

# Preparation and Characterization of Inclusion Complexes of Poly(dimethylsiloxane)s with $\gamma$ -Cyclodextrin Without Utilizing Sonic Energy

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**Abstract**  $\gamma$ -cyclodextrin ( $\gamma$ -CD) formed inclusion complexes with poly(dimethylsiloxane)s (PDMS) under sonic energy and the products were crystalline compounds. In this study an inclusion complex between PDMS and  $\gamma$ -CD was synthesized at room temperature in the presence of light and mixing, in the absence of light and in the absence of mixing. These inclusion complexes (ICs) were characterized by XRD, DSC,  $^1\text{H}$  NMR, UV–Vis and FT-IR spectroscopy. The findings suggest that the reaction conditions change the crystalline structure and mole ratios of the complexes (monomer unit/ $\gamma$ -CD) determined by  $^1\text{H}$  NMR spectroscopy for all of the ICs with  $\gamma$ -CD; which is 2 at room temperature, 1.5 under sonic energy, 3 without light and mixing. The UV–Vis results indicate an IC between  $\gamma$ -CD and PDMS.

**Keywords** Poly(dimethylsiloxane) (PDMS) ·  $\gamma$ -Cyclodextrin · Inclusion complex formation · Sonic energy

## 1 Introduction

Complexes of CDs with silicon-containing polymers are formed as new organic-inorganic hybrids with exact stoichiometric relationships. Cyclodextrins are cyclic oligosaccharides the most common consisting of 6, 7, and 8 glucopyranose units linked by *R*-1,4 glucosidic

bonds; they are called alpha-cyclodextrin ( $\alpha$ -CD),  $\beta$ -cyclodextrin ( $\beta$ -CD) and  $\gamma$ -cyclodextrin ( $\gamma$ -CD), respectively [1–3]. They present a truncated cone shape with a hydrophobic core, which can accommodate non-polar compounds [4, 5] and two hydrophilic rims composed of –OH groups. The inclusion complex (ICs) formation depends on internal parameters (the nature of the CD, polymer and solvent media) as well as on external parameters (temperature and pressure). Accordingly, new strategies are developed to fabricate novel supramolecular hydrogels via several routes. Recently, attention has been paid on ICs formed by CDs and inorganic polymers which offer different sites of binding and may be selectively threaded by CDs [4–8]. In 1990, Harada and Kamachi discovered an inclusion complexation of many  $\alpha$ -CDs and poly(ethylene glycol) (PEG) that resulted in the formation of polypseudorotaxanes [7]. This paper describes the preparation and characterization of inclusion complexes of CDs with PDMS under various conditions. The results indicated that light and mixing are necessary for the formation of an inclusion complex between cyclodextrins and PDMS and may change the structure of the polyrotaxane. However light and mixing may change the crystal structure. DSC analysis confirmed the existence of the complex with an endothermic melting peak of  $\gamma$ -cyclodextrin at about 110 and the one at 310°C disappearing.

## 2 Experimental

### 2.1 Material

Bis(hydroxyalkyl)-terminated PDMS (HO-PDMS-OH) with an average molecular weight of 5600 g mol<sup>-1</sup> (a value reported by the manufacturer) was obtained from

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Aldrich and used without further purification. According to its molecular weight and the data reported in the literature [9, 10] the structure of HO-PDMS-OH can be shown as HO-R-PDMS<sub>70</sub>-R-OH. Anhydrous tetrahydrofuran (THF) (Sigma-Aldrich, = 99.9%, inhibitor-free), dimethyl formamide (DMF) (Merck, = 99.9%), methanol (MeOH) (Merck, = 99.9%),  $\gamma$ -cyclodextrin ( $\gamma$ -CD) (Applichem, = 98%) were used without further purification.

