# The Solid Channel Structure Inclusion Complex Formed Between Guest Styrene and Host γ-Cyclodextrin

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## Abstract

The solid complex of guest styrene included inside the channels of host γ-cyclodextrin (styrene/γ-CD$_{channel}$-IC) was formed in order to perform polymerization of styrene in a confined environment (γ-CD channels). The experimental molar ratio of styrene to γ-CD in styrene/γ-CD$_{channel}$-IC was found to be 2:1, which is consistent with molecular modeling studies, utilizing Quantum Mechanics PM3 parameters that indicate the γ-CD/two styrene molecular complex is the most energetically favorable. Consistent with modeling of the γ-CD/two styrene molecular complex, no experimental indication of intermolecular π–π interactions between the pairs of included styrene molecules inside the γ-CD channels was observed. Once included in the host γ-CD cavities, the thermal stability of normally volatile bulk styrene to elevated temperatures (much above its boiling point) was observed until the γ-CD host molecules themselves began to degrade at ∼300 °C. In addition, the thermal degradation of host γ-CD from the styrene/γ-CD$_{channel}$-IC was observed to be different from that of pure γ-CD due to co-degradation of styrene and γ-CD.

## Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6, 7, and 8 units of 1,4-linked glucose units, and are named alpha (α), beta (β) and gamma (γ)-cyclodextrins, respectively (Figure 1). Although the depth of the cavities for the three CDs is the same (∼7.8 Å), their cavity diameters are ∼6, 8, and 10 Å, respectively [1]. Due to the unique chemical structure of CD molecules, the inner side of the cavity is hydrophobic and the outer side is hydrophilic. The hydrophobic nature of the CD cavities facilitates the ability of CDs to act as hosts for both nonpolar and polar guests, which include small molecules as well as polymers [1–4]. Once the inclusion compound is formed, the stability of the guest molecules increases due to the binding forces (van der Waals attractions, hydrogen bonding, hydrophobic attractions, etc.) between the host CD and guest molecules [5–6].

Solution or solid inclusion complexes of monomers i.e., styrene [7–8], methyl methacrylate [9], pyrrole [10], bithiophene [11], aniline [12–13], etc., with α-, β- and γ-CDs have been studied. In solution complexes, CDs show unique characteristic in which water-insoluble, hydrophobic monomers become water-soluble when they are complexed with host CD molecules, and this characteristic was used to synthesize polymers in aqueous media [8–10]. In the case of solid monomer-CD complexes, the monomer resides in the CD cavities and can be polymerized by solid-state polymerization [14] or by suspending the crystals of monomer-CD inclusion compound into a solution where the inclusion compound is not soluble [7]. In order to obtain polymer, the CDs have to adopt continuous channel-type packing (Figure 1d) in which the monomer molecules reside in the channels and further react with each other once the polymerization is initiated. Polymerization cannot be achieved in cage-type monomer-CD ICs (Figure 1c), since the monomers are entrapped in the CD cavities and are segregated from each other by neighboring host CD molecules.

Polymerization of vinyl monomers, like styrene, that are located as guests in the narrow channels of their cyclodextrin-inclusion compound (CD-IC) crystals can potentially lead to polymers with microstructures that are distinct from those attained during homogeneous polymerizations of the same monomers, since certain microstructures resulting from homogeneous polymer-

