

A NOVEL SUPRAMOLECULAR CLATHRATE OF RODLIKE *p*-BUTOXYBENZYLIDENE-*p'*-DODECOXYANILINE TRAPPED WITHIN POLYORGANOSILOXANE PORE*

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Abstract A novel supramolecular polysiloxane clathrate, POS/C, has been prepared by in-situ encapsulating rodlike *p*-butoxybenzylidene-*p'*-dodecoxyaniline (BBDA), one kind of Schiff base liquid crystal molecule, within the pore of polyorganosiloxane (POS) which is prepared by hydrosilylation coupling reaction of polyvinylsilsesquioxane (Vi-T) with tetramethyldisiloxane (H-MM). Investigation by polarized light microscopy (PLM), differential scanning calorimetry (DSC), infrared spectroscopy (IR), atomic force microscopy (AFM) and molecular simulation gives a preliminary support to the existence of the title supramolecular clathrate.

Keywords Supramolecular clathrate; Polyorganosiloxane pore; Hydrosilation; Encapsulation; Characterization

INTRODUCTION

The applicable prospect of the host-guest system, especially macromolecule-based host-guest supramolecular system, has excited worldwide interest among polymer and material scientists. It is well known that inorganic or organic porous materials with hollow tubular structure can be used as host to include a variety of guest molecules with special properties, which could herald new generations of improved catalysts, biosensors, novel optical-electrical materials and a range of other applications. Many kinds of complexes of zeolites as hosts with guest molecules

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have been reported^[1~9]. Wu and Thoms reported the preparation of polyaniline filaments in the 3-nanometer hexagonal channel of aluminosilicate MCM-41^[10], which represents a new step toward the design of nanometer electronic devices. Carbon nanotubes, with hollow tubular structure, can also be used as hosts to construct supramolecular clathrate^[11~14]. A team of British researchers has encapsulated a variety of metals and metal compounds in carbon nanotubes using chemical technique^[15]. These filled nanotubes could have different industrial applications such as catalysts, micro-electronic and micro-magnetic devices etc.. Harada et al^[16] reported that a series of cyclodextrin (CD) could complex with polymers such as poly(ethylene glycol), poly(propylene glycol), and polyisobutylene as guests to form polyrotaxanes which are the precursors for constructing tubular polycyclodextrins. In addition, other types of organic microtubules such as tubular polyacetylene^[17], poly(3-methylthiophene)^[18], polypyrrole^[19,20] and polyaniline^[20,21] have attracted much attention due to their novel properties and application potentials in drug delivery systems^[22,23], microwave component after coating with metal, electronic and electro-optical devices^[24].

However, most of the macromolecules mentioned above as hosts are insoluble and hard to melt, that make them difficult to process and let alone to construct host-guest systems. Besides, the size, shape and chemical affinity of the 'hollow' or 'cage' of the hosts are difficult to be regulated, which restricts the range of guests to be confined and narrows their applications.

This paper deals with the synthesis and characterization of a novel supramolecular clathrate which encapsulate rodlike guest liquid crystalline molecule *p*-butoxybenzylidene-*p'*-dodecoxyaniline (BBDA) within the host molecule polyorganosiloxane (POS) possessing nanotube structure, which is prepared by hydrosilylation coupling reaction of ladderlike polyvinylsilsesquioxane (Vi-T) with tetramethyldisiloxane (H-MM) as coupling agent in the presence of Pt-complex as catalyst.

EXPERIMENTAL

Materials and techniques

BBDA ($C_4H_9OC_6H_4-CH=N-C_6H_4OC_{12}H_{25}$), Vi-T and catalyst Cp_2PtCl_2 were prepared according to the following literatures^[25~27] respectively. H-MM (> 98% GC pure) was purchased from Fluka Chemika Co. All the solvents are commercially available and of analytical grade.

The IR spectra were recorded on Specord 75-IR (Carl Zeiss, Jena) and FT-IR

spectrophotometer, PE-80. The DSC measurement was conducted on Perkin-Elmer DSC-7 differential scanning calorimeter. The birefringent behavior was examined on XPIA-XINTIAN polarized light microscope with a hot stage. The molecular simulations were carried on Pentium-133 MHz PC, using Alchemy III V 3.0 for Win 95 (Tripos Associate, Inc.), Molgen 4.0 Real (Single) for DOS. Atomic force microscope (AFM) was detected with Nanoscope III.

