

Chapter 2

Polyrotaxane Based on Inclusion Complexes of OH-PDMS-OH and Br-PDMS-Br with γ -Cyclodextrin Without Utilizing Sonic Energy

Abstract γ -Cyclodextrin (γ -CD) was found to form inclusion complexes with poly(dimethylsiloxane)s (PDMS) under sonic energy and the products were crystalline compounds in high yields, which have been investigated extensively in the past. In this study, an inclusion complex between PDMS and γ -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, ^1H -NMR and FT-IR spectroscopy. The findings suggest that the reaction conditions change the crystalline structure and mole ratios of the complexes (monomer unit/ γ -CD) determined by ^1H -NMR spectroscopy for all of the ICs with γ -CD.

Keywords Poly(dimethylsiloxane) (PDMS) • γ -Cyclodextrin(γ -CD) • Inclusion complex formation • Sonic energy

2.1 Introduction

γ -cyclodextrin (γ -CD) formed inclusion complexes with bis(hydroxyalkyl)-terminated poly(dimethyl siloxane) (OH-PDMS-OH) and bis(2-bromoisobutyrate)-terminated poly(dimethyl siloxane) (Br-PDMS-Br) at room temperature for 7 days without utilizing sonic energy which gives crystalline compounds. 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 α -cyclodextrin (α -CD), β -cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD), respectively [1–3]. They present a truncated cone shape with a hydrophobic core, which can accommodate nonpolar compounds [4, 5] and two hydrophilic rims composed of -OH groups. The inclusion complex (IC) 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 were 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 α -CDs and poly(ethylene glycol) (PEG) that resulted in the formation of polypseudorotaxanes [6]. This chapter describes the preparation and characterization of inclusion complexes of CDs with OH-PDMS-OH and Br-PDMS-Br at room temperature for 7 days.

The results indicated the successfully formation of an inclusion complex between γ -CD/PDMS and γ -CD/Br-PDMS-Br. Differential scanning calorimetry (DSC) analysis confirmed the existence of the complex with an endothermic melting peak of γ -CD at about 110 °C and the one at 310 °C disappearing [6–8].

2.2 Inclusion Complex of γ -CD and OH-PDMS-OH and Br-PDMS-Br

^1H -NMR of the functionalized OH-PDMS-OH was used to verify the quantitative modification of the end groups to the terminal bromine atoms (Fig. 2.1). The volatiles were removed under vacuum from the final product. GPC analysis showed $M_n = 14,800$, with a MWD = 1.93, maximum yield determined gravimetrically is 82 %. ^1H -NMR (CDCl_3) indicated $\delta = 0.0\text{--}0.3$ ppm for protons of methyl groups of $-\text{Si}(\text{CH}_3)_2\text{O}$, $\delta = 2.0$ ppm for methylene group next to the bromide [6, 9–11] (Scheme 2.1).

When OH-PDMS-OH or Br-PDMS-Br (liquid) was added to aqueous solutions of γ -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 γ -CD forms a complex with inorganic polymers at room temperature without sonic energy. Table 2.1 shows the results of the complex formation between γ -CD and OH-PDMS-OH or Br-PDMS-Br at room temperature for 7 days. γ -CD forms a complex as soon as OH-PDMS-OH or Br-PDMS-Br is added and the reaction yield becomes higher after 6 days at the room temperature without sonic energy. The yield of γ -CD/OH-PDMS-OH and γ -CD/Br-PDMS-Br is 79 and 71 % respectively. The cavity of the γ -CD is large enough to accommodate PDMS [7, 12–14].

2.3 Stoichiometries

The complex formation of γ -CD with OH-PDMS-OH or Br-PDMS-Br was studied quantitatively. The amount of the complex formed increased with an increase in the amount of OH-PDMS-OH or Br-PDMS-Br added to the aqueous solution of γ -CD.

