

THE HYDROSILYLATION REACTION OF LADDERLIKE POLYVINYLSILSESQUIOXANE WITH 1,1,3,3-TETRAMETHYLDISILOXANE*

CAO Xinyu (曹新宇) XU Hui (许 辉) WANG Letian (王乐天) LI Ze (李 泽)
CAO Ming (曹 明) XIE Ping (谢 萍) and ZHANG Rongben (张榕本)**

(PCLCC^(a), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China)

ZHU Chuanfeng (朱传凤) and WANG Chen (王 琛)

(Youth Laboratory of Nanoscience and Technology,
Chinese Academy of Sciences, Beijing 100080, China)

Abstract The hydrosilylation reaction of ladderlike polyvinylsilsesquioxane (Vi-T) with 1, 1, 3, 3-tetramethyldisiloxane (H-MM) catalyzed by dicyclopentadienyl-dichloroplatinum (Cp_2PtCl_2) was carried out well in tetrahydrofuran (THF) to produce a soluble white solid. This product was characterized by IR, ^1H -NMR, ^{13}C -NMR, ^{29}Si -NMR, DSC, X-ray diffraction method, gel permeation chromatography (GPC), vapour pressure osmometry (VPO), atomic force microscopy (AFM) and molecular simulation. These results prove that the product contains nanoscale tubular structure.

Keywords Hydrosilylation; Polyorganosiloxane; Tubular structure; Characterisation

INTRODUCTION

Study on the microstructure and microenvironment of macromolecules is very interesting for a wide range of scientific and practical view point. To control the molecular stereoconfiguration is one of the key processes to regulate the polymer properties. For linear polymer with single main chain, transition metal-catalyzed especially metallocene-catalyzed coordination polymerization enables olefin to produce polymer with regular structure and a narrow molecular weight distribution

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a) Polymer Chemistry Laboratory, the Chinese Academy of Sciences and China Petrol-Chemical Corporation

**To whom correspondence should be addressed

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better than ordinary free radical polymerization. For three dimensional polymer, one perfect example of controlled molecule is dendrimer. However, the control of two- and three-dimensional molecular polymers, in general, seems more difficult than that of linear polymers. Usually the structure of three dimensional polymers is a random networks.

Most recently, much attention was switched to the nano-scale self-assembling structures like tubular polymers. Inorganic and natural organic material were studied more widely. Zeolite possess channel molecular structure which exhibits an extremely narrow pore size distribution^[1~3]. But they are insoluble gels. For more practical use of molecular devices, individual tubular structure is needed. Carbon nanotubes can partly meet such requirement. Recently, by condensation of a laser-vaporized carbon-nickel-cobalt mixture at 1200°C, fullerene single-wall nanotubes (SWNTs) have been produced in more than 70 percent yield^[4].

To construct microtubes of smaller size, direct chemical synthesis may be a more convenient way. Harada et al. reported a series of cyclodextrin (CD) complexes as crystalline products^[5]. One interesting work they did is the first synthesis of tubular polymer from threaded CDs. It can be served as a template, and can be unthreaded after the polymerization of CDs.

However, publications concerning the synthetic organic tubular polymers are still very limited so far. The synthetic organic polymers with their irreplaceable advantages, such as easy to be modified and easy to be tailored, play an important and valuable role in the future application of supramolecular system. In this paper, ladderlike polyvinylsilsesquioxane (Vi-T) was reacted with tetramethyldisiloxane (H-MM) in the presence of Cp_2PtCl_2 as catalyst via hydrosilylation, resulting in the formation of a polyorganosiloxane (POS) containing nanotube structure. The product was characterized by IR, ^1H -NMR, ^{13}C -NMR ^{29}Si -NMR, DSC, X-ray diffraction method, GPC, vapour pressure osmometry (VPO), atomic force microscopy (AFM) and molecular simulation.

EXPERIMENTAL

Materials and Techniques

Vi-T was synthesized by precoupling method from vinyltrichlorosilane^[6]. Cp_2PtCl_2 catalyst was prepared by referring to literature^[7]. H-MM (>98% GC) was purchased from Fluka Chemika Co.. All the solvents are commercially available and of analytical grade.

