

THE HYDROSILATION REACTION OF LADDERLIKE POLYALLYLSILSESQUIOXANE (ALLYL-T) AND POLYHYDROSILSESQUIOXANE (H-T)*

Yong Zhang, Ze Li, Chun-qing Liu and Rong-ben Zhang**

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

Chuan-feng Zhu and Chen Wang

Youth Laboratory of Nanoscience and Technology, Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China

Abstract The one plus one (1 + 1) mode of hydrosilation reaction of ladderlike *cis*-isotactic polyallylsilsesquioxane (Allyl-T) and polyhydrosilsesquioxane (H-T) using dicyclopentadienylplatinumdichloride (Cp_2PtCl_2) as the catalyst leads to the formation of a new polyorganosiloxane (POS). The presence of nanoscale tubular structure in the product POS was preliminarily proved by IR, ^1H -NMR, differential scanning calorimetry (DSC), X-ray diffraction (XRD), gel permeation chromatography (GPC), atomic force microscopy (AFM) and molecular simulation.

Keywords Hydrosilylation, Polyorganosiloxane, Self-assembly, Tubular structure

INTRODUCTION

Recently, study of the microstructure and microenvironment of macromolecules has attracted great interest on the part of polymer scientists, and much attention has switched to the structure-controlled polymers such as tubular polymers (TPs). Up to now, most of the investigations on TPs were focused on inorganic and organic TPs derived from natural compounds. For example, carbon nanotubes with hollow tubular structure, can be prepared by physical method^[1-3]. Meanwhile, Harada *et al.* first reported a series of organic TPs prepared from threaded cyclodextrin (CD) complexes^[4, 5]. However, one of the main limitations of these inorganic and organic tubular polymers is that their microstructures and chemical affinity are very difficult to regulate precisely.

It is known that a direct chemical synthetic method can be a convenient way to construct the TPs, which possess irreplaceable advantages, such as ease of being modified and tailored. These TPs can play an important role in developing new advanced materials such as carriers for catalysts and other adsorbents, reaction vessels or templates as well as separating material according to the size and chemical affinities of the molecules to be separated and so on.

However, publications concerning the synthetic organic TPs are still very scant so far. Recently, our research group synthesized a novel polyorganosiloxane (POS) having a nanoscale tubular structure via two plus two (2 + 2) tube-forming mode of a new route, "Stepwise Coupling Polymerization" (SCP) previously proposed by us^[6, 7]. The cross-section of the tube consists of two structural units of reactive, *cis*-isotactic ladderlike Vi-T molecules with two reactive, α,ω -coupling agents (1,1,3,3-tetramethyldisiloxane, H-MM)^[8, 9]. These macro-

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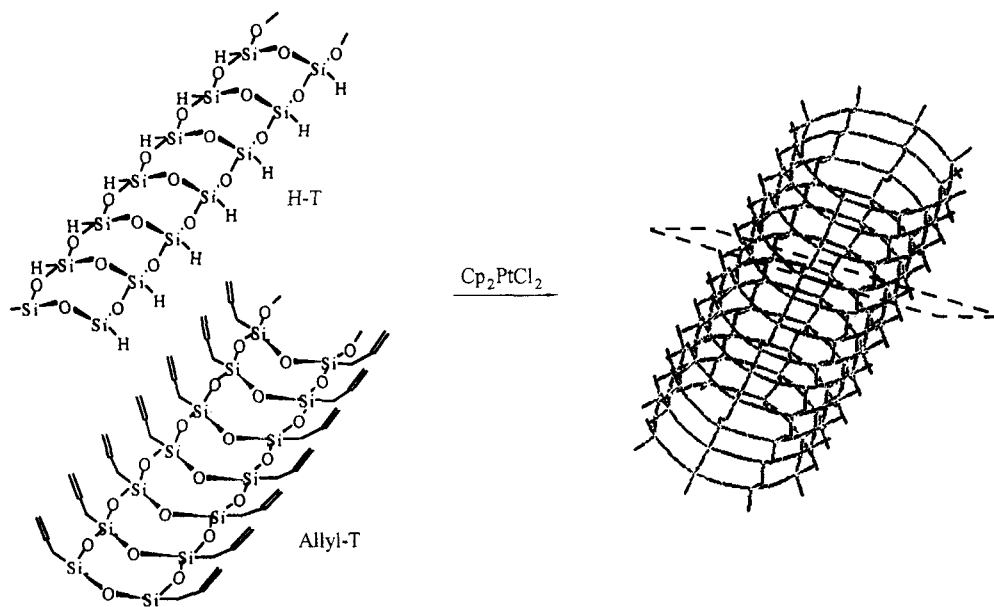
** Corresponding author: Rong-ben Zhang (张榕本), E-mail: zhangrb@infoc3.icas.ac.cn

*** Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation

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molecular ladderlike polysilsesquioxanes (LPSs) used were prepared by preamminolysis reaction, which is also a kind of SCP. For example, a series of LPSs have been successively synthesized until now, including polymethylsilsesquioxane (Me-T)^[10, 11], Ph-T^[12], polyalkylsilsesquioxane^[13] and ladder polyphenylene-bridged-siloxanes^[14], especially reactive H-T^[15, 16], Vi-T or Allyl-T^[17], copolymethylepoxysilsesquioxane^[18] polyester-silsesquioxane (E-T)^[19], the related supramolecular TP's clathrates prepared by *in-situ* tube-closure and trapping europium compound^[20–22], rodlike Schiff-base liquid crystal molecule, *p*-butoxybenzylidene-*p*'-dodecoxyaniline (BBDA) within the pores of the tubular structure^[23, 24], respectively.

In this paper, another kind of one plus one (1 + 1) tube-forming mode of the hydrosilation reaction of the ladderlike Allyl-T with H-T was successfully synthesized for the first time and resulted in the formation of a POS containing nanoscale tubular structure, as shown in Scheme 1. The cross-section of the tubular structure of POS formed was consisted of one structural unit of reactive *cis*-isotactic Allyl-T and another structural unit of reactive *cis*-isotactic H-T. The existence of nanoscale tubular structure in the product has been preliminarily confirmed by above-mentioned methods.



Scheme 1 Hydrosilation reaction of Allyl-T and H-T

EXPERIMENTAL

Materials and Techniques

All the reaction reagents and solvents were commercially available and of analytical grade. Some reagents were treated as follows prior to use. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Toluene was washed with concentrated H₂SO₄ to remove thiophene or methylthiophene and distilled from sodium sand. Allyl-T and H-T were synthesized by the precoupling of allyltrichlorosilane and hydrotrichlorosilane with 1,4-phenylenediamine (PDA) respectively^[15–17] and by subsequent hydrolysis and polycondensation. Allyl-T was obtained as a white solid with a molecular weight (MW) of 4000. Meanwhile H-T with MW of 3000 was obtained as a toluene solution of 8.0×10^{-3} g/mL. Catalyst Cp₂PtCl₂ was prepared according to the reference^[25] and dissolved in THF to form a 1.0×10^{-3} g/mL solution. Trimethylchlorosilane was dissolved in THF to form a 1.0×10^{-4} g/mL solution.

IR spectra were recorded on a Specord 75-IR spectrophotometer (Carl Zeiss, Jena) and a FT-IR spectrometer (PE-80). ¹H-NMR spectra were measured on a JNH-FX100 spectrometer (JBOX). The DSC measurements were performed on a Perkin-Elmer DSC-7 instrument at a heating rate of 10 K/min. XRD analysis

was carried out on a Rigaku DMAX/2400 diffractometer with Cu-K α radiation. GPC was undertaken on C-R2AX instrument (Shimadzu, Japan) with polystyrene as the standard. Molecular simulations were performed on a Pentium-133 MHz PC, using Alchemy III V 3.0 for Win 95 (Tripos Associate, Inc.), Molgen 4.0 Real (Single) for DOS. AFM was observed with a Nanoscope III (Digital Ins., USA).