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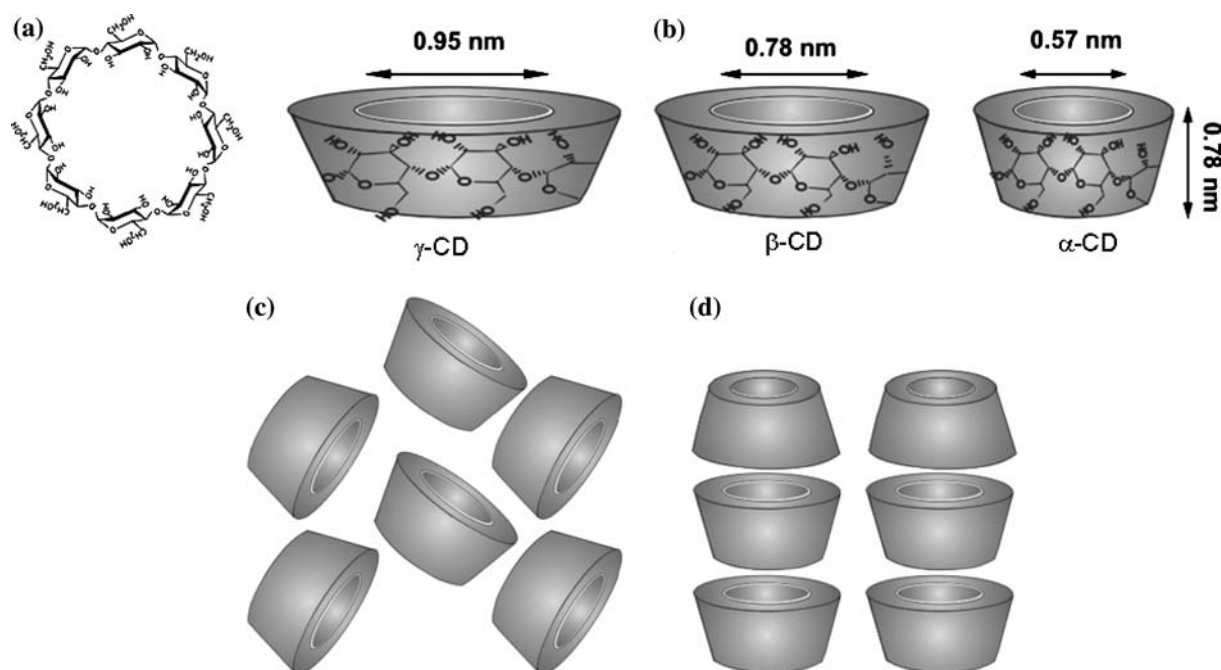
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*Figure 1.* (a) γ-CD chemical structure; (b) approximate dimensions of α-, β- and γ-CDs; schematic representation of packing structures of (c) cage-type and (d) head-to-head: tail-to-head: tail-to-tail channel-type γ-CD crystals.

izations may be prevented by the conformational restrictions placed on them by the narrow CD-IC channels. For example, when propylene monomer was formed into an IC with perhydrotriphenylene (PHTP) host and then free-radically polymerized *in situ*, the resulting PP was found to be predominantly syndiotactic [15], consistent with the conformational modeling of PP stereoisomers in channels (D ~5 Å) appropriate to PHTP-ICs [16].

Based on our conformational modeling of stereo-isomeric polystyrenes (PSs) in narrow channels, we suggested that polystyrene with unusual microstructures might be obtained *via* constrained polymerization of styrene in its γ-CD-IC crystals [17]. It is crucial to have full complexation of styrene inside the γ-CD$_{channel}$ crystals prior to polymerization, since the presence of any uncomplexed styrene would jeopardize the confined polymerization. For this purpose, the solid inclusion complex of styrene inside γ-CD channels (styrene/γ-CD$_{channel}$-IC) was formed. Modeling of the styrene/γ-CD-IC was also performed with the semi-empirical Quantum Mechanics PM3 method in order to get a better understanding of the stoichiometry and interactions between guest styrenes and the host γ-CD molecules. It is essential to perform extensive characterization and modeling of styrene/γ-CD$_{channel}$-IC, so, we can better interpret the results of the constrained solid-state polymerization. The focus of this paper is to summarize the results of the formation and characterization of the solid complex of guest styrene included in host γ-CD channels, while the polymerization of styrene inside these γ-CD channels will be the subject of a future paper (see reference [7] for a preliminary report).

