

MORE ON THE STRUCTURES OF POLYPHENYLSILSESQUOXANES

ZHANG Xinsheng (张心胜), SHI Lianghe^{*}(施良和), HUANG Chaoran(黄超然)

(Institute of Chemistry, Academia Sinica, Beijing)

ABSTRACT

The steric tacticity of polyphenylsilsesquioxanes is discussed based on both structure transformation consideration and the results of calculations, X-ray diffraction patterns, fluorescence emission spectroscopy, and scanning electron microscopy. All of the results show that *cis*-isotactic conformation is the most probable one for ladderlike polymer polyphenylsilsesquioxane though other conformations such as *cis*-syndiotactic may also be present in the macromolecules depending upon the preparation conditions.

In the previous papers^[1,2], we studied the relationship between the configurations of polyphenylsilsesquioxanes (PPS) and preparative methods, and two criteria were obtained to judge the regularity of ladderlike structures. PPS's steric tacticity was believed to be *cis*-syndiotactic which was first suggested by Brown and coworkers^[3,4] based on the results of infrared, ultraviolet spectroscopy, X-ray patterns and calculations of angles between the bonds. This conformational concept was widely accepted^[5] but no further investigation was made to confirm its reality. Indeed, there were several papers published, concerning PPS's structures^[6-8], but most of them directed to the defective and branching structures. In the present work, the steric tacticity of PPS was considered, based on the results of calculations, X-ray patterns, and two new techniques, fluorescence emission spectroscopy and scanning electron microscopy (SEM). Infrared and ultraviolet spectroscopy were also used, but they are not effective tools in studying the tacticity of PPS.

EXPERIMENTAL

Materials

All of the materials used in the present studies were prepared by the methods described elsewhere^[2]. The defects were characterized by ¹H, ²⁹Si NMR, IR, and solution properties^[1,2].

X-ray patterns

The diffraction patterns were obtained with a Rigaku equipment with a scanning speed of 2°/min. from 3 to 30°. Studies were also performed in 30–60°, and in 0–3° with another Rigaku instrument for films piled up but no peak was found in these ranges.

Fluorescence Spectra

The investigations were carried out on a Hitachi MPF-4 equipment with an excitation wavelength of 260nm in chloroform solutions ranging from 1.0×10^{-4} – 10^{-2} mol(Si)/ml.

SEM

Work was done on a S-530 model instrument made in Japan.

Received December 27, 1986

* To whom correspondence should be addressed.

RESULTS AND DISCUSSIONS

1. From the consideration of monomer-macromolecule structure transformations

It was reported that PPS and several kinds of cage-like products (e.g. T_8) could be converted to one another with ease^[4].

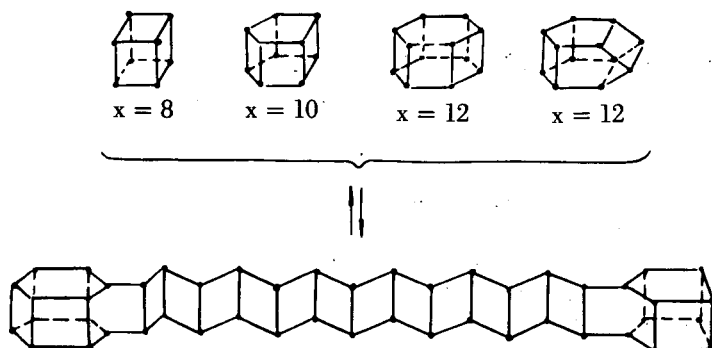


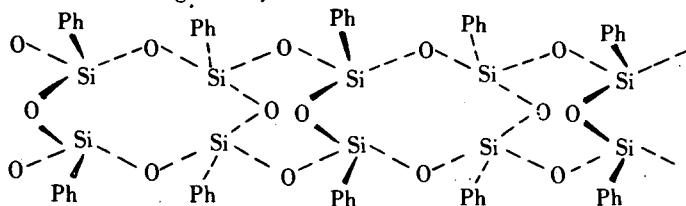
Fig. 1 T_x ($x = 8, 10, 12$)-double chain equilibrium in phenylsilsesquioxanes