Synthesis of POS Containing Nanoscale Tubular Structure from Allyl-T and H-T

A 250 mL round-bottomed flask equipped with a refluxing condenser, a magnetic stirrer and a three-way cock was evacuated and purged three times cyclically with dry argon. Then the flask was charged with 0.2 g of Allyl-T, 2.0 mL of Cp₂PtCl₂ solution and 200 mL of THF and stirred at room temperature for 30 min and subsequently warmed up to 50°C, then 12.5 mL of H-T solution was added. The resulting mixture was stirred for 30 h, followed by addition of 4.0 mL of trimethylchlorosilane solution. Heating was then stopped and the resulting mixture was stirred for additional 10 h down to the room temperature. The product was dried under vacuum and the protection of dry argon at room temperature for 12 h. 0.3 g of a white soluble solid ($M_w = 11,000$) was obtained with a yield of nearly 95%.

RESULTS AND DISCUSSION

Result of Synthesis

In general, all reactions are accelerated at higher temperature, but in this preparative work it is advisable to keep the reaction temperature lower than 50°C because the precursors, both the silanol-terminated Allyl-T and H-T, are thermally unstable and can be gelled at a temperature higher than 50°C.

This reaction is also sensitive to the polarity of solvent. When toluene was chosen as the reaction solvent which can dissolve both Allyl-T and H-T, some undesired gel was produced and stuck on the wall of reaction flask. Therefore, the reaction did not proceed very well. Thus toluene was not an appropriate solvent for this reaction. A series of toluene/THF mixtures in the ratio of 100/20, 100/40, 100/60 and up to 100/100, were tried and the results of reactions remained unsatisfactory. However, THF shows good solubility for both the starting materials and the product which guarantees satisfactory completion of the reaction.

It is worthy of mention here that the hydrogen-bonding assisted self-assembling during the formation of H-T^[15, 16] and Allyl-T^[17] makes the stereoregularity of Allyl-T and H-T to be mainly *cis*-isotactic, which have been proved by XRD, molecular simulation and AFM image of Allyl-T. Obviously, this *cis*-isotactic configuration of LPs is a prerequisite for the formation of nanoscale tubular structure rather than a random network.

Evidently, elimination of gelation is much more difficult for the reaction of (1 + 1) mode between two long polymer chains than for the (2 + 2) mode where two polymer chains were coupled with two small coupling molecules. Thus, it was conducive to carry out the hydrosilation reaction in very diluted solution (no more than 2 mg/mL), in which the LPS chains are unfolded and their reactive side-groups can stretch out unrestrainedly and react freely with each other.

Results of Characterization

The relevant characterization data of Allyl-T, H-T and the titled product POS are listed in Table 1.

IR determination

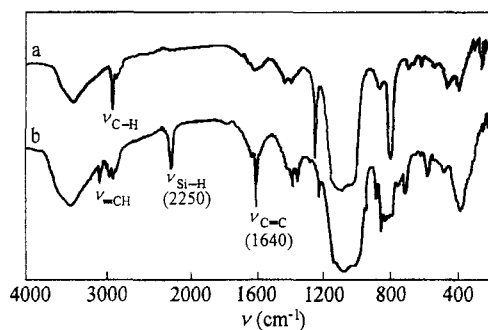
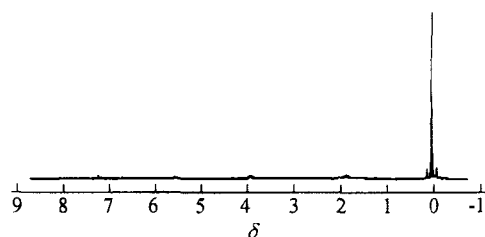
In the IR spectrum of POS (Fig. 1), the peak assigned to Si—H group (2250 cm⁻¹) has disappeared and the peak assigned to Si—CH₂CH=CH₂ group (1640 cm⁻¹) has almost disappeared too after hydrosilation reaction. These results indicate that the hydrosilation reaction runs to completion.

¹H-NMR determination

Similarly, in the ¹H-NMR spectrum of POS (Fig. 2), the peaks which are assigned to Si—H ($\delta = 4.72$), —CH=CH₂ ($\delta = 5.0, 5.8$) and Si—CH₂ adjacent to —CH=CH₂ ($\delta = 1.62$) have also disappeared, respectively. Also the result indicates the hydrosilylation reaction was accomplished completely.