## Experimental section

### Materials

γ-cyclodextrin was purchased from Cerestar (Hammond, IN). Styrene (99.9%, Aldrich) was vacuum distilled prior to use. All the other chemicals used in this study were reagent grade and used without further purification. The water used in this study was deionized (DI-H$_2$O).

### Formation of solid styrene/cyclodextrin inclusion compounds (styrene/CD$_{channel}$-IC)

The as-received γ-CD has a cage-type crystalline structure (Figure 1c). Two different approaches can be followed to form styrene/γ-CD inclusion compounds (styrene/γ-CD$_{channel}$-ICs), where the resulting CD-IC has a channel packing structure. The first approach is a "suspension method" in which the preformed γ-CD$_{channel}$ is suspended into styrene to form the inclusion compound [7]. The second approach is a "precipitation method", which is comparatively more convenient. In this method, styrene is added directly to an unsaturated CD aqueous solution and precipitation occurs as the styrene molecules form the IC with CD molecules, where the resulting styrene/CD-IC has a channel structure. Here, we used the precipitation method to form all styrene/CD inclusion compounds.

A quantity of as-received γ-CD$_{cage}$ (6.5 g, 0.005 mol) was dissolved in 100 ml of deionized water at room temperature (RT). Styrene (1.3 g, 0.0125 mol) was added drop-wise to the clear aqueous solution of γ-CD,

while the solution was stirred and kept at RT. The clear $\gamma$-CD solution became turbid and a white precipitate formed immediately after addition of styrene, which indicated formation of the styrene/$\gamma$-CD-IC. The resulting white suspension was stirred for an additional 24 h at RT, and the filtered precipitate was dried in the fume hood for 24 h.

X-Ray confirmed the channel packing structure for the styrene/$\gamma$-CD-IC. The presence and molar ratio of styrene to $\gamma$-CD ($\sim$2:1) was determined with solution [1]H-NMR upon dissolution of the styrene-$\gamma$-CD-IC in d-DMSO. For comparison, a physical mixture of styrene and $\gamma$-CD (2:1 mol ratio of styrene to $\gamma$-CD) was prepared by mixing as-received cage structure $\gamma$-CD crystals with liquid styrene monomer.

### Wide-angle X-ray diffraction (WAXD)

WAXD measurements were performed with a Siemens type-F X-ray diffractometer using a Ni-filtered CuK$_\alpha$ radiation source ($\lambda = 1.54$ Å). The diffraction intensities were measured every 0.1° from $2\theta = 5$ to 30° at a rate of $2\theta = 3°$/min. The supplied voltage and current were 30 kV and 20 mA, respectively.

### Differential scanning calorimetry (DSC)

Experiments were performed with a Perkin–Elmer DSC-7 under nitrogen purge gas. Indium was used as a standard for calibration. The samples were subjected to heating and cooling cycles consisting of: 1.0 min hold at $-50$ °C, ramp to 25 °C at 20 °C/min, hold at 25 °C for 1 min, and quench to $-50$ °C at a cooling rate of 200 °C/min.

### Nuclear magnetic resonance (NMR)

^{1}H-NMR spectra were recorded on a Mercury 300 spectrometer in DMSO-d6, using tetramethylsilane (TMS) as the internal standard. Solid-state NMR experiments were performed on a Bruker DSX-300 instrument operating at a field strength of 7.05 $T$, corresponding to a 300 MHz [1]H Larmor frequency, using 7 mm zirconium oxide rotors. [13]C cross-polarization/magic angle spinning/with high power dipolar ^{1}H decoupling (CP-MAS/DD) spectra and single-pulse MAS/DD spectra were recorded with 4 kHz MAS and 3.5 $\mu$s $\pi/2$ pulse widths. Radio-frequency field strengths for ^{1}H decoupling (DD) were 70–73 kHz. The cross-polarization contact time was 1 ms, and the delay between two consecutive scans was 3 s, while single-pulse spectra were acquired with cycle delay times of 1 s.