Preparation of supramolecular clathrate POS/C by in-situ encapsulation

A 250 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was evacuated and purged with dry argon for three times. Then the flask was charged with 350 mg (~ 2.215 mmol of units) of Vi-T, 25 mg (0.057 mmol) of BBDA, 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 (2.254 mmol) of H-MM was added. The resulting mixture was stirred and subsequently warmed up to 50°C for 20 h. Most volatile compounds were removed at reduced pressure below 40°C to leave 10 mL residue, which was dried by natural evaporation in air and then further dried in vacuum at room temperature for 12 h. Finally, a slight yellow solid was obtained in 95% yield.

Preparation of blend of BBDA and POS

For comparison, the blend of BBDA and POS was prepared. 200 mg (~ 0.345 mmol of units) of pure POS and 18 mg (0.041 mmol) of BBDA were dissolved in 50 mL THF. The solution was stirred for two days at room temperature. Then most of the solvent was removed at reduced pressure below 40°C to leave 5 mL solution which was dried in air and then dried in vacuum at room temperature for 12 h. Similarly, a slight yellow solid was obtained.

RESULTS AND DISCUSSION

It is known that an essential prerequisite for forming a nanotube structure is a *cis*-isotactic configuration of the precursor Vi-T (shown in Fig.1), which was proposed based on the synthetic mechanism^[26].

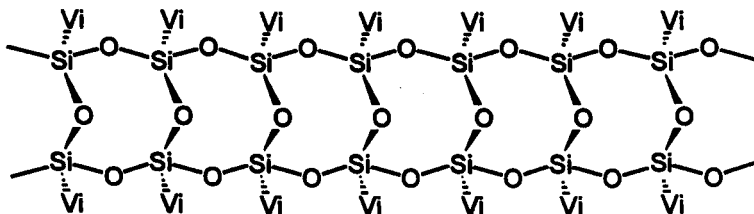


Fig. 1. Configuration of the *cis*-isotactic Vi-T

This kind of configuration is favorable to form POS possessing mainly nanotube structure rather than random network structure after coupling with H-MM. The characterization results are described below.

Solubility test

In comparison with the low solubility of Vi-T in polar solvent THF or chloroform, the high solubility of POS and its clathrate POS/C in these polar solvents demonstrates that the precursor Vi-T with outward vinyl-terminated side chains should be well dissolved in nonpolar solvent such as benzene, meanwhile the POS and its clathrate POS/C without vinylterminated side chain, which was exhausted after hydrosilylation, should be insoluble in nonpolar solvent. The difference in solubility is a preliminary evidence to prove the above prediction on the formation of the POS and its clathrate POS/C. The further characterization results of the title products are shown below.

Polarized light microscopy observation

As shown in Fig. 2, it is evident that the blend of BBDA and POS has obvious birefringence while the clathrate POS/C does not. The birefringence results from the aggregated crystal of BBDA molecules, which means that the blend of BBDA and POS undergoes phase separation leading to the aggregation of BBDA molecules. On the contrary, the absence of birefringence in the clathrate suggests that BBDA molecules are probably trapped into POS pores at molecular level so that BBDA molecules are incapable of forming crystalline aggregates. The amount of BBDA

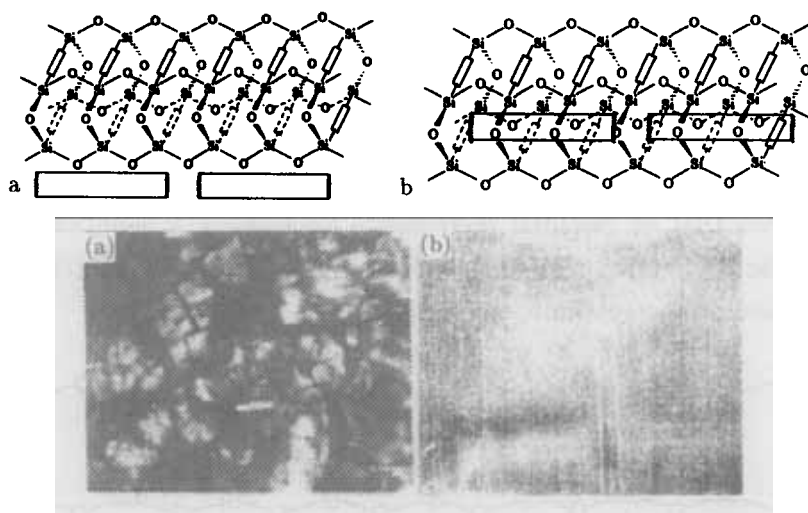


Fig. 2. Comparison of the polarized light microscopy of (a) the blend of BBDA and POS and (b) the clathrate POS/C