● represents C_6H_5Si group

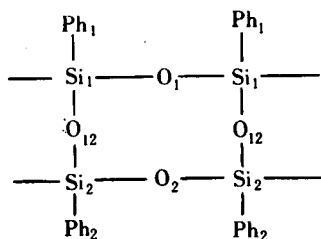
Now we take T_8 as an example. Because of the restrictions of both bond angles and steric hinderance of phenyl groups, "syndiotactic" conformation can not exist in cage-like structure. This can be proved with a model and simple calculations. In other words, as far as cage-like configuration is concerned, all of the phenyl groups should lie in the outside of the ring. Then the formation of *cis*-syndiotactic polymer from cyclic species needs all of the 8 Si—O—Si bonds in the chains broken simultaneously (the other 4 Si—O—Si bonds between the chains should rotate at the same time), that is to say, the cage-like structure must be smashed into pieces before the formation of tactic polymer. Same thing should happen in the process of converting syndiotactic polymer (if there is) into cage-like products. We regard it impossible. In contrast, *cis*-isotactic polymer can be converted into cage-like species just by the breakage of two bonds. In fact, cage-like conformation similar to T_8 can even be approached without any stress only by the rotation of oxygen atoms.

2. From the results of fluorescence emission spectroscopy

Steric structure of PPS given by Brown and coworkers^[3,4] is shown below



For the convenience of discussion, we use some signs to designate the groups and atoms in two jointed chains as indicated in the following:



The angles between Ph_1 and Ph_2 in Brown's model is about 68° (Fig. 2a). Through the movement of O_{12} round $\text{Si}-\text{O}_{12}-\text{Si}$, about 8° angle can be approached (see Fig. 5b), but occurrence of stress would prohibit the existence of such conformation (this can be proved by the results of X-ray which will be discussed later). On the other hand, in *cis*-isotactic conformation, two neighbouring phenyl groups, Ph_1 and Ph_1 , or Ph_2 and Ph_2 , have the preference to lie nearly parallel (Fig. 2b) because of volume exclusion of the polymer chain which also would limit $\text{O}_1(\text{O}_2)$ lying opposite to $\text{Ph}_1(\text{Ph}_2)$.

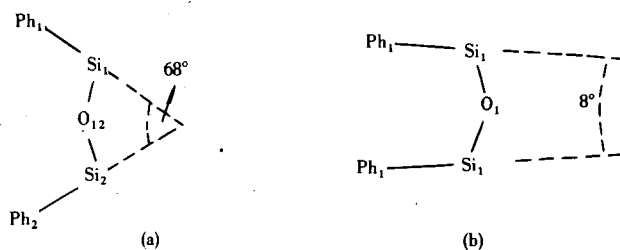


Fig. 2 Angles between neighbouring Ph groups in PPS

(a) in both syndiotactic and isotactic conformations; (b) only in isotactic conformation.

It can be expected from the above statement that PPS chains with *cis*-syndiotactic conformation should have prominent intensity of monomer fluorescence, and with *cis*-isotactic, the intensity of excimer fluorescence ought to be predominant. The fluorescence spectra of PPS are shown in Fig. 3. That almost only excimer fluorescence can be seen supports the prediction from *cis*-isotactic conformation. It also needs to point out that under some preparation conditions, a tail in the range of monomer fluorescence can be observed (Fig. 3c) indicating the existence of irregular steric structures in long range. More detailed data on PPS fluorescence will be published elsewhere^[9].

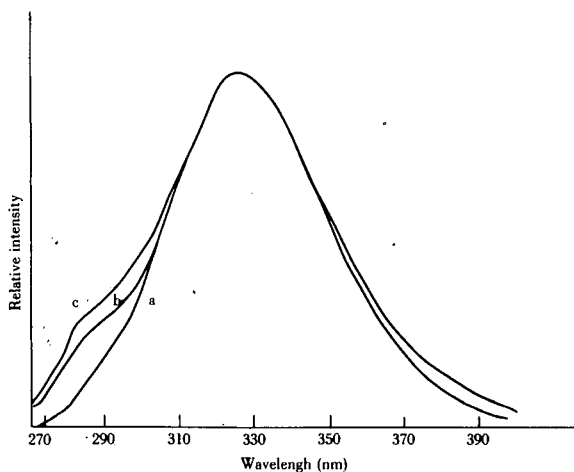


Fig. 3 Fluorescence spectra of PPS

(a) in solid state; (b) prepared from hydrolyte in toluene;

