

H-BONDING SELF-ASSEMBLED TEMPLATE-CONTROLLED SYNTHESIS OF A NOVEL SOLUBLE AND REACTIVE AMIDE-BRIDGED LADDERLIKE POLYHYDROSILOXANE*

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Abstract A novel soluble and reactive amide-bridged ladderlike polyhydrosiloxane (ALPHS) was first synthesized by an amido H-bonding self-assembled template. ALPHS with molecular weight $\bar{M}_n = 18300$ has very highly ordered ladderlike structure, which was confirmed by a sharp resonance absorption peak of $[-\text{Si}(\text{H})\text{O}_{2/2}]$ moiety with the half peak width $\Delta_{1/2} < 0.5$ in ^{29}Si -NMR spectrum. Presence of the reactive Si—H groups gives ALPHS an opportunity to further derive a variety of functional polymers by versatile Si—H reactions such as hydrosilylation, condensation, and so on.

Keywords: Ladderlike; Polyhydrosiloxane; Amido H-bonding template.

INTRODUCTION

In 1960 Andrianov^[1, 2] attempted to synthesize 1,4-phenylene-bridged ladderlike polymethyl-siloxane (PLPMS), but unexpectedly, only insoluble network gel was obtained because a π - π stacking template of bridged phenylene groups cannot withstand 100°C during the polymerization process. Thirty years later, Fukuyama^[3] *et al.* have also mentioned PLPMS, but no characterization data were given except an imaginary ladderlike structure. Recently, our group developed a novel supramolecular chemistry-controlled stepwise coupling polymerization approach (SCP) to prepare organobridged ladderlike polysiloxanes^[4]. We synthesized the stereoregular ladderlike polysiloxane, PLPMS, by means of π - π stacking templates^[5, 6] and 2,5-dipropylhydroquinone-bridged ladderlike polymethylsiloxane *via* hydroquinone H-bonding template^[7]. Recently, we prepared highly regular aryl amide-bridged ladderlike polymethylsiloxanes with the $\Delta_{1/2} < 0.6$ ^[8, 9] by aryl amide H-bonding template. It is noteworthy that in contrast to all aforementioned polymers with inert side groups, the ladderlike organo-bridged polyhydrosiloxane with reactive Si—H side groups is a more promising precursor for preparing a wide variety of functional polymeric materials.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was refluxed and distilled over sodium benzophenone. Triethylamine (TEA) was refluxed over potassium hydroxide and distilled before use. Trichlorosilane (HSiCl_3) was distilled and collected the distillate at 30–32°C. Other reagents were commercially available and were of analytical grade.

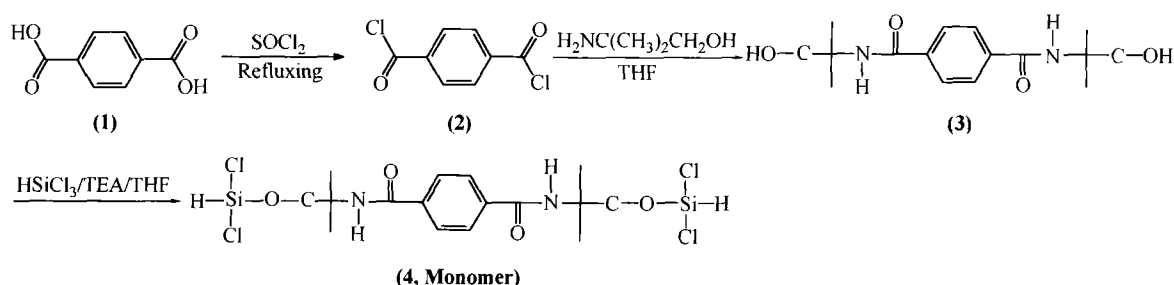
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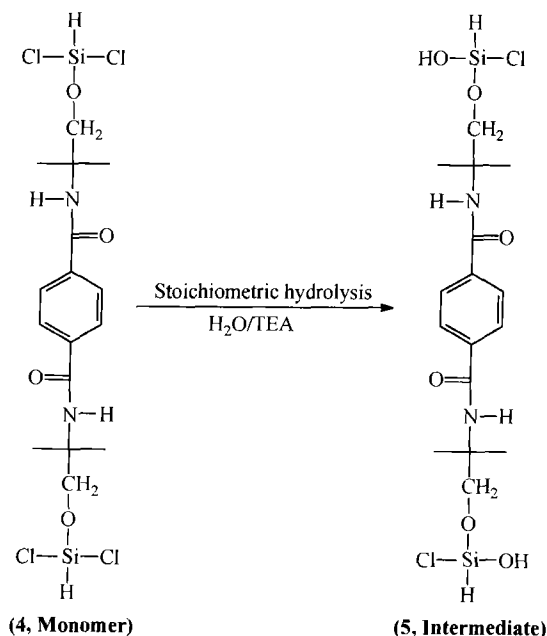
Measurements

