

Note

SYNTHESIS OF NEW HIGH MOLECULAR WEIGHT AND REACTIVE LADDERLIKE POLYSILSESQUOXANES*

Huai-zhong Pan, Chun-qing Liu, Ming Cao, 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 polychloropropylsilsesquioxane (CP-T) was first synthesized by “stepwise coupling polymerization”. The molecular weight of CP-T is as high as 1.7×10^5 . It is a tough, elastic reactive ladderlike polymer and has good heat-resistant and adhesive properties. CP-T can further react with many nucleophilic reagents to generate new ladderlike reactive polysilsesquioxanes, which can be used as potential precursors in the synthesis of functional ladderlike polymers.

Keywords Stepwise coupling polymerization, Reactive ladderlike polymer, Nucleophilic substitution

INTRODUCTION

Ladderlike polyphenylsilsesquioxane (Ph-T) was first synthesized by Brown *et al.*^[1] by equilibrating the condensation product of phenylsilanetriol. Since then, much attention has been paid to this area because of its special structure and properties such as thermostability, though 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. Much work has also been done on the synthesis of reactive ladderlike polysilsesquioxanes. The reactive ladderlike polysilsesquioxanes can be subjected to further modification, such as hydrosilylation, oxidation, condensation, or cross-linking with other polymers. They can be used to prepare organic/inorganic hybrid materials, microscopically controllable supramolecules and low decay nonlinear optical (NLO) polymers, etc.

Nakahama^[3] tried to synthesize polyvinylsilsesquioxane (V-T) by Brown's method, but they only obtained a crosslinked gel. Shiba^[4] and Ito^[5] patented the preparation of polyallylsilsesquioxane (A-T) and V-T in 1987, but they did not give a convincing structural characterization. Zhang and Shi *et al.*^[6-12] have also made extensive studies on these polymers, concerning their structural characterization and physical properties.

Our group has synthesized a series of ladderlike polysilsesquioxanes including V-T, A-T, ladderlike polyhydrosilsesquioxane (H-T), etc. by “stepwise coupling polycondensation”^[13-15], which involves preaminolysis of trichlorosilane followed by hydrolysis and polycondensation. The regularities of the ladderlike polymers are usually better than those synthesized by other methods^[16].

V-T, A-T or H-T can be functionalized by hydrosilylation, oxidation or condensation reaction. A series of functional ladderlike polysilsesquioxanes were prepared by grafting functional groups onto the ladderlike main chain, including non-linear optical polymers, fishbone-like (end-on fixed type) and rowboat-like (side-on fixed type) liquid crystalline polymers^[17-23].

* This project is financially supported by National Natural Science Foundation of China (No. 29874034).

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

Received January 20, 2000

In this paper, we report a new reactive ladderlike polychloropropylsilsesquioxane (CP-T), which can be further functionalized by nucleophilic substitution reaction.

EXPERIMENTAL

Materials and Measurement

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

3-Chloropropyltrichlorosilane was purchased from Hongxing Chemical Company and distilled before use. 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. Other solvents and reagents were purified by standard methods. All the solvents are commercially available and of analytical grade.

Synthesis of Ladderlike Polychloropropylsilsesquioxane (CP-T)

21.2 g (0.1 mol) of 3-chloropropyltrichlorosilane and 300 mL of toluene was added to a 1000 mL three-necked flask. A solution of 10.1 g (0.1 mol) of triethylamine and 5.4 g (0.05 mol) of *p*-phenylenediamine (PDA) in 250 mL of THF was added dropwise to the flask under stirring at $-15\sim -20^\circ\text{C}$ within 6 h. The reaction system was stirred for 30 min at -15°C . After addition, 3.6 g (0.2 mol) of water in 150 mL of THF was added dropwise to the flask under -15°C within 6 h. The reaction system was further stirred at about 25°C for a few hours, then filtered to remove the salt. To the filtrate, 1 mL of triethylamine and 1–3 g of CaH_2 were added and stirred for 24–48 h at room temperature. After completion of the condensation reaction the solution was washed with water until neutral. The solvent was removed under vacuum, 9.1 g white solid was obtained in a yield of 70%.

Synthesis of Ladderlike Polyiodopropylsilsesquioxane (IP-T)

5 g of CP-T was dissolved in 100 mL of acetone, then 10 g of NaI was added to the solution. The reaction mixture was refluxed for 1 h, then filtered to remove the precipitated NaCl. The product was precipitated by adding water and washed thoroughly with water, then dried under vacuum. 8 g of product was obtained in a yield of 94%.

