

# Novel Supramolecules Based on Architecturally Variant $\alpha$ -Cyclodextrin Polyrotaxanes and Nanorod-Like $\alpha$ -Cyclodextrin Self-Assembly

J. W. Chung<sup>\*</sup>, B.-Y. Yu<sup>\*\*</sup> and S.-Y. Kwak<sup>\*\*\*</sup>

School of Materials Science and Engineering, Seoul National University, San 56-1,  
Sillim-dong, Gwanak-gu, Seoul 151-744, Korea

<sup>\*</sup>cwfrank5@snu.ac.kr, <sup>\*\*</sup>yby3735@snu.ac.kr, <sup>\*\*\*</sup>sykwak@snu.ac.kr

## ABSTRACT

SA-ICs (self-assembled ICs) were successfully prepared by the reorganization of the initially formed  $\alpha$ -CD inclusion complexes ( $\alpha$ -CD ICs) with PCLs having different architecture when exposed in THF. Furthermore, nanorod-like  $\alpha$ -CD self-assembly was successfully obtained by recrystallization  $\alpha$ -CD in THF without guest molecule. It was confirmed that all of the SA-ICs (excepting SA-IC with SPCL) had well defined supramolecular structure attributed to continuous packing of microfibril, but no supramolecular structure was observed in SA-IC with SPCL due to radial structure of SPCL. In particular, morphologies of SA-IC showed dependence of architecture of PCL. Interestingly, these supramolecular structures were obtained by only THF treatment. In addition,  $\alpha$ -CD showed self-assembled behavior in THF, and resulted in the nanorod-like  $\alpha$ -CD self-assembly in spite of the absence of guest molecules. Furthermore pore structure was formed by the random aggregation of nanorod-like  $\alpha$ -CD self-assembly.

**Keywords:** Cyclodextrin, inclusion complex, self-assembly, microfibril, nanorod-like  $\alpha$ -CD self-assembly.

## 1 INTRODUCTION

Cyclodextrins (CDs) have been the most intensively studied as host molecules, on account of their good water-solubility and ability to selectively include a wide range of guest molecules [1]. CDs are cyclic oligosaccharides with six ( $\alpha$ -), seven ( $\beta$ -), or eight ( $\gamma$ -) glucose units linked by 1,4- $\alpha$ -glucosidic bonds. CDs have a shallow truncated cone shape and a hydrophobic cavity that is apolar relative to the outer surface. The average diameters of the cavities are 4.5 Å for  $\alpha$ -CD, 7.0 Å for  $\beta$ -CD, and 8.5 Å for  $\gamma$ -CD. It is known that the CD cavity can act as a host for a great variety of small or long guest molecules, resulting in IC formation [2]. For polymeric guests with a long chain-like nature, it was found that the CD molecules were threaded along the polymer chain, where the resulting ICs typically formed channel-type crystalline structures [3]. Due to their novel architectures and applications in various fields, CD ICs with polymers have been extensively studied. However, most investigations have focused on the threading of linear

polymeric guests into the cavities of CDs [4]. Few study on the self-assembly based on CD ICs found in the literature. Moreover, there is no report to discuss the effect of difference in the architecture of the polymeric guests on self-assembly of ICs. In particular, no self-assembled behavior of  $\alpha$ -CD in specific solvent and its morphology have ever been reported.

Herein we report on the self-assembly of ICs composed of  $\alpha$ -CD and various PCLs with radial, conical, blocked, or linear molecular architecture and the self-assembly of  $\alpha$ -CD with nanorod-like shape in specific solvent. The formation and structure of these supramolecular self-assembly were investigated, and it can be seen that the molecular architecture of the guest molecule and the choice of solvent play an important role in formation of these supramolecular structure.

