

# STUDIES ON THE EXCIMER FLUORESCENCE AND THE STERIC TACTICITY OF POLYPHENYLSILSESQUIOXANES

HUANG Chaoran (黄超然), XU Guangzhi (徐广智), ZHANG Xinsheng (张心胜),  
and SHI Lianghe (施良和)

(Institute of Chemistry, Academia Sinica, Beijing)

## ABSTRACT

The steric tacticity of polyphenylsilsesquioxanes (PPS) was studied by excimer fluorescence spectroscopy. It was found that the fluorescence of PPS come mainly from its intramolecular excimers. The experimental results indicated that the steric-structure of PPS is most probably *cis*-isotactic rather than the *cis*-syndiotactic as suggested in the literature. With the increase in defect content monomer fluorescence intensity increases because of the enhanced mobility of phenyl groups. Molecular weights and molecular weight distributions do not affect the fluorescence spectra of PPS.

## INTRODUCTION

The formation of intramolecular excimer needs strict coordination of steric position. For example, the excited fluoropher must lie parallel to the unexcited one and the distance between the two fluorophers should be about  $3\text{\AA}$  in order to form an excimer. For the compound of  $\text{Ph}-(\text{CH}_2)_n-\text{Ph}$  ( $\text{Ph} = \text{C}_6\text{H}_5$ ), it was found that the best condition for the existence of excimer was limited to  $n = 3$ <sup>[1]</sup>. Such a rule of  $n = 3$  which gives a complete formation of excimer is also true for the compounds containing C—O bonds and Si—O bonds<sup>[2,3]</sup>. As the formation of intramolecular excimer is restricted in a strict spacial position, the study of excimer fluorescence can be used as a probe in approaching the steric structures of molecules. Up to now the excimer fluorescence of some macromolecules, especially, the polymer containing styrene as a monomer, have been studied extensively<sup>[4,5]</sup>, but the data about polyorganosiloxanes were very scarce in literature.

In the present work, the fluorescence spectra of ladderlike polyphenylsilsesquioxanes (PPS) and several related polyorganosiloxanes were determined for the purpose of the investigation of PPS's steric structure. The existence of excimer in UV excited PPS molecules was studied. Also, the effects on fluorescence spectra of molecular weights, defects, and copolymerization were reported in this paper.

## EXPERIMENTAL

### 1. Sample preparation

#### A. Monomer $\text{PhSi}(\text{OC}_2\text{H}_5)_3$

Excessive water free ethanol (A.R) was dropped slowly into  $\text{PhSiCl}_3$  with rotation. After the complete reaction, the products were separated and  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  was carefully distilled twice. The structure and purity of  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  were determined by IR,  $^{29}\text{Si}$  NMR, and elementary

analysis.

### B. Polyphenylsilsesquioxanes

Prepolymers were obtained by hydrolysis of  $\text{PhSiCl}_3$  in toluene (prepolymer A) or ether (prepolymer B). Polymers were prepared from the prepolymers under various conditions. Fractionation was conducted at  $25^\circ\text{C}$  with toluene/methanol as solvent/non-solvent. The structures were characterized by  $^{29}\text{Si}$  NMR,  $^1\text{H}$  NMR and IR. The molecular weights and defect contents of PPS samples were listed in Table 1. Detailed descriptions were given elsewhere<sup>[6,7,8]</sup>.

Table 1 Molecular weights and defect contents of PPS

| Sample              | Solvent for hydrolysis | Molecular weight      | Defect <sup>d)</sup> content(mol%) |
|---------------------|------------------------|-----------------------|------------------------------------|
| prepolymer A        | toluene                | $1.1 \times 10^{3b)}$ | 17                                 |
| prepolymer B        | ether                  | $2.8 \times 10^{3b)}$ | 50                                 |
| PPS-1 <sup>a)</sup> | toluene                | $8.6 \times 10^{3c)}$ | <1                                 |
| PPS-2 <sup>a)</sup> | ether                  | $3.4 \times 10^{5c)}$ | <0.1                               |
| PPS-3 <sup>a)</sup> | ether                  | $5.5 \times 10^{5c)}$ | <0.1                               |
| PPS-4 <sup>a)</sup> | ether                  | $5.7 \times 10^{3b)}$ | <0.1                               |

Note: a. PPS-1, prepared from prepolymer A;  
 PPS-2, prepared from prepolymer B;  
 PPS-3 and PPS-4, fractions from PPS-2.

b.  $M_n$ , determined by VPO in benzene.

c.  $M_w$ , determined by small angle laser light scattering in THF.

d. See reference<sup>[7]</sup>.