The Fourier transform infrared (FTIR) measurements were performed with a Perkin Elmer 80 spectrometer. ^1H -NMR and ^{29}Si -NMR measurements were carried out on a Varian 200 (USA) instrument with chloroform- d (CDCl_3) or THF as the solvent, respectively. Tetramethylsilane (TMS, $\delta = 0.0$) was used as reference for ^1H -NMR and chromium (III) acetylacetonate as a relaxation agent for ^{29}Si -NMR. The molecular weight of polymers was determined by vapor pressure osmometry (VPO) at 40°C with THF as the solvent. Mass-spectrometric data and elemental analysis result were obtained with a Biflex III MALDI-TOF mass spectrometer (Bruker Analytical, Inc) and a Heraeus CHN-Raped Dated System, Inc (Germany), respectively.

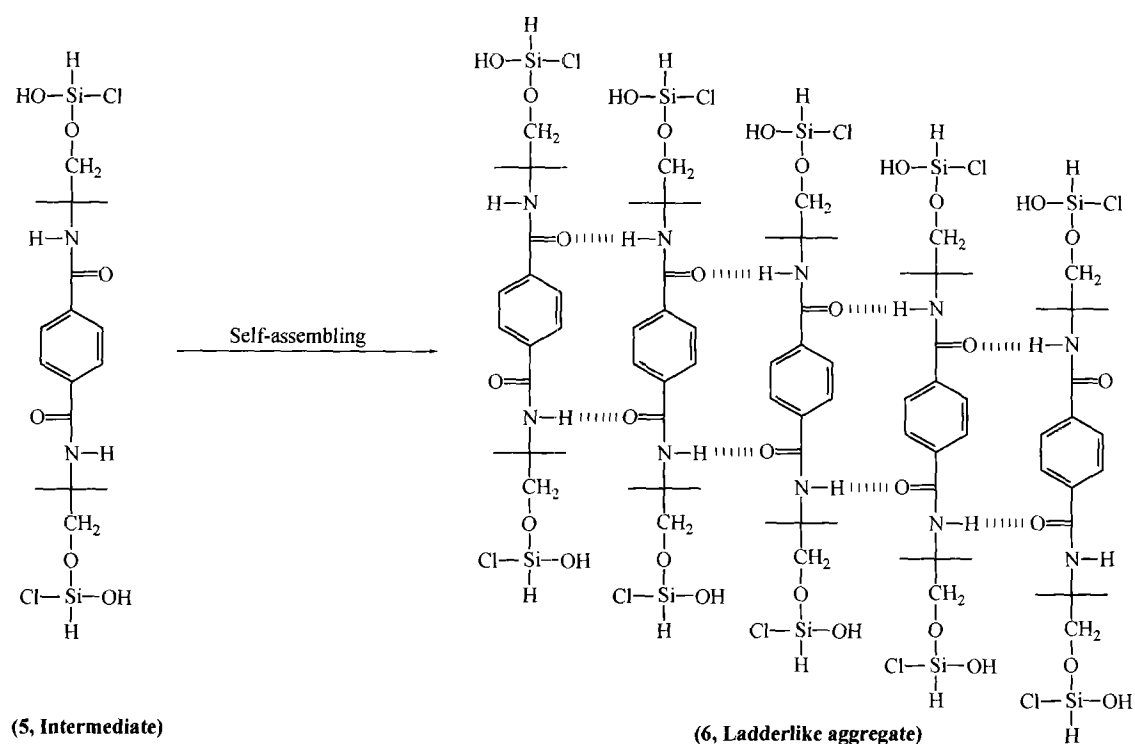
The synthetic route for the titled polymer ALPHS is denoted as the following five steps: (a) preparation of the coupled monomer **M** (compound **4**), as shown in Scheme 1; (b) "stoichiometric hydrolysis", as shown in Scheme 2; (c) formation of the amido H-bonding self-assembled ladderlike aggregates, as shown in Scheme 3; (d) dehydrochlorination condensation, as shown in Scheme 4; and (e) $\text{Me}_3\text{SiO}-$ capped reaction, as shown in Scheme 5.