### UV-Vis spectrometry (UV-Vis)

Solution UV-Vis spectra of styrene were recorded in methanol on a Varian Cary 3 UV-Visible spectropho-tometer. Diffuse reflectance measurements for styrene-CD$_{channel}$-IC powder were carried out on a Cary 3 e UV-Visible spectrophotometer equipped with an integrating sphere. Spectra were measured following calibration with a pressed polytetrafluoroethylene powder standard. Reflectance spectra were collected and $K/S$ data obtained using the standard Kubelka-Munk equation [18], $K/S = (1-R)^2/2R$.

### Thermogravimetric analyses (TGA)

TGA of the samples were performed with a Perkin–Elmer Pyris 1 thermogravimetric analyzer. Thermal decompositions were recorded between 25 and 500 °C. The heating rate was of 20 °C/min and nitrogen was used as a purge gas.

### Direct insertion probe pyrolysis mass spectrometry (DIP-MS)

DIP-MS system consisted of a 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system. 0.01 mg samples were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of 20 °C/min and the scan rate was 2 scans/s.

### Computational modeling methods

The structures of styrene, $\gamma$-CD, and their ICs were optimized by performing an optimized geometry calculation in MOPAC using PM3 parameters [19]. The UV spectrum of styrene was predicted using ZINDO-CI/INOD1 (Zerner Intermediate Neglect of Differential Overlap-Configuration Interaction) [20] with CI = 26. In the cases of $\gamma$-CD and the styrene/$\gamma$-CD-ICs, the MO-ZYME algorithm [21] was used to speed up the calculations. The calculations were conducted at 298.15 K and 1 atm and executed on a Pentium 4-MCPU 2.66 GHz with 768 of RAM.

## Results and discussion

### WAXD

$\gamma$-CD can exist in two classes of crystal structures called "cage' and "channel" [22]. In the cage structure (Figure 1c), the $\gamma$-CD molecules have a "herring-bone" arrangement, where each $\gamma$-CD cavity is blocked by neighboring molecules. In the channel packing (Figure 1d), the $\gamma$-CD molecules are stacked on top of each other to form long cylindrical channels in which guest molecules can reside. For $\gamma$-CD, a cage-type complex has only been obtained with water as the guest [23], i.e., pure $\gamma$-CD, whereas for other guest molecules, both small molecules and macromolecules, the channel-type structure is formed [23–24]. It was reported that the orientation of $\gamma$-CD channels is head-to

head:tail-to-head:tail-to-tail, resulting in a 3-$\gamma$-CD repeating unit (Figure 1d) [23].

WAXD is a useful characterization technique for investigating the crystalline phase transition between the cage structure of as-received $\gamma$-CD·7H$_2$O and the channel structure of styrene/$\gamma$-CD-ICs. Once the guest styrene molecules are included in the $\gamma$-CD cavities, it is expected that the resulting inclusion compound crystals adopt a channel-type structure. Figure 2 shows WAXD patterns for as-received $\gamma$-CD, channel $\gamma$-CD formed by a re-crystallization method [7], and styrene/$\gamma$-CD-IC. The styrene/$\gamma$-CD-IC exhibits the finger-print diffraction pattern of the $\gamma$-CD channel-type reported in the literature [25].

The crystallographic characteristics of channel $\gamma$-CD and styrene/$\gamma$-CD-IC crystals are summarized in Table 1. The calculated d-spacings from the two-dimensional tetragonal unit cell having [25] a = b = 23.7 Å are in good agreement with the observed values seen in Table 1. It was observed that the d-spacings for $\gamma$-CD channel crystals and styrene/$\gamma$-CD-IC are almost the same, suggesting that guest styrene molecules are only included in the $\gamma$-CD channels. The WAXD data represents the first evidence that $\gamma$-CD molecules formed a channel structure IC with the possible inclusion of styrene guests residing in the $\gamma$-CD cavities.