## 2 EXPERIMENTAL

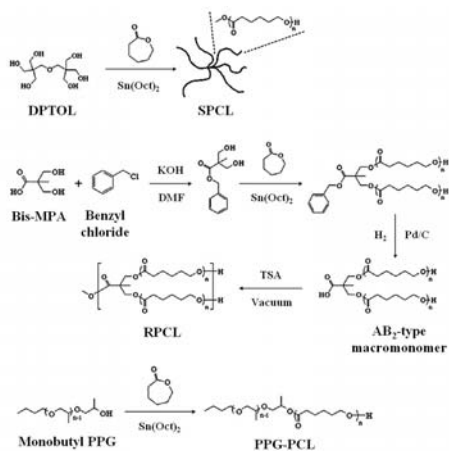
### 2.1 Materials

Dipentaerythritol (DPTOL), 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), potassium hydroxide (KOH), benzyl bromide,  $\epsilon$ -caprolactone (CL), poly(propylene glycol) monobutyl ether (monobutyl PPG,  $M_n = ca. 1,200$ ), tin (II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>), palladium on activated carbon (Pd/C, 5 wt% palladium), and *p*-toluenesulfonic acid (*p*-TSA) were all purchased from Aldrich Chemical Co. and used as received.  $\alpha$ -CD was supplied by Walker-GmbH. *N,N*-Dimethylformamide, diethyl ether, toluene, methanol, tetrahydrofuran, Acetone, Methylene chloride, and ethyl acetate were all purchased from Daejung Chemicals & Metals and used without any additional purification. The supplier, Aldrich Chemical Co., informed us that the number-average molecular weight of the polycaprolactone diol (LPCL), as a linear counterpart of the star-shaped poly( $\epsilon$ -caprolactone) (SPCL), random branched poly( $\epsilon$ -caprolactone) (RPCL), and diblock poly( $\epsilon$ -caprolactone) (PPG-PCL) prepared in this study, was 2,000.

### 2.2 Preparation of Samples

Various PCLs used as templates of SA-ICs were simple ring opening polymerization as shown in scheme 1. The SA-ICs were prepared as follows.  $\alpha$ -CD (10 mmol) was

dissolved in distilled water (75 ml) at 60 °C. Each PCL was dissolved in 20 ml of acetone, respectively. Then, PCL solutions were added dropwise to the  $\alpha$ -CD solution at 60 °C with vigorous stirring for 24 h. The resulting mixtures were cooled to room temperature and further stirred for 24 h. The precipitated products (ICs) were collected by filtration, and washed with distilled water and acetone to remove free  $\alpha$ -CD and PCLs. The ICs were dried overnight *in vacuo*, and then vigorously stirred in THF for a few hours to trigger the SA-ICs. The dispersed products (SA-ICs) in THF were collected by filtration and dried overnight *in vacuo*. The SA-IC of with SPCL, RPCL, PPG-PCL, and LPCL are referred to herein as SPCL/ $\alpha$ -CD, RPCL/ $\alpha$ -CD, PPG-PCL/ $\alpha$ -CD, and LPCL/ $\alpha$ -CD, respectively.



Scheme 1: Polymerization of PCLs.

## 2.3 Characterization

$^1\text{H}$  NMR spectra were recorded at 500 MHz in either  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  on a Bruker Avance 500 spectrometer. WAXD patterns were obtained on a MAC/Science MXP 18XHF-22SRA diffractometer with a  $\text{Cu K}\alpha$  radiation source. (50 kV and 100 mA) Powder samples were mounted on a sample holder and scanned at a rate of  $2\theta = 5^\circ \text{ min}^{-1}$ . The morphologies of the  $\alpha$ -CD, PCLs, ICs, and SA-ICs were visualized by FE-SEM (JEOL JSM-6330F). SAXS patterns of the SA-ICs were obtained on a Bruker AXS Nanostar with a  $\text{Cu K}\alpha$  radiation source. (40 kV and 35 mA) Nitrogen adsorption-desorption isotherms were at 77 K collected on a Micrometrics ASAP 2000 apparatus. The specific surface areas were estimated by BET method and the pore size distributions were determined by the BJH method using the nitrogen desorption branches of isotherms.

## 3 RESULTS AND DISCUSSION

### 3.1 Synthetic Results of PCLs

PCLs with different molecular architectures (SPCL, RPCL, and PPG-PCL) were successfully prepared by the

ring-opening polymerization of CL triggered by the hydroxyl groups of DPTOL, bis-MPA, and monobutyl PPG, respectively. As shown in Scheme 1, SPCL has a radial geometry and RPCL has a fanwise conical shape. PPG-PCL is a block copolymer consisting of PPG and PCL chains with a linear shape. The detailed synthetic results are summarized in Table 1.

Table 1: detailed synthetic results of PCLs.

Sample	$M_{n,\text{GPC}}$ (g/mol)	Polydispersity <sup>a</sup>	Number of CL / branches	Number of terminal hydroxyls
SPCL	13,000	1.2	14	6
RPCL	14,000	1.5	17	4
PPG-PCL	4,000	1.3	15	1
LPCL	2,000	-	17	2

<sup>a</sup> Polydispersity index determined by GPC.