### C. $-(\text{PhSiO}_{1.5})_x-(\text{Me}_2\text{SiO})_y-$

$\text{PhSiCl}_3$  was cohydrolyzed in ether with equal weight  $\text{Me}_2\text{SiCl}_2$ , purified, and then polymerized. The product was precipitated twice with toluene/methanol, and dried in vacuum at  $50^\circ\text{C}$  to constant weight.

#### 2. Fluorescence spectra

Work was done on Hitachi MPF-4 equipment. Surface fluorescence emission was recorded by cell rotation for  $30^\circ$ . Refined UV pure chloroform was used as solvent, and no effect of the solvent was found on fluorescence spectra under the experimental conditions. The solution concentrations were in the range of  $10^{-2}$ — $10^{-4}$  Ph mol/dm<sup>3</sup>.

## RESULTS AND DISCUSSION

$\text{PhSi}(\text{OC}_2\text{H}_5)_3$  has the same UV absorption spectrum as PPS (Fig. 1, b) indicating no dimer present in PPS molecule. Exciting spectra were measured for recordings of emission fluorescence at 285nm and 325nm for  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  and PPS, respectively, and the results showed that both  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  and PPS had the maximum absorption at 272nm (Fig. 1c, d) which coincide with the values from UV absorption spectra. It can be deduced that the fluorescence at 285nm for  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  and 325nm for PPS are resulted from the same absorption of 272nm. So the

difference in fluorescence between  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  and PPS indicates the different state of phenyl groups. From the structure consideration of these two molecules, we owe the fluorescence at 325nm to the excimer in PPS.

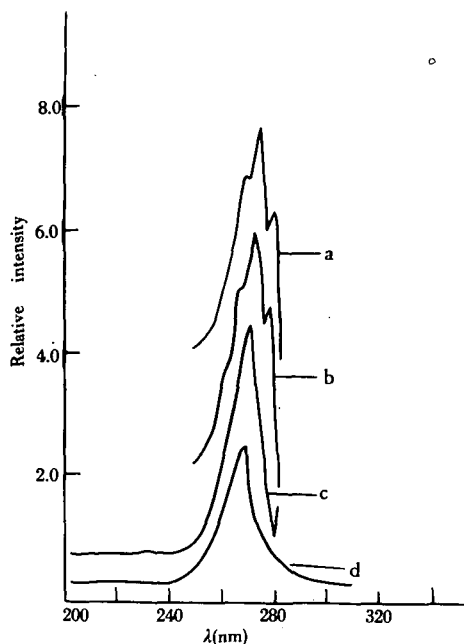


Fig. 1 UV absorption and fluorescence exciting spectra.

- a. UV absorption spectrum of  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$ ,
- b. UV absorption spectrum of PPS,
- c. exciting spectrum of  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$ ,
- d. exciting spectrum of PPS.

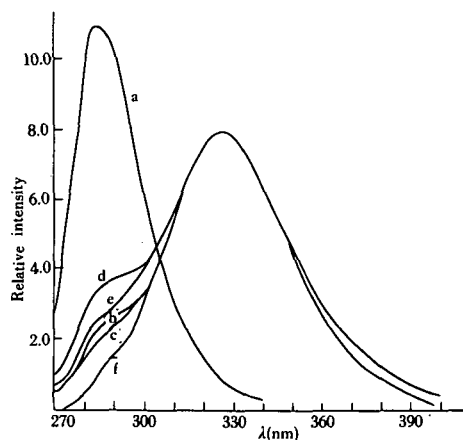


Fig. 2 Fluorescence spectra of  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  and PPS.

- a.  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  ; b. prepolymer A; c. PPS—1;
- d. prepolymer B; e. PPS—2; f. film of PPS.

Fluorescence spectrum of  $\text{PhSi}(\text{OC}_2\text{H}_5)_3$  gives an emission peak of phenyl monomer at 285nm (Fig. 2a) when excited by UV light with a wavelength of 260nm. Under the same condition, PPS has a strong excimer fluorescence peak at 325nm with a very weak emission at 285nm corresponding to the emission of monomers (Fig. 2c,e)  $I_e/I_m$ , the ratio of emission intensities at 325nm ( $I_e$ ) and at 285nm ( $I_m$ ) keeps constant in the concentration range of  $10^{-2}$ — $10^{-4}$  Ph mol/dm<sup>3</sup>. In the same concentration range, no red shift of the peak was found. This is the character of intramolecular excimer fluorescence. These results illustrate the existence of intramolecular excimer in PPS.

