

SYNTHESIS AND CHARACTERIZATION OF A NOVEL REACTIVE LADDER-LIKE POLYSILSESQUIOXANE WITH LATERAL BROMOPHENYL GROUPS*

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Abstract A novel soluble, reactive ladder-like polysilsesquioxane (**L**) with lateral bromophenyl groups was synthesized successfully by stepwise coupling polymerization (SCP) method including preaminolysis, hydrolysis and polycondensation steps. The monomer 3-trichlorosilylpropoxy-4-bromobenzene (**M**) was first prepared via hydrosilylation reaction catalyzed by dicyclopentadienylplatinum (II) dichloride (Cp_2PtCl_2). The title polymer (**L**) was characterized by $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, FTIR, X-ray diffraction (XRD), DSC and vapor pressure osmometry (VPO). The experimental results indicate that the polymer (**L**) possesses a typical ladder-like structure.

Keywords Ladder-like, Polysilsesquioxane, Stepwise coupling polymerization, Hydrosilylation

INTRODUCTION

As early as 1960, Brown *et al.*^[1] first reported a linear, soluble ladder-like polyphenylsilsesquioxane by equilibration polymerization of phenyltrichlorosilane hydrolyte in the presence of an alkaline catalyst at 250°C. Unlike usual insoluble random network polymers, the unique double-chain ladder-like structure results in its significant film-forming ability, thermal resistance, and mechanical properties, which have interested many polymer chemists^[2–9]. However, this method can not be used to prepare ladder-like polysilsesquioxanes containing reactive side groups such as Si—H group *etc.* due to the harsh reaction conditions.

Recently, on the basis of hydrogen bonding self-assembly, a new route named “stepwise coupling polymerization” (SCP) was designed to synthesize ladder-like polysiloxanes by our group^[10]. SCP involves preaminolysis of trichlorosilane, hydrolysis and polycondensation (Scheme 1). A series of novel ladder-like polysilsesquioxanes containing non-reactive and reactive side groups such as phenyl, methyl, vinyl, allyl, hydroxy, ester, epoxy groups *etc.* were synthesized under mild reaction conditions through this route^[11–19]. Moreover, several kinds of organo-bridged ladder-like polysiloxanes were prepared by SCP too^[20–22].

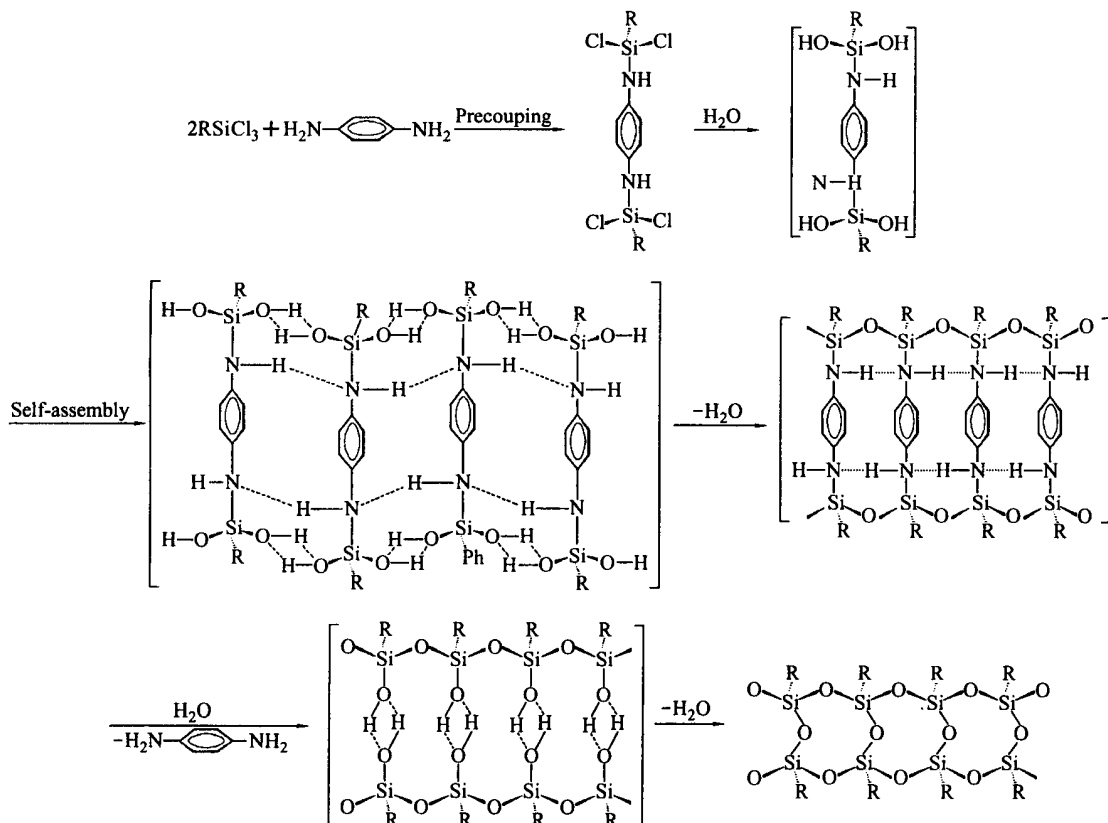
Because of the unique double-chain structure, the functional polymers based on the ladder-like polysilsesquioxanes have excellent thermal, thermo-oxidative and electronic properties. Several kinds of liquid crystalline polysilsesquioxanes have been prepared by hydrosilylation reaction of a vinyl-terminated liquid crystalline compounds with ladder-like polyhydrosilsesquioxane or random copolymethylhydrosilsesquioxane^[23, 24]. However, there are some limitations to preparing functional polymers in this way due to the unstability of Si—H groups therein. Since bromophenyl groups can be further functionalized, a variety of