Table 1. Characterization data of Allyl-T, H-T and POS

Item	Allyl-T	H-T	POS
Appearance and solubility	Transparent solid film, soluble in THF, toluene	Transparent solid film, soluble in THF, toluene	Transparent solid film, soluble in THF but insoluble in toluene
Molecular weight (by GPC)	4000	3000	11000
IR	1640 cm^{-1} Assigned to $\text{Si}-\text{CH}_2\text{CH}=\text{CH}_2$	2250 cm^{-1} Assigned to $\text{Si}-\text{H}$	No peaks assigned to $\text{Si}-\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{Si}-\text{H}$
$^1\text{H-NMR}$ (δ)	5.0, 5.8 Assigned to $-\text{CH}=\text{CH}-$	4.72 Assigned to $\text{Si}-\text{H}$	No peaks assigned to $\text{Si}-\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{Si}-\text{H}$
X-ray diffraction (d in nm)	$d_1 = 1.07$ $d_2 = 0.408$	$d_1 = 0.718$ $d_2 = 0.390$	$d_1 = 1.088$ $d_2 = 0.431$
DSC	$T_g = 129^\circ\text{C}$	Almost a horizontal straight line	Nearly a horizontal line with a pair of upward and downward peaks
Molecular simulation	<i>Cis</i> -isotactic helix soft configuration with side-group stretched The distance between two adjacent chains is in the order of POS (0.34 nm) < Allyl-T (0.39 nm).	<i>Cis</i> -isotactic helix configuration and soft framework	Rigid frame of chains without free side-group
AFM	The average width of the protruding part of chain is in the order of POS (0.26 nm) $\approx$ Allyl-T (0.28 nm). The AFM data are identical to the results of molecular simulation.		

**Fig. 1** IR spectra of POS (a) and a mixture of Allyl-T and H-T (b)**Fig. 2** $^1\text{H-NMR}$ spectrum of Allyl-T and POS

As is well known, in NMR experiments each nucleus in a different environment experiences a different local magnetic field due to the circular motion of electrons around the neighbouring bonds and to through-space effects. A different applied magnetic force is therefore required for resonance and absorption occurs in the different regions of the spectrum, thus the position of an absorption peak will alter. The phenomenon termed shielding effect making the chemical shifts to upper fields is often observed in ring compounds. For example, the spectrum of crown ether prefers to show the stronger shielding effect of the electronic circulation in the ring causing upfield shift of the methylene absorption, rather than to show the de-shielding effect of the electronegative oxygen causing downfield shift of the methylene absorption, as the typical chemical shift ca. $\delta = 3-4$. In the $^1\text{H-NMR}$ spectrum here, the new multiple peaks of POS appeared at about $\delta = 0.2$ further upfield relative to the typical chemical shift of the methylene absorption, which can be ascribed to the shielding effect of the ring compound mentioned above. Thus, the result supports the point of view that the product POS contains nanoscale tubular structure characteristics.

Solubility test

The good solubility of the POS indicates that it is not a random network polymer. Besides, there is a marked difference in polarity features between the product POS and the starting materials Allyl-T. POS is soluble in

highly polar solvents such as THF, chloroform, cyclohexanone *etc.*, and insoluble in non-polar solvents such as benzene or toluene in which Allyl-T can be completely dissolved. It can be explained by the difference in the structures of Allyl-T and POS if the transverse sections of TP and Allyl-T are taken into account. The section of POS with tubular structure consists of two polar Si—O bonds and six methylene linkers while the section of the ladderlike Allyl-T consists of one polar Si—O bond and two non-polar allyl terminals. In addition, POS with tubular structure is very rigid as compared with the soft and spiral Allyl-T. This demonstrates the changes of molecular morphology and polarity taking place during the process from the starting ladderlike polymer to POS with tube structure.

DSC measurement

The DSC curves of POS (Fig. 3) show the differences between the first scan (a) and the second scan (b). It indicates that the POS macromolecule is more rigid in comparison with that of the parent Allyl-T with T_g 129°C. Probably, a small peak at 120.02°C ($\Delta H = -87.05$ J/g) on curve (a) may be attributed to the condensation of some irregular silanol groups in POS. As for the peak at 190°C, according to the results of X-ray and AFM, it can be ascribed to some regular structure of POS.

XRD analysis

As shown in Fig. 4, there are two peaks in the XRD pattern of the POS, similar to that of Allyl-T. The first peak, which appeared in the small angle region, representing the longer-range sequence, is not as sharp as that of Allyl-T. This shows that the product POS has longer period regular structure, although many stereo-chemical defects still exist in the molecular structure.

