

SYNTHESIS AND CHARACTERIZATION OF A SOLUBLE LADDERLIKE POLYSILSESQUIOXANE CONTAINING REACTIVE ESTER GROUPS*

Yang Liu, Chun-qing Liu, Zhong-rong Shen, Ping Xie and Rong-ben Zhang**

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

Chao-bin He and Tai-shung Chung

Institute of Materials Research and Engineering, National University of Singapore, Singapore 119260

Abstract A novel soluble ladderlike polysilsesquioxane containing reactive ester groups (Ester-T) was synthesized for the first time by stepwise coupling polymerization including preammonolysis, controlled hydrolysis and polycondensation. The monomer, 3-trichlorosilylpropoxy 4-acetoxybenzoate (**M**), was synthesized by hydrosilylation of allyloxy 4-acetoxybenzoate with trichlorosilane in the presence of dicyclopentadienylplatinum (**II**) chloride (Cp_2PtCl_2) catalyst. Combination of FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{29}\text{Si-NMR}$, XRD, DSC, TGA and VPO methods was used to demonstrate that the polymer obtained has an ordered ladderlike structure. The synthesized Ester-T may have promising applications as a precursor of advanced functional polymers.

Keywords Ladderlike polysilsesquioxane, Stepwise coupling polymerization, Hydrosilylation, Characterization

INTRODUCTION

As early as in 1960, Brown *et al.* first reported a linear, soluble, ladderlike polyphenylsilsesquioxane (Ph-T) obtained by equilibration polymerization^[1]. Unlike usual insoluble random network polymers, the unique double-chain ladderlike structure of Ph-T results in its significant film-forming ability, resistance to heat and mechanical properties, and has interested many polymer chemists^[2-9]. However, this method can not be used to synthesize reactive ladderlike polysilsesquioxanes such as polyhydrosilsesquioxane (H-T), polyvinyl(or allyl)silsesquioxane (Vi-T or Allyl-T) due to the harsh reaction conditions (at 250 °C in the presence of KOH) required.

If a ladderlike polysilsesquioxane (LPS) has certain functional side groups such as vinyl, allyl, amino, hydroxy, carboxyl, or ester groups, it would be an excellent functional polymer or a precursor for advanced functional polymers. But work on LPS containing functional groups is still very limited^[10-12]. Since ester groups can be further functionalized, a variety of advanced functional polymers can be derived from Ester-Ts. There are two known approaches for preparing Ester-T. One is through the hydrosilylation reaction between LPS containing Si-H groups and either vinyl- or alkynyl-terminated ester molecules. The other is through the direct synthesis of Ester-T from trichlorosilane monomers possessing ester groups synthesized via hydrosilylation. We have tried to synthesize Ester-T by the first method, but unfortunately the target product can not be obtained due to the relatively low grafting efficiency and the difficulty in separating the unreacted vinyl-terminated molecules containing ester groups. In this paper, we report the direct synthesis of a novel soluble ladderlike

* The authors are grateful to the National Natural Science Foundation of China (No. 29874034), Dow Corning Corporation and Institute of Materials Research and Engineering, National University of Singapore for their financial supports.

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

*** An abbreviation for Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation
Received March 20, 2000

polysilsesquioxane containing reactive ester groups (Ester-T) by the stepwise coupling polymerization (SCP) of an ester containing trichlorosilane monomer under mild reaction conditions.