## 2.2 Characterization

The solid-state<sup>1</sup>H NMR spectra were recorded with a Bruker DRX 500 spectrometer (500 MHz) in deuterated chloroform. The X-ray diffraction (XRD) measurements were performed on powder samples with an Xpert Philips diffractometer (USA) and nickel filtered Cu K $\alpha$  radiation was used in this work. Data were collected at a rate of  $^{\circ}2\theta$  min over the  $5^{\circ}\approx 60^{\circ}$  range of  $2\theta$  [11]. Fourier transform infrared (FTIR) spectra of the inclusion complexes (solids) were recorded on an EQUINOX 55 Bruker FTIR Spectrophotometer. The UV–Vis spectra were recorded on a Perkin Elmer lambda 17 UV–Vis spectrophotometer. The infrared spectrum was recorded within the range of 4000–400 cm<sup>-1</sup> by a German Nicolet FT-IR Nexus-670 IR spectrophotometer in KBr flake. The differential scanning calorimetry (DSC) curves of the samples were recorded on a differential scanning calorimeter in the temperature of  $-100$ – $250^{\circ}\text{C}$  at a scanning rate of  $10^{\circ}\text{Cmin}^{-1}$ . The measurements were performed on 5 mg of the sample in closed aluminum containers under a nitrogen atmosphere [11].

## 2.3 Complex Formation of $\gamma$ -CD / PDMS

### 2.3.1 Preparation of $\gamma$ -CD-PDMS inclusion complexes in the presence of stirring and light at the room temperature

PDMS (300 mg, 4.3 mmol) was added to a saturated aqueous solution of  $\gamma$ -CD (300 mg,  $2.4 \times 10^{-1}$  mmol) (Table 1) at room temperature. The mixture was stirred

at room temperature for a week and then allowed to stand overnight at room temperature. The complexes were isolated by centrifugation and filtration and washed with tetrahydrofuran to remove nonincluded PDMS, dried, and then washed with water to remove uncomplexed CD and dried again (Table 1: Reaction 1) [7, 12].

### 2.3.2 Preparation of CDs-PDMS inclusion complexes with sonic energy

PDMS (300 mg, 4.3 mmol) was added to a saturated aqueous solution of  $\gamma$ -CD (300 mg,  $2.4 \times 10^{-1}$  mmol) (Table 1) at room temperature. The mixture was stirred at room temperature and ultrasonically (with a KS-750 Sonicator from Kesheng(China)) agitated for 15 min then allowed to stand overnight at room temperature. The complexes were isolated by centrifugation and filtration and washed with tetrahydrofuran to remove nonincluded PDMS, dried, and then washed with water to remove uncomplexed CD and dried again (Table 1: Reaction 2) [7, 12].

### 2.3.3 Preparation of $\gamma$ -CDs-PDMS inclusion complexes in the presence of stirring without light

PDMS (300 mg, 4.3 mmol) was added into a test tube containing a saturated aqueous solution of  $\gamma$ -CD (300 mg,  $2.4 \times 10^{-1}$  mmol) which was coated with aluminum foil at room temperature. The mixture was stirred at room temperature for a week and then allowed to stand overnight at room temperature. The complexes were isolated by centrifugation and filtration and washed with tetrahydrofuran to remove nonincluded PDMS, dried, and then washed with water to remove uncomplexed CD and dried again. The results are summarized in Table 1 (Reaction 3) [7, 12].

### 2.3.4 Preparation of CDs-PDMS inclusion complexes without stirring and light

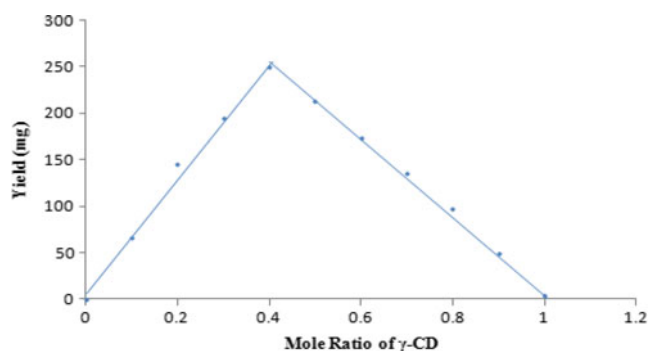
PDMS (300 mg, 4.3 mmol) was added to a saturated aqueous solution of  $\gamma$ -CD (300 mg,  $2.4 \times 10^{-1}$  mmol) which the tube coated with alumina foil at room tem-