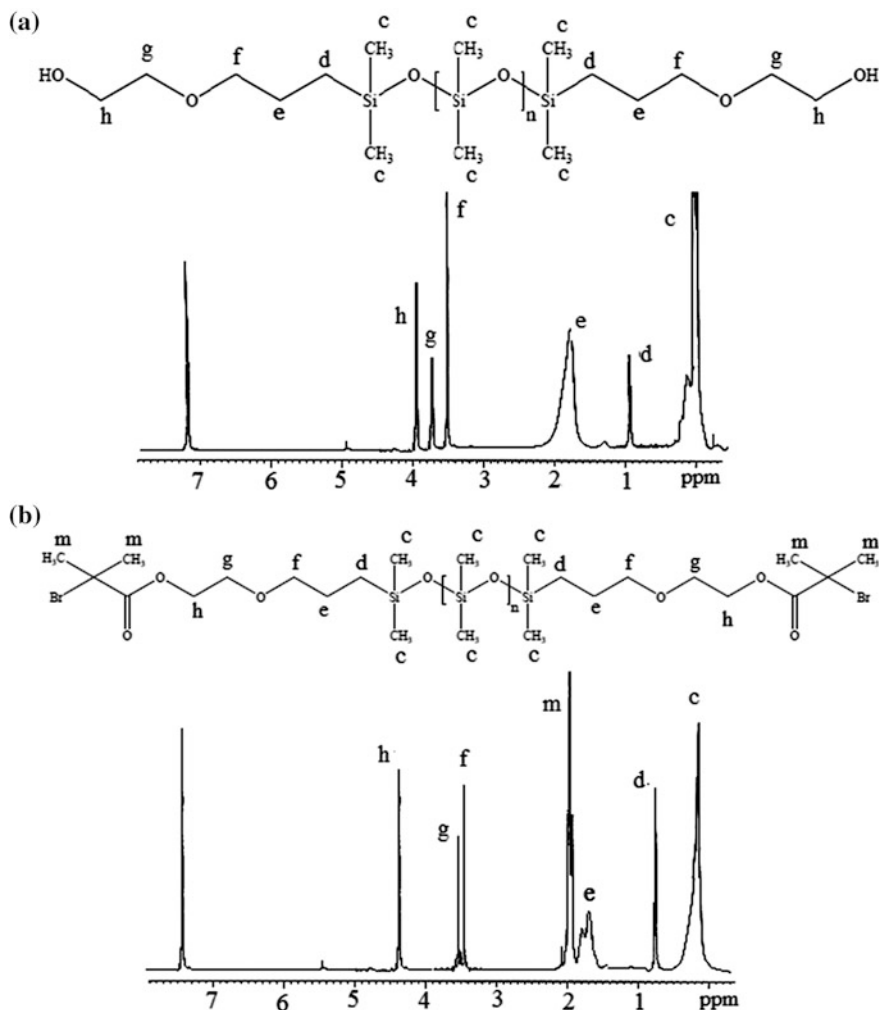
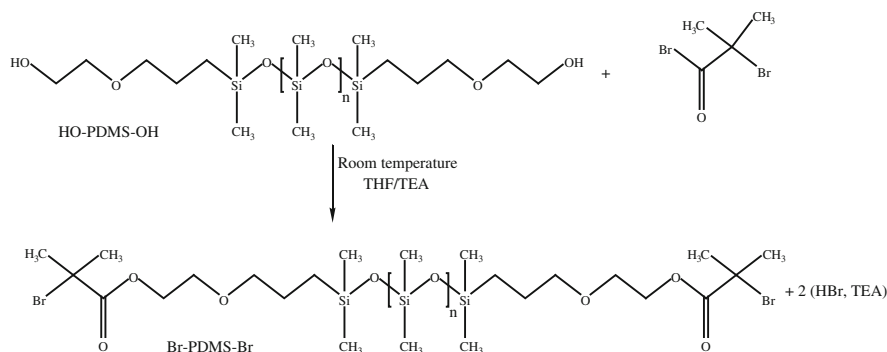


Fig. 2.1 ^1H -NMR spectra of **a** HO-PDMS-OH and **b** Br-PDMS-Br macroinitiator in the CDCl_3 solvent

The amount of the complex showed similar values even if excess amounts of OH-PDMS-OH or Br-PDMS-Br were used; this indicates the stoichiometric complexation. The continuous variation plot for the formation of the complex between γ -CD and OH-PDMS-OH or Br-PDMS-Br is at maximum level in 2:3 and 1:1 stoichiometry (monomer unit: γ -CD) respectively (Fig. 2.2). The stoichiometry was confirmed by the use of ^1H -NMR spectroscopy. The length of the 1.5 monomer units corresponds to the depth of the γ -CD cavity.