EXPERIMENTAL

Materials

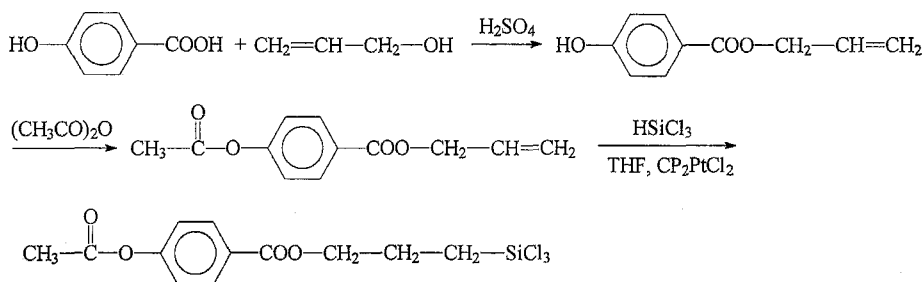
All solvents were commercially available and of analytical grade. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Toluene was dehydrated over CaCl_2 and then sodium. 4-Hydroxybenzoic acid, allyl alcohol, acetic anhydride, trichlorosilane, 1,4-phenylenediamine (PDA), and anhydrous Na_2SO_4 were purchased from Beijing Chemical Factory and were of analytical grade. Cp_2PtCl_2 catalyst was prepared according to the literature^[13]. Triethylamine (TEA) was purchased from Beijing Chemical Factory and dried with CaH_2 prior to use.

Techniques

FTIR spectra were performed on a PE-80 FTIR spectrometer. ^1H -NMR and ^{13}C -NMR spectra were obtained from a JNH-FX100 (JBOX) 300 MHz NMR spectrometer. ^{29}Si -NMR measurement was performed on a Varian Unity 200 MHz NMR instrument. Molecular weight was measured using a Knauer vapor pressure osmometer using THF as the solvent. TGA measurement was conducted on a Perkin-Elmer 7 thermal analysis system under N_2 with a temperature scan rate of 20 K/min. XRD analysis was carried out on a Rigaku D/MAX 2400 X-ray diffractometer.

Preparation of Monomer: 3-Trichlorosilylpropoxy 4-acetoxybenzoate **M**

Monomer **M** was synthesized in three steps as described in Scheme 1.



Scheme 1 Synthetic route of monomer **M**

Synthesis of allyloxy 4-hydroxybenzoate **1**

A mixture of 27.6 g (0.2 mol) 4-hydroxybenzoic acid and 70 mL (1.0 mol) allyl alcohol was stirred with a magnetic stirrer at 80 °C. 1.5 mL concentrated sulphuric acid was added dropwise into the flask after the powders had dissolved. The solution was then refluxed for 20 h and nearly 3 mL water was separated with an oil-water separator. The product was obtained as colorless crystals by removing the allyl alcohol and recrystallizing with a mixture of water and ethanol (1:1) in a yield of 60%. ^1H -NMR (CDCl_3 , δ): 8.0, 6.9 (*dd*, 4H, C_6H_4); 6.0–6.1, 5.3–5.5 (*m*, 3H, $\text{CH}_2=\text{CH}$) and 4.9 (*d*, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$).

Synthesis of allyloxy 4-acetoxybenzoate **2**

12.6 g (0.07 mol) **1** was dissolved in 28 mL (0.28 mol) acetic anhydride. After adding 1 mL phosphoric acid slowly as drops, the solution was stirred at 85 °C for 0.5 h. The reaction solution was then cooled to room temperature, and 30 mL distilled water was added. The organic layer was separated and washed with aqueous NaHCO_3 solution (10 wt%) until neutral. After drying over anhydrous sodium sulfate, **2** was obtained in 90 % yield. FTIR (film, cm^{-1}): 1604, 1505 (C_6H_4); 1762, 1723, 1271 and 1197 (COO). ^1H -NMR (CDCl_3 , δ): 8.1, 7.2 (*dd*, 4H, C_6H_4); 6.0–6.1, 5.3–5.4 (*m*, 3H, $\text{CH}_2=\text{CH}$); 4.8 (*d*, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$) and 2.3 (*s*, 3H, CH_3COO).

Synthesis of 3-trichlorosilylpropoxy 4-acetoxybenzoate **M**

To a 100 mL round-bottomed flask equipped with a reflux condenser, a magnetic stirrer and a two-way stop-cock

was added 6.6 g (0.03 mol) **2**. The flask was evacuated and flushed with dry argon three times. Then 1 mL THF solution of Cp_2PtCl_2 (1 mg/mL) and 30 mL THF were added. This mixture was stirred at room temperature for 30 min before 4 mL (0.04 mol) HSiCl_3 was added. This mixture was stirred and subsequently warmed to 35°C for 36 h. Then the volatile components were removed under reduced pressure below 40°C, and the product **M** was obtained as a light yellow liquid in 95 % yield. The characterization results are listed in Table 1.

