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STRUCTURAL INVESTIGATION OF A NEW
POLYORGANOSILOXANE CONTAINING NANOTUBULAR CAVITIES
USING ORGANIC FLUORESCENT PROBES*

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Abstract Fluorescent molecules — *p*-dimethylaminobenzonitrile (DMABN) and *trans*-stilbene (TSB) — were used as probes to investigate the inner structure of the nanotubular cavities contained in a new polyorganosiloxane (POS) which was prepared by the hydrosilylation coupling reaction of *cis*-isotactic ladderlike polyvinylsilsesquioxane (Vi-T) with 1,1,3,3-tetramethyldisiloxane (H-MM) as coupling agent in the presence of catalyst dicyclopentadienyldichloroplatinum (Cp₂PtCl₂). The results from FTIR spectra and fluorescence spectra in combination with molecular simulation reveal that the cross-section of the nanotubular cavity is nearly rectangular in shape, and is about 0.62 nm in width and about 0.38 nm in height. This work gains in-depth knowledge into the inner structure of the nanotubular cavities of POS and furthermore provides a guide to the selection of proper guest molecules in constructing functional supramolecular clathrate based upon POS.

Keywords Polyorganosiloxane, Nanotubular cavities, Fluorescent probes

INTRODUCTION

Recently we reported a novel inorganic-organic hybrid — nanotube-contained polyorgano-siloxane (POS)^[1, 2] — which was prepared by the hydrosilylation coupling reaction of *cis*-isotactic ladderlike polyvinylsilsesquioxane (Vi-T)^[3] with 1,1,3,3-tetramethyldisiloxane (H-MM) as coupling agent in the presence of catalyst dicyclopentadienyldichloroplatinum (Cp₂PtCl₂) (Scheme 1). Although a variety of other structures may also exist in the POS, the nanotubular structure as shown in Scheme 1 should be the main structure because the *cis*-isotactic conformation of Vi-T is conducive to the formation of such a tubular structure^[1, 2]. In addition, the existence of nanotubular cavities in the POS has been confirmed by a set of characterization techniques including IR, NMR, X-ray diffraction, GPC, vapour pressure osmometry (VPO), two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY), DSC, atomic force microscopy (AFM), and molecular simulation^[1, 2].

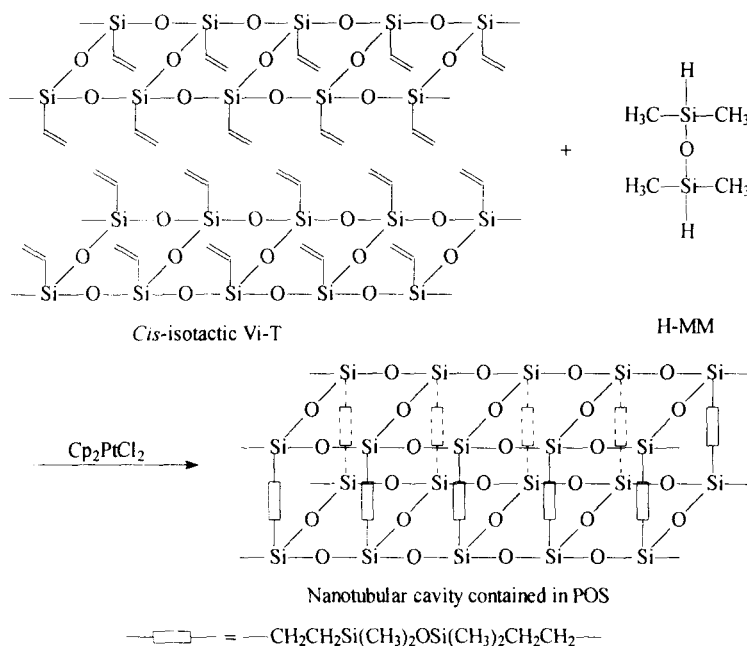
However, the inner structure of the nanotubular cavities, such as their shape and size still