## DSC

DSC is a useful tool to determine whether or not the guest molecules are included inside the CD cavities: thermal transitions, such as the melting point ($T_m$) for guests, would be observed if there is any uncomplexed guest molecules present in the CD-ICs. Figure 3 shows the DSC scans of styrene/$\gamma$-CD-IC and the physical mixture of styrene and $\gamma$-CD. It was observed that the

DSC scans of the physical mixture of styrene and $\gamma$-CD exhibited a melting point for styrene at −30 °C, whereas no melting point was observed for the styrene/$\gamma$-CD-IC, suggesting that the styrene molecules were all included inside the CD channels.

## NMR

NMR is a powerful technique to determine the presence and molar ratio of guest molecules in CD-ICs. The presence of styrene in the styrene/$\gamma$-CD-IC was confirmed by solution $^1$H-NMR, and the molar ratio of styrene to $\gamma$-CD was found to be ∼2:1 for the complex. Solid-state $^{13}$C-NMR has also been carried out to get further evidence for the complexation of styrene and $\gamma$-CD. Figure 4 shows the $^{13}$C CP/MAS NMR spectra of the styrene/$\gamma$-CD-IC and the physical mixture of styrene with $\gamma$-CD. Cyclodextrin molecules assume a less symmetrical conformation in their cage structure crystals when not including a guest (other than water) in their cavities. In the CP/MAS spectrum of the physical mixture of styrene and $\gamma$-CD, the $\gamma$-CD peaks show several resolved resonances for each of the carbon types (Figure 4a). In the case of the styrene/$\gamma$-CD-IC CP/MAS spectrum, each carbon in each glucose unit can be observed as a single somewhat broadened peak (Figure 4b), which indicates that $\gamma$-CD adopts a more symmetrical conformation and each $\gamma$-CD molecule is in a similar environment due to the presence of included styrene guest molecules, whose resonances and therefore presence is also confirmed. A closer examination and comparison of the styrene resonances in the physical mixture and in the inclusion compound revealed some differences in their resonance frequencies/chemical shifts, which may due to possible interactions between $\gamma$-CD and styrene in the inclusion compound.
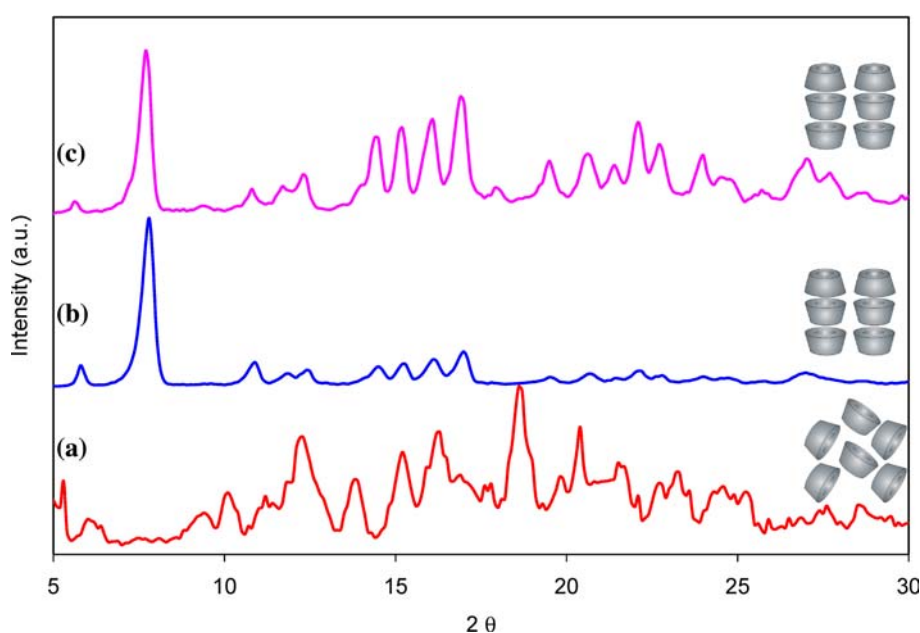


*Figure 2.* X-ray diffraction patterns of (a) $\gamma$-CD$_{cage}$, (b) $\gamma$-CD$_{channel}$ and (c) styrene/$\gamma$-CD$_{channel}$-IC.