Table 1. Characterization results of monomer **M**

Items of characterization	Results
Appearance	Light yellow liquid
Solubility	Soluble in toluene, THF, chloroform, acetone <i>etc.</i>
FTIR (in cm^{-1})	1760, 1718, 1277, 1199 ($-\text{OCO}-$); 1605, 1505 ($-\text{C}_6\text{H}_4-$)
$^1\text{H-NMR}$ (δ)	8.0, 7.1 (<i>dd</i> , 4H, C_6H_4); 4.3 (<i>t</i> , 2H, $-\text{CH}_2\text{CH}_2\text{OCO}-$); 2.2 (<i>s</i> , 3H, $\text{CH}_3\text{COO}-$); 1.9 (<i>m</i> , 2H, $-\text{CH}_2\text{CH}_2\text{OCO}-$); 1.5 (<i>t</i> , 2H, $\equiv\text{SiCH}_2\text{CH}_2-$)
$^{13}\text{C-NMR}$ (δ)	168.4 ($\text{CH}_3\text{COO}-$); 165.2 ($-\text{CH}_2\text{OCO}-$); 154.2, 130.9, 127.2, 121.4 ($-\text{C}_6\text{H}_4-$); 67.6 ($-\text{COOCH}_2-$); 25.3 ($-\text{COOCH}_2\text{CH}_2-$); 20.8 ($\text{CH}_3\text{COO}-$); 20.5 ($\equiv\text{SiCH}_2\text{CH}_2-$)
$^{29}\text{Si-NMR}$ (δ)	13.03

Preparation of Ladderlike Polymer: Ester-T

The synthetic route leading to Ester-T is shown in Scheme 2.

A solution of 1.35 g (12.5 mmol) PDA, 6.8 mL triethylamine and 70 mL THF was added dropwise to a 500 mL three-necked flask containing 8.89 g (25.0 mmol) **M** in 70 mL toluene at -10°C within 1.5 h. Then the reaction solution was stirred for another 30 min at low temperature (-5°C to -10°C). After which, 0.9 mL water and 80 mL THF were then added dropwise at -5°C . This prepolymer solution was washed with water until neutral and dried with anhydrous Na_2SO_4 overnight. Then the solution was filtered, and some anhydrous Na_2SO_4 and CaH_2 were added to the solution. The polycondensation process was carried out using triethylamine as the catalyst at about 50°C for 72 h. Then the polymer solution was washed with water until neutral and dried with anhydrous Na_2SO_4 . For endcapping the terminal silanol ($\text{Si}-\text{OH}$) groups of the polymer, silylation was carried out by using trimethylchlorosilane as the endcapper: 0.4 mL pyridine was added to the above mentioned polymer solution before 0.5 mL (4.5 mmol) trimethylchlorosilane in 20 mL toluene was added dropwise at room temperature under stirring. A white turbidity gradually appeared. The mixture was stirred at room temperature for 24 h and the residual trimethylchlorosilane and pyridine were removed under vacuum. The solution was washed neutral with water and dried with anhydrous Na_2SO_4 . Upon the removal of the solvent under vacuum, the residual light yellow solid was dried under vacuum at room temperature for 48 h to give the product Ester-T in 82% yield.