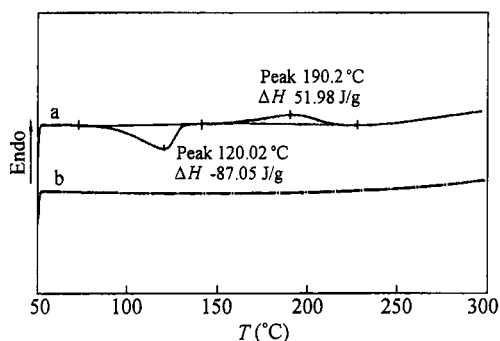


Fig. 3 DSC curves of POS
a) First scan; b) Second scan

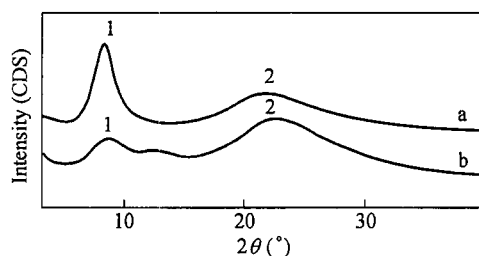


Fig. 4 X-ray diffraction of Allyl-T (a) and POS (b)

Molecular weight determination

The molecular weight of POS measured by GPC is 11,000 dalton, about 1.5 times larger than the sum of that of Allyl-T (4000) plus H-T (3000). This result indicates that the tubular structure in the product contains some defects instead of having an infinite crosslinking network structure.

AFM observation

The AFM image depicted in Fig. 5 shows that the POS chains array themselves more regularly than do the Allyl-T chains containing free allyl side groups. The width of the bright lines representing the POS chains was similar to that of Allyl-T while the distance between the two adjacent POS chains is smaller than that of Allyl-T chains. In fact, the width of the bright lines on the AFM image does not stand for the real width of the macromolecular chains. It is smaller, to some extent, than the real width because the bright part only stands for the protruding part mainly formed of the Si—O—Si framework that can be detected by the AFM probe. Moreover, the nanoscale tubular structure would shrink somewhat when the solvents are evaporated out. The interaction force between the probe and the POS substrate molecules could also affect the width of the POS chains. However, the decrease of

the distances between the adjacent chains from Allyl-T to POS in the AFM images is consistent with that calculated by molecular simulation.

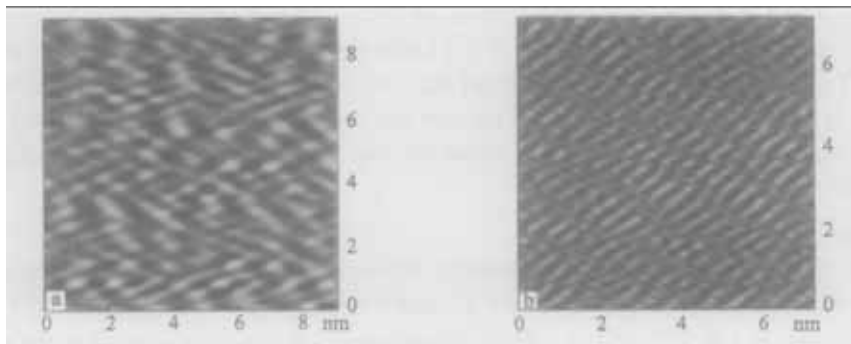


Fig. 5 AFM image of Allyl-T (a) and POS (b)

a) Allyl-T, the average width of the protruding part of chain is 0.28 nm, the average distance between adjacent chains is 0.37 nm.

b) POS, the average width of the protruding part of chain is 0.26 nm, the average distance between each adjacent chains is 0.32 nm.

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

Molecular simulation

From the simulation of the molecular structure, we find that almost all the parent LPSs have similar widths of the ladderlike Si—O—Si framework, *i.e.* ca. 0.45 nm. The structure of H-T is shown as an example of the helix structure of *cis*-isotactic LPS when the molecule is sufficiently long. Allyl-T has a helix molecular structure similar to H-T but has the allyl side groups stretched out freely. For tubular structure, we propose a typical and reasonable model (Fig. 6). The simulations show that it has an outer diameter of 0.45 to 0.7 nm, and an inner diameter of 0.2 to 0.3 nm as shown in Table 1. The molecular simulation is valid only in an ideal environment, the real molecular shapes and morphological structures are definitely affected by the interaction of solvents.

