

CONCERTED H-BONDING TEMPLATE SYNTHESIS OF AN ORDERED LADDER POLYSILSESQUIOXANE*

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Abstract A novel soluble regular ladder poly(benzoyl-3-aminopropyl) silsesquioxane (LPBAS) was facilely prepared under effective assistance of concerted H-bonding self-assembly of amido groups of side chains and silanol groups, respectively, of a new template monomer [1,3-bis(benzoyl-3-aminopropyl)-1,1,3,3-tetraethoxydisiloxane] (M). The ordered ladder structure of LPBAS is manifested in: (1) the presence of two Bragg peaks representing the ladder width (d) and ladder thickness (t) in X-ray diffraction (XRD) pattern; (2) narrow base-line width ($w = 6$) of resonance absorption for $-\text{CH}_2\text{SiO}_{3/2}$ moiety in ^{29}Si -NMR and (3) high glass transition temperature $T_g = 112^\circ\text{C}$ in differential scanning calorimetry (DSC) analysis.

Keywords: Concerted H-bonding template; Self-assembly; Ladder polysilsesquioxane.

INTRODUCTION

The synthesis of ladder polysilsesquioxane (LPS) and organobridged ladder polysiloxane (OLPS) is of growing interest for its unique structures and properties in silicone polymer chemistry^[1,2]. Historically, a soluble ladder polyphenylsilsesquioxane (Ph-T) was first reported by Brown *et al.*^[3] in 1960. Matsumoto *et al.*^[4] reported the synthesis of crystalline pentacyclic laddersiloxane. Yamamoto *et al.*^[5] also prepared ladder Ph-T with low molecular weight (M_w ca. 1400) in 2004. Noticeably, a series of OLPSs with high M_w have been synthesized using the stepwise coupling polymerization put forward by our group^[6–10]. Among them, phenylene-diamine bridged OLPSs have been converted to LPSs *via* further hydrolysis of SN bridges of OLPSs and condensation^[10–12].

Here, we report a new approach to synthesize LPS *via* concerted H-bonding template. Importantly, a new template monomer [1,3-bis(benzoyl-3-aminopropyl)-1,1,3,3-tetraethoxydisiloxane] (M) first forms ladder supramolecular aggregate (4) by self-assembly, which then, is directly converted to the ordered LPBAS *via* careful hydrolysis/condensation.

EXPERIMENTAL

Materials

All the reagents and solvents were commercially available and of analytical grade. Triethylamine (TEA) was refluxed with KOH for 24 h and distilled before use. Tetrahydrofuran (THF) and 1,4-dioxane were distilled over sodium and benzophenone.

* This work was financially supported by NSFC (Nos. 50073028, 29974036 and 20174047).

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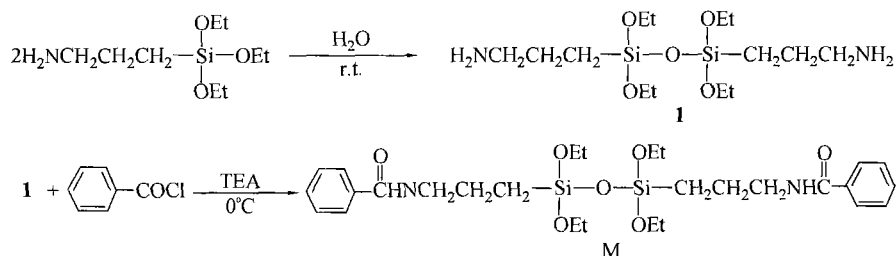
Received December 12, 2005; Revised January 12, 2006; Accepted January 19, 2006

Characterizations

The Fourier transform infrared spectra (FTIR) were recorded with a Perkin Elmer 80 spectrometer. The XRD was performed on a Rigaku D/max 2400 diffractometer. ^1H - and ^{29}Si -NMR measurements were carried out on a Bruker 300 MHz spectrometer using deuterated acetone or THF as a solvent, respectively. The DSC experiment was performed on a Mettler Toledo Star 822 differential scanning calorimeter under N_2 atmosphere. Vapor pressure osmometry (VPO) analysis was measured in THF at 40°C on a Knauer VPO instrument. Elemental analysis results were obtained with a Heraeus CHN-RAPID DATEL system instrument.

Synthesis of Template Monomer (M)

The synthetic route to M is shown in Scheme 1. 7.36 g (20 mmol) of 1,3-bis(3-aminopropyl)-1,1,3,3-tetraethoxydisiloxane **1** and 16.16 g (160 mmol) of TEA were dissolved in 60 mL anhydrous THF in an ice-bath. A solution of 5.62 g (40 mmol) benzoyl chloride dissolved in 50 mL THF, was added dropwise into **1** solution under vigorous stirring. The reaction mixture was stirred in an ice-bath for 3 h and then filtered to remove TEA·HCl salts. After removing the volatile components from the filtrate, the white solid M was purified by column chromatography using petroleum ether/THF (10:3) as eluent with an yield of 79%.