RESULTS AND DISCUSSION

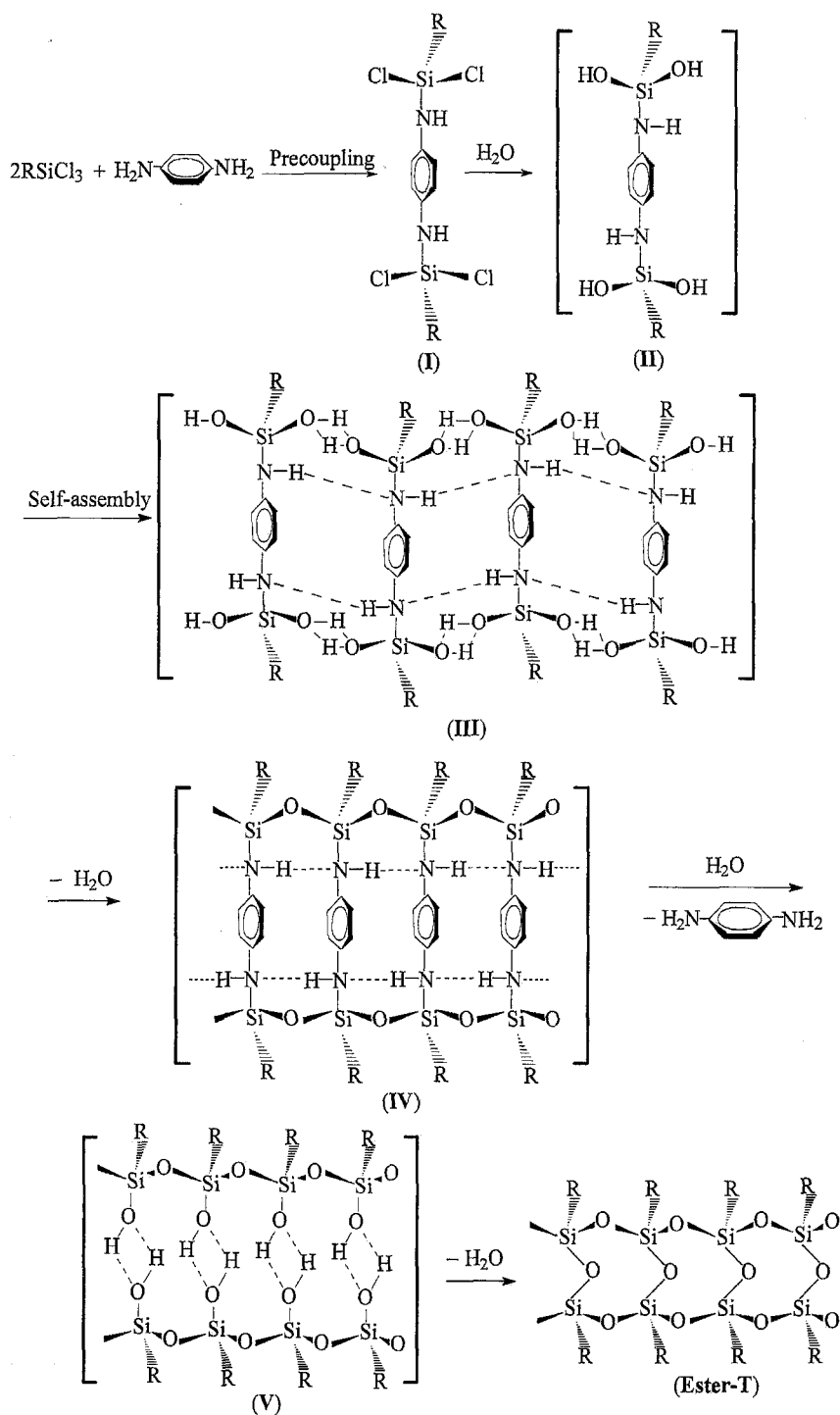
Synthesis and Characterization of Monomer **M**

As shown in Scheme 1, compound **1** was synthesized by normal esterification of 4-hydroxybenzoic acid with allyl alcohol. Then acetic anhydride was used to react with compound **1** to give compound **2**. Monomer **M** was synthesized successfully for the first time by hydrosilylation of trichlorosilane with compound **2**. Characterization results are listed in Table 1. It is worth mentioning that the hydrosilylation reaction must be protected by dry argon and the monomer obtained must be stored under dry argon as the $\text{Si}-\text{Cl}$ bond of the monomer is easily hydrolyzed. With careful control of the reaction conditions, the yield of monomer **M** can be very high. It is also noted that compound **1** should not be used directly for the hydrosilylation reaction due to the existence of the side reaction between the hydroxyl groups in compound **1** and the $\text{Si}-\text{H}$ groups. In our experiment, the hydroxyl groups were protected by acetyl groups.