*Table 1.* Crystallographic characteristics of $\gamma$-CD$_{channel}$ and styrene/$\gamma$-CD$_{channel}$-IC crystal structures

| $\gamma$-CD$_{channel}$ | | | Styrene/$\gamma$-CD$_{channel}$-IC | | |
|---|---|---|---|---|---|
| *Hkl* | $2\theta$ (observed) (°) | d (observed) (Å) | $2\theta$ (observed) (°) | d (observed) (Å) | d (calculated)[a] (Å) |
| 110 | 5.8 | 15.22 | 5.6 | 15.75 | 16.76 |
| 200 | 7.8 | 11.32 | 7.7 | 11.48 | 11.85 |
| 220 | 10.9 | 8.11 | 10.8 | 8.18 | 8.38 |
| 310 | 12.4 | 7.13 | 12.3 | 7.18 | 7.49 |
| 132 | 14.5 | 6.10 | 14.4 | 6.14 | 6.21 |
| 400 | 15.2 | 5.82 | 15.2 | 5.83 | 5.93 |
| 330 | 16.1 | 5.50 | 16.1 | 5.5 | 5.59 |
| 420 | 17.0 | 5.21 | 16.9 | 5.24 | 5.3 |
| 620 | 24.0 | 3.70 | 24 | 3.7 | 3.75 |

[a]Calculated assuming a tetragonal unit cell with $a = b = 23.7$, $c = 22.2$ Å [25].
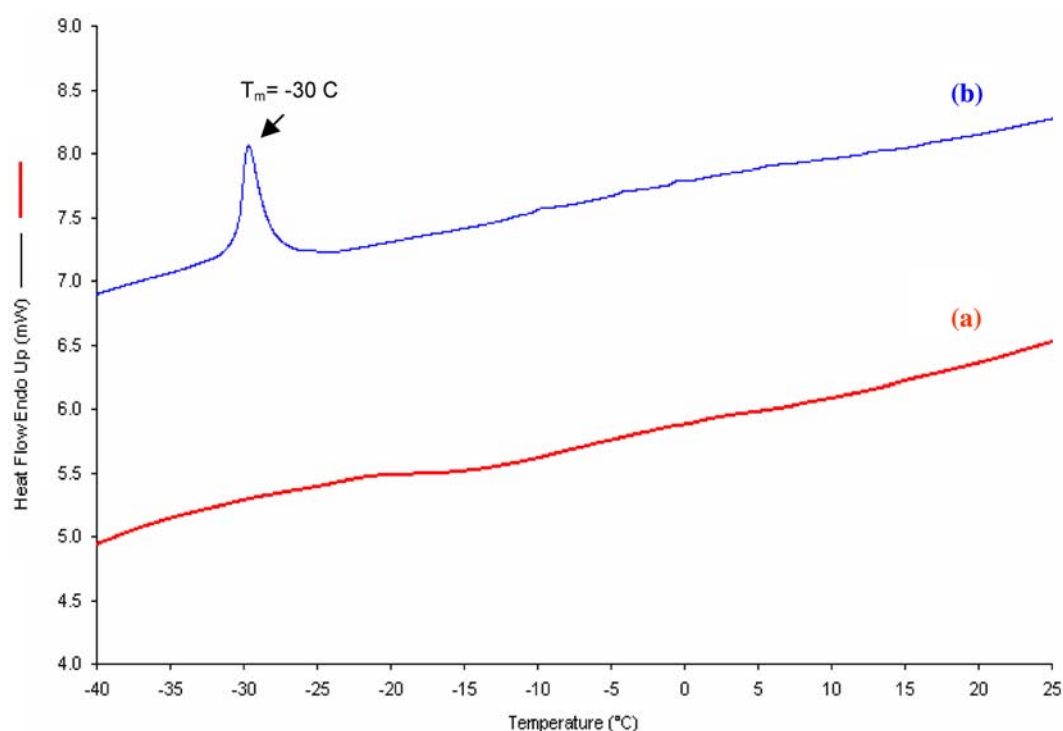