From the consideration of structures, PPS can mainly have two types of conformation, that is, *cis*-syndiotactic (Fig. 3a) which was first suggested by Brown and coworkers<sup>[9]</sup>, and *cis*-isotactic (Fig. 3b). The formation of intramolecular excimers as stated above shows that the position of neighbouring phenyl groups meets the demand of excimer formation. Though from the first look, <sup>1</sup>Ph may form excimer with <sup>3</sup>Ph in *cis*-Syndiotactic (Fig. 3a) or with <sup>2</sup>Ph and <sup>3</sup>Ph in *cis*-isotactic (Fig. 3b), the results based on models and calculations of bond angles and lengths as well as X-ray diffractions eliminate the possibility of existence of <sup>1</sup>Ph—<sup>3</sup>Ph excimer. Also, the restrictions of bond angles and lengths are advantageous to the formation of <sup>1</sup>Ph—<sup>2</sup>Ph excimers which is

only possible in *cis*-isotactic conformation. More detailed data will be published elsewhere<sup>[8]</sup>. All of these results indicate that the conformation form of PPS is mainly *cis*-isotactic rather than the *cis*-syndiotactic.

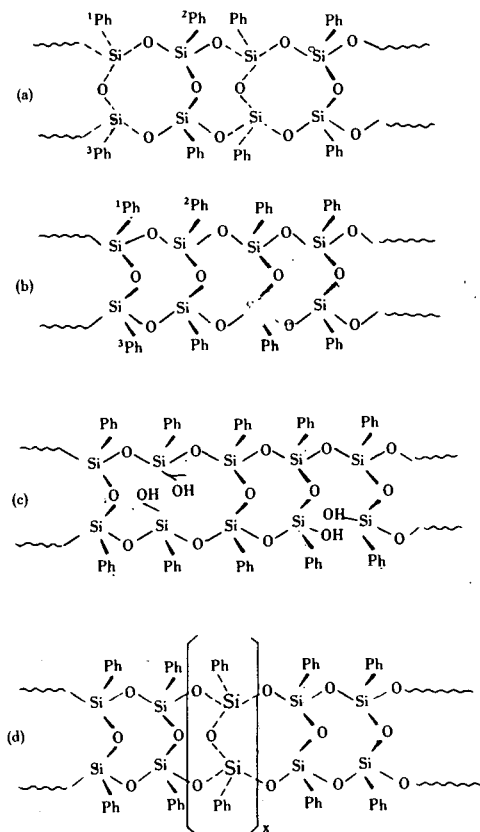


Fig. 3 Schematic representation of PPS structure.

- a. *cis*-syndiotactic; b. *cis*-isotactic;  
c. *cis*-isotactic containing defects; d. *cis*-isotactic containing irregular units.

It can be seen from Fig. 2c,e that there is some difference in fluorescence spectrum in the region of 270nm to 300nm when PPS was prepared from different prepolymers. PPS—1 prepared from prepolymer A has a weaker fluorescence emission than PPS—2 from prepolymer B in 270—300nm showing more tactic conformation in PPS—1. In other words, PPS—2 chain contains sterically more irregular units such as “syndiotactic ones” (Fig. 3d).

The effect of ladderlike regularity (or defects) on fluorescence spectra was also studied in the present work. PPS can have two types of defect (“interchain” or “intrachain”) as shown in Fig. 3c. Interchain defect provides phenyl groups with the possibility of rotation around O—Si—O bonds which as a consequence may increase the fluorescence intensity of monomers (at about 285nm). Curves presented in Fig. 2 is in keeping with this expectation. The fluorescence spectra of films is represented in Fig. 4 which also show some differences between differently constructed polyphenylsilsesquioxanes.

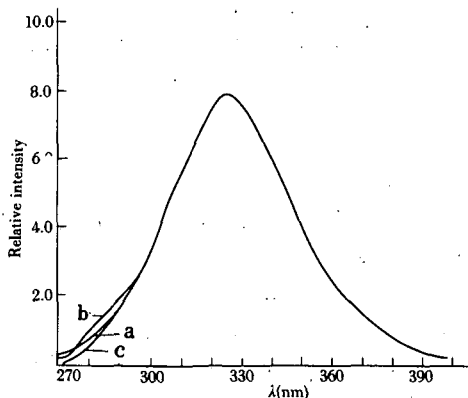


Fig. 4 Fluorescence spectra of polyphenylsilsequioxanes film.

a. prepolymer A; b. prepolymer B; c. PPS.