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functional polymers such as liquid crystalline and NLO polymers can be prepared using the ladder-like polysilsesquioxanes with lateral bromophenyl groups as precursors. In this paper, the above mentioned novel reactive ladder-like polysilsesquioxane (L) was synthesized by SCP, and its structure was elucidated by a combination of $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, FTIR, XRD, VPO and DSC methods.



Scheme 1 Synthetic route of SCP

EXPERIMENTAL

Materials

All the reagents and solvents were commercially available and of analytical grade. Trichlorosilane, 1,4-phenylenediamine (PDA), allyl bromide, methanol, tetrahydrofuran (THF) and toluene were purchased from Beijing Chemical Factory, 4-bromophenol was obtained from Acros Co. THF and toluene were distilled from a sodium-benzophenone complex. Trichlorosilane was distilled and then stored in a dry container before use. Dicyclopentadienyl platinum dichloride (Cp_2PtCl_2) used as the hydrosilation catalyst was prepared by a published method^[25].

Characterization

FTIR spectra were recorded on a Bruker EQUINOX55 spectrometer. The $^1\text{H-NMR}$ spectrum of the monomer was obtained from a JNH-FX100 (JBOX) 300 MHz spectrometer, with chloroform- d (CDCl_3) as the solvent. $^1\text{H-NMR}$ measurements of the polymer and $^{29}\text{Si-NMR}$ measurements of both monomer and polymer were performed on a Varian Unity 200 MHz instrument and $^{29}\text{Si-NMR}$ spectra were referenced ($\delta = 6.9$) to external standards (hexamethyldisiloxane). X-ray diffraction (XRD) analysis was carried out on a Rigaku D/MAX 2400 X-ray diffractometer. Differential scanning calorimetry (DSC) experiments were performed on a Mettler Toledo Star-822 differential scanning calorimeter under N_2 at a scanning rate of 10 K/min. The number-average molecular

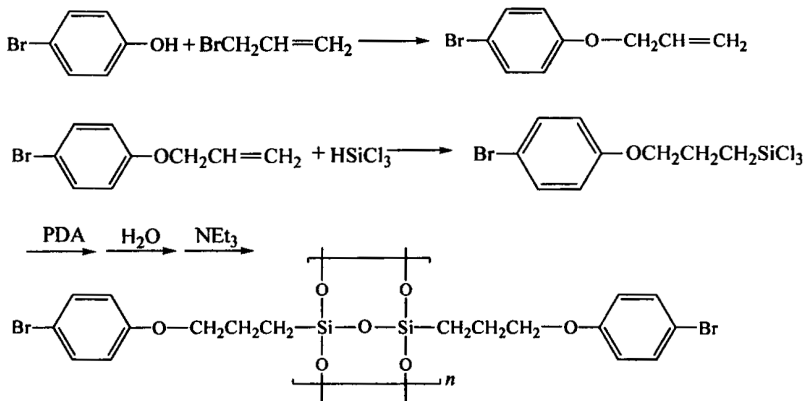
weight (M_n) was determined by a Knauer vapor pressure osmometer (VPO) with THF as the solvent.

Synthesis

The synthetic route of the ladder-like polysilsesquioxane with lateral bromophenyl group is shown in Scheme 2.