*Figure 3.* DSC scans of (a) styrene/$\gamma$-CD-IC and (b) physical mixture of styrene and $\gamma$-CD.

We have also carried out single pulse $^{13}$C-NMR experiments for styrene/$\gamma$-CD-IC (Figure 4c), to learn if the styrene molecules in the $\gamma$-CD channels are involved in any kind of styrene–styrene $\pi$–$\pi$ interactions. Judging from a comparison of $^{13}$C-NMR chemical shifts observed for pure styrene (not shown) and those observed for styrene included in the channels of its $\gamma$-CD-IC, no specific interactions between the styrene molecules in the channels were observed, which is consistent with both the UV-Vis and modeling data discussed below.

*TGA*

Thermogravimetric results observed for pure $\gamma$-CD indicated two weight loss stages (Figure 5(i)a). The one below 150 °C was attributed to removal of water and the second, with a maximum at around 360 °C and corresponding to the major weight loss, was associated with the main degradation of $\gamma$-CD [26]. The TGA thermogram of the physical mixture of styrene and $\gamma$-CD (Figure 5(i)c) is almost identical with the thermogram of pure $\gamma$-CD, which indicates that there is only a very small amount of styrene left in the mixture prior to the TGA experiment. Since styrene is volatile, most of the styrene is evaporated from the mixture, which proves that there is no complexation between styrene and $\gamma$-CD in the physical mixture. In the case of complexation, the stability of a volatile guest molecule would be expected to increases due to guest–host interaction, which was the case for styrene/$\gamma$-CD-IC. In the TGA thermogram of styrene/$\gamma$-CD-IC (Figure 5(i)b), there was a continuous