used should not exceed 9 wt% of Vi-T in the preparation of clathrate, otherwise there will emerge birefringence too, because the amounts of BBDA are more than what the POS hollows can hold.

DSC measurement

DSC measurement shows that the thermogram of the clathrate, POS/C, is almost a smooth curve without any indication of the melting point of BBDA, while the blend of BBDA and POS has a peak at 102°C which is near to the melting point 99°C of BBDA (Fig. 3). This means that BBDA molecules in the clathrate are homogeneously dispersed in POS on a molecular scale, while the blend of BBDA and POS is heterogeneous phase hence BBDA molecules are aggregated as crystal so as to display the melting point. Therefore, the DSC results are identical to that mentioned above by PLM and further prove that the clathrate is formed through encapsulation of BBDA into POS pores.

IR spectroscopic result

In comparison of the IR spectra of pure POS with that of the clathrate POS/C and the blend of BBDA and POS, both show the appearance of new peaks at 1510 cm^{-1} and 1610 cm^{-1} which can be assigned to the phenylene groups of BBDA. After extraction with methanol, for the clathrate POS/C the two new peaks still exist, while for the blend of BBDA and POS the two new peaks disappear (Fig. 4). This means that the BBDA molecules are difficult to be extracted out from the clathrate because BBDA molecules are included in POS pores, while in the blend of BBDA and POS the BBDA molecules are easy to be separated and extracted out.

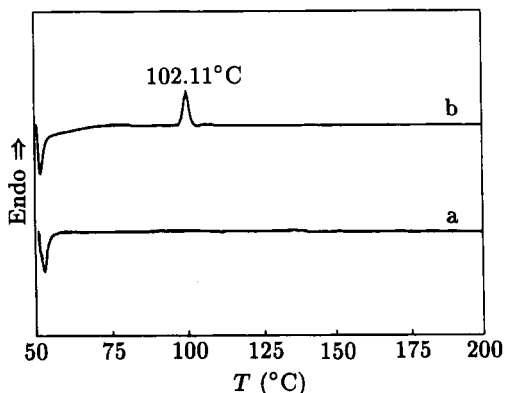


Fig. 3. DSC thermogram of (a) the clathrate POS/C and (b) the blend of BBDA and POS

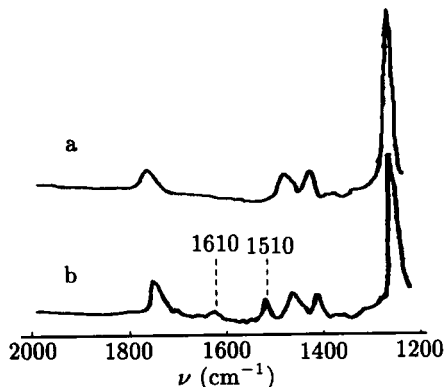


Fig. 4. The comparison of IR spectra of (a) the blend of BBDA and POS and (b) the clathrate POS/C after extraction with methanol

Atomic force microscopy (AFM) observation

As shown in Fig. 5, comparison of the AFM images of Vi-T, pure POS and the clathrate POS/C, it can be found that the bright stripes representing the polymer chain alignment become wider from Vi-T to pure POS and to the clathrate POS/C, which is consistence with the theoretical consideration and molecular simulation results.