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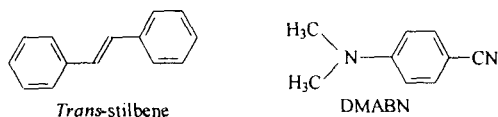
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remains unclear, which prevents us from understanding the structure and properties of the POS as a whole and furthermore, from intentionally designing and preparing POS-based supramolecular clathrate. To detect the inner structure of a material, one should bear in mind that probe technique, especially the fluorescent probe technique (FPT)^[4], which acquires structural information from the fluorescence variation of probe molecules included in the host materials, is usually an effective and practical method in this regard. Fortunately, the POS thus obtained has good solubility in many organic solvents such as THF, chloroform and so on^[1], which makes it convenient to implement FPT which is generally conducted in solutions. In this paper, two small organic fluorescent molecules, *p*-dimethylaminobenzonitrile (DMABN) and *trans*-stilbene (TSB) (Scheme 2) were adopted as probes in consideration of the relative small size of the nanotubular cavities. The FTIR spectra, fluorescence spectra in conjunction with molecular simulation were employed to carry out such an investigation.



Scheme 1 The schematic process for the formation of nanotubular cavity of POS



Scheme 2 The structure of *trans*-stilbene and DMABN

EXPERIMENTAL

Materials

DMABN was obtained from the Aldrich Co., and TSB was obtained from the Beijing Chemical Factory. They are both of analytical grade and stored under dry conditions all the time. H-MM (>98% GC) was available from Fluka Chemie AG Co.. Cp_2PtCl_2 was synthesized according to Ref. [5]. Vi-T was prepared by referring to Ref. [3]. Analytical grade THF was refluxed with blue sodium benzophenone ketal before use.

Measurements

FTIR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. The steady-state

fluorescence spectra of the polymer were measured on a Hitachi MPF-4 fluorescence spectrophotometer, with THF as solvent at room temperature (25°C). The concentrations of the samples for fluorescence determination were listed in Table 1. Molecular simulation was conducted on a Pentium-133MHz PC, using Alchemy 2000 V 1.0 for Windows 95 (Tripos Associate, Inc.) as simulation tool based on the molecular mechanics method which employs the potentials for the MM2 force field.

Table 1 The concentrations of samples for fluorescence determination

Sample	Concentration (mol/L)
DMABN	1.37×10^{-5}
Blend (DMABN + POS)	$1.37 \times 10^{-5} + 5.14 \times 10^{-5}$ *
Inclusion system of DMABN	6.85×10^{-5} **
TSB	1.11×10^{-5}
Blend (TSB + POS)	$1.11 \times 10^{-5} + 5.14 \times 10^{-5}$
Inclusion system of TSB	6.85×10^{-5}

* The molar concentration of the POS is calculated based upon the molecular weight of one recurring unit of POS;

** The calculation of the concentration of inclusion system is simplified by neglecting the included fluorescent molecules within POS due to its minute quantity in comparison with POS.

Preparation of Inclusion Systems

To a 50 mL round-bottomed flask equipped with a refluxing condenser and a magnetic stirrer were added 100 mg (~0.633 mmol of unit) of Vi-T and 10 mg of DMABN. The flask was then evacuated and purged with dry argon three times. 0.4 mg of Cp_2PtCl_2 and 20 mL of THF were added and the mixture was stirred at room temperature for 30 min, then 85 mg (~0.637 mmol) of H-MM was added, and subsequently heated to 40°C for 24 h. After cooling, THF was allowed to evaporate and the resulting solid was repeatedly washed with methanol to remove those DMABN molecules which were not included in POS. After drying under vacuum, 182 mg of white POS product was obtained. The procedure of encapsulating TSB is similar to that for DMABN given above.

RESULTS AND DISCUSSION

The probe molecules were included into the nanotubular cavities of the POS by the *insitu* encapsulation method, i.e. probe molecules were introduced into the reaction mixture of Vi-T, H-MM, catalyst, and solvent THF, and were entrapped simultaneously as the nanotubes formed. The products were thoroughly washed with methanol to remove free probes in order to avoid unnecessary fluorescent disturbance.

