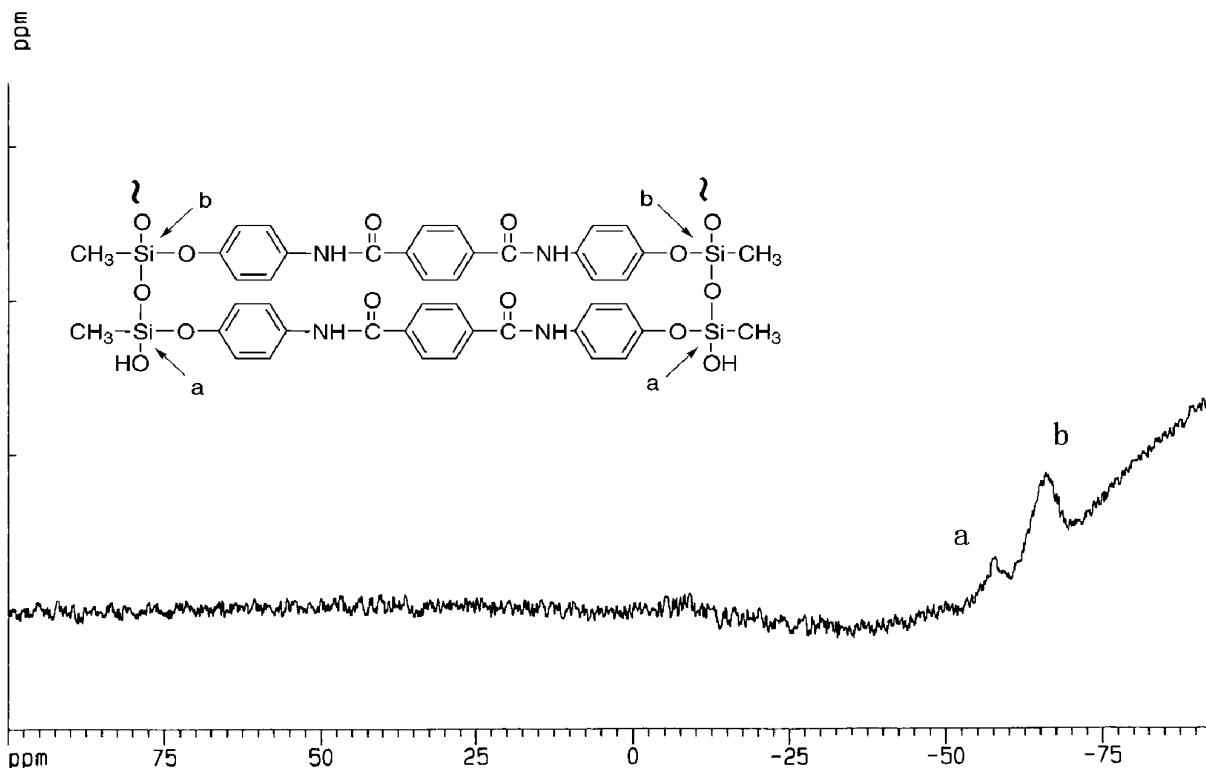


Fig. 3.  $^{29}\text{Si}$  NMR spectrum of polymer ALPS.

