

Note

SYNTHESIS OF LADDERLIKE POLYHYDROXYPROPYLSILSESQUIOXANE*

Huai-zhong Pan, Chun-qing Liu, Zhong Jin, Ming Cao, Jian-hua Luo,
Ping Xie and Rong-ben Zhang**

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Yu-hui Lin and Neal Tai-sheng Chung

Institute of Materials Research and Engineering, Singapore 117602, Singapore

Abstract Ladderlike polyhydroxypropylsilsesquioxane (HO-T) was synthesized by alcoholysis of ladderlike poly(3-propionyloxy-propyl)silsesquioxane. The HO-T was characterized by GPC, IR, NMR, DSC, TGA and X-ray diffraction methods. Through hydrogen-bonding interaction, ladderlike polymer (HO-T) can form a supramolecular complex with somewhat regular structure.

Keywords Ladderlike polyhydroxypropylsilsesquioxane, Hydrogen-bond interaction, Supramolecular complex

INTRODUCTION

Ladderlike polyphenylsilsesquioxane (Ph-T) was first synthesized in 1960 by Brown *et al.*^[1] by equilibrating the condensation products of phenylsilanetriol. Although Frye^[2] pointed out that the polymer synthesized by equilibration polymerization does not have a highly ordered ladderlike structure, and there are many structural defects such as branches and some kinds of cage-like oligomers in the polymer. Because of its special structure and properties, many investigations have been done in this area. Shiba^[3] and Ito^[4] patented the preparation of ladderlike polyallylsilsesquioxane (A-T) and polyvinylsilsesquioxane (V-T) in 1987, but they did not give a convincing structural characterization.

Our group has synthesized various kinds of ladderlike polysilsesquioxanes including V-T, A-T, ladderlike polyhydrosilsesquioxane (H-T), etc.^[5-8] by “stepwise coupling polymerization (SCP)”, which involves preaminolysis of trichlorosilane followed by hydrolysis and polycondensation. The regularities of the ladderlike polymers prepared by SCP are usually better than those synthesized by other methods^[8]. V-T, A-T or H-T can be functionalized by hydrosilylation, oxidation or condensation reaction. Various functional ladderlike polysilsesquioxanes were prepared by grafting functional groups to the ladder-like main chain, including non-linear optical polymers, fishbone-like (end-on fixed type) and rowboat-like (side-on fixed type) liquid crystalline polymers^[9-15].

Here we report a ladderlike polymer containing hydroxy groups. Because of the interaction between hydrogen bonds, the ladderlike polymer can self-assemble under suitable conditions.

EXPERIMENTAL

Materials and Measurement

IR spectra were recorded on a Specord 75-IR (Carl Zeiss, Jena) spectrophotometer, ¹H-NMR spectra were

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** Corresponding author: Rong-ben Zhang (张榕本), E-mail: zhangrb@infoc3.icas.ac.cn

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obtained with a JNH-FX100 (JBOX) spectrometer. The molecular weight of the polymer was measured by GPC (Shimadzu LC-4A) using polystyrene as the standard and THF as eluent at a flow rate of 1 mL/min. DSC measurements were performed on a Perkin-Elmer DSC-7 instrument at a heating rate of 10 K/min. TGA was performed on a Perkin-Elmer 7 thermal analysis system under N_2 at a heating rate of 10 K/min.

Allyl propionate and trichlorosilane were distilled before use. Cp_2PtCl_2 catalyst was prepared by referring to the literature^[16]. THF was dried by anhydrous Na_2SO_4 and distilled over sodium. Toluene was washed with concentrated H_2SO_4 to remove thiophene and distilled over sodium. Triethylamine was refluxed with ninhydrin and distilled, then dried by KOH. All the other solvents and reagents are commercially available and of analytical grade. They were purified by standard methods.