(c) prepared from hydrolyte in ether

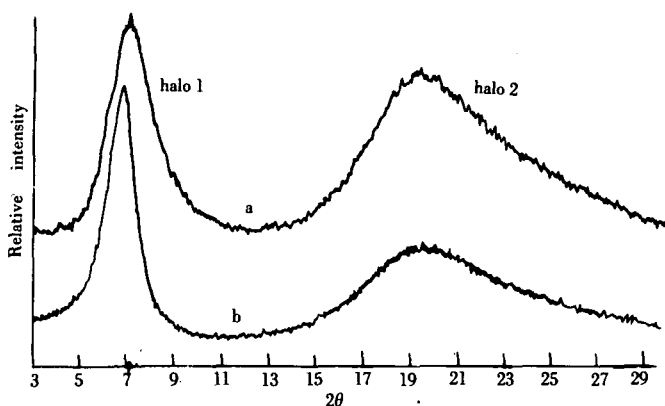


Fig. 4 X-ray patterns of PPS

(a) PPS with 50% (chain unit) defects; (b) PPS with perfect ladderlike structure

3. From the results of X-ray

X-ray patterns (Fig. 4) of PPS show two diffraction halos in good agreement with Andrianov and coworkers' results^[5].

The first sharp halo represents a plane-to-plane distance of about $12.5\text{ \AA}$ which was found to be corresponding with the chain-to-chain distance from the calculations of bond angles and lengths (Fig. 5a). The results also show us that the distribution of chain-to-chain distance is narrow. The conformation as indicated in Fig. 5b which is the only form that could be used in explaining the excimer fluorescence for *cis*-syndiotactic PPS is impossible because its chain-to-chain distance is less than $8\text{ \AA}$.

The second halo which is diffuse covers a wide range of diffraction angle with a peak locating at $2\theta \simeq 19.4^\circ$ which gives a plane-to-plane distance approximately $4.6\text{ \AA}$. Several calculations were made and only the thickness of the polymer chains with *cis*-isotactic conformation is nearer to the value found.

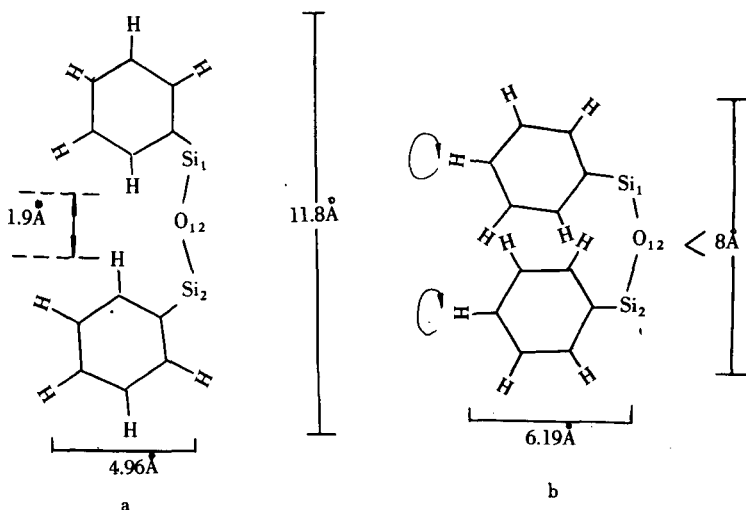
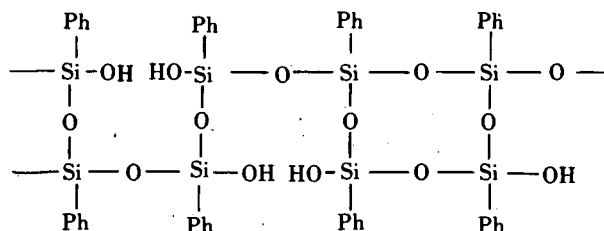


Fig. 5 Schematic representation of PPS chain-to-chain distances and chain thicknesses.

It is also noticed that the relative intensity of halo 1 compared with halo 2 decreases sharply as the defect content of the following kind^[1,2] increases (Fig.6). This is the consequence of disorder



Defective PPS

in main chain which, as expected, leads to a reduction in d_1 (chain-to-chain distance, corresponding to halo 1) but no distinct effect found on d_2 (corresponding to halo 2) (Table 1).