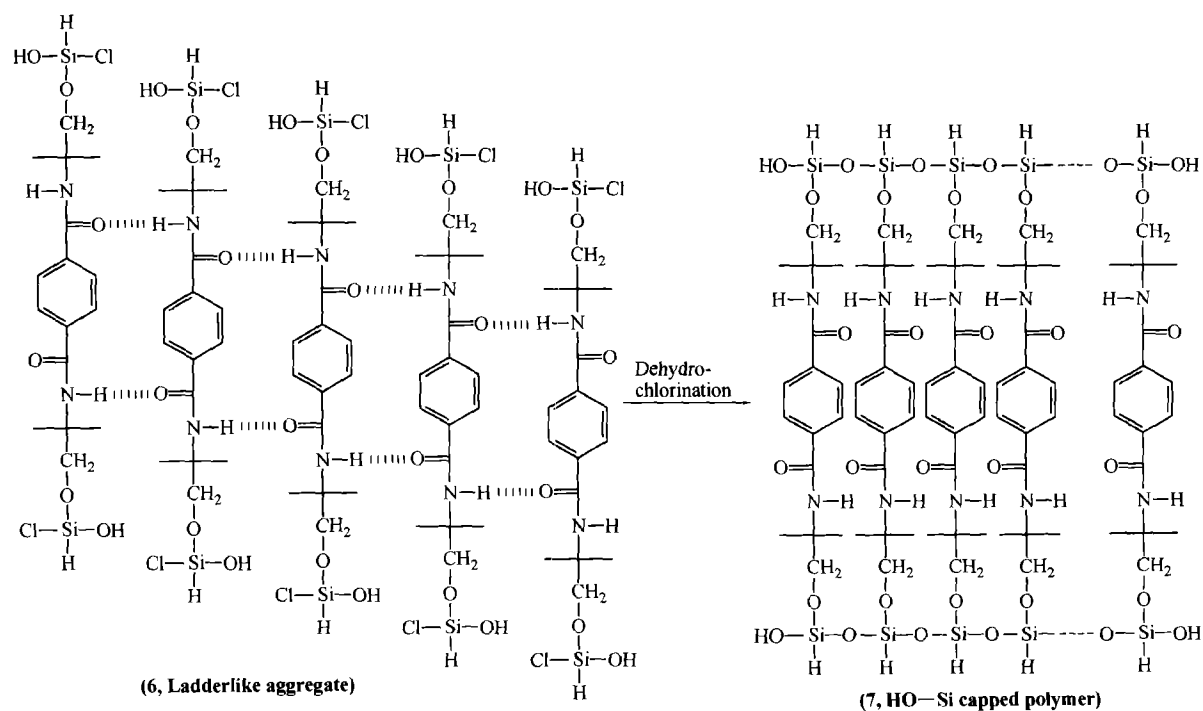
Scheme 1 Synthesis of monomer **M**



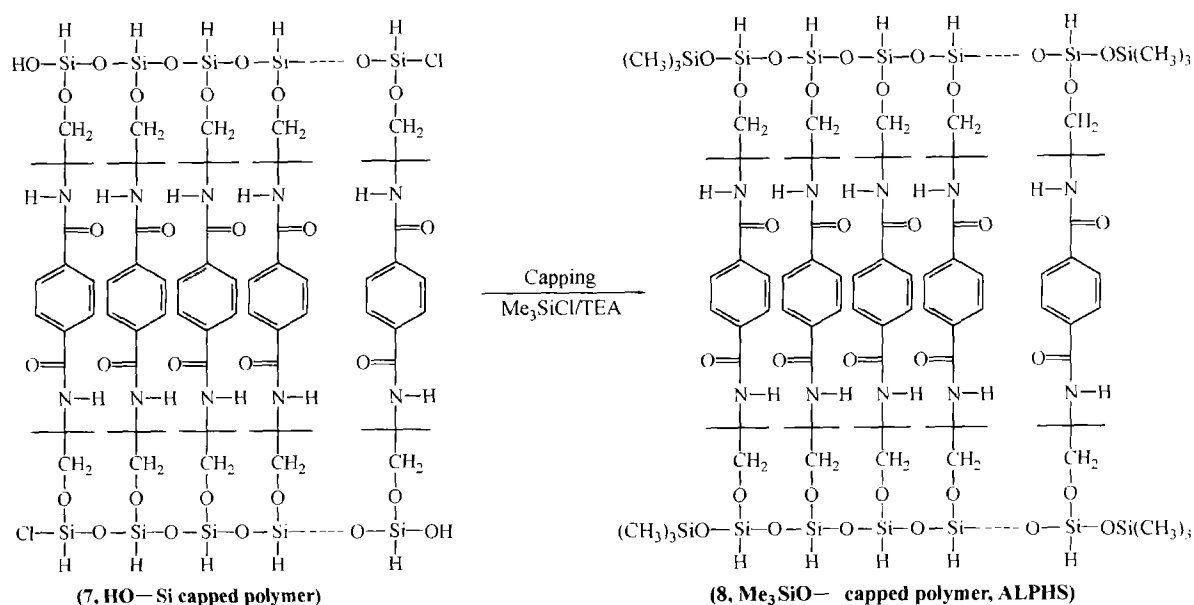
Scheme 2 Synthesis of intermediate



Scheme 3 Self-assembling process of intermediate



Scheme 4 Dehydrochlorination of ladderlike aggregates

Scheme 5 Me₃SiO-capping process

Synthesis of Monomer **M** (Compound **4**)

As shown in Scheme 1, compound **2** was prepared according to Ref. [10]. 28.42 g (0.14 mol) of compound **2** was dissolved in 150 mL of THF and dropped into a flask which had been charged with 65 mL (0.68 mol) of 2-amino-2-methyl-1-propanol and 100 mL of THF. The mixture was stirred in an ice-water bath. The reaction was continued for 1 h after the addition. The reaction product was filtered, washed (with 3 portions of 100 mL H₂O) and recrystallized (in EtOH). 24.70 g of white crystal of compound **3**, was obtained in 70% yield. FTIR (KBr, cm⁻¹): 3343 (st, NH), 2974, 2933, 2874 (st, CH₃), 1639 (st, C=O), 1548 (δ, NH), 1501, 1459 (st, phenyl), 1395, 1363 (δ sy, C (CH₃)₂) and 1061 (st, C—O). ¹H-NMR (CDCl₃, δ): 7.8 (C₆H₄), 6.2 (NH), 3.7 (CH₂O), 1.8 (OH) and 1.5 (CH₃). MS: 309.3, 331.3. Elem. Anal. Calcd. for C₁₆H₂₄N₂O₄ (%): C 62.32, H 7.84, N 9.08. Found (%): C 62.31, H 7.83, N 9.22. Then 3 mL (2.97 × 10⁻² mol) of HSiCl₃ was added into a Schlenk flask charged with 3.08 g (1.00 × 10⁻² mol) of compound **3**, 100 mL of dried THF and 2.81 mL (2.00 × 10⁻² mol) anhydrous TEA was stirred at room temperature for 5 h. Monomer **M** (compound **4**) was obtained after excess HSiCl₃ and a part of THF was moved by vacuum evaporation.

Synthesis of ALPHS (Compound **8**)