Synthesis of 1-Allyloxy-4-bromobenzene

4-Bromophenol was alkylated with allyl bromide and potassium carbonate according to the procedure in the literature^[26]. 1-Allyloxy-4-bromobenzene was purified through a silica gel column using CH_2Cl_2 as eluent to give a colorless oil in a yield of 96%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ); 7.34 (d, 2H, $-\text{C}_6\text{H}_4-$), 6.77 (d, 2H, $-\text{C}_6\text{H}_4-$), 5.98 (m, 1H, CH=), 5.32 (m, 2H, $\text{CH}_2=$) and 4.46 (d, 2H, $-\text{CH}_2\text{O}-$).



Scheme 2 Synthetic route of the polymer L

Synthesis of 3-Trichlorosilylpropoxy-4-bromobenzene (M)

Hydrosilylation reaction was carried out by standard Schlenk techniques. A solution of 4.26 g (0.02 mol) of 1-allyloxy-4-bromobenzene, 1 mg of Cp_2PtCl_2 catalyst and 8 mL of trichlorosilane in 30 mL toluene were stirred for 48 h at ambient temperature under the protection of argon. Then the volatile components were removed under reduced pressure, and the product M was obtained as a pale yellow liquid in 98 % yield. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ) 7.37 (d, 2H, $\text{Br}-\text{C}_6\text{H}_4-$), 6.78 (d, 2H, $-\text{C}_6\text{H}_4-\text{O}$), 3.90 (t, 2H, $-\text{OCH}_2-$), 1.97 (m, 2H, $-\text{CH}_2-\text{CH}_2-$) and 1.52 (t, 2H, $-\text{CH}_2-\text{Si}$); $^{29}\text{Si-NMR}$ (200 MHz, CDCl_3 , δ), 13.58 ($-\text{SiCl}_3$).

Synthesis of Ladder-like Polysilsesquioxane (L) with Lateral Bromophenyl Groups

A solution containing 1.08 g (0.01 mol) PDA and 2.8 mL TEA in 70 mL THF was added dropwise to a solution of 0.02 mol M dissolved in 80 mL toluene under vigorous stirring at -10°C for 1.5 h. Then the reaction solution was stirred for another 0.5 h. A solution containing 0.72 mL (0.04 mol) of water and 5.6 mL TEA in 70 mL THF was added dropwise at -5 to 0°C , then the mixture was slowly raised to ambient temperature and stirring continued for 10 h. After being filtered and neutralized, the solution was concentrated to about 50 mL. Some anhydrous Na_2SO_4 and a small amount of tetramethylammonium hydroxide pentahydrate ($(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$) were added to the toluene solution and stirred for 12 h. After filtration, the process was repeated three times. Next, some anhydrous CaSO_4 was added and the solution was stirred at 50°C for another 48 h. The solution was filtered and washed with saturated brine and water until neutral, then dried over anhydrous Na_2SO_4 . The solution was concentrated to about 10 mL followed by the dropwise addition of 40 mL methanol. Some precipitates appeared gradually, which were collected and redissolved in toluene; then the process was repeated twice. Finally, the precipitates were collected and dried at 50°C in a vacuum oven for 24 h to give a white solid polymer L in a yield of 67%.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of Monomer *M*

Monomer *M* was synthesized successfully by hydrosilylation of 1-allyloxy-4-bromobenzene with trichlorosilane. It is worth mentioning that the hydrosilylation reaction must be protected by dry argon and the monomer *M* obtained must be stored under a dry argon atmosphere.

Generally, hydrosilylation reactions were carried out using THF as the solvent. However, in this system, we found that there was always some residual THF, which could not be removed completely even under high vacuum and high temperature. According to the literature^[27], THF could undergo coordination with trichlorosilane in the ratio of 1:1. Since the residual trichlorosilane can take part in the following hydrolysis reaction, it must be removed completely. Therefore toluene was used as the solvent instead of THF in this step.

Since there are two kinds of adducts (α and β adducts) in the hydrosilylation reaction catalyzed by H_2PtCl_2 , we employed Cp_2PtCl_2 as catalyst to reduce the amount of α -adducts. As can be seen from the ^1H -NMR spectrum (Fig. 1) and ^{29}Si -NMR spectrum (Fig. 2) of *M*, β -adduct is the dominant product after hydrosilylation and almost no detectable α -adduct appears under the reaction conditions used. This is mainly attributed to the high steric hindrance of Cp_2PtCl_2 , which leads to higher steric hindrance of the intermediate complex for the formation of α -adduct than of β -adduct.