RESULTS AND DISCUSSION

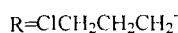
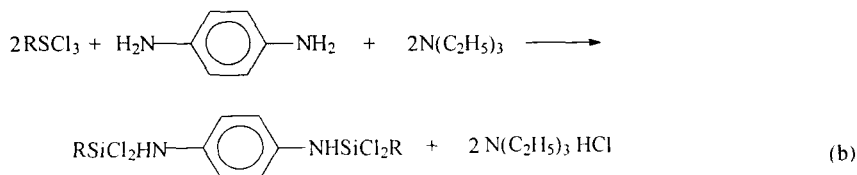
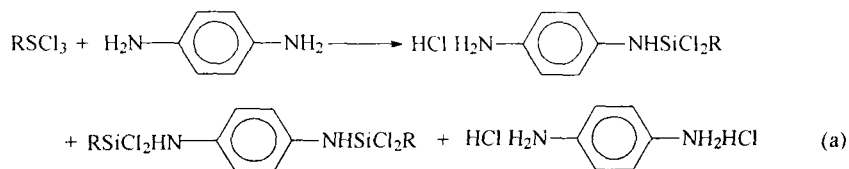
Synthesis and Properties of CP-T

CP-T have been synthesized by “stepwise coupling polymerization”, which involves the preaminolysis of organotrichlorosilane followed by hydrolysis and polycondensation. This method has been used to synthesize various kinds of ladderlike polysilsesquioxanes. The regularities of the ladderlike polymers synthesized by “stepwise coupling polymerization” are usually better than those synthesized by other methods. They can be used to synthesize tubular polymers.

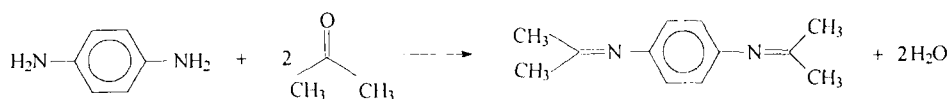
In the present work the preaminolysis reaction has been improved. Originally, organotrichlorosilane was aminolysized by equal moles of *p*-phenyldiamine (PDA) during preaminolysis reaction. But as shown in Scheme 1a, the reaction may produce $\text{RSiCl}_2-\text{NH}-\text{C}_6\text{H}_4-\text{NH}_2 \cdot \text{HCl}$, $\text{RSiCl}_2-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{SiCl}_2\text{R}$ and $\text{HCl} \cdot \text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \cdot \text{HCl}$. In Scheme 1b, triethylamine was used instead of PDA to absorb the produced HCl. The mole ratio of RSiCl_3 :PDA:triethylamine is 1:0.5:1. During the reaction, PDA reacted with RSiCl_3 to form $\text{RSiCl}_2-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{SiCl}_2\text{R}$, and the produced HCl was absorbed by triethylamine. The reaction system was kept slightly acidic, so that a colorless product can be obtained. During the preaminolysis reaction, acetone was originally used as the solvent to dissolve PDA, but as shown in Scheme 2, acetone can also react with PDA, and this reaction will change the ratio of RSiCl_3 to PDA. The produced H_2O can also react with RSiCl_3 during preaminolysis reaction. In order to avoid the occurrence of this reaction, THF was used instead of

acetone, though more THF should be used. As this side-reaction is eliminated, the regularity of the ladderlike polysilsesquioxane will be improved.

Cl—CH₂— groups can also react with Et₃N during the reaction, so Et₃N and PDA were added dropwise into the reaction system at low temperature and kept the ratio of Cl/N in the reaction system at > 1.



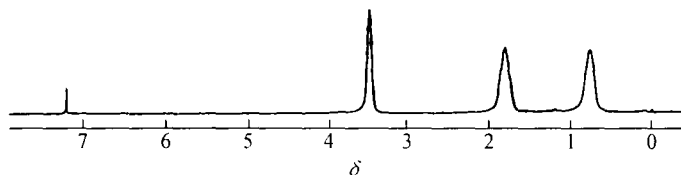
Scheme 1



Scheme 2

CP-T is a colorless tough and elastic material. Because the side reactions were avoided, the regularity of CP-T was improved. CP-T is not cross-linked even at much high molecular weight. The molecular weight of CP-T measured by GPC can reach as high as 1.7×10^5 without network gel. The high molecular weight provides CP-T with elastic properties.