**Table 1** Inclusion complex of  $\gamma$ -CD/ PDMS at various conditions ( $C_{\gamma\text{-CD}} = 2.4 \times 10^{-1}$  mmol,  $C_{\text{PDMS}} = 4.3 \times 10^{-4}$  mmol)

Reaction no.	Light ( $\lambda =$ )	Mixing (250 rpm)	Sonic energy
1	☀	☀	–
2	☀	–	–
3	–	☀	–
4	–	–	–

**Table 2** Conversion of  $\gamma$ -CD/ PDMS at various conditions

Condition	Conversion%
Room temperature (7 days)	71
Sonic energy (15 min)	56
Without light and mixing (7 days)	34
Without light (7 days)	49
At room temperature (7 days) PDMS-Br	67



**Fig. 1** Continuous variation plot for complex formation between  $\gamma$ -CD and PDMS under sonic energy

perature. The mixture was stand at room temperature for a week. The complexes were isolated by centrifugation and filtration and washed with tetrahydrofuran to remove nonincluded PDMS, dried, and then washed with water to remove the uncomplexed CD and dried again (Table 1:Reaction 4) [7, 12].

### 3 Results and Discussion

#### 3.1 Complex Formation of $\gamma$ -CD with PDMS

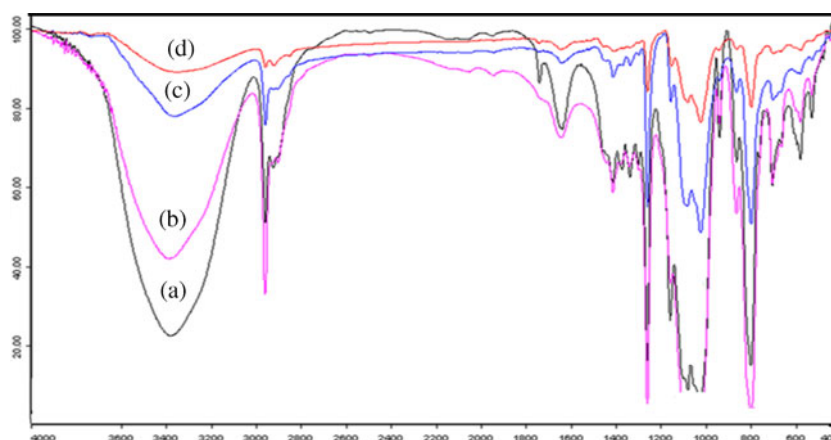
When PDMS (liquid) was added to aqueous solutions of  $\gamma$ -CD (diameter of the cavity: 7.0 Å) and the mixture was mixed at room temperature for 7 days, the heterogeneous solution became turbid and the complexes were formed as crystalline precipitates. This is the first observation in which  $\gamma$ -cyclodextrin forms a complex with inorganic polymers at room temperature without sonic energy. Table 2 shows the results of the complex formation between  $\gamma$ -CD and PDMS under various conditions. The  $\gamma$ -CD forms a complex as soon as PDMS is added and the reaction yield becomes

higher after 6 days at the room temperature without sonic energy. The cavity of the  $\gamma$ -CD is large enough to accommodate PDMS [7, 12–14]. At the presence of sonic energy for 15 min, the yield of the complex between  $\gamma$ -CD and PDMS is lower than at room temperature (Table 2) [12, 13]. Table 2 shows that sonication afforded a lower yield. It is well known that ultrasonication is frequently used for complexation of axle and ring molecules. Usually the sonication promotes a reaction to make a homogeneous system. In this manuscript, perhaps complexation was also promoted under sonication condition; however it was too fast to form large particle, actually turbid solution was observed. These tiny particles of the complex could not be caught by filtration and precipitation by centrifugation. When PDMS (liquid) was added to aqueous solutions of  $\gamma$ -CD under sonic energy, the heterogeneous solution became turbid and the complex formed as a crystalline precipitate [15, 16].