### 3.2 Inclusion Structure of SA-ICs

FT-IR spectra showed that the  $\text{C}=\text{O}$  stretching band of PCL ( $1725 \text{ cm}^{-1}$ ) was shifted to a higher frequency ( $1736 \text{ cm}^{-1}$ ) in the spectra of the SA-ICs. DSC exhibited that the peak corresponding to the melting of the PCL block disappeared for SA-ICs, and SA-ICs were found to have higher decomposition temperatures relative to free  $\alpha$ -CD through TGA. These results indicate that  $\alpha$ -CD was stably complexed with the PCL single chain as well as that there are no free PCLs in the SA-ICs. Stoichiometry (CL/CD) of the SA-ICs was evaluated from  $^1\text{H}$  NMR spectra. 1.1, 2.2, 1.5, and 0.8 of stoichiometry was observed for LPCL/ $\alpha$ -CD, SPCL/ $\alpha$ -CD, RPCL/ $\alpha$ -CD, and PPG-PCL/ $\alpha$ -CD, respectively. Thus, it is considered that SPCL/ $\alpha$ -CD, RPCL/ $\alpha$ -CD, and PPG-PCL/ $\alpha$ -CD have the separated block structure, consisting of complexed and uncomplexed component such as polymer-*block*-polypseudorotaxanes, due to the block-selected inclusion complexation of  $\alpha$ -CD depending on the architecture of PCLs (Figure 1).

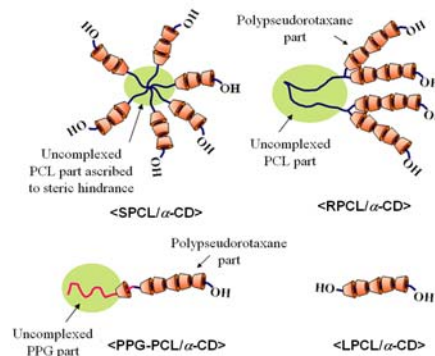


Figure 1: Inclusion structure of SA-ICs.

From WAXD, prominent peaks at *ca.*  $7.6^\circ$  (100),  $12.8^\circ$  (110), and  $19.6^\circ$  (210) were observed in all of the SA-ICs, while the major crystalline peaks for the PCLs were notably

absent. These results indicate that all of the SA-ICs have the hexagonal and channel-type crystalline structures;  $\alpha$ -CDs penetrated to a PCL chain (so-called “single IC strand”) were hexagonally aligned in the horizontal direction and  $\alpha$ -CDs were closely packed along PCL chain in the vertical direction, as schematically illustrated in Figure 2.

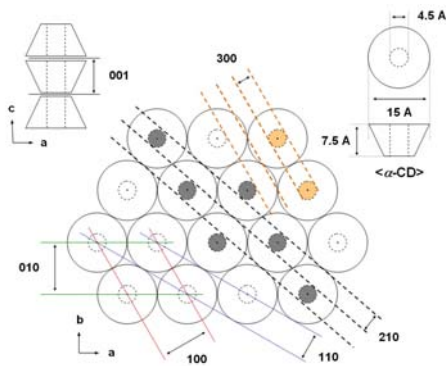


Figure 2: crystalline structure of SA-ICs.

### 3.3 Self-Assemble Supramolecular Structure of SA-ICs

Figure 3 is FE-SEM images of the  $\alpha$ -CD and RPCL. These images exhibited that  $\alpha$ -CD had a rugged morphology ascribed to the random aggregation of  $\alpha$ -CDs, whereas RPCL showed the smooth surface morphologies.

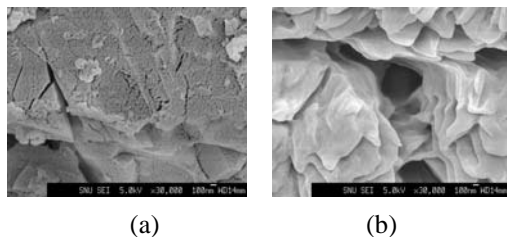


Figure 3: Morphologies of (a)  $\alpha$ -CD and (b) RPCL. (Other PCL also showed a similar morphology to RPCL)

Figure 4 is FE-SEM images of ICs with SPCL and RPCL before THF treatment. It was found that these ICs also had the hexagonally channel-shaped structure by WAXD (not shown in this paper).