Figure 1 is the ¹H-NMR spectrum of CP-T. The peaks at $\delta = 0.78$, 1.85 and 3.53 is assigned to α -, β - and γ -H respectively. Figure 2 is the IR spectrum of CP-T. The peak at 1000~1100 cm⁻¹ is assigned to the Si—O—Si group and the peak at 700 cm⁻¹ is assigned to the C—Cl bond.

Fig. 1 ¹H-NMR spectrum of CP-T

The thermoresistant property of CP-T was measured by TGA. As shown in Fig. 3, the decomposition temperature (T_d) was found to be 363.4°C. Because of the high polarity of Cl—C bond, CP-T has good adhesion property toward common materials. So it may be used as a heat-resistant adhesive.

CP-T also has excellent film forming properties. It can form a very thin, uniform and transparent film on the surface of many materials.

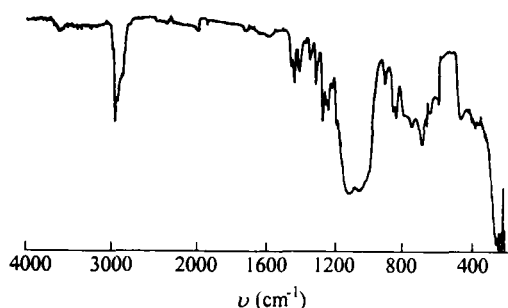


Fig. 2 IR spectrum of CP-T

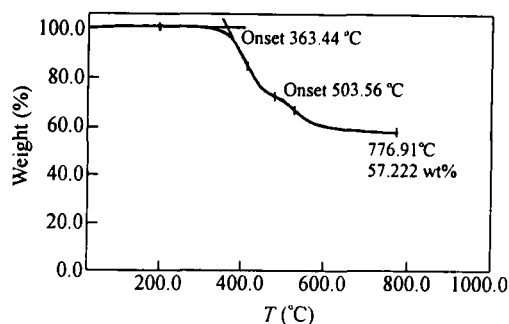
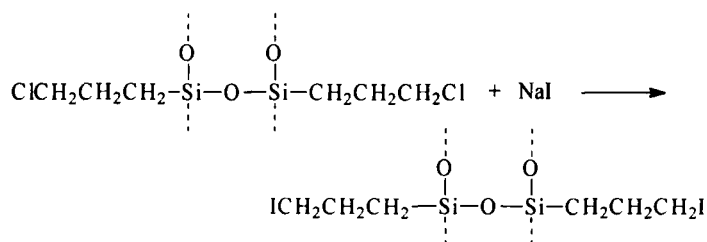


Fig. 3 TGA curve of CP-T

Reaction of CP-T

Due to the reactivity of the Cl— group, CP-T can react with many nucleophilic reagents to form other functional ladderlike polymers such as non-linear optical polymers, liquid crystalline polymers, etc. CP-T can also react with NaI to form more reactive ladderlike polymers.



Scheme 3

As shown in Scheme 3, IP-T was prepared by substituting CP-T with NaI. During substitution, NaCl was rapidly precipitated from the reaction system, and IP-T was obtained as a slightly yellowish solid. It is also a tough and elastic ladderlike polymer, and has good film forming and adhesive properties.

Figure 4 is the $^1\text{H-NMR}$ spectrum of IP-T. Compared with the $^1\text{H-NMR}$ spectrum of CP-T, the chemical shift of IP-T is slightly shifted to high field by *ca.* $\delta = 0.1$, because the electronegativity of the iodine atom is lower than that of the chlorine atom. Figure 5 is the IR spectrum of IP-T. Compared with the IR spectrum of CP-T, the absorption peak of the I-C bond appears at $400\text{--}460\text{ cm}^{-1}$.

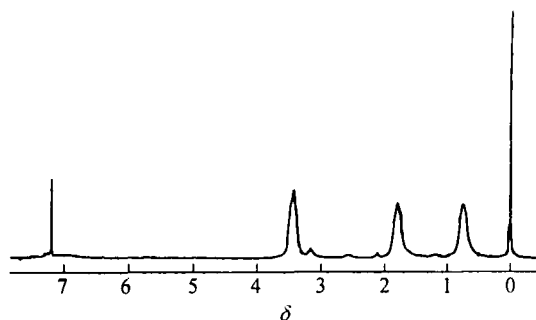
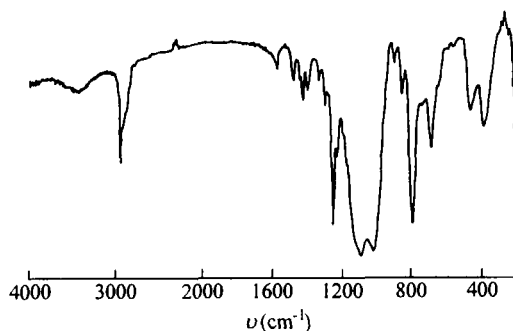
Fig. 4 $^1\text{H-NMR}$ spectrum of IP-T