#### 3.2 Stoichiometries

The complex formation of  $\gamma$ -CD with PDMS was studied quantitatively. The amount of the complex formed increases with an increase in the amount of PDMS added to the aqueous solution of  $\gamma$ -CD. The amount of the complex showed similar values even if excess amounts of PDMS were used; this indicates the stoichiometric complexation. The continuous variation plot for the formation of the complex between  $\gamma$ -CD and PDMS is at maximum level at 0.40, i.e. 2:3 (monomer unit:  $\gamma$ -CD) stoichiometry (Fig. 1). This result suggests that 1.5 units were bound in each  $\gamma$ -CD cavity. The stoichiometry was confirmed by the use of  $^1\text{H}$  NMR spectroscopy. The length of the 1.5 monomer units corresponds to the depth of  $\gamma$ -CD cavity.

**Fig. 2** FTIR of  $\gamma$ -CD/PDMS complexes at various conditions **a** PDMS- $\gamma$ -CD 7 days at room temperature **b** PDMS- $\gamma$ -CD under sonic energy at room temperature **c** PDMS-Br 7 days at room temperature **d** PDMS- $\gamma$ -CD without mixing and light at room temperature



**Table 3** Assignments of FTIR of PDMS/ $\gamma$ -CD

Wavenumber( $\text{cm}^{-1}$ )	Assignment
2960	$\nu(\text{C-H})$ in $\text{CH}_3$
1259.90	$\delta(\text{C-H})$ in $\text{Si-CH}_3$
791	$\nu_a(\text{Si-O-Si})$ in $\text{Si-O-Si}$
723	$\nu_s(\text{Si-O-Si})$ in $\text{Si-O-Si}$
601	$\rho(\text{C-H})$ in $\text{Si-CH}_3$
3369	$\Upsilon(\text{O-H})$ in $\gamma\text{-CD}$

$\nu$  = stretching mode,  $\nu_a$  = asymmetric stretching,  $\nu_s$  = symmetric stretching,  $\delta$  = in-plane bending or scissoring,  $\rho$  = in-plane bending or rocking

### 3.3 Properties

The complexes were isolated by centrifugation, then washed, and dried. The inclusion complexes were thermally stable. The complexes were insoluble in water, even in boiling conditions [12, 15]. The FTIR spectrum of PDMS- $\gamma$ -CD is provided in Fig. 2. The spectrum showed strong Si-O-Si stretching absorptions at 400–800  $\text{cm}^{-1}$ , which is characteristic of a siloxane backbone. The complete list of FTIR structure assignments is given in Table 3.

### 3.4 XRD Analysis

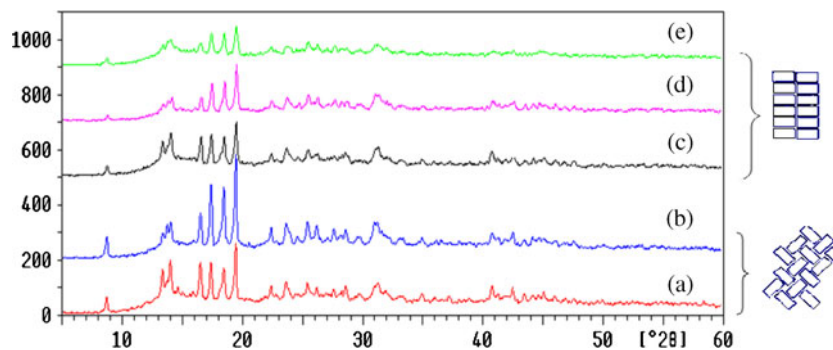
The X-ray diffraction pattern of the complex between  $\gamma$ -CD and PDMS shows that the complexes are crystalline. The complexes are soluble in dimethyl sulfoxide, dimethyl formamide, and pyridine. The X-ray diffraction studies (powder) show that all of the complexes are crystalline, although linear PDMS is a liquid. Harada reported that the crystal structures of CD complexes are classified mainly into three types: channel-type, cage-type, and layer-type [12, 15]. Figure 3 shows the powder X-ray diffraction patterns of  $\gamma$ -CD/PDMS