The inclusion systems thus obtained were subjected to FTIR spectral and fluorescence spectral analyses as discussed below.

FTIR Analysis of the Inclusion Systems

The FTIR spectra of DMABN and TSB inclusion systems are shown in Fig. 1. The primary concern is whether the addition of probe molecules in the reaction mixture would influence the hydrosilylation coupling reaction. As exhibited in Figs. 1a and 1b, the characteristic peaks at around 1600 cm^{-1} and 3050 cm^{-1} ^[3], attributed to the active group $-\text{Si}-\text{CH}=\text{CH}_2$ of the precursor Vi-T, almost completely disappeared in the resulting POS, indicating the hydrosilylation coupling reaction has proceeded to completion, similar to that for preparing pure POS^[1]. This demonstrates that the addition of DMABN or TSB does create a negative effect on the reaction. In other words, *insitu* encapsulation is wholly feasible for the preparation of inclusion systems.

In the FTIR spectrum of the inclusion system of DMABN (Fig. 1a), there is a set of weak peaks at 2225, 1609, 1517 and 1366 cm^{-1} which are all ascribed to DMABN, indicating DMABN

has indeed been encapsulated into the nanotubular cavities of POS. In addition, the stretching vibration of $\text{C}\equiv\text{N}$ shifted from 2212 cm^{-1} (in free state of DMABN) to 2225 cm^{-1} (in entrapped state). This is probably caused by the weakening of the coordination effect of $\text{C}\equiv\text{N}$ and benzyl ring due to steric effect which could decrease the *co*-planarity of $\text{C}\equiv\text{N}$ and benzyl ring, or merely resulted from the interactions between DMABN and the inner cavities of POS.

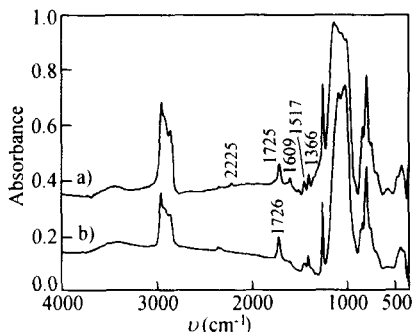


Fig. 1 FTIR spectrum of the inclusion system of a) DMABN and b) TSB

In the FTIR spectrum of the inclusion system of TSB (Fig. 1b), nevertheless, the characteristic peaks of TSB are not detected, which implies TSB is probably not included in the POS. Of course, this supposition needs to be further clarified from the fluorescence determination herein after.

By the way, it should be pointed out that the new peak at around 1725 cm^{-1} , appearing in both FTIR spectra, is actually attributed to the entrapped THF by referring to the standard IR spectrum of THF.

Fluorescence Study of the Inclusion Systems

The fluorescence characteristics of the two probe molecules DMABN and TSB are described at first.

DMABN exhibits dual fluorescence in a variety of organic solvents^[6]. The two emissions are generally believed to occur from two conformationally distinct excited singlet states — the short wavelength emission from a planar state, and the long one from a twisted intramolecular charge transfer (TICT) structure^[7]. The TICT excited state is believed to be formed from the planar excited state by twisting around the phenyl-nitrogen bond and appears to be sensitive to the environment such as polarity of solvents, geometric confinement and so on^[8]. Because of its strong response to environmental effects, DMABN has been successfully used as a fluorescence probe in micelles and in cyclodextrin inclusion complexes^[9, 10].

TSB emits typical luminescence while *cis*-stilbene (CSB) emits no luminescence at all, and TSB can be easily converted to CSB upon exposure to UV light^[11]. Such characteristics of stilbene offer an advantage to investigate the structure of host materials, that can be performed specifically here by first encapsulating TSB into the cavities of POS followed by UV irradiation. By comparing the fluorescence of the inclusion system before and after the UV irradiation, it is possible to infer the structure of the nanotubular cavities.