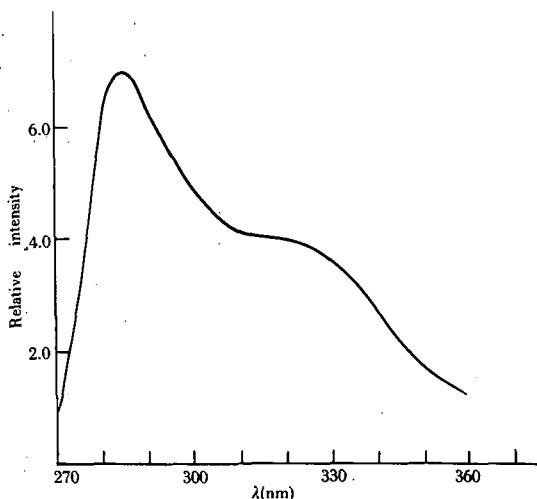


Fig. 5 Fluorescence spectrum of copolymer

The following copolymer has many "defect" as ladderlike structure is concerned. Its fluorescence spectrum shows a strong monomer emission intensity (Fig. 5). This result also indicates the formation of intramolecular excimers in contrast to intermolecular excimer in the polymer.

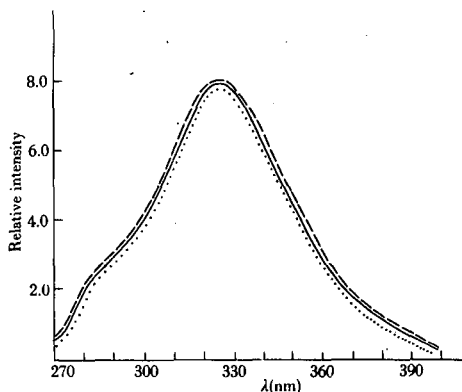
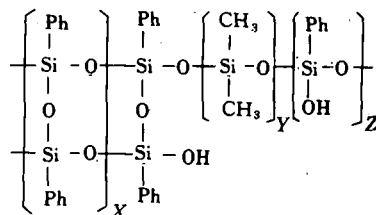


Fig. 6 Fluorescence spectra of different molecular weights and molecular weight distributions

a. ....PPS-3; b. ....PPS-4; a. — PPS-2,  $M_w/M_n = 10$ .

It was reported that the ratio  $I_e/I_m$  varies with molecular weights for polystyrene (PS) solution with a concentration of  $10^{-3}$  Ph mol/dm<sup>3</sup>[10]. This can be explained as an increased coil density in

solution while the molecular weight of PPS increases. Two fractions of PPS with molecular weights of  $5.5 \times 10^5$  (PPS—3) and  $5.7 \times 10^3$  (PPS—4) were studied in our work, and the experimental results showed that these two samples had the same fluorescence spectrum (Fig. 6). Comparing curves a and d with c in Fig. 6, we can see that the molecular weight distribution also does not affect the fluorescence spectra of PPS.

### CONCLUSIONS

The stated results give the following conclusion:

1. PPS has very strong excimer fluorescence emission both in bulk and solution state. The excimers were proved to be intramolecular rather than intermolecular ones.

2. Combined with the other experimental results and the consideration of PPS's structure, the mode of conformation in PPS segments is mainly *cis*-isotactic though in long range the conformation may be irregular. The methods of sample preparation have distinct effect on PPS fluorescence spectra due to the different constructions of PPS chains under different conditions.

3. Increase in defect content increases monomer fluorescence intensity because of the enhanced mobility of phenyl groups. Copolymer of  $\text{PhSiO}_{1.5}$  with  $\text{Me}_2\text{SiO}$  also has a higher monomer peak than PPS.

4. Molecular weights and molecular weight distributions do not affect the fluorescence spectra of PPS.

### Keywords:

Polyphenylsilsesquioxanes; Fluorescence; Excimer; Steric tacticity.

### REFERENCES

- [1] Hirarams, F., *J. Chem. Phys.* **1964**, 42, 3136.
- [2] David, C.; Piens, M. and Geukeus, G., *Eur. Polym. J.*, **1972**, 8, 1291.
- [3] 吴世康、姜永才, 科学通报, 1980 年数理化专辑, *KEXUE TONGBAO; A Special Issue of Mathematics, Physics, & Chemistry*, 259 页.
- [4] Vala, M. T.; Haebig, J. and Rice, S. A., *J. Chem. Phys.* **1965**, 43, 886
- [5] 钱人元、曹 锦、陈尚贤、白凤莲, 中国科学 B 辑, *SCIENTIA SINICA* **1983** 12 1080.
- [6] Zhang Xinseng, and Shi Lianghe, *Chinese J. Polym. Sci.*, **1987**, 5(3), 197.
- [7] Zhang Xinseng; Chen Suming and Shi Lianghe, *Chinese J. Polym. Sci.*, **1987**, 5(2)162.
- [8] Zhang Xinseng; Shi Lianghe and Huang Chaoran, *Chinese J. Polym. Sci.*, **1987**, 5(4),
- [9] Brown, J. F. and Vogt, L. H., *J. Amer. Chem. Soc.*, **1960**, 82, 6194.
- [10] Ishii, T., Handa, T. and Matsunaga, S., *Macromolecules*, **1978**, 11(1), 40.