IR spectra were recorded on Specord 75-IR (Carl Zeiss, Jena) and FT-IR spectrophotometer, PE-80. ^1H -NMR, ^{13}C -NMR and ^{29}Si -NMR spectra were performed on JNH-FX100 (JBOX). The DSC measurement was made on Perkin-Elmer DSC-7 differential scanning calorimeter with a temperature rising rate of $10\text{ }^\circ\text{C}/\text{min}$. X-ray diffraction analysis was carried out on a Rigaku DMAX/38 diffractometer with $\text{Cu-K}\alpha$ radiation. GPC was measured on C-R2AX instrument (Shimadzu, Japan) with polystyrene as standard. VPO were measured on a KNAUER-Vapour Pressure Osmometer. Molecular simulations were performed on a Pentium-133 MHz PC, using Alchemy III V3.0 for Win 95 (Tripos Associate, Inc.), Molgen 4.0 Real (Single) for DOS. AFM was observed with Nanoscope III (Digital Ins., USA).

Synthesis of polyorganosiloxane (POS) containing nanotube structure from Vi-T and H-MM

A 250 mL round-bottomed flask equipped with a refluxing condenser, a magnetic stirrer and a three-way cock was, at first, evacuated and charged with dry argon. This operation was repeated three times. Then the flask was added with 0.35 g of Vi-T, 1 mg of Cp_2PtCl_2 and 120 mL of THF. The mixture was stirred at room temperature for 30 min, then 0.4 mL of H-MM was added. The resulting mixture was stirred and subsequently warmed up to 50°C for 20 h. Most volatile components were removed at reduced pressure below 40°C to leave 10 mL solution, which was dried in air and then in vacuo at room temperature for 12 h. A white (sometimes a light yellow) soluble solid was obtained. The yield was nearly 100%.

RESULTS AND DISCUSSION

In consideration of the hydrogen bonding self-assembling during the formation of Vi-T^[6] and the results obtained from X-ray diffraction method, molecular simulation, and AFM image of Vi-T, we propose that the configuration of Vi-T is mainly cis-isotactic, which is conducive to the formation of nanotube structure rather than random network structure. The good solubility of obtained product in THF after hydrosilylation reaction also gives a support to this point of view.

The main characterization data of Vi-T and POS were listed in Table 1.

In the IR spectrum of POS (Fig. 1), the peaks assigned to Si—H group (2120 cm^{-1}), and Si—CH=CH₂ group (1602 cm^{-1}) disappeared. Similarly, in the ^1H -NMR spectrum of POS (Fig. 2), peaks assigned to Si—H ($\delta = 4.72$) and Si—CH=CH₂ ($\delta = 5.9$) also disappeared. The disappearance of these characteristic peaks indi-

cates that the hydrosilylation reaction proceeds to completion.

Table 1 Characterization data of Vi-T and POS

Item	Vi-T	POS
Solubility	Transparent solid film soluble in toluene	Transparent solid film soluble in THF but insoluble in toluene
IR, ^1H -NMR, ^{13}C -NMR, ^{29}Si -NMR	Showed the peaks assigned to $\text{Si}-\text{CH}=\text{CH}_2$	No peak assign to $\text{Si}-\text{CH}=\text{CH}_2$
X-ray Diffraction (d. in nm)	$d_1=0.938$, $d_2=0.400$	$d_1 = 1.156$, $d_2 = 0.527$
DSC	Almost a horizontal straight line	Almost a horizontal straight line
Molecular weight (by GPC and VPO)	ca. 2,000 (Dalton)	ca. 10,000 (Dalton) (ca. 5 times of the precursor Vi-T versus the calculated 3.8 times)
Molecular simulation*	cis-isotactic configuration is reasonable	The inner hollow of proposed structure (I) (shown in Fig. 6) can fit the size of toluene and THF
AFM	The distances between two adjacent chains is in the order of Vi-T (0.28 nm) < POS (0.702 nm) The widths of the bright chain is in the order of Vi-T (0.15 nm) < POS (0.33 nm) the AFM data are identical to the results of molecular simulation	

* The geometry optimization and conformation analysis of designed molecular structure is based upon molecular mechanics method which employs the potentials for the MM2 force field. The influence of hydrogen bonding is included in the calculations. The electrostatic interactions are approximated by the dipole-dipole interaction.

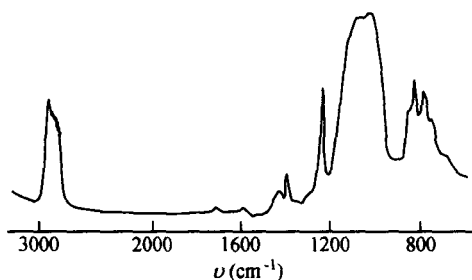


Fig. 1 The IR spectrum of POS

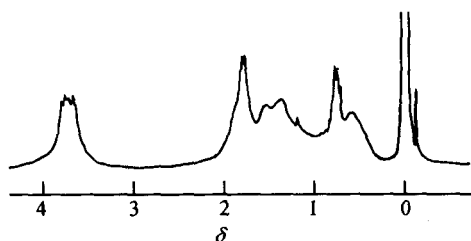


Fig. 2 The ^1H -NMR spectrum of POS

In addition, in the ^1H -NMR spectrum of POS, there appeared two new peaks at $\delta = 1.75$ and $\delta = 3.65$ which are attributed to THF. We also found the corresponding peaks of THF in ^{13}C -NMR spectrum, which appear at $\delta = 67.3$ and $\delta = 27.8$, respectively. Nevertheless, it was noted that no peaks attributed to toluene were