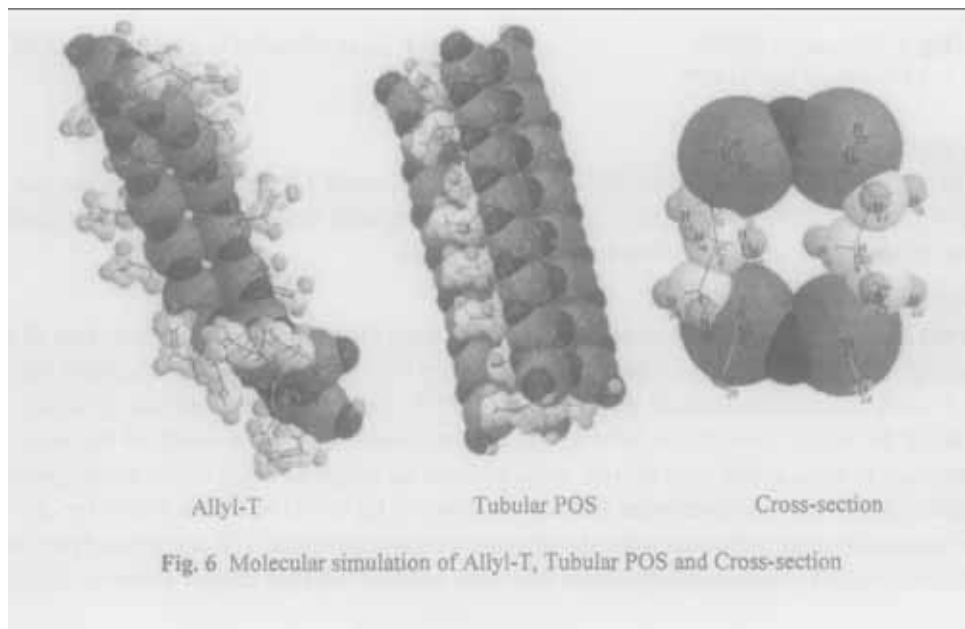
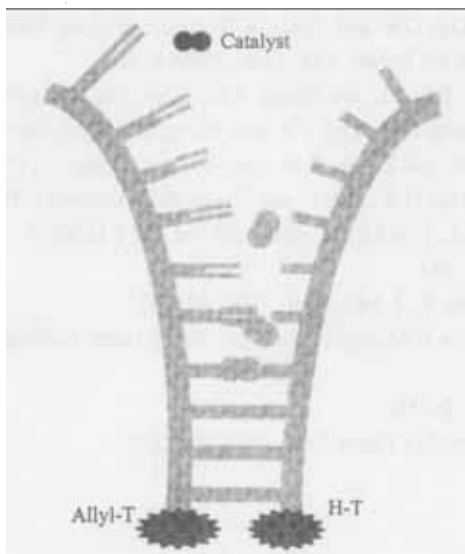


Fig. 6 Molecular simulation of Allyl-T, Tubular POS and Cross-section

As mentioned above, the yield for the tube formation is very high because this kind of multifunctional polymerization easily leads to the formation of a new polymer despite the many irregular units remaining in the product. On the other hand, the reaction mechanism that we proposed was related to the interaction of Allyl-T and the Pt-complex catalyst. The reaction probably is continuous in zipping process as shown in Scheme 2, which may be similar to the reaction of nucleation and propagation in nucleic acid self-assembly^[26-29]. The further study on this mechanism is still undertaken.



Scheme 2 Schematic representation of a possible zipping mechanism for the construction of tubular structure

CONCLUSION

A new polyorganosiloxane POS containing nanoscale tubular structure was prepared by the (1 + 1) mode of hydrosilation reaction of Allyl-T and H-T. The product which is soluble in many polar organic solvents was characterized by IR, ¹H-NMR, and their results indicate that the reaction proceeded very well. Characterization data obtained from GPC, XRD, DSC, AFM and molecular simulation indicate the existence of some regular nanoscale tubular structures in the product different from the parent Allyl-T and H-T. However, some structure defects still exist in the tubular structure.