Synthesis of Ester-T

Scheme 2 shows the synthetic route of the supramolecular hydrogen-bonding assisted synthesis of Ester-T. The three main steps include the pre-ammonolysis reaction with α,ω -diamine (PDA), the controlled hydrolysis and

the polycondensation in the presence of TEA catalyst. Based on different activities of the three chlorine atoms in the starting monomer **M**, the pre-ammonolysis reaction can be carried out using PDA as the precoupling agent, which not only protects the most active Cl atoms in **M** from crosslinking but also links the two **M** molecules.



Scheme 2 Synthetic route of Ester-T

Consequently, a precoupled intermediate **I**, which acts as the template to ensure further formation of the ordered ladderlike macromolecule, was formed.

The hydrolysis of intermediate **I** leads to the production of intermediate **II**, which can self-assemble to form possible ladderlike oligomeric aggregate **III** by supramolecular interaction of hydrogen-bonds between N and H atoms of the $-\text{NH}$ groups, and between the silanols which can form square-planar hydrogen-bonds^[14–16]. Due to the tetrahedral configuration of the silicon atom and supramolecular hydrogen-bonds, ladderlike **III** may have a *cis*-isotactic configuration. It is worth mentioning that many insoluble compounds will immediately form in the hydrolysis process if the concentration of intermediate **I** is too high, and the hydrolysis is carried out at high temperature or water is introduced rapidly. These compounds are probably insoluble three-dimensional network gels (unrelated to the ladderlike structure), due to the rapid random condensation which creates links between polymers. For the above reason, the hydrolysis reaction of intermediate **I** should be carried out at low temperature, in dilute solution, and water should be introduced very slowly.

Through the self-assembly and condensation of silanols, possible ladderlike **III** can be condensed to form possible intermediate **IV**. Then the bridged PDA can be eliminated gradually because the $\text{Si}-\text{N}$ bonds are readily hydrolyzed, possibly allowing the formation of intermediate **V** and the final product Ester-T, in which *cis*-isotactic configuration may exist. Further experiments are in progress to demonstrate the existence of *cis*-isotactic configuration in the ladderlike Ester-T.

Characterization of Ester-T

Characterization results for ladderlike polymer Ester-T are listed in Table 2.

Table 2. Characterization results of Ester-T

Items of characterization	Results
Appearance	Light yellow solid
Solubility	Soluble in toluene, THF, chloroform, acetone <i>etc.</i>
FTIR (in cm^{-1})	1761, 1717, 1274, 1197, 1161 ($-\text{OCO}-$); 1444, 1370 ($\text{CH}_3\text{COO}-$); 1049~1100 ($=\text{Si}-\text{O}-\text{Si}=$); 1604, 1505, 846 ($-\text{C}_6\text{H}_4-$);
$^1\text{H-NMR}$ (δ)	8.0, 7.0 (<i>b</i> , 4H, C_6H_4); 4.2 (<i>b</i> , 2H, $-\text{CH}_2\text{CH}_2\text{OCO}-$); 2.3 (<i>b</i> , 3H, $\text{CH}_3\text{COO}-$); 1.8 (<i>b</i> , 2H, $-\text{CH}_2\text{CH}_2\text{OCO}-$); 0.8 (<i>b</i> , 2H, $=\text{SiCH}_2\text{CH}_2-$)
$^{13}\text{C-NMR}$ (δ)	168.8 ($\text{CH}_3\text{CO}-$); 165.4 ($-\text{CH}_2\text{OCO}-$); 154.2, 131.0, 127.6, 121.5 ($-\text{C}_6\text{H}_4-$); 66.6 ($-\text{COOCH}_2-$); 22.2 ($-\text{COOCH}_2\text{CH}_2-$); 21.1 ($\text{CH}_3\text{CO}-$); 1.5 ($=\text{SiCH}_2\text{CH}_2-$)
T_g (by DSC, $^\circ\text{C}$)	107.6
T_d (by TGA, $^\circ\text{C}$)	367.2
M_n (by VPO, in Dalton)	2.4×10^4
$^{29}\text{Si-NMR}$ (δ)	-66.4 ($\text{SiO}_{3/2}$); -53.8~-61.2 (HOSiO)
Distance [d (nm) / 2θ ($^\circ$)] by XRD	1.92/4.6; 0.44/20.4