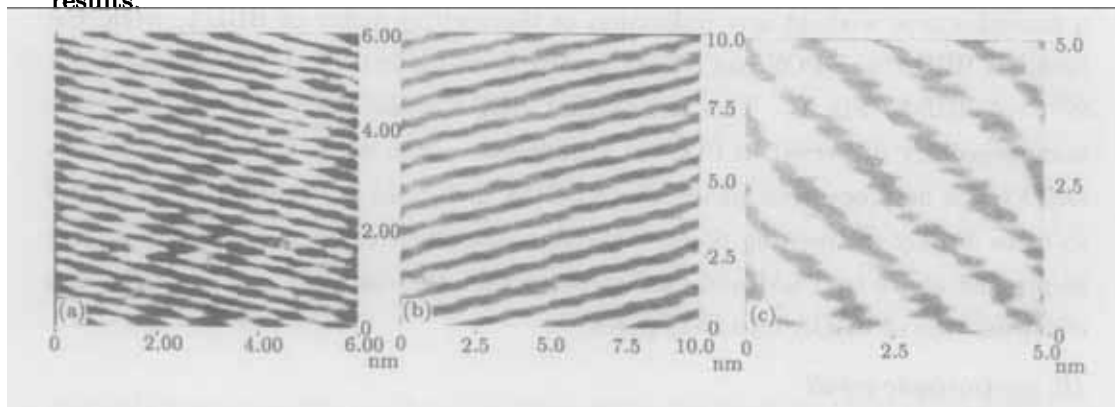


Fig. 5. The comparison of the AFM images of (a) Vi-T, (b) POS and (c) the clathrate POS/C

The AFM photographs show that the width of the bright stripes is 0.72 nm for pure POS, while the width of the bright stripe is about 1.0 nm for the clathrate POS/C. It is because that, there would occur shrinkage of the hollow structure in pure POS when solvents are evaporated out, nevertheless, if BBDA molecules are inside the hollow of the POS, the shrinkage will be greatly reduced, and furthermore the hollow might be enlarged by the insertion of BBDA. In conclusion, the encapsulation of BBDA can account for the ca. 0.3 nm wider of the bright stripes of the clathrate POS/C than that of pure POS.

Molecular simulation

Molecular simulation for the rodlike liquid crystal molecule BBDA shows that the most wide part of the molecule is about 0.5 nm, similar to the width of benzene, the length of the molecule is about 3.2 nm if the molecule is stretched fully (see Fig. 6).

Molecular simulation also demonstrates the inner size of the hollows of the POS is about 0.7 nm. So it is possible for the POS to accommodate the BBDA molecules in its hollows when the BBDA molecules enter the hollows through the cross-section, although it might leave a tail outside and produces some defects.

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 of many irregular units remaining in the product. On the other hand, the

mechanism for the formation of the tubelike polymer is not clear so far, to which a lot of efforts have been devoted. The preliminary presumption is that BBDA, a LC molecule, has an affinity to Vi-T and hence BBDA is likely to come close to Vi-T prior to hydrosilylation reaction which favours the encapsulation of BBDA when POS is formed. Another reason is that coordination catalysis mechanism of hydrosilylation proceeds as a zipper and plays an important role on the formation of nanotube structure. Additionally, the result of molecular weight measurement indicates that molecular weight of POS is about 5 times as large as that of Vi-T. It is somewhat higher than the theoretical value 3.8 times calculated on the base of an ideal (2+2) way of construction. The result means that the obtained POS nanotube is not wholly regular, there may exist some irregular defects such as branches and so on, which is probably due to the involvement of more than two Vi-T chain in the construction of one nanotube or arises from the defects of Vi-T itself. Further study is undertaken in an attempt to improve the regularity of POS and make clear the mechanism of preparation process.

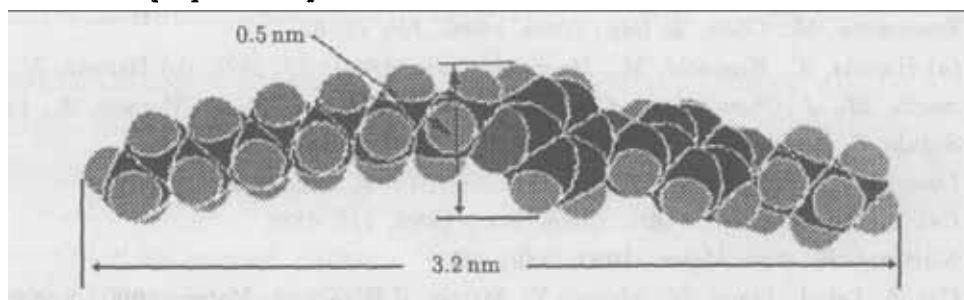


Fig. 6. Molecular model of BBDA

CONCLUSION

By in-situ encapsulation, guest molecule BBDA was trapped into pore of the host macromolecule POS forming a novel soluble supramolecular clathrate POS/C. Solubility test, PLM, DSC, IR, AFM and molecular simulation on the POS/C show the existence of the title clathrate in contrast to the blend of BBDA and POS.