Scheme 1 Synthetic route to the template monomer (M)

^1H -NMR (acetone- d_6 , δ): 7.92 (s, $-\text{NHCH}_2\text{CH}_2-$), 7.89–7.41 (d, t, t, 4H, 4H, 2H $-\text{C}_6\text{H}_5$), 3.86 (m, 8H, $-\text{SiOCH}_2\text{CH}_3$), 3.39 (t, 4H $-\text{NCH}_2\text{CH}_2-$), 2.05 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 1.18 (t, 12H, $-\text{SiOCH}_2\text{CH}_3$), and 0.71 (t, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$). ^{29}Si -NMR (THF, δ): -49.24 (s, $-\text{Si}-\text{O}-\text{Si}-$). Elemental Anal. Calcd. for $\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_7\text{Si}_2$ (%): C 58.25, H 7.63, N 4.85, O 19.42; Found (%): C 58.17, H 7.80, N 4.72, O 19.57.

Synthesis of the Titled LPBAS

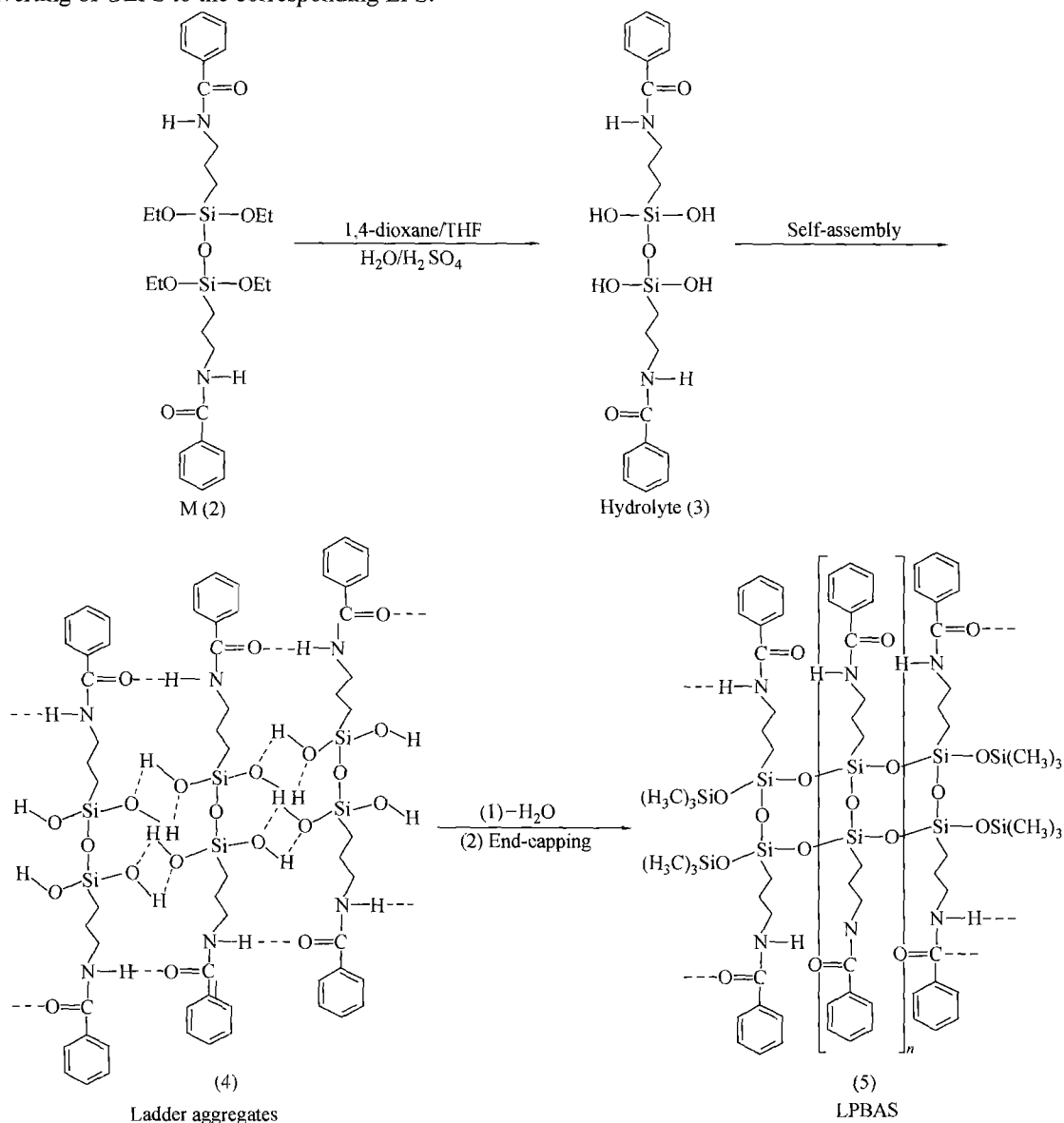
2.88 g (5 mmol) M was dissolved in 80 mL 1,4-dioxane/THF (4:1) at room temperature (r.t.) under stirring. A solution containing several drops of concentrated H_2SO_4 as catalyst and 20 mL 1,4-dioxane was then added into the monomer solution. A mixture of 0.36 mL (20 mmol) deionized water and 80 mL 1,4-dioxane was added dropwise in 4 batches and within 3 h for each time. The reaction system was stirred at r.t. for another 24 h, followed by addition of 300 mL water as precipitation agent to give a white silanol-uncapped polymer. To end-cap the terminal silanols, the mixture of the dried silanol-uncapped polymer, 0.054 g (0.5 mmol) trimethylchlorosilane, 0.051 g (0.5 mmol) TEA and 60 mL anhydrous THF was stirred at r.t. for 24 h. Finally, the titled polymer LPBAS (**5**) was obtained by precipitating with water, filtering and then dried at 50°C for 12 h, with an yield of 71%.