The strong absorption band at 1049~1100 cm^{-1} in the FTIR spectrum (Fig. 1) of Ester-T (which does not appear in the FTIR spectrum of monomer **M**) is assigned to the $\nu_{\text{Si}-\text{O}}$ of the $\text{Si}-\text{O}-\text{Si}$ bond. Moreover, two strong absorption bands at 1761 cm^{-1} ($-\text{C}_6\text{H}_4-\text{OOC}-$) and 1717 cm^{-1} ($-\text{C}_6\text{H}_4-\text{COO}-$) indicating there are two different kinds of ester bond. The absorption bands at 1604 cm^{-1} and 1504 cm^{-1} are assigned to $\text{C}-\text{H}$, $\text{C}=\text{C}$ stretching and/or bending vibrations of the phenylene groups.

In the $^1\text{H-NMR}$ spectrum (Fig. 2) of Ester-T, the broad peaks are assigned to $\text{Si}-\text{CH}_2-$, $-\text{CH}_2-\text{OCO}-$ and $-\text{OCOCH}_3$ of Ester-T and the peaks in the $^{13}\text{C-NMR}$ spectrum (Fig. 3) are assigned to $\text{Si}-\text{CH}_2$, $\text{Si}-\text{CH}_2-\text{CH}_2-$, $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{O}-$, $-\text{C}_6\text{H}_4-\text{COO}-$, $-\text{OCOCH}_3$, $-\text{OCOCH}_3$ and $-\text{C}_6\text{H}_4-\text{COO}-$ of Ester-T, respectively.

The T_g of Ester-T is 107.6 $^\circ\text{C}$ measured by DSC. The TGA curve of Ester-T (Fig. 4) reveals a thermal decomposition temperature of 367.2 $^\circ\text{C}$, indicating that Ester-T possesses relatively high resistance to heat.

FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, DSC and TGA results demonstrate that monomer **M** has been hydrolyzed and condensed to form a polymer containing Si—O—Si bonds. The M_n of the polymer Ester-T determined by VPO is about 2.4×10^4 .