Scheme 2.1 Reaction scheme for the synthesis of bis(2-bromoisobutyrate)-terminated PDMS macroinitiator from bis(hydroxyalkyl)-terminated PDMS

Table 2.1 Assignments of FTIR of PDMS/ γ -CD

Wavenumber (cm^{-1})	Assignment
2960	$\nu(\text{C-H})$ in CH_3
1259.90	$\delta(\text{C-H})$ in Si-CH_3
791	$\nu_a(\text{Si-O-Si})$ in Si-O-Si
723	$\nu_s(\text{Si-O-Si})$ in Si-O-Si
601	$\rho(\text{C-H})$ in Si-CH_3
3369	$\nu(\text{O-H})$ in $\gamma\text{-CD}$

ν = stretching mode, ν_a = asymmetric stretching, ν_s = symmetric stretching, δ = in-plane bending or scissoring, ρ = in-plane bending or rocking

2.4 Characterization Inclusion Complex Formation

The complexes were isolated by centrifugation, then washed, and dried. The inclusion complexes were thermally stable. The complexes were insoluble in water, even under boiling conditions [12, 15]. The FTIR spectrum of the PDMS/ γ -CD is provided in Fig. 2.3. The spectrum showed strong Si-O-Si stretching absorptions at $400\text{--}800\text{ cm}^{-1}$, which is characteristic of a siloxane backbone. The complete list of FTIR structure assignments is given in Table 2.1.

The X-ray diffraction pattern of the complex between $\gamma\text{-CD/OH-PDMS-OH}$ and $\gamma\text{-CD/Br-PDMS-Br}$ complexes at room temperature for 7 days shows that the complexes are crystalline (Fig. 2.4). The X-ray diffraction studies (powder) show that all of the complexes are crystalline, although linear PDMS is a liquid at room temperature. Harada reported that the crystal structures of CD complexes are classified mainly into three types: channel-type, cage-type, and layer-type [6].

The complexes were found to have a cage-type structure at room temperature (Fig. 2.4a, b). The reflection peaks $\gamma\text{-CD/OH-PDMS-OH}$ and $\gamma\text{-CD/Br-PDMS-Br}$ complexes are different from those of the $\gamma\text{-CD}$ [12]. Figure 2.5 shows the $^1\text{H-NMR}$

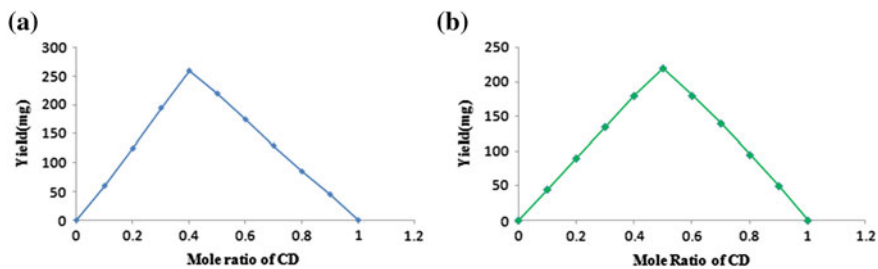


Fig. 2.2 Continuous variation plot for complex formation between γ -CD and **a** OH-PDMS-OH and **b** Br-PDMS-Br at room temperature for 7 days