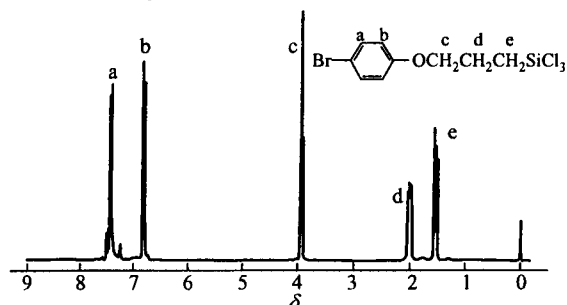


Fig. 1 ^1H -NMR spectrum of monomer *M*

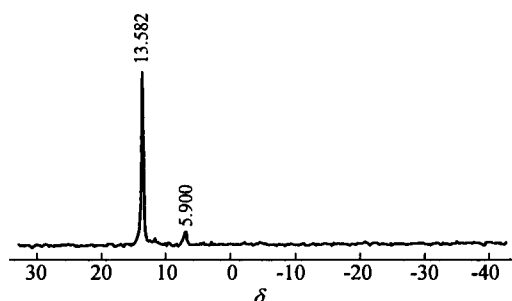


Fig. 2 ^{29}Si -NMR spectrum of monomer *M*

Synthesis of Ladder-like Polymer *L*

The titled ladder-like polymer *L* was successfully synthesized from 3-trichlorosilylpropoxy-4-bromobenzene by SCP method in three steps including preaminolysis reaction with α,ω -phenylenediamine (PDA), controlled hydrolysis and polycondensation. Note that PDA plays two important roles during the reaction process: (1) coupling two silicon atoms to form an intermediate template; (2) assisting the self-assembly of the intermediates through hydrogen-bonds.

In the polycondensation step, a strong base, $(\text{CH}_3)_4\text{NOH}$, was used as the condensation catalyst, which could easily increase the molecular weight.

Some desiccants were also used to remove small amounts of water produced by the reaction system. Since hydrated Na_2SO_4 is unstable above 32.5°C because the bonded water is easily released at $> 50^\circ\text{C}$, CaSO_4 was used to remove water during the last condensation process to increase the molecular weight of polymer.

The narrow distributed polymeric components were obtained by precipitation method using methanol as the precipitant.

CHARACTERIZATION OF POLYMER *L*

Appearance and Solubility

The title polymer is a white solid, which is soluble in acetone, toluene, chloroform and THF but insoluble in methanol and ethanol *etc.* Besides, the polymer solution exhibits good film-forming ability.

Number-Average Molecular Weight

The molecular weight of the polymer *L* is measured by VPO instead of the usual GPC method, because polymer *L* is a relatively stiff wormlike macromolecule with a double-chained skeleton; nevertheless, the standard

compound (polystyrene) usually used for calibrating a GPC instrument is a flexible linear polymer that assumes a coil-like conformation in THF. The number-average molecular weight (M_n) of the polymer measured by VPO is 10,400.

FTIR Spectrum

The FTIR spectrum of the titled polymer is shown in Fig. 3. The strong and broad band at 1128–1000 cm^{-1} belongs to the stretching vibration of Si—O—Si; the band at 3445 cm^{-1} is attributed to the stretching vibration of uncondensed Si—OH. Bands at 1245 and 1287 cm^{-1} are assigned to the vibration of Si—CH₂ and several absorption peaks (1578, 1591, 1489 and 1406 cm^{-1}) belong to the vibration of phenylene. The band at 1073 cm^{-1} is assigned to the vibration of the Br—C₆H₄— group.

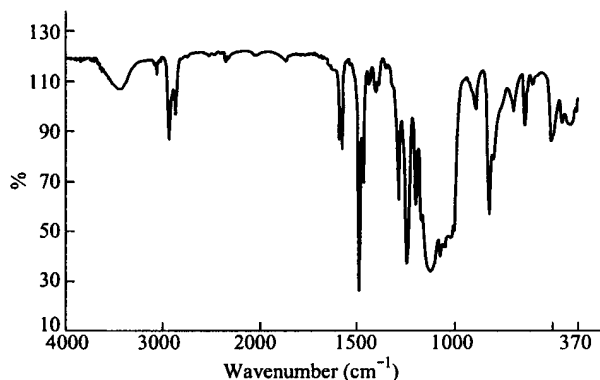


Fig. 3 FTIR spectrum of polymer L

¹H-NMR and ²⁹Si-NMR Spectra

¹H-NMR and ²⁹Si-NMR spectra are shown in Fig. 4 and Fig. 5, respectively.

There is an apparent shift (from $\delta = 1.52$ to 0.74) of the peak assigned to the proton near to the silicon atom in the ¹H-NMR spectrum compared to that of the monomer M. Simultaneously, the peaks are all broad peaks as compared with sharp peaks in the ¹H-NMR spectrum of the monomer.