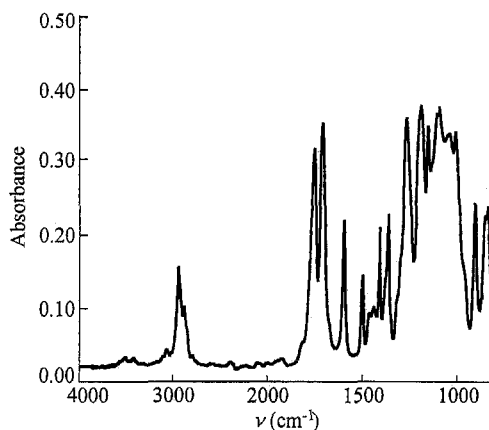


Fig. 1 FTIR spectrum of Ester-T

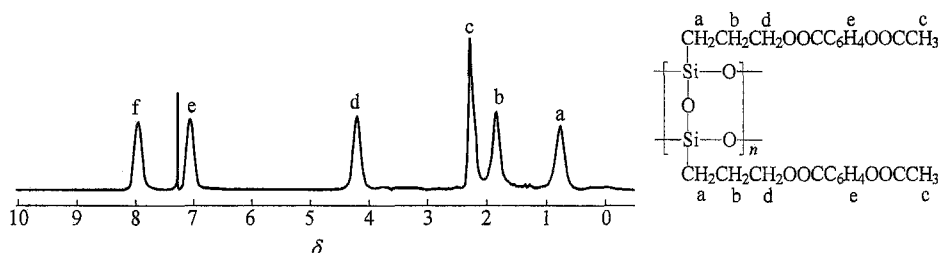


Fig. 2 $^1\text{H-NMR}$ spectrum of Ester-T

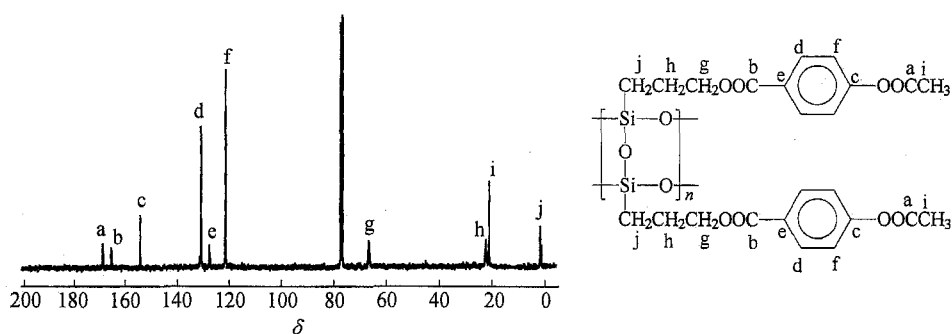


Fig. 3 $^{13}\text{C-NMR}$ spectrum of Ester-T

The $^{29}\text{Si-NMR}$ spectrum of Ester-T (Fig. 5) reveals two groups of peaks. The larger peak (D^2) appearing at $\delta = -66.4$ indicates the fully condensed Si atoms of $\text{SiO}_{3/2}$ unit in the ladderlike double chain, while the smaller broad peak (D^1) at $\delta = -53.8 \sim -61.2$ reflects the defective Si atoms connected with hydroxy groups.

The XRD pattern of Ester-T (Fig. 6) shows two distinct halos and it is in good agreement with previous work^[1, 17, 18]. The first narrow halo at 1.92 nm (d_1) indicates the intramolecular chain-to-chain distance (*i.e.*, the width of each double chain) in the double-chain ladderlike molecule. It is also indicated that Ester-T has a

sufficiently rigid skeleton that its movement around the longitudinal axis is restricted, and therefore it has practically invariable conformation. The second diffused halo covering a wide range of diffraction angles indicates that the average thickness of the ladderlike polymer chain is about 0.44 nm (d_2).

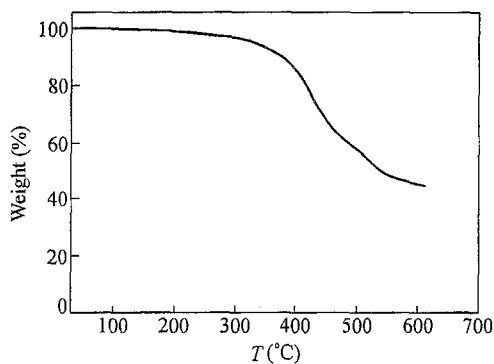


Fig. 4 TGA curve of Ester-T

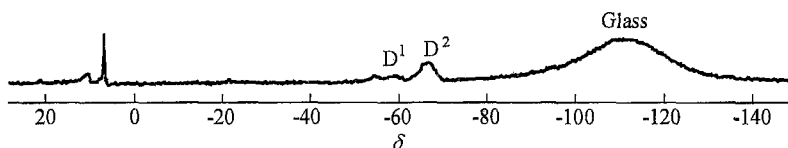


Fig. 5 ^{29}Si -NMR spectrum of Ester-T

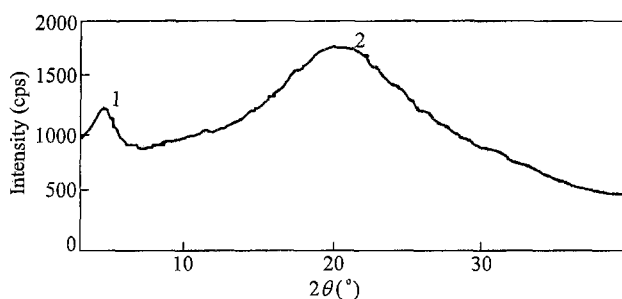


Fig. 6 XRD pattern of Ester-T

The Ester-T formed before silylation is soluble in common organic solvents such as toluene, THF, chloroform, cyclopentanone, and acetone *etc.* and can form a light yellow transparent film after the solvent is evaporated.