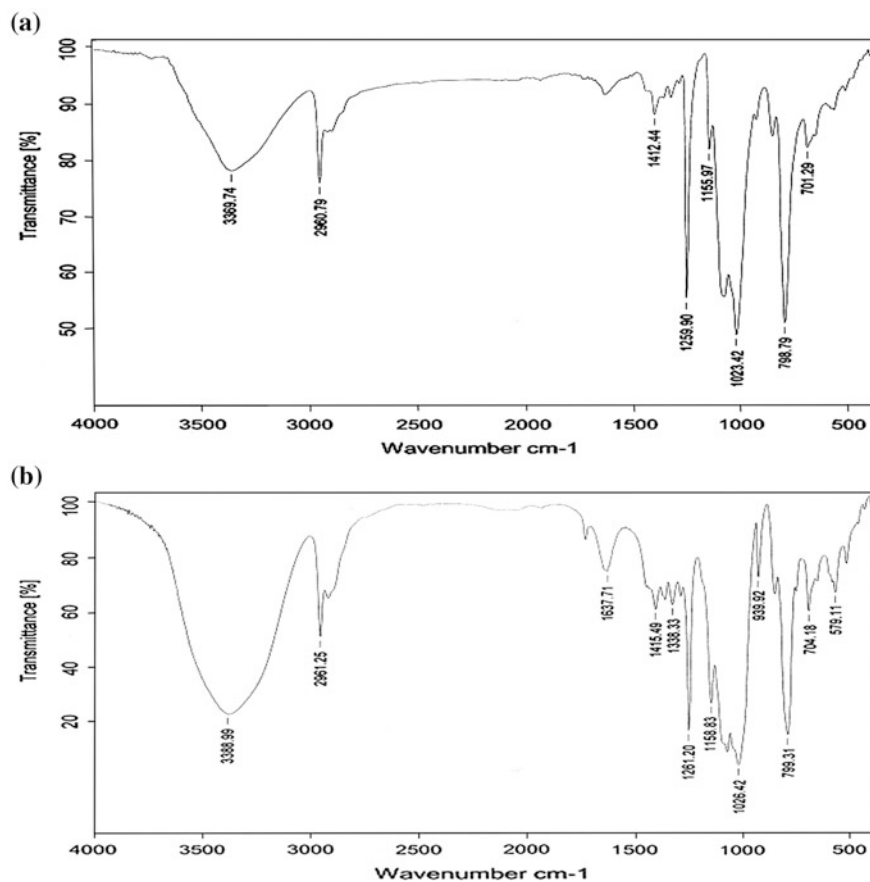


Fig. 2.3 FTIR of complex formation between γ -CD and **(a)** OH-PDMS-OH and **(b)** Br-PDMS-Br at room temperature for 7 days

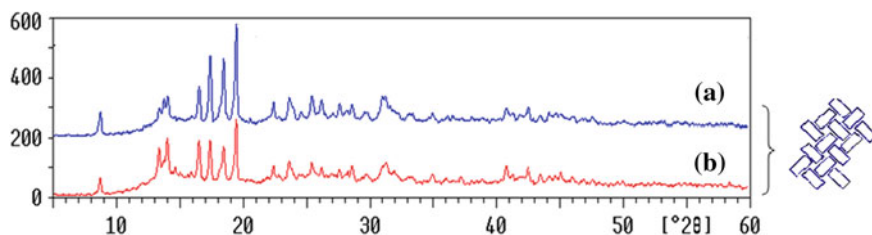


Fig. 2.4 XRD of the complex formation between γ -CD and **a** OH-PDMS-OH and **b** Br-PDMS-Br at room temperature for 7 days

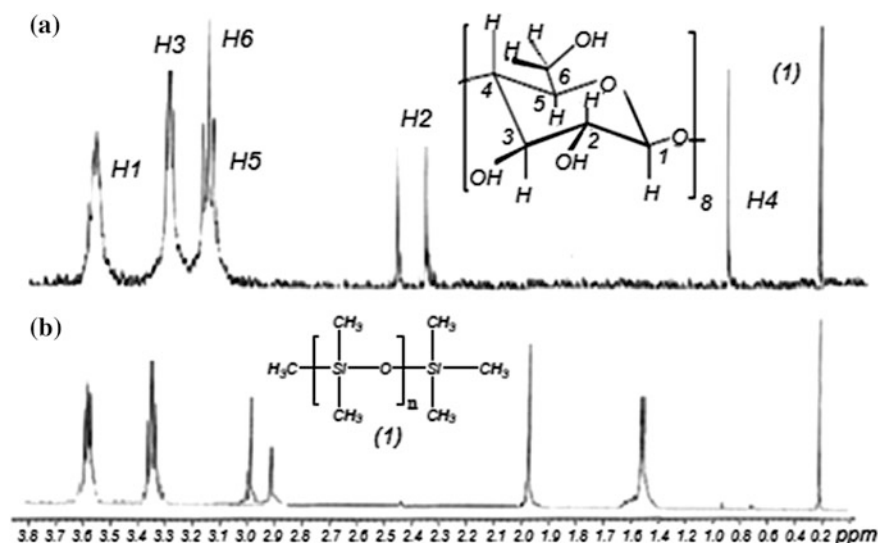


Fig. 2.5 ^1H -NMR spectrum of the complex between **a** OH-PDMS-OH/ γ -CD 7 and **b** Br-PDMS-Br/ γ -CD 7 day at room temperature