RESULTS AND DISCUSSION

Molecular Design and Reaction Condition

The template monomer [1,3-bis(benzoyl-3-aminopropyl)-1,1,3,3-tetraethoxydisiloxane] (M) was designed, in which its $-\text{Si}-\text{O}-\text{Si}-$ moiety was directly used as the ladder-rung of ladder LPBAS and four reactive $\text{Si}-\text{OEt}$ groups were used for the construction of $-\text{Si}-\text{O}-\text{Si}-$ ladder main chain through hydrolysis/condensation. The concerted H-bonding template involved here refers to the strong amido H-bonding interactions of

(N—H···O=C) in side group and square-planar H-bonding system of Si—OH group according to the literature^[13, 14]. A proposed mechanism for the preparation of LPBAS is shown in Scheme 2. It is noted that the most important factor to form ordered LPBAS is how to bring the template effect of M into full play throughout the whole synthetic process. First, in order to ensure the formation of stronger H-bonding interaction in the ladder aggregates (4), the low-polar mixed solution [1,4-dioxane/THF (4:1)] was selected as the reaction medium. Second, in consideration of balancing the suitable reaction speed and the strong H-bonding template effect in the synthetic process, the reaction was carried out at room temperature. The concerted H-bonding interaction of amido and square-planar H-bonding system of the Si—OH groups in the hydrolyte (3) leads to the reconstruction of more stable ladder aggregates (4). Third, the latter can be timely fixed in the form of covalent bond by the condensation between Si—OH groups. It is worthwhile to state that the —Si—O—Si— moiety in template monomer (M) can be directly used as the ladder-rung of LPBAS, avoiding the decrease in ladder regularity in converting of OLPS to the corresponding LPS.



Scheme 2 A proposed mechanism for the synthesis of LPBAS

Characterization of the Titled LPBAS

As shown in Table 1, a variety of sophisticated techniques including FTIR, XRD, ^1H -NMR, ^{29}Si -NMR, DSC, VPO and elemental analysis were used to substantiate the ladder structure of LPBAS.

Table 1. Characterization data of LPBAS

Characterization items	Results
Appearance	White solid
Solubility	Soluble in THF, 1,4-dioxane etc.
Elemental analysis	For LPBAS ($\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_5\text{Si}_2$) _n Calcd. (%): C 56.07, H 5.61, N 6.54; Found (%): C 55.87, H 5.68, N 6.32
$\overline{M}_n$ (by VPO, g/mol)	1.86×10^4
FTIR (KBr, in cm^{-1})	3319 (st, NH); 3064 (m, C_6H_4); 2927, 2886 (st, CH_2); 1640 (st, C=O); 1604 (st, C_6H_4); 1032 (st, Si—O—Si)
Distance d and t (nm)/ 2θ ($^\circ$) by XRD & (simulated by HyperChem Release 7)	Ladder width: $d=1.65$ nm/5.34 (1.56 nm) Ladder thickness: $t=0.42$ nm/20.96 (0.40 nm)
^1H -NMR (δ)	8.6–7.8 (2H, NH); 7.9, 7.3 (10H, C_6H_5); 3.3 (4H, NCH ₂); 1.7 (4H, SiCH ₂ CH ₂); 0.66 (4H, SiCH ₂)
^{29}Si -NMR (δ)	Main peak: -61.03 ($-\text{CH}_2\text{SiO}_{3/2}$) Minor peak: -17.12 ($\text{Me}_3\text{SiO}_{1/2}$)
T_g (by DSC, $^\circ\text{C}$)	112