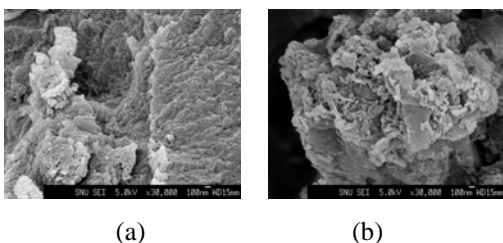


Figure 4: Morphology of ICs with (a) SPCL and (b) RPCL. (Other ICs also show a similar morphology to RPCL)

However, no specific morphologies expected from the hexagonally organized CD structure were observed in ICs and morphologies of ICs were very rough, though the hexagonally aligned CD formation as shown in Figure 2 was verified to be present in these ICs by WAXD. Considering above WAXD and FE-SEM results, it is regarded that long natured CD agglomerate (so-called “microfibril”) formed by hexagonally aligned packing of some IC strands were present in all of the ICs, and rough morphologies of ICs is thought to ascribe to random aggregation of microfibril in ICs. However, the morphologies of the SA-ICs formed from THF treatment were quite different from those of  $\alpha$ -CD, PCLs, and ICs. (Figure 5) In Figure 5, all of the SA-ICs exhibited the formation of hexagonally well defined supramolecular structure on a micrometer scale, with the exception of SPCL/ $\alpha$ -CD.

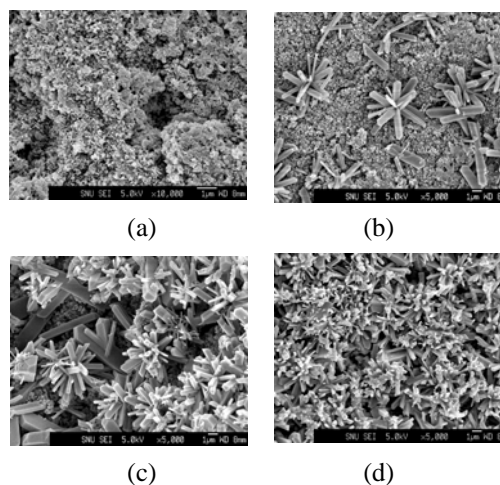


Figure 5: Morphology of ICs with (a) SPCL and (b) RPCL.

This supramolecular structure may be due to reorganization of the microfibrils in ICs by THF; it is thought that microfibrils composed of the hexagonally organized IC strands were continuously aligned in SA-ICs. SPCL/ $\alpha$ -CD exhibited a very rough morphology similar to the morphologies of ICs before self-assembly. This implies that the regularly hexagonal packing of microfibrils for the formation of the supramolecular structure was not accomplished on account of radial architecture and geometrical constraints of SPCL to hinder the formation of the regularly arranged structure. Meanwhile, LPCL/ $\alpha$ -CD was found to have the roughest surface morphology in the SA-ICs, excepting SPCL/ $\alpha$ -CD, whereas both RPCL/ $\alpha$ -CD and PPG-PCL/ $\alpha$ -CD had smooth surfaces. This result implies the occurrence of microphase separation between the complexed and uncomplexed components in RPCL/ $\alpha$ -CD and PPG-PCL/ $\alpha$ -CD by THF.

### 3.4 Reorganization of Solid-State Morphology in SA-IC

Reorganization of microfibrils can be verified by SAXS experiments. Figure 6 is SAXS profiles for the SA-ICs.

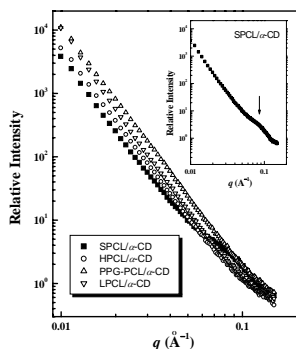


Figure 6: SAXS profiles of SA-ICs.

In Figure 6, it was found that SPCL/ $\alpha$ -CD had a broad peak at the range between  $q=0.06$  and  $0.12 \text{ \AA}^{-1}$ . This indicates that the structural scattering units corresponding to the size between 5.3 and 10.5 nm are present in a disordered state, which is regarded as random aggregation of microfibrils. However, no peak was observed in other SA-ICs with supramolecular structure. This implies continuous packing of microfibril in RPCL/ $\alpha$ -CD, PPG-PCL/ $\alpha$ -CD, and LPCL/ $\alpha$ -CD

### 3.5 Nanorod-like $\alpha$ -CD Self-Assembly

WAXD experiments were carried out to investigate the effect of THF on self-assembled behavior of  $\alpha$ -CD.