Synthesis of 3-Trichlorosilanylpropyl Propionate (Ester-SiCl₃)

To a 500 mL three-necked flask equipped with a reflux condenser and a dropping funnel, 50 mL of allyl propionate and small amount of Cp_2PtCl_2 were added. The flask was cooled to 0 °C. Then 50 mL of $HSiCl_3$ was added to the reaction mixture slowly. After addition, the reaction mixture was stirred for about 24 h at room temperature and gently refluxed for about 6 h, then the remaining $HSiCl_3$ was removed by distillation under vacuum (110 °C/133 Pa). 104 g of the title compound was obtained with a yield of 91%.

Synthesis of Ladderlike Poly(3-propionyloxy-propyl)silsesquioxane (Ester-T)

25 mL (0.1 mol) of ester-SiCl₃ and 200 mL of toluene were added to a 1000 mL three-necked flask. A solution of 5.4 g (0.05 mol) of *p*-phenylenediamine (PDA) and 14 mL (0.1 mol) of triethylamine in 140 mL of THF was added dropwise into the flask under stirring in 6 h at -10~-15 °C. After addition, the reaction system was stirred continuously for 30 min at -10 °C. Then 2.7 mL (0.15 mol) of water in 50 mL of THF was added dropwise to the flask at -15~-20 °C within 5~6 h. The reaction system was further stirred at room temperature for about 5 h and then filtered to remove the salt. The filtrate was washed with water until neutral and dried by anhydrous Na_2SO_4 overnight. To the filtrate, 7~8 drops of triethylamine and several grams of CaH_2 were added and stirred for 24~48 h at room temperature, then about 0.5~1 mL of Me_3SiCl was added to the system and stirred for another 24 h. After the completion of reaction, the solution was washed with water until neutral to obtain the title compound (16 g) in a yield of 95%.

IR (KBr, cm^{-1}): 1000~1200 (Si-O-Si), 1730 (C=O); ^1H -NMR ($CDCl_3$, δ): 0.68 (2H, Si-CH₂-), 1.13 (3H, CH₃CH₂CO-), 1.74 (2H, SiCH₂CH₂-), 2.31 (2H, CH₃CH₂CO-) and 4.05 (2H, SiCH₂CH₂CH₂-).

Synthesis of Ladderlike Poly(3-hydroxy-propyl)silsesquioxane (HO-T)

100 mL (containing 7 g) of ester-T solution and 200 mL of methanol were added to a 500 mL flask equipped with a reflux condenser. 3~5 drops of $SOCl_2$ was added to the flask. The reaction mixture was refluxed for *ca.* 1 day. After reaction, the excess methanol and the by product methyl propionate were removed under vacuum. Then some methanol was added to the toluene solution of the product which was dried over anhydrous Na_2SO_4 . 3.9 g product was obtained in a yield of 79%.