spectrum of the complex between γ -CD and PDMS. We calculated the mole ratio of OH-PDMS-OH or Br-PDMS-Br to γ -CD in the complexes. The moles ratios of the complexes are 2:3 and 1:1 (monomer unit: γ -CD) for OH-PDMS-OH/ γ -CD and Br-PDMS-Br/ γ -CD respectively, which is similar to those obtained from the conversion of complex (Fig. 2.1). The length of 2 monomer units corresponds to the depth of the γ -CD cavity.

DSC thermograms of γ -CD and the inclusion complex of OH-PDMS-OH/ γ -CD and Br-PDMS-Br/ γ -CD in the temperature range from -100 to $+350$ °C are shown in Fig. 2.6. DSC has been used to characterize the 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

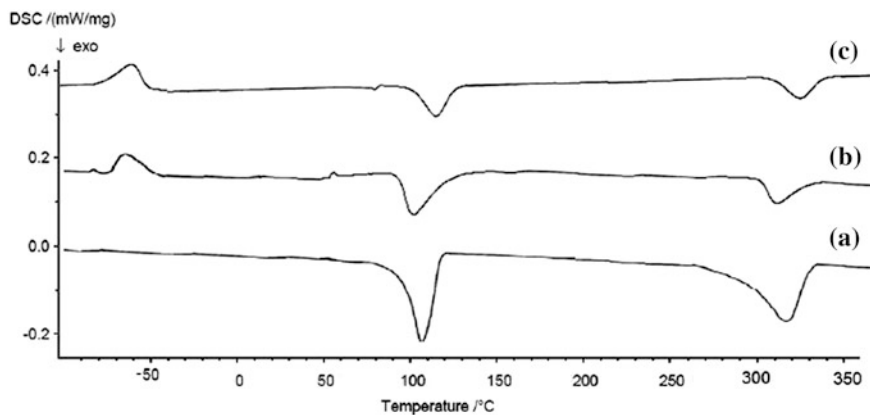


Fig. 2.6 DSC spectrum of **a** γ -CD, **b** the complex between OH-PDMS-OH/ γ -CD and **c** Br-PDMS-Br/ γ -CD 7 days at room temperature

the physiochemical state of the guest inside the CD complexes. The DSC plot of γ -CD, showed that two endothermic peaks were observed in the temperature range between 100 and 110 °C due to the loss of water and near 320 °C due to the γ -CD fusion [16, 17]. Glass transition temperature (T_g) of PDMS cannot be observed in Fig. 2.6, because its value has been reported to be about -120 °C [18–20]. The DSC thermograms for the OH-PDMS-OH/ γ -CD and Br-PDMS-Br/ γ -CD systems show shifting the persistence exothermic peak of PDMS (at -120 °C) in all products. These results are characteristic of the microphase separated morphology of the inclusion complex. On the basis of DSC results, one can conclude that the inclusion complex of OH-PDMS-OH/ γ -CD and Br-PDMS-Br/ γ -CD has successfully been synthesized.

2.5 Summary

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 γ -CD and OH-PDMS-OH or Br-PDMS-Br. The results showed that monomer structure may affect the monomer unit/ γ -CD calculated through $^1\text{H-NMR}$. The DSC results indicated that the inclusion complexes of OH-PDMS-OH/ γ -CD and Br-PDMS-Br/ γ -CD have successfully been synthesized.

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Silicon Containing Copolymers

Amiri, S.; Semsarzadeh, M.A.; Amiri, S.

2014, X, 53 p. 38 illus., 17 illus. in color., Softcover

ISBN: 978-3-319-09224-9