complexes under various conditions. The  $\gamma$ -CD/PDMS and  $\gamma$ -CD/PDMS-Br complexes were found to cage type structure at room temperature (Fig. 3a, b) but for  $\gamma$ -CD/PDMS complexes in other conditions adopt a head-to head channel-type structure in which  $\gamma$ -CD molecules are stacked along a PDMS axis to form a cylinder (Fig. 3c, d, e). The reflection peaks of  $\gamma$ -CD -PDMS complexes are similar to those of the  $\gamma$ -CD/PDMS complex and different from those of  $\gamma$ -CD [12].

Figure 4 shows the  $^1\text{H}$  NMR spectrum of the complex between  $\gamma$ -CD and PDMS. We calculated the mole ratio of PDMS to  $\gamma$ -CD in the complex. Comparing the integral of the CD(1H) peak and that of the methyl group on PDMS, 2 monomer units were found to bind to a  $\gamma$ -CD molecule. The mole ratios of the complexes (monomer unit/ $\gamma$ -CD) at room temperature are 2, which is similar to those obtained from the conversion of complex (Fig. 1). However the length of 2 monomer units corresponds to the depth of the  $\gamma$ -CD cavity. But the mole ratios of the complexes (monomer unit/ $\gamma$ -CD) are 1.5, 3 and 1 for (monomer unit/ $\gamma$ -CD) under sonic energy, without light and mixing and PDMS-Br at room temperature respectively [7, 12].

### 3.5 Differential Scanning Calorimetry (DSC)

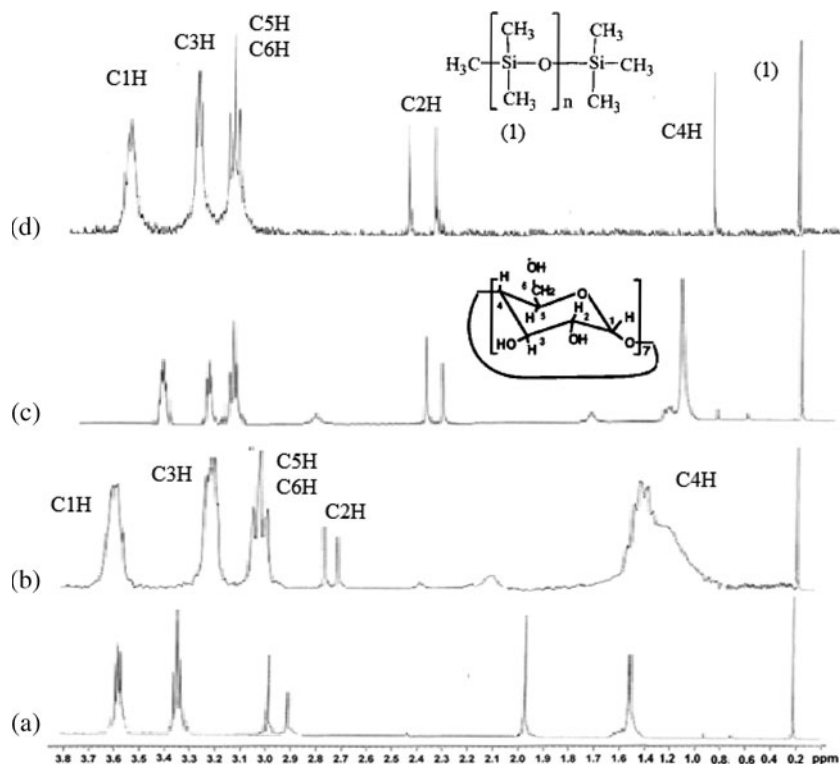
DSC was used to characterize thermal and structural properties of many compounds. DSC is a useful tool to determine the melting and crystallization temperatures, which can provide both quantitative and qualitative information about the physiochemical state of guest inside the CD complexes. DSC thermograms of cyclodextrin and inclusion complex of PDMS/ $\gamma$ -CD in the temperature range from  $-100^\circ\text{C}$  to  $+350^\circ\text{C}$  are shown in Fig. 5. The DSC plot of  $\gamma$ -CD, showed two endothermic peaks were observed in the temperature range between