The fluorescence spectrum of inclusion system of DMABN was compared to that of pure DMABN and the blend of DMABN and POS (cf. Fig. 2a, b and c). The broad peak A centered around 350 nm corresponds to the emission from the planar state of DMABN, and the broad peak B centered around 430 nm corresponds to the emission from the TICT state of DMABN. It was found that for this inclusion system, there was only peak A, while peak B was almost undetectable in comparison with that of pure DMABN. This provides evidence that, other than the previous FTIR analysis, DMABN is actually included into the nanotubular cavities of POS. In addition, it is

realized that the disappearance of TICT luminescence, resulting from the restriction of the rotation of phenyl-nitrogen bond, is mainly due to the geometric confinement of the cavities of POS. The effect of polarity can be neglected, since the polarity of solvent THF is similar to that of POS, which is proved by the comparison of the fluorescence of DMABN (Fig. 2b) with that of the blend of DMABN and POS (Fig. 2c). The addition of POS to the DMABN solution does not affect the normal luminescence of the DMABN. The above results suggest two aspects with regard to the structure of nanotubular cavities. Firstly, the size of the cavities including length and inner diameter should be larger than that of the DMABN molecule; secondly, the shape of inner cavities is not circular but more likely oval or rectangular, such that it could confine the rotation of phenyl-nitrogen bond due to the steric effect.

For the inclusion system of TSB, however, the characteristic fluorescence of TSB (cf. Fig. 3a, the weak broad peak centered around 370 nm is ascribed to the luminescence of the POS itself) was not observed even before UV irradiation, and the lack of luminescence is not due to the possible quench effect of the POS exerted on the fluorescence of TSB because the addition of POS into the solution of TSB (i.e. the blend of POS and TSB, cf. Fig. 3c) does not affect the normal luminescence of TSB (Fig. 3b). This result confirms that TSB is not included in the cavities of POS. In this case, apparently, it is impossible to detect the structure of the cavities of the POS by using TSB as a probe as planned before. Nevertheless, we can at least deduce that the width of TSB should be near to or larger than the width of the nanotubular cavities since TSB is a pancake shaped molecule.

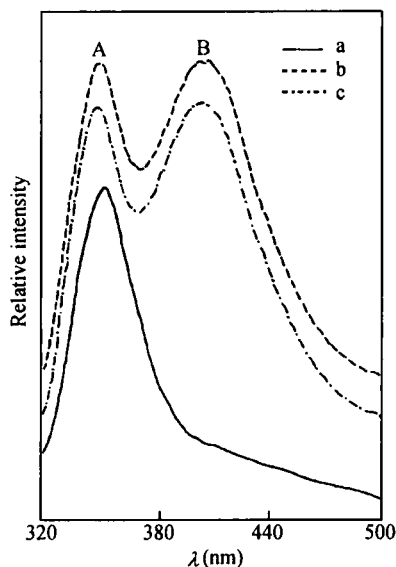


Fig. 2 Fluorescent spectra of a) inclusion system of DMABN, b) DMABN and c) the blend of DMABN and POS

$\lambda_{\text{ex}} = 295 \text{ nm}$

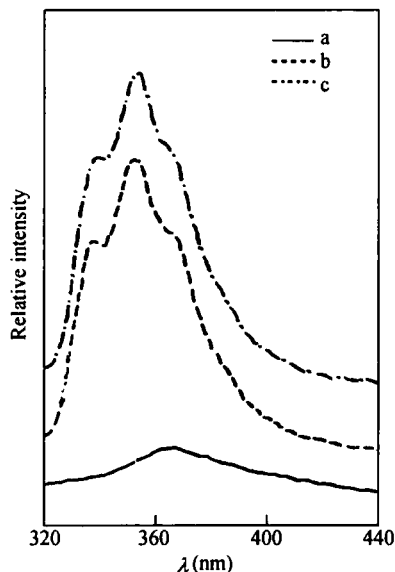


Fig. 3 Fluorescent spectra of a) inclusion system of TSB, b) TSB and c) the blend of TSB and POS

$\lambda_{\text{em}} = 300 \text{ nm}$

Molecular Simulation

In order to verify the above experimental results, the molecular mechanics method was employed to simulate the structures of DMABN, TSB, and the nanotubular cavity of POS (Fig. 4), from which their size were measured (Table 2).