observed in the NMR spectra of POS although toluene also existed in reaction mixture as a part of solvent. These results suggest that THF molecules were probably included in the holes of POS due to the strong interaction between THF and POS, which was proved by two-dimensional nuclear overhauser effect spectroscopy (2D NOESY), whereas the toluene was unable to enter the holes of POS probably due to the lack of interactions between them. There are also other reports with regard to the inclusion of THF in organic silicon xerogels^[8,9].

The DSC curve of POS (Fig. 3) is almost a horizontal straight line, which indicates the great rigidity of the POS macromolecule. The difference between curve (a) and (b) may be attributed to the escape of THF at high temperature.

There are two peaks in the X-ray diffraction pattern of the POS, similar to that of Vi-T (Fig. 4), but the first peak is shifted to smaller angle region and is not as sharp as that of Vi-T. This means that the POS has longer period regular structure, but still with many stereochemical defects in the molecular structure.

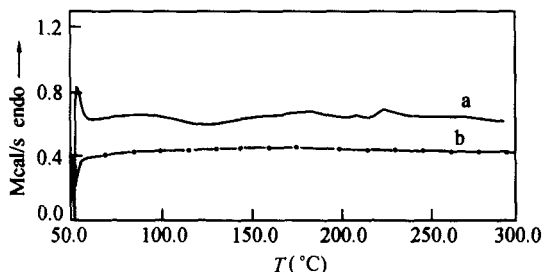


Fig. 3 The DSC curves of POS
(a) first scan; (b) second scan

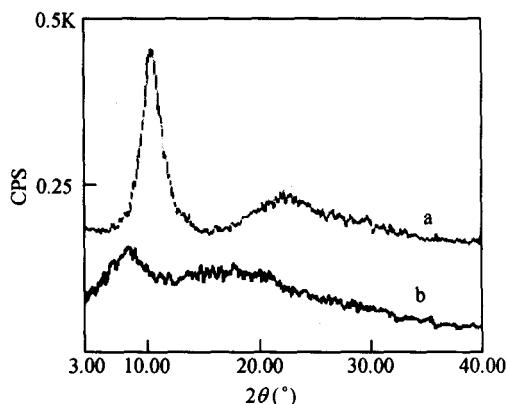


Fig. 4 The X-ray patterns of Vi-T (a) and POS (b)

The AFM image (Fig. 5) showed that the POS chains array regularly similar to that of Vi-T, but the width of the bright lines representing the POS chain alignment increased. In fact, the width of the bright lines on the photos does not stand for the real width of macromolecular chain. It is smaller, to some extent, than the real size because the bright part only stand for the protruding part which can be detected by the probe, and moreover, the nanotube structure will shrink when solvents are evaporated. The interaction force between the probe and molecules could also affect the size. Even though, the increase of the chain width from Vi-T to POS in the AFM images is tallied with that calculated by molecular simulation.

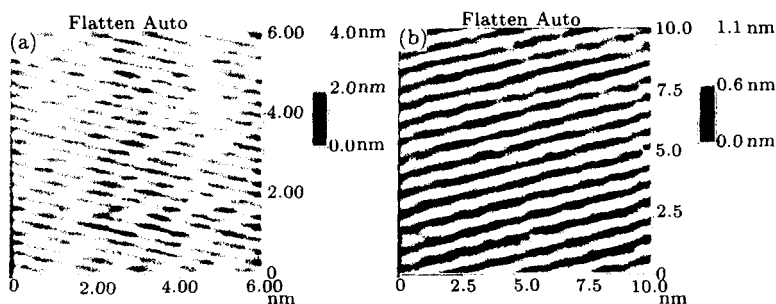


Fig. 5 The AFM image of (a) Vi-T, the average distance between each two chains is 0.28 nm
(b) POS, the average distance between each two chains is 0.70 nm

Note: AFM was measured by Prof. Bai Chunli's research group, Institute of Chemistry, the Chinese Academy of Sciences. Vi-T and POS are dissolved in THF respectively to form a solution of ca. 10^{-4} mol/L. A piece of mica is stuck on a stainless steel base which is placed on the desk coating spreader. The fresh and smooth surface of the mica was disclosed by scotch tape. One drop of the THF solution of sample is dropped on the surface of mica, and followed by 20 seconds of spinning

From the main peak of the GPC curves and the data of VPO, the molecular weight of POS is about 4 to 6 times larger than that of Vi-T against the calculated value of 3.8 times according to tabular model (Fig. 6, I). From the GPC curves of POS, it was found that there were still some low molecular weight oligomers. These results suggest that there may exist the following possible structures in the product.