A mixture of H₂O (0.36 mL, 2 × 10⁻² mol), THF (40 mL) and TEA (5.62 mL, 4.00 × 10⁻² mol) was added dropwise into the monomer/THF solution for 12 h at 40°C to obtain a partially hydrolyzed intermediate **5**, which was self-assembled into a ladderlike supramolecular aggregate (compound **6**) through H-bonding. The reaction continued for 10 h to obtain silanol-terminated polymer (compound **7**). Finally, excess (CH₃)₃SiCl (0.170 g) and TEA (0.112 g) were added to end-capping the terminal silanol groups of compound **7**. The whole above-mentioned process was completed under the protection of Ar gas for 24 h. The crude reaction product was filtered, washed with CHCl₃ and dried under vacuum at 40°C. 2.23 g of ALPHS in the form of white solid was obtained in 52% yield.

RESULTS AND DISCUSSION

Because monomer **M** is exceedingly air-sensitive to be further purified. **M** was characterized by ²⁹Si-NMR method. The main peak at δ = -26.66 stands for the =SiCl₂ moiety of **M**, with a very small amount of residue HSiCl₃ (δ = -35.14).

Synthesis and Characterization of ALPHS

Because Si—H bonds are readily hydrolyzed in basic condition while Si—O—C bonds are readily hydrolyzed in acidic condition, therefore, a nearly neutral condition is maintained. Furthermore, it is essential to bring the amido H-bonding template into full play throughout the formation of self-assembled ladderlike aggregates and polycondensation process. Hence, several important factors should be emphasized as follows.

Choice of appropriate solvent

In order to run the reaction in a homogeneous system we should select a strongly polar solvent which is capable of dissolving the highly polar intermediate **5**. However, a strongly polar solvent normally can weaken the H-bonding association between the intermediate molecules (compound **5**). Moreover, the amide solvents such as DMF and DMA *etc.* can cause the Si—H groups to decompose slowly even at room temperature. Thus, an aprotic solvent THF with fair polarity (dielectric constant $\epsilon = 7.58$) was chosen although a very low solubilizing power cannot be avoided.