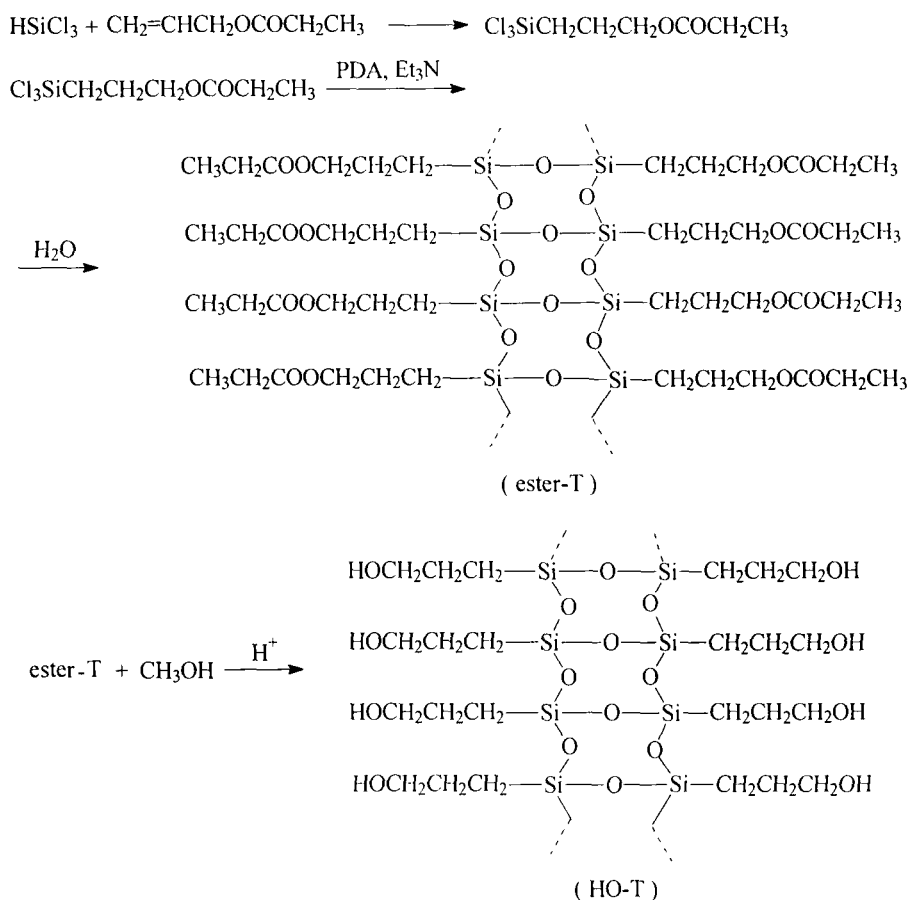
Measurement of Alignment Order of HO-T

To a 250 mL flask, 20 mL of HO-T methanol solution was added, then 50 mL of toluene was added slowly to the flask with stirring. The precipitate was separated by centrifugation, and dried under vacuum. The molecular arrangement of HO-T was measured by X-ray diffraction.

RESULTS AND DISCUSSION

Synthesis of Ladderlike Polyhydropropylsilsesquioxane (HO-T)

Hydroxy groups are introduced into the ladderlike polymers so that the ladderlike polymer can self-assemble to the suitable supramolecular complex under proper conditions. Hence, trichlorosilylpropyl propionate was synthesized at the first step, then coupled to the ladderlike polymer, ester-T (Scheme 1).



Scheme 1

The ladderlike polyhydrosilsesquioxane (HO-T) was obtained by alcoholysis of ester-T.

The average molecular weight of HO-T obtained from GPC measurement is around 2×10^3 on using polystyrene as the standard. HO-T can dissolve in methanol, ethanol and slightly dissolve in water and THF, but not dissolve in toluene. So HO-T can self-assemble to a supramolecular complex by adding toluene to the methanol solution of HO-T.

Figures 1 and 2 are the $^1\text{H-NMR}$ and IR spectra of HO-T, respectively. The peaks at 0.55, 1.47 and 3.56 in the $^1\text{H-NMR}$ spectrum are due to α -, β - and γ -H of HO-T respectively. Because the resonance peak of the γ -H of HO-T overlaps with H_2O in $\text{DMSO-}d_6$, the integral value of the peak at 3.56 is larger than that of others. In IR the spectrum, the absorption bands for Si—O—Si bond and —OH group appear at $1000\sim 1200\text{ cm}^{-1}$ and $\sim 3400\text{ cm}^{-1}$, respectively, but there is no absorption band at 1730 cm^{-1} which is characteristic for the C=O group.

The thermostability of HO-T was measured by TGA. The decomposition temperature (T_d) is 388°C . The glass transition temperature (T_g) of HO-T was measured by DSC. It indicates that HO-T is rather rigid polymer with a high glass transition temperature (T_g) of 142°C . Because of the weak interaction energy of hydrogen bonds, no heat-absorbing peak is observed under 100°C .

The hydrogen bond interaction can be confirmed by temperature-variable FT-IR spectra. As shown in Fig. 3, with increasing temperature, the peak intensity at 3380 cm^{-1} indicating the hydrogen bond interaction of HO-T was weakened. When the temperature is higher than 100°C , almost all the hydrogen bonds were broken.