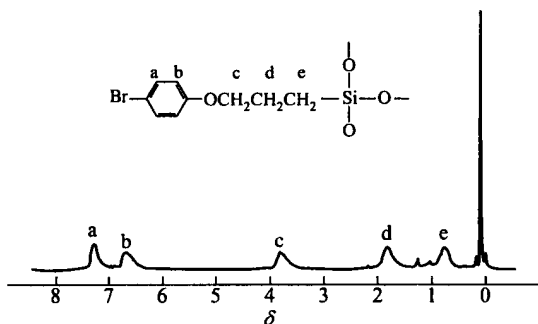


Fig. 4 ¹H-NMR spectrum of polymer L

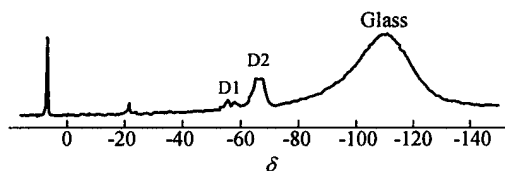


Fig. 5 ²⁹Si-NMR spectrum of polymer L

It can be seen from the ²⁹Si-NMR spectrum of polymer L (Fig. 5) that there are two distinct peaks (D₁, $\delta = -56$ and D₂, $\delta = -67$) for silicon atoms. The peak D₂ represents the fully condensed silicon atom with three siloxane bonds and one silicon-carbon bond in the ladder-like double chain, whereas the peak D₁ stands for the silicon atom with one uncondensed silanol group. The ²⁹Si-NMR signals of the polymer are all broad peaks, for example the width of the peak D₂ is about 8. Several different stereo-configurations (*cis*-isotactic, *cis*-syndiotactic, *etc.*) may coexist in ladder-like polymers, which probably is the main reason for broadening of the ²⁹Si-NMR peaks.

XRD patterns

There are two distinct peaks in the XRD pattern of polymer L (Fig. 6). The first halo appearing at d_1 (0.738 nm)

may indeed be considered as the intermolecular chain-to-chain distance in the ladder-like polysilsesquioxane, namely the width of the polymer (L). The second halo ($d_2 = 0.432$ nm), covering a wide range of diffraction angles, is related to the thickness of the ladder-like polysilsesquioxane, with reference to Brown *et al.*^[1] and Andrianov *et al.*^[28]. This XRD pattern shows that polymer L has rod-like skeletons with good regularity.

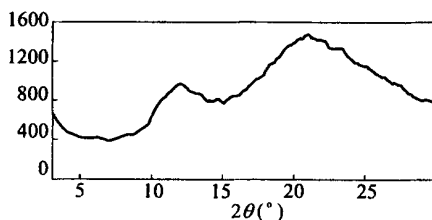


Fig. 6 The XRD spectrum of polymer L

DSC Curve

The DSC curve of polymer L is shown in Fig. 7. The sample was scanned from 50 to 250°C at a rate of 10 K/min and then cooled in liquid N₂ immediately. With a second scan, a distinct glass transition temperature T_g appeared at 74°C. As is well known, the single-chained polysiloxanes are flexible and have very low T_g values. For examples, the T_g of polydimethylsiloxane is -120°C, and T_g of polymethylphenylsiloxane (35 mol% Ph) is -100°C^[29]. Obviously, the T_g of the polymer L is much higher than that of single-chain polysiloxanes due to its comparatively rigid double-chain structure.

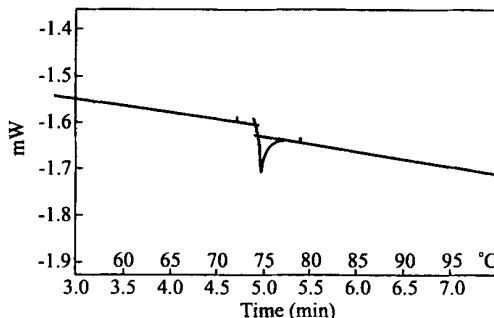


Fig. 7 DSC curve of polymer L

The characterization data from ¹H-NMR, ²⁹Si-NMR, XRD spectra, DSC curve, VPO, as well as the good solubility of polymer L in a series of organic solvents, indicate that polymer L possesses an ordered ladder-like structure.

CONCLUSIONS

A novel ladder-like polysilsesquioxane with reactive bromophenyl side groups, which may have potential applications as a precursor for advanced functional materials, has been prepared successfully by a stepwise coupling polymerization method. The structure of the polymer was elucidated by FTIR, ¹H-NMR, ²⁹Si-NMR, XRD, DSC and VPO. The characterization results show that this polymer possesses an ordered ladder-like structure.

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