**Fig. 3** Powder X-ray diffraction patterns (solid state) of  $\gamma$ -CD/PDMS complexes at various conditions **a** PDMS- $\gamma$ -CD 7 days at room temperature **b** PDMS-Br 7 days at room temperature

**c** PDMS- $\gamma$ -CD under sonic energy at room temperature **d** PDMS- $\gamma$ -CD without mixing at room temperature **e** PDMS- $\gamma$ -CD without mixing and light at room temperature

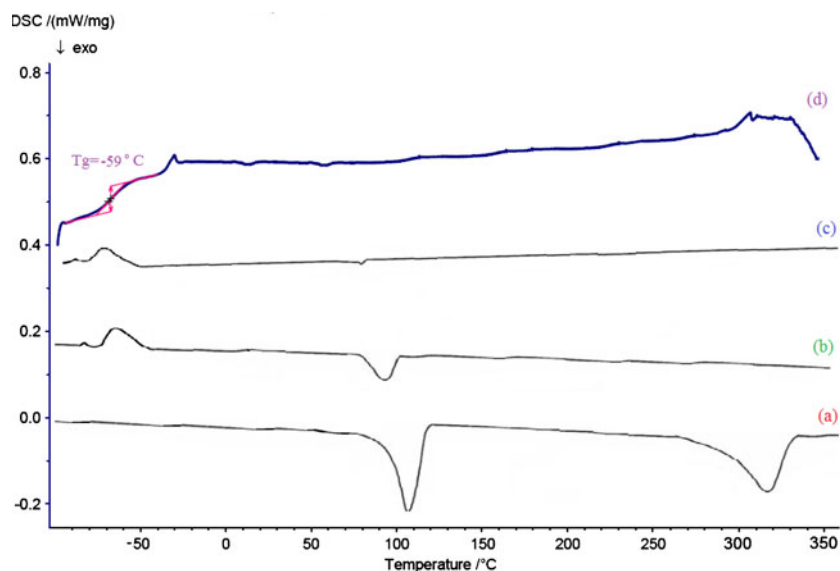
**Fig. 4**  $^1\text{H}$  NMR spectrum of the complex between  $\gamma$ -CD /PDMS complexes at various conditions **a** PDMS- $\gamma$ -CD 7 days at room temperature **b** PDMS- $\gamma$ -CD under sonic energy at room temperature **c** PDMS- $\gamma$ -CD without mixing and light at room temperature **d** PDMS-Br 7 days at room temperature



100–110°C due to the loss of water and near 320°C, it is observed and endothermic peak that corresponds to the  $\gamma$ -CD fusion [17]. The glass transition temperature ( $T_g$ ) of PDMS cannot be observed in the Fig. 5, because its value has been reported to be about  $-120^\circ\text{C}$  [18–22]. The DSC thermograms for the PDMS/  $\gamma$ -CD systems

show persistence of the exothermic peak of PDMS in all products. These results show characteristic of the microphase separated morphology of the inclusion complex. On the basis of the DSC results, one can conclude that inclusion complex of PDMS/ $\gamma$ -CD has successfully been synthesized.

**Fig. 5** DSC scan of **a**  $\gamma$ -cyclodextrin and the complex between PDMS/ $\gamma$ -CD **b** 7 days at room temperature without mixing and light, **c** under sonic energy at room temperature, **d** 7 days at room temperature



#### 4 Conclusion

This is the first observation that cyclodextrins have formed a complex with inorganic polymers at room temperature without sonic energy. These kinds of complexes may provide a new way of creating new organic-inorganic hybrids and other functional supramolecular architectures, especially inclusion complexes of  $\gamma$ -CD and PDMS. The results showed that the reaction condition may affect the monomer unit/ $\gamma$ -CD calculated through  $^1\text{H NMR}$ . The DSC results indicated that the inclusion complex of PDMS/ $\gamma$ -CD has successfully been synthesized.

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