As the products can bind up THF and its main molecular weight is approximate to the theoretical value, we presume that the nanoscale tubular structure of (I) preferentially exists in the reaction product (Fig. 6).

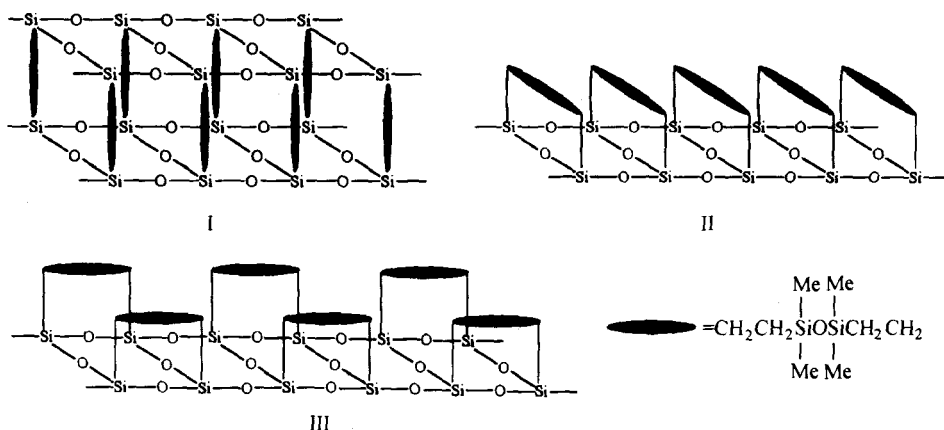


Fig. 6 Some existed possible structures in the product

The reaction mechanism that we proposed was related to the interaction of Vi-T

and the complex catalytic action of Pt catalyst. The reaction probably is continued as zipping mechanism (Fig. 7), which is similar to the reaction of nucleation and propagation in nucleic acid self-assembly^[10~13]. The study on this mechanism is still undertaken.

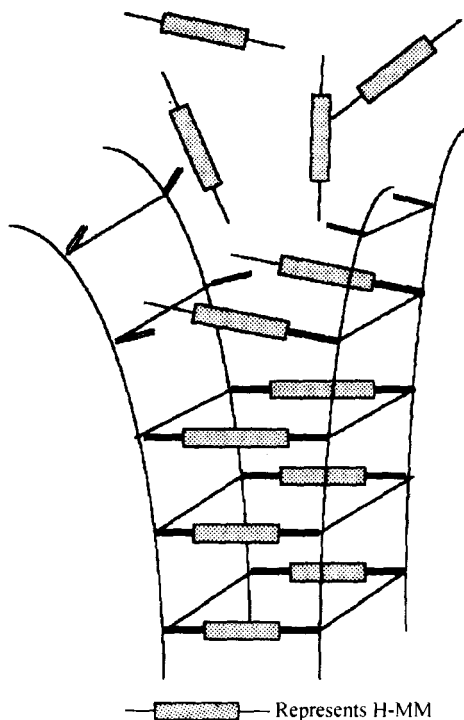


Fig. 7 Schematic representation of a possible zipping mechanism for the construction of tubular structure

The following potential applications of the product can be anticipated for POS: 1) to be used as a carrier for catalysts and other adsorbents; 2) to be used as a fixing agent for gases and harmful substances; 3) as a separating agent to separate molecules according to their size and chemical affinities; 4) to be used as a reaction reactor or templates and 5) their clathrates could be used as electronic devices, sensors and release-controlled encapsulated medicines.

CONCLUSION

A polyorganosiloxane POS containing nanotube structure was prepared by hydrosilylation coupling of Vi-T with H-MM. The product is soluble in many organic solvents such as THF, chloroform and so on. Characterizations by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{29}\text{Si-NMR}$ spectra showed that the reaction was carried out very well.

The further characterizations by GPC, VPO, X-ray diffraction, DSC, AFM and molecular simulation indicate that there may mainly contain nanotube structure in the product. In addition, some other kinds of structures may exist too.

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