REFERENCES

- 1 Smalley, R.E., *Science*, 1994, 266: 1219
- 2 Ebbesen, T.W. and Ajayan, P.M., *Nature*, 1992, 358: 220
- 3 Iijimam, S. and Ichihashi, T., *Nature*, 1993, 363: 63
- 4 Harada, A., Li, J. and Kamachi, M., *Nature*, 1993, 364: 516
- 5 Harada, A., Li, J. and Kamachi, M., *Nature*, 1992, 356: 325
- 6 Zhang, R.B., Dai, D.R., Cui, L., Xu, H., Liu, C.Q. and Xie, P., *Mater. Sci. Eng. C.*, 1999, 3: 13
- 7 Zhang, R.B., Xie, P., Dai, D.R. and Liu, C.Q., *Chinese J. Polym. Sci.*, 2000, 18(3): 195.
- 8 Cao, X.Y., Xu, H., Wang, L.T., Li, Z., Cao, M., Xie, P. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1998, 16(3): 226
- 9 Zhang, R.B., Cao, X.Y., Xie, P., Wang, L.T. and Li, Z., 1997, CN Pat., 97 1 12236.9
- 10 Xie, Z.S., He, Z.Q., Dai, D.R. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1989, 7(2): 183

- 11 Xie, Z.S. and Zhang, R.B., *Coating Industry* (in Chinese), 1991, 2: 5
- 12 Xie, Z.S., Dai, D.R. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1991, 9(3): 266
- 13 Zhang, L.Y., Dai, D.R., Li, Z. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1999, 17(1): 71
- 14 Cao, X.Y., Wang, L.T., Li, B. and Zhang, R.B., *Polym. Adv. Tech.*, 1997, 8: 657
- 15 Xie, Z.S., Dai, D.R. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1992, 10(4): 361
- 16 Zhang, R.B., Li, Z., Xie Z.S., Xie, P., Dai, D.R. and Liu, D.S., 1997, CN Pat., ZL 94 1 00507.0
- 17 Li, Z., Cao, X.Y., Xu, H., Xie, P., Cao, M. and Zhang, R.B., *React. Polym.*, 1999, 39(1): 1
- 18 Cao, M., Li, Z., Zhang, Y., Xie, P., Dai, D.R. and Zhang, R.B., *React. & Funct. Polym.*, 2000, 45: 119
- 19 Zhang, L.Y., Dai, D.R. and Zhang, R.B., *Polym. Adv. Tech.*, 1997, 8: 662.
- 20 Xu, H., Zheng, M., Cao, M., Xie, P., Bai, F.L. and Zhang, R.B., *Science in China (B)*, 1999, 42(4): 351
- 21 Liu, C.Q., Xie, P., Dai, D.R. and Zhang, R.B., Zhu, C.F. and Wang, C., *Polym. Adv. Tech.*, 2001, 12: 1
- 22 Liu, C.Q., Liu, Z.H., Xie, P., Dai, D.R. and Zhang, R.B., Zhu, C.F. and Wang, C., *Polym. Adv. Tech.*, 2001, in press
- 23 Xu, H., Cao, X.Y., Li, Z., Cao, M., Dai, D.R., Xie, P. and Zhang, R.B., *Chinese J. Polym. Sci.*, 1998, 16(3): 253
- 24 Zhang, R.B., Xu, H., Xie, P., Wang, L.T. and Li, Z., 1997, CN Pat., 97 1 12268.7
- 25 Aptel, M.A., *Anal. Chem.*, 1985, 57: 651
- 26 Craig, M.E., Crothers, D.M. and Doty, P., *J. Mol. Biol.*, 1971, 62: 383
- 27 Porschke, D., in "Chemical Relaxation in Molecular Biology", ed. by Pecht, I., Rigler, R., Springer-Verlag, Berlin, 1977, p.191
- 28 Lindsey, J.S., *New J. Chem.*, 1991, 15: 153
- 29 Lawrence, D.S., Jiang, T. and Levett, M., *Chem. Rev.*, 1995, 95: 2229