Utilizing “stoichiometric hydrolysis” method

The so-called “stoichiometric hydrolysis” means that the amount of water used for hydrolyzing 2 Si—Cl groups instead of 4 Si—Cl groups in the monomer **M** molecule is employed. Actually, in “stoichiometric hydrolysis” process the partially hydrolyzed product generally forms with 1–4 Si—OH groups. For simplicity, intermediate **5** with statistical 2 Si—OH and 2 Si—Cl groups is taken. They self-assemble to form the ladderlike aggregate **6**, which immediately undergoes dehydrochlorination condensation with numerous surrounding monomers **M** with Si—Cl groups to produce covalent polymer **7** in a homogeneous THF solution. As pointed out by Cojnowski^[11, 12], the dehydrochlorination reaction is smoothly carried out in an anhydrous condition in the presence of catalyst TEA, which also acts as HCl-absorbent.

Choice of appropriate reaction temperature

Appropriate temperature ($\sim 40^\circ\text{C}$) was chosen to get a balance between the acceleration of polycondensation and the dissociation of amido H-bondings. Meanwhile, the strong H-bond association between amido groups still exists at this temperature. Similar experimental data concerning changes in the strength of association of the amido H-bonds at different temperatures have been reported by our group elsewhere^[8].

End-capping

To avoid the happening of self-condensation between Si—OH groups and hetero-condensation between Si—H and Si—OH groups, ALPHS should be capped with $(\text{CH}_3)_3\text{SiO}-$ groups completely.

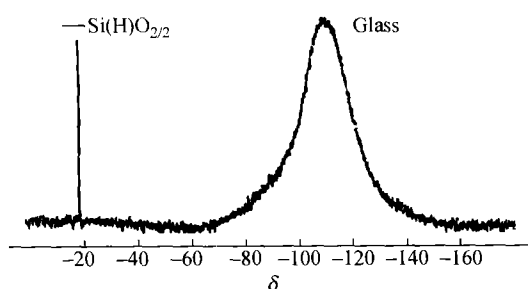


Fig. 1 ^{29}Si -NMR spectrum of the polymer ALPHS

The characterization data were tabulated in Table 1. The FT-IR spectrum shows two peaks at 2252 cm^{-1} (Si—H) and 1149 cm^{-1} (Si—O—Si & Si—O—C). The molecular weight was determined by VPO method instead of the usual gel permeation chromatography (GPC) because principle of GPC method is based on the volume-repulsion action by using spherical shape polystyrene as standard and it is not suitable for the semi-rigid rod-like polymer ALPHS macromolecule. Besides, according to the literatures^[13, 14] the XRD analysis demonstrate two diffraction peaks: one is located at $2\theta = 6.42^\circ$ corresponding to the ladder width $d_1 = 1.376\text{ nm}$ and the other one is at 19.72° corresponding to the ladder thickness $d_2 = 0.450\text{ nm}$, indicating that ALPHS

possesses ladderlike structure. It is particularly noteworthy that ^{29}Si -NMR measurement shows a very sharp resonance absorption peak with the half peak width $\Delta_{1/2} < 0.5$ of the moiety $[-\text{Si}(\text{H})\text{O}_{2/2}]$, as shown in Fig. 1. This value is smaller than any other ladderlike polysiloxanes reported before, proving that ALPHS has a highly regular ladderlike structure.

Table 1. Characterization results of ALPHS

Item	Results
Appearance	White solid
Solubility	Soluble in THF
FT-IR (KBr, cm^{-1})	3343 (st, NH); 2975, 2934, 2875 (st, CH_3); 2252 (st, SiH); 1640 (st, C=O); 1548 (δ , NH); 1501, 1459 (st, C_6H_4); 1392, 1364 (δ , sy, C (CH_3) ₂); 1149 (st, Si—O—Si & Si—O—C), 1063 (st, C—O)
Distance (nm)/ 2θ ($^\circ$) by X-ray diffraction	Ladder width $d_1 = 1.376/6.42$ Ladder thickness $d_2 = 0.450/19.72$
^{29}Si -NMR (δ)	-18.45, $[-\text{Si}(\text{H})\text{O}_{2/2}]$
DSC	No T_g was observed before decomposition
$\overline{M}_n$ (by VPO, g/mol)	1.83×10^4

CONCLUSION

A novel soluble, reactive and highly stereoregular amide-bridged ladderlike polyhydrosiloxane (ALPHS) was successfully synthesized by means of an amido H-bonding self-assembled template. It is essential to bring the amido H-bonding template into full play throughout the preparative process.

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