REFERENCES

- [1] Kyotani, T., Nagai, T., Inoue, S., Tomita, A., *Chem. Mater.* **1997**, *9*, 609
- [2] Gilbert, M.T., Knox, J.H., Kaur, B., *Chromatographia*, **1982**, *16*, 138
- [3] Kamegawa, K., Yoshida, H., *Bull. Chem. Soc. Jpn.*, **1990**, *63*, 3683
- [4] Pekela, R.W., Hopper, R.W., *J. Mater. Sci.*, **1987**, *22*, 1840

- [5] Behrens, P., *Adv. Mater.*, **1993**, 5, 127
- [6] Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., Schlenker, J.L., *J. Am. Chem. Soc.*, **1992**, 114, 10834
- [7] Monnier, A., Schüth, F., Huo, Q., Kumar, D., Margolese, D., Maxwell, R.S., Stucky, G.P., Krishnamurty, M., Petroff, P., Firouzi, A., Janiche, M., Chmelka, B.F., *Science*, **1993**, 261, 1299
- [8] Hamilton, B., Rimmer, J.S., Anderson, M., Leigh, D., *Adv. Mater.*, **1993**, 5, 583
- [9] Ramamurthy, V., Sanderson, D.R., Eaton, D.F., *J. Am. Chem. Soc.*, **1993**, 115, 10438
- [10] (a) Wu Chun-Guey, Thoms, B., *Science*, **1994**, 246, 17, (b) Wu Chun-Guey, Thoms, B., *Chem. Mater.*, **1994**, 6, 1109
- [11] Iijima, S., Ichihashi, T., *Nature*, **1993**, 363, 603
- [12] Bethune, D.S., Kiang, C.H., de Vries, M.S., Gorman, G., Savoy, R., Vazquez, J., Beyers, R., *Nature*, **1993**, 363, 605
- [13] Ebbesen, T.W., Hiura, H., Bisher, M.E., Treacy, M.M.J., Shreave-Keyer, J.L., Haushalter, R.C., *Adv. Mater.*, **1996**, 8, 155
- [14] Han, Q., Fan, S.S., Li, Q.Q., Hu, Y.D., *Science*, **1997**, 277, 1287
- [15] Freemantle, M., *Chem. & Eng., News*, **1996**, July 15, 62
- [16] (a) Harada, A., Kamachi, M., *Macromolecules*, **1990**, 23, 2821, (b) Harada, A., Kamachi, M., *J. Chem. Soc., Chem. Commun.*, **1990**, 1322, (c) Harada, A., Li, J., Suzuki, S., Kamachi, M., *Macromolecules*, **1993**, 26, 5267
- [17] Liang, W., Martin, C.R., *J. Am. Chem. Soc.*, **1991**, 112, 9666
- [18] Cai, Z., Martin, C.R., *J. Am. Chem. Soc.*, **1989**, 111, 4138
- [19] Martin, C.R., *Adv. Mater.*, **1991**, 3 (9), 457
- [20] Cai, Z., Lei, J., Liang, W., Menon, V., Martin, C.R., *Chem. Mater.*, **1990**, 3, 960
- [21] Martin, C.R., Parthasarathy, R., Menon, V., *Synth. Met.*, **1993**, 55, 1165
- [22] Rudolph, A.S., Calvert, J.M., Schoen, P.E., in "Biotechnological Applications of Lipid Microstructures", ed. by Caber, B.P., Schnur, J.M. Chapman D, Plenum, New York, **1988**, p.305
- [23] Pool, R., *Science*, **1990**, 247, 1410
- [24] Tabony, J., Tob, D., *Nature*, **1990**, 346, 448
- [25] Cheng, G., Zhang, R.B., *Chin. J. Polym. Sci.*, **1990**, 9, 339
- [26] Li, Z., Cao, X.Y., Xu, H., Xie, P., Cao, M., Zhang, R.B., *Reactive & Functional Polymers*, **1997**, in press
- [27] Aptel, M. A., *Anal. Chem.*, **1985**, 57, 651