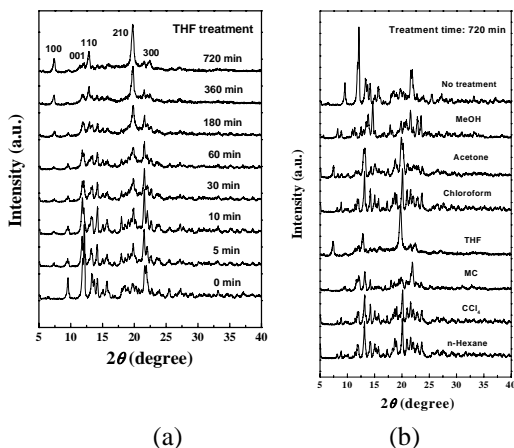


Figure 6 (a) and (b) are WAXD profiles of  $\alpha$ -CD treated by THF with varied times and by other solvents for 720 min, respectively.

As shown in Figure 6 (a), crystalline structure of  $\alpha$ -CD varied by the THF treatment. Moreover, distinct (100), (001), (110), (210), and (300) peaks were observed for  $\alpha$ -CD treated by THF for 720 min, which implies the formation of  $\alpha$ -CD self-assembly with the hexagonally aligned channel-type crystalline structure. In particular,

this structure was only observed by THF treatment, as shown in Figure 6 (b). These results reveal that THF can bring about the self-assembly of  $\alpha$ -CD attributed to the slow recrystallization. In addition, it was confirmed that  $\alpha$ -CD self-assembly had pore structure by  $N_2$  adsorption-desorption and FE-SEM analysis, as shown in Figure 7. This may ascribe to the random aggregation of nanorod-like  $\alpha$ -CD self-assembly.

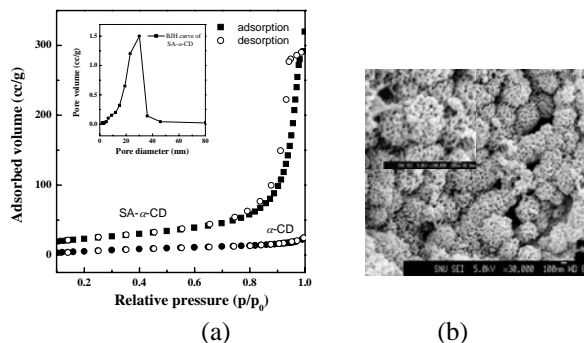


Figure 7: Porous materials attributed to random aggregation of nanorod-like CD assembly; (a)  $N_2$  adsorption-desorption results and (b) FE-SEM image.

## 4 CONCLUSIONS

SA-ICs with four types of PCLs having distinct molecular architectures - SPCL (radial), RPCL (conical), PPG-PCL (diblock), and LPCL (linear) - were successfully prepared by the reorganization of the initially formed  $\alpha$ -CD ICs when exposed in THF. SPCL/ $\alpha$ -CD, RPCL/ $\alpha$ -CD, and PPG-PCL/ $\alpha$ -CD had a polymer-*block*-polypseudorotaxanes type structure based on the architecture of PCL. In addition, all of the ICs were found to have a hexagonally channel-type crystalline structure. From results of FE-SEM and SAXS, it was found that RPCL/ $\alpha$ -CD, PPG-PCL/ $\alpha$ -CD, and LPCL/ $\alpha$ -CD had the well defined supramolecular structure attributed to the alignment of hexagonally shaped microfibrils, whereas no supramolecular structure was observed in SPCL/ $\alpha$ -CD because of the radial structure of SPCL. Particularly, the self-assembled structure of IC was only found to form in THF. In addition,  $\alpha$ -CD in THF showed self-assembled behavior, resulting in nanorod-like self-assembly and porous material.

## REFERENCES

- [1] G. Wenz, *Angew. Chem., Int. Ed. Engl.*, 33, 803, 1994.
- [2] W. Saenger, *Angew. Chem., Int. Ed. Engl.*, 19, 344, 1980.
- [3] J. Lu, I. D. Shin, S. Nojima, A. E. Tonelli, *Polymer*, 41, 5871, 2000.
- [4] A. Harada, S. Takahashi. *J. Chem. Soc., Chem. Commun.* 654, 1984.