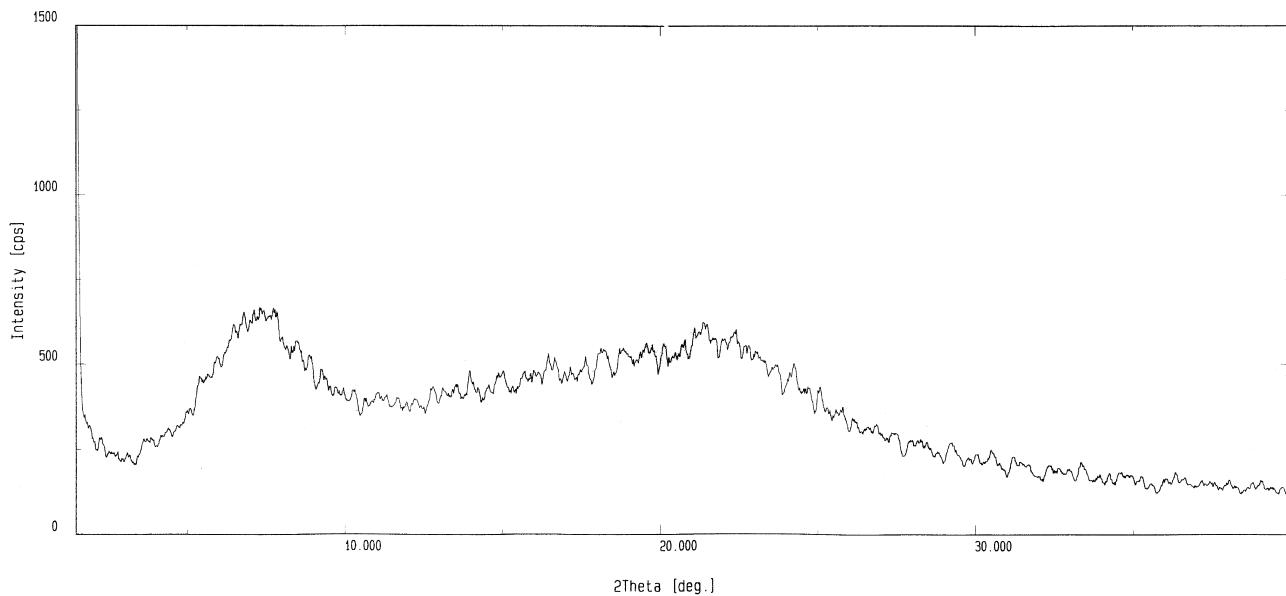


Fig. 4. XRD pattern of polymer ALPS.

to evaluate the flexibility of macromolecular chain of polymers. In contrast to the common flexible single-chain polysiloxane which has a very low  $T_g$  ( $< -100$  °C), the  $T_g$  of polymer ALPS is about 150.6 °C (Fig. 5). A possible explanation for this discrepancy is that polymer ALPS has a unique double chain structure and rigid ladder-rung of strong H-bonding interactions, which remarkably restricts the internal rotation of Si–O–Si bond and greatly increased the stiffness of macromolecular chain of ALPS.

The molecular weight of polymer ALPS was measured by light scattering instead of gel permeation chromatog-

raphy (GPC) since GPC measurements are based on size exclusion principle using polystyrene as a standard, a poor reference for polymer ALPS possessing a semi-rigid double-chain structure. The weight-averaged molecular weight ( $M_w$ ) of polymer ALPS is determined as  $4.7 \times 10^5$  g/mol.

#### 4. Conclusions

A novel soluble, high molecular weight organo-bridged

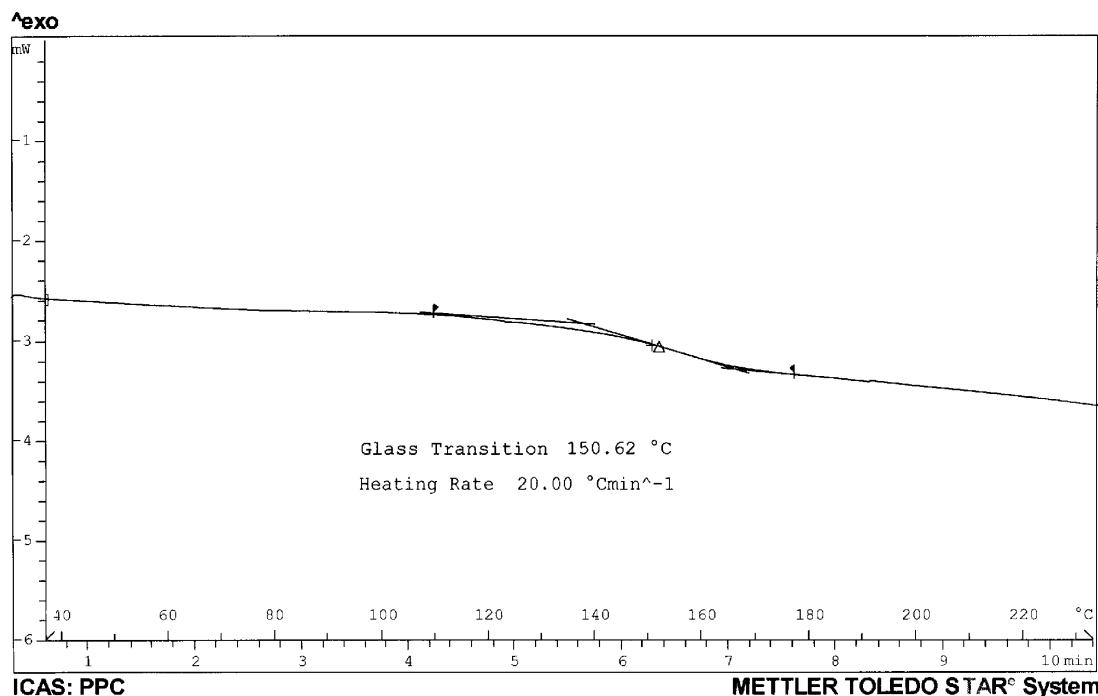


Fig. 5. DSC curve of polymer ALPS.

ladder-like polymethylsiloxane has been synthesized by amido H-bonding assisted template polymerization of monomer *N,N'*-di(4-methyldiethoxysiloxyl-phenyl)-terephthaloyl amide which was prepared by dehydrocoupling reaction of *N,N'*-di(4-hydroxy-phenyl)-terephthaloyl amide with methyldiethoxysilane. The polymer was characterized by FTIR, <sup>1</sup>H NMR, <sup>29</sup>Si NMR, XRD, DSC, and light scattering techniques and the results show that this polymer is a semi-rigid, ordered ladder-like architecture macromolecule. The H-bonding-assisted synthetic strategy may be widely applied to prepare other kinds of organo-bridged ladder-like polysiloxanes.

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