The ^{29}Si -NMR and XRD results of Ester-T as well as its good solubility in organic solvents indicate that this polymer may have ordered ladderlike structure, but still contains defective branched structure.

It is worth mentioning that the acetyl groups in the side chains of Ester-T can be easily substituted by reactive hydroxyl groups to form a new kind of functional ladderlike polymer through intra- and inter-molecular hydrogen bondings. This kind of polymer may have potential applications in controlled release of catalysts, hydrogen-bonding-assisted alignment layers in liquid crystal displays and so on.

CONCLUSIONS

A novel soluble ladderlike Ester-T was successfully synthesized by stepwise coupling polymerization using ester group-containing trichlorosilanes as the starting monomer. The characterization results from FTIR, ^1H -NMR, ^{13}C -NMR, ^{29}Si -NMR, XRD, DSC, TGA, and VPO measurements demonstrate that Ester-T has ladderlike structure, although some structure defect still exists. Further experiments on its functionalization and application in organic/inorganic hybrid materials and supramolecular clathrates are in progress.

REFERENCES

- 1 Brown, J.F.Jr., Vogt, L.H.Jr., Katchman, A., Eustance, K.M., Kiser, K.M. and Krantz, K.W., *J. Am. Chem. Soc.*, 1960, 82: 6194
- 2 Brown, J.F.Jr., *J. Polym. Sci., Part C*, 1963, 1: 83
- 3 Maciel, G.E., Sullivan, M.J. and Sindorf, D.W., *Macromolecules*, 1981, 14: 1608
- 4 Frye, C.L. and Klosowski, J.M., *J. Am. Chem. Soc.*, 1971, 93: 4599
- 5 Tsvetkov, V.N., Andrianov, K.A., Makarova, N.N., Vitovskaya, M.G., Rjuntsev, E.I. and Shtennikova, I.N., *Eur. Polym. J.*, 1973, 9: 27
- 6 Martynova, T.N. and Korchkov, V.P., *J. Organomet. Chem.* 1983, 248: 241
- 7 Zhang, X.S. and Shi, L.H., *Chinese J. Polym. Sci.*, 1987, 5: 197
- 8 Puyenbroek, R., Grampel, J.C. van de, Rousseeuw, B.A. and Drift, E.W.J.M. van der, *Polymer*, 1994, 35: 3131
- 9 Kanemitsu, Y., Suzuki, K. and Masumoto, Y., *Solid State Commun.*, 1993, 86: 545
- 10 Zhang, R.B., Dai, D.R., Cui, L., Xu, H., Liu, C.Q. and Xie, P., *Mat. Sci. Eng. C.*, 1999, 10: 13
- 11 Xie, Z.S., Dai, D.R. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1991, 9: 266
- 12 Li, Z., Cao, X.Y., Xu, H., Xie, P., Cao, M. and Zhang, R.B., *React. Fun. Polym.*, 1999, 39: 1
- 13 Apfel, M.A., Finkelmann, H., Janini, G.M., Laub, R.J., Lühmann, B.H., Price, A., Roberts, W.L., Shaw, T.J. and Smith, C.A., *Anal. Chem.*, 1985, 57: 651
- 14 Kakudo, M. and Watase, T., *J. Chem. Phys.*, 1953, 21: 167
- 15 Kakudo, M., Kasai, N. and Watase, T., *J. Chem. Phys.*, 1953, 21: 1894
- 16 Kasai, N. and Kakudo, M., *Bull. Chem. Soc. Japan*, 1954, 27: 605
- 17 Andrianov, K.A., Zhdanov, A.A. and Levin, V.Yu., *Annual. Rev. Mater. Sci.*, 1978, 8: 313
- 18 Zhang, X.S., Shi, L.H. and Huang, C.R., *Chinese J. Polym. Sci.*, 1987, 5: 353