As shown in Fig. 1, two main Bragg peaks were recorded. According to the literature^[6–10], the first sharp peak at 1.65 nm/5.34 (2θ $^\circ$) stands for the width (d) of the ladder polymer, and the second one at 0.42 nm/20.96 (2θ $^\circ$) can be ascribed to the thickness (t) of the ladder macromolecule or intermolecular spacing between the polymers. These results are consistent with those obtained by molecular simulation. Interestingly, a weak peak appearing at 0.71 nm/12.40 (2θ $^\circ$) assumably relates to the distance between amido groups in the two sides of LPBAS due to the strong H-bonding interactions. Significantly, the first sharp and strong Bragg peak indicates the existence of high long-range order of the ladder structure on the macromolecular framework.

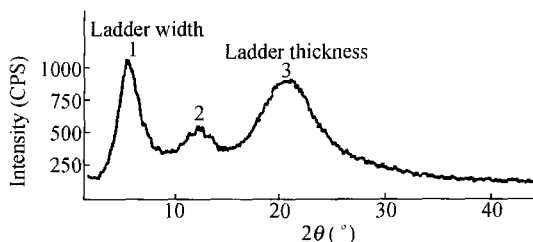
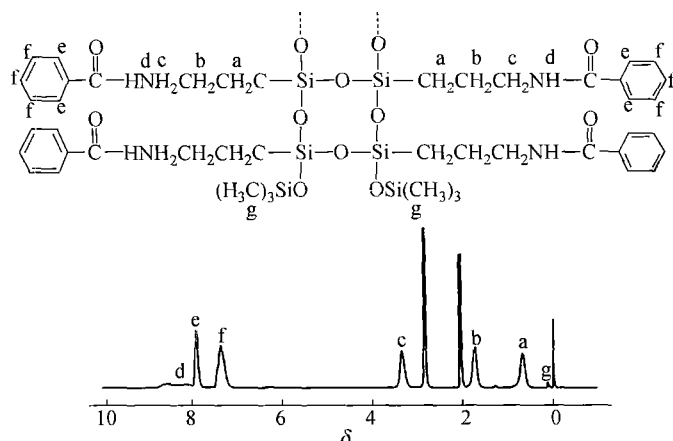
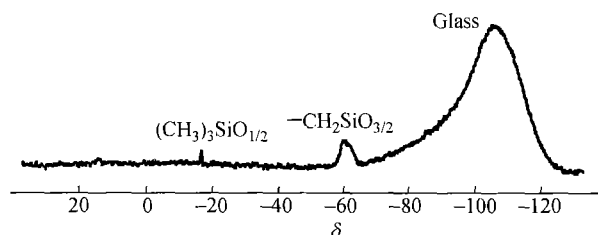


Fig. 1 XRD pattern of LPBAS

No obvious resonance peaks assigned to Si—OEt groups in the ^1H -NMR of LPBAS (as shown in Fig. 2) were found, suggesting that the Si—OEt groups have been hydrolyzed completely. The weak absorption of end-capping group ($-\text{SiMe}_3$) appeared at $\delta=0.16$, is compatible with the expected structure of LPBAS.

^{29}Si -NMR spectrum (Fig. 3) shows an important information about the ladder structure of LPBAS. Only two distinct types of Si-atom in LPBAS were recorded and the resonance signal related to Si-atom in the monomer M has disappeared thoroughly. One type of Si-atom at $\delta=-61.03$ is attributed to internal silicon atom of ($-\text{CH}_2\text{SiO}_{3/2}$) units in the LPBAS backbone, and another one at $\delta=-17.12$ represents the terminal silicon atom of ($\text{Me}_3\text{SiO}_{1/2}$). Most importantly, the considerably narrow base-line width ($w=6$) of the main chain unit ($-\text{CH}_2\text{SiO}_{3/2}$) indicates that LPBAS has regular ladder main chain.

Fig. 2 ^1H -NMR spectrum of LPBASFig. 3 ^{29}Si -NMR spectrum of LPBAS

Additionally, compared with the low T_g of single-chain polydimethylsiloxane ($< -100^\circ\text{C}$), the T_g of the titled polymer LPBAS is as high as 112°C . The obvious difference can be attributed to the highly rigid ladder double-chain structure and strong H-bonding interactions, which greatly restrict the internal rotation of $-\text{Si}-\text{O}-\text{Si}-$ main chain.

CONCLUSIONS

In summary, LPBAS has been successfully synthesized under the assistance of concerted H-bonding self-assembling template of amido and $\text{Si}-\text{OH}$ groups, respectively. The results obtained from the characterization data indicate that LPBAS is a macromolecule with semi-rigid and ordered ladder architecture. This facile synthetic method can be employed to prepare other kind of regular LPSs.

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