Fig. 5 IR spectrum of IP-T

After the substitution of the Cl— group with the I— group, the reactivity of the ladderlike polymer should obviously increase. Both CP-T and IP-T may be used as potential precursors in the synthesis of functional polymers having special structures and good film forming and heat-resistant properties.

CONCLUSION

CP-T was synthesized by “stepwise coupling polymerization”. After making some improvements to the synthesis method, the regularity of the ladderlike polymer was increased. CP-T does not cross-link even if the molecular weight reaches as high as 1.7×10^5 . CP-T is a tough, elastic reactive ladderlike polymer and has good heat-resistant and adhesion properties. CP-T can react with many nucleophilic reagents, e.g. it can react with NaI to form IP-T. CP-T adhesive and IP-T are potential precursors in the synthesis of functional ladderlike polymers.

REFERENCES

- 1 Brown, J.F. Jr, Vogt, L.H. Jr, Katchman, A., Eustamce, J.W., Kiser, K.M. and Krantz, K.W., *J. Am. Chem. Soc.*, 1960, 82: 6194
- 2 Frye, C.L. and Klosowski, J.M., *J. Am. Chem. Soc.*, 1971, 93: 4599
- 3 Yamazaki, N., Nakahama, S. and Goto, J., *Contemp. Top. Polym. Sci.*, 1984, 4: 105
- 4 Shiba, S., Fukuyama, S. and Yoneda, Y., 1988, JP 63,118,739
- 5 Ito, T., Yamashita, Y. and Kawazu, T., 1987, JP 62,283,128
- 6 Zhang, X.S. Chen, S.M. and Shi, L.H., *Chinese J. Polym. Sci.*, 1987, 5: 162
- 7 Zhang, X.S. and Shi, L.H., *Chinese J. Polym. Sci.*, 1987, 5: 197
- 8 Shi, L.H., Zhang, X.S., Si, Y.D., Li, M. and Li, D.C., *Chinese J. Polym. Sci.*, 1987, 5: 359
- 9 Zhang, X.S., Shi, L.H. and Huang, C.R., *Chinese J. Polym. Sci.* 1987, 5: 353
- 10 Huang, C.R., Xu, G.Z., Zhang, X.S. and Shi, L.H., *Chinese J. Polym. Sci.*, 1987, 5: 347
- 11 Fang, Z.P., Li, D., Qin, A.W. and Yu, T.Y., *Chinese J. Polym. Sci.*, 1987, 5: 332
- 12 Fang, Z.P., Qiu, A.W. and Yu, T.Y., *Chinese J. Polym. Sci.*, 1987, 5: 340
- 13 Xie, Z.S., Dai, D.R. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1991, 9: 266
- 14 Xie, Z.S., Jin, S.Z., Wan, Y.Z. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1992, 10: 361
- 15 Xie, Z.S., Dai, D.R. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1989, 7: 183
- 16 Li, Z., Cao, X.Y., Xu, H. and Zhang, R.B., *React. Funct. Polym.*, 1998, 39: 1
- 17 Xie, P., Xie, Z.S., Wan, Y.Z. and Zhang, R.B., *Mol. Cryst. Liq. Cryst.*, 1996, 289: 59
- 18 Xie, P., Wan, Y.Z., Zhang, R.B., Zhou, B.S., Hou, J.N., Dai, D.R., Li, Z. and Liu, D.S., *Makromol. Physics & Chem.*, 1996, 197: 745
- 19 Xie, P., Guo, J.S. and Zhang, R.B., *Mol. Cryst. Liq. Cryst.*, 1996, 289: 45
- 20 Wan, Y.Z., Xie, P. and Zhang, R.B., *Macromol. Symp.*, 1996, 105: 249
- 21 Zhang, L.Y., Dai, D.R. and Zhang, R.B., *Polym. Advan. Technol.*, 1997, 8: 662
- 22 Wan, Y.Z., Xie, P. and Zhang, R.B., *Liquid Crystals*, 1998, 24: 871
- 23 Zhang, L.Y., Dai, D.R., Li, Z. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1999, 17: 71