From a top view of the nanotubular cavity, it is observed that the cavity is rectangular in shape with a distinct difference in width and height. DMABN, with a width of 0.50 nm and a height of

0.25 nm in its planar state, is certainly able to be included into the cavity of POS. However, in its vertical (twisted) state, the height of DMABN should be about 0.48 nm, which is larger than the height of the cavity, 0.38 nm. Therefore DMABN cannot twist around its phenyl-nitrogen bond when it is included in the POS, especially if van der Waals radii of DMABN are taken into account. This explains why the inclusion system of DMABN does not exhibit TICT luminescence. In other words, geometric confinement of the inner cavity may suppress the formation of TICT state of DMABN.

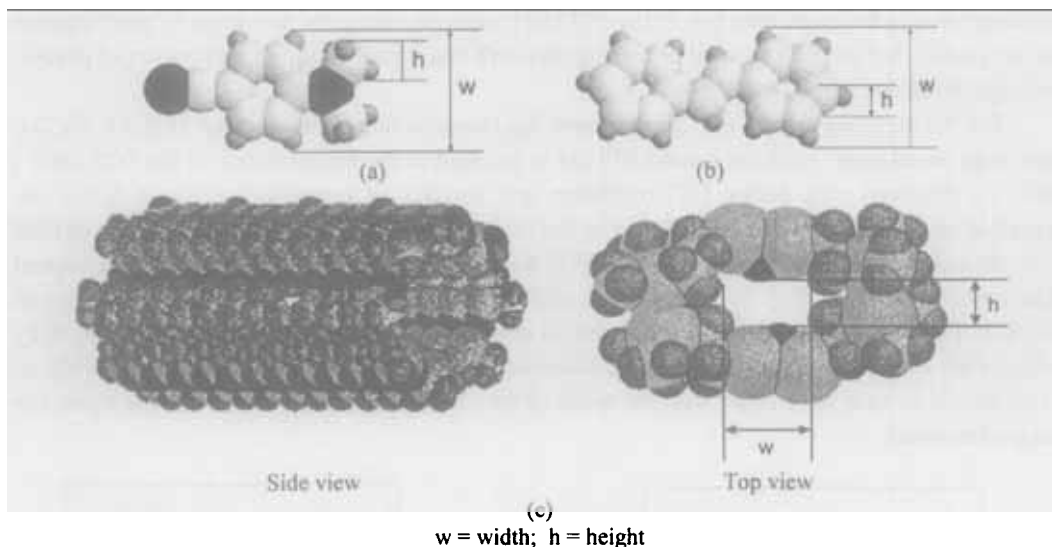


Fig. 4 Molecular model of a) DMABN, b) TSB and c) Nanotubular cavity existed in POS

Table 2 The size of DMABN, TSB molecules and the nanotubular cavity of POS resulted from molecular simulation

Object	Size (nm)	
	Width	Height
DMABN	0.50	0.25/0.48*
TSB	0.57	0.15
Nanotubular cavity of POS	0.62	0.38

* represents the planar/vertical state

TSB, though with its width seemingly smaller than that of the inner cavity, is however, difficult to include into the cavity on account of the van der Waals radii of TSB that could be larger than the width of the nanotubular cavity.

CONCLUSION

Fluorescent probe DMABN can be included into the nanotubular cavities of the POS, but at the expense of its TICT emission, while TSB cannot be included into the cavities of the POS completely. From these facts, it is possible to roughly estimate the inner size and shape of the nanotubular cavities. Molecular simulation supports the results from a theoretical point of view. In general, this work elucidates a relatively precise inner structure of the nanotubular cavities in the POS and in particular, provides a guidance for the selection of proper guest molecules in constructing POS-based functional supramolecular clathrate. Due to the small size of the cavity, the guest molecules to be selected are greatly restricted, and applications are limited. At present, work on the preparation of POS with larger nanotubular cavities is still in progress.

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