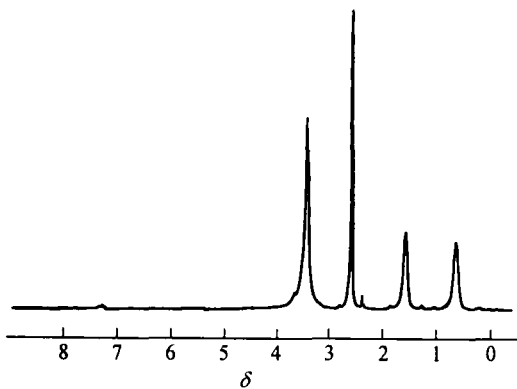


Fig. 1 ¹H-NMR spectrum of HO-T

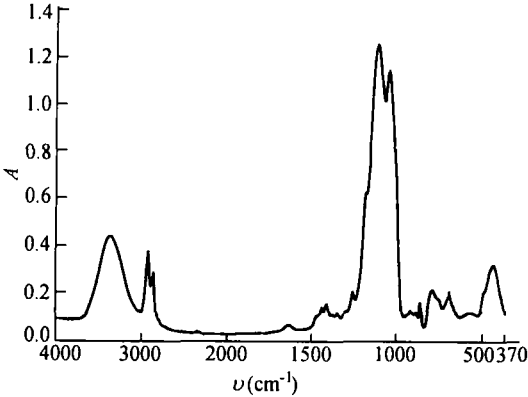


Fig. 2 IR spectrum of HO-T

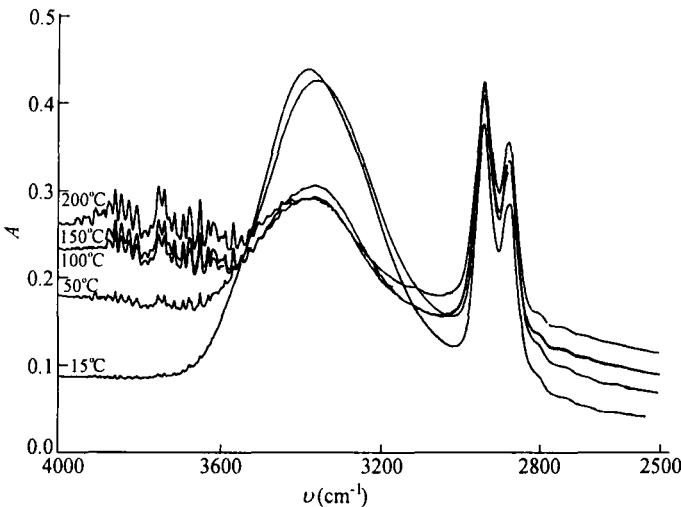


Fig. 3 Temperature dependence of FT-IR spectrum of HO-T

The structure of HO-T that precipitated from methanol solution was measured by X-ray diffraction and is shown in Fig. 4. It can be seen from the diffraction pattern that HO-T appears somewhat orderly after precipitation with toluene. It has long- and short-range ordered structure. Thus HO-T may self-assemble to a more regular structure after precipitation from solution.

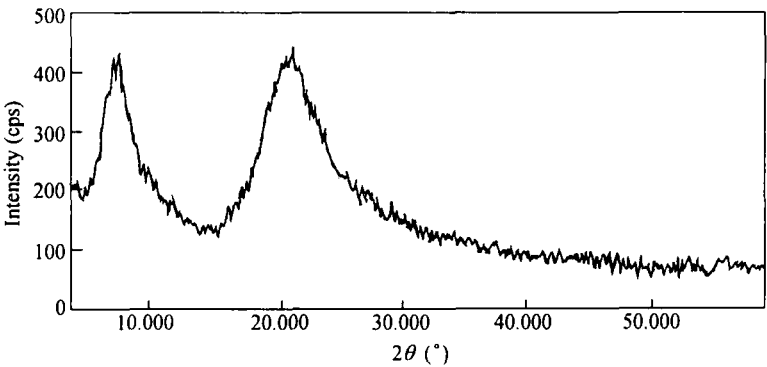


Fig. 4 X-ray diffraction pattern of HO-T

CONCLUSION

The ladderlike polyhydropropylsilsesquioxanes have been synthesized and can self-assemble to a somewhat regular supermolecular complex, which may be used as the precursor for synthesis of functional polymers containing special structures.

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