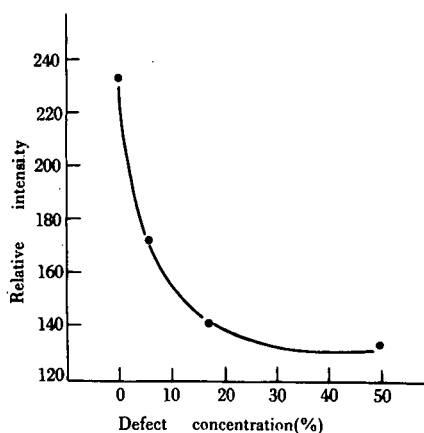


Fig. 6 The relationship between relative intensity (halo 1/halo 2) and defect concentration

Table 1 Effect of defects on d_1 and d_2

Defect content (%)	d_1 (Å)	d_2 (Å)
less than 0.1	12.9	4.5
5.8	12.6	4.6
17	12.7	4.6
50	12.3	4.6

4. Other evidences

Micrographs of SEM for PPS fracture surfaces show the tiny spherical particles with diameters from 200 Å to 800 Å for the film cast from the surfaces of mercury (Fig. 7). From a model one can easily see that PPS with *cis*-isotactic conformation have high tendency to curve while *cis*-syndiotactic ones are more likely to form strips. When 4.96 Å is taken as the chain thickness, and assuming that PPS chains is curved in the form of isotactic conformation, we can have the diameters of PPS coils in 250 Å to 850 Å for molecular weight ranging from 100,000 to

1,000,000, very near to the values found. Although a particle may not be one molecule curved, it indeed indicates that the submolecular structure is not fibrous as that of rodlike macromolecules usually is. The curved PPS molecules were also supported by the studies of solution properties of PPS which suggest a rigid coil conformation of PPS molecules rather than any of other stiff chains^[7,8].

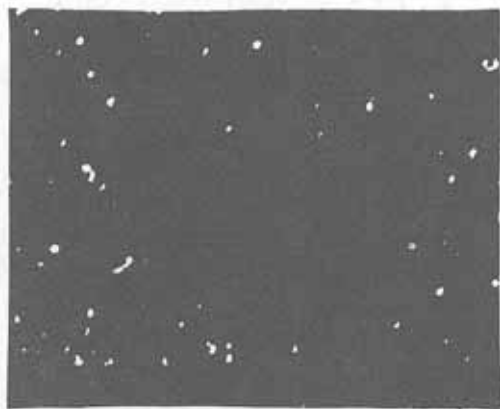


Fig. 7 SEM micrograph for PPS fracture surface of PPS film cast from the surface of mercury

CONCLUSION

All of the stated results show that *cis*-isotactic conformation is the most probable one for ladderlike polymer PPS though other conformations such as *cis*-syndiotactic may also be present in the macromolecules depending upon the preparation conditions. Also, the combination of a variety of different methods gives us a more reliable way to approach the structural elucidation of PPS.

Keywords:

Polyphenylsilsesquioxanes; X-ray diffraction patterns; Fluorescence emission spectroscopy; Scanning electron microscopy

REFERENCES

- [1] ZHANG Xinsheng; CHEN Suming and SHI Lianghe, *Chinese J. Polym. Sci.*, **1987**, 5(2), 162.
- [2] ZHANG Xinsheng and SHI Lianghe, *Chinese J. Polym. Sci.*, **1987**, 5(3), 197.
- [3] Brown, J. F., Jr.; Vogt, L. H., Jr.; Katchman, A.; Eustance, J. W.; Kiser, K. M., and Krantz, K. W., *J. Amer. Chem. Soc.*, **1960**, 82, 6194.
- [4] Brown, J. F., Jr.; *J. Polym. Sci., Part C*, **1963**, (1), 83.
- [5] Andrianov, K. A.; Zhdanov, A. A. and Levin, L. Yu., *Annual Rev. Mater. Sci.*, **1978**, 8, 313.
- [6] Kovar, J.; Mrkvickova-Vaculova, L. and Bohdanecky, M., *Makromol. Chem.* **1975**, 176, 1829.
- [7] Bohdanecky, M.; Mrkvickova-Vaculova, L. and Kovar, J., *Collect. Czech. Chem. Commun.*, **1975**, 40, 2616.
- [8] Helminiak, T. E. and Berry, G.C., *J. Polym. Sci., Polym. Symp.*, **1978**, 65, 107.
- [9] HUANG Chaoran; XU Guangzhi; ZHANG Xinsheng and SHI Lianghe, *Chinese J. Polym. Sci.*, **1987**, 5(4), 347.