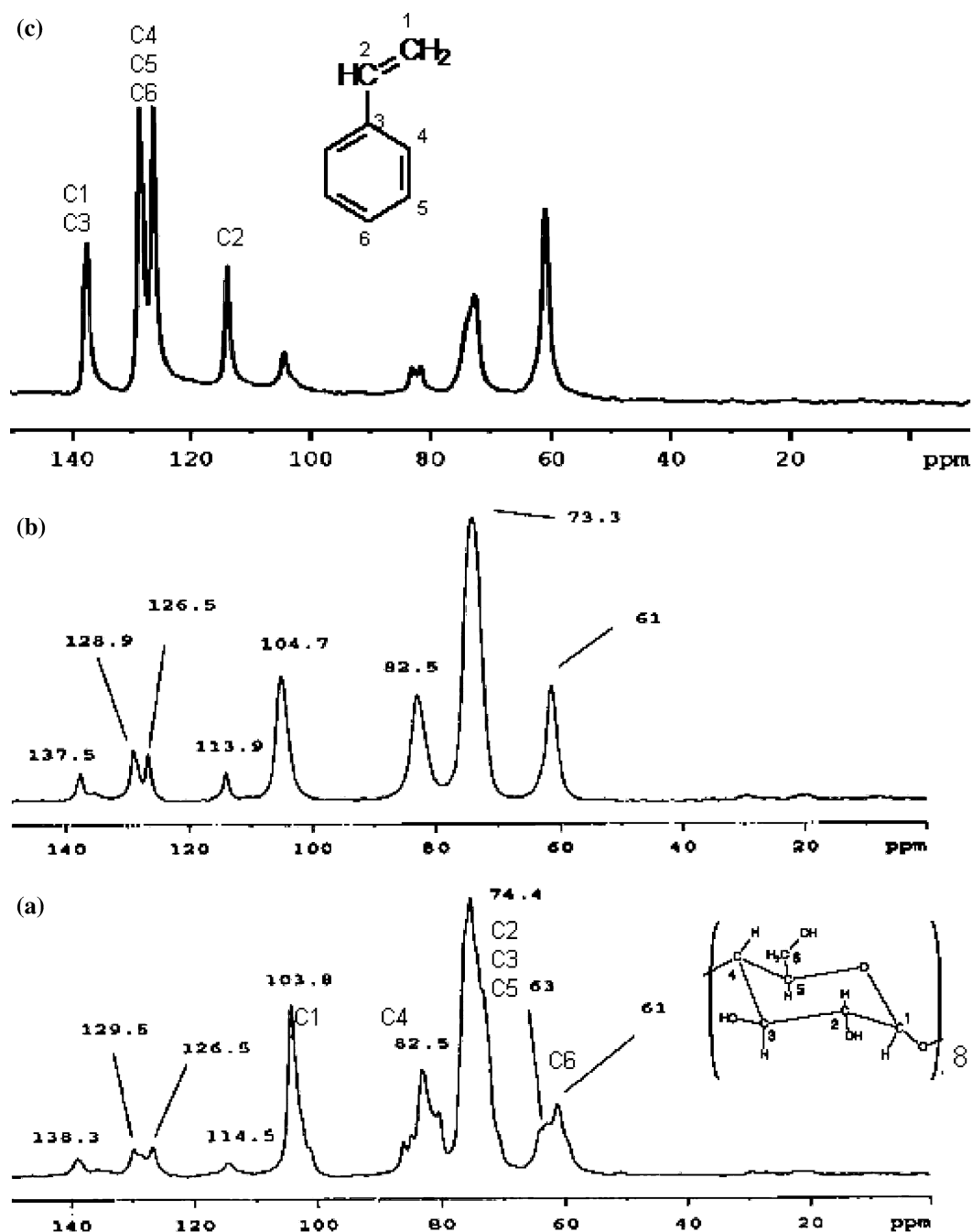
*Figure 4.* CP/MAS $^{13}$C-NMR of (a) physical mixture of styrene and $\gamma$-CD, (b) styrene/$\gamma$-CD$_{channel}$-IC, and (c) single pulse $^{13}$C-NMR of styrene/$\gamma$-CD$_{channel}$-IC.

weight loss up to the main degradation of $\gamma$-CD suggesting the presence of styrene and its stability at temperatures much higher than its boiling point (styrene $T_b$ = ~138 °C). The presence and higher thermal stability of styrene at elevated temperatures is further strong evidence for the complexation of styrene with $\gamma$-CD in this sample.

Isothermal TGA study of the styrene/$\gamma$-CD-IC has also been carried out at elevated temperatures (Figure 5(ii)). The weight loss percentages were found to be 18.4, 19.8, 21.9, and 23.4% as the temperature was kept constant at 180, 200, 220, and 265 °C, respectively, for 100 min of thermal treatment. The higher the treatment temperature, the higher the weight loss observed for the styrene/$\gamma$-CD-IC. This finding reveals that some of the styrene molecules are still present inside the $\gamma$-CD channels even at elevated temperatures, though less styrene remains in the $\gamma$-CD cavities after prolonged heating at elevated temperatures. Nevertheless, the presence of styrene molecules was still detected by pyrolysis mass spectrometry up until the main degradation of $\gamma$-CD (above 300 °C), indicating the co-degradation of the remaining styrene with $\gamma$-CD. This observation suggests that CD-ICs may provide a means to deliver volatile additives to polymers in the form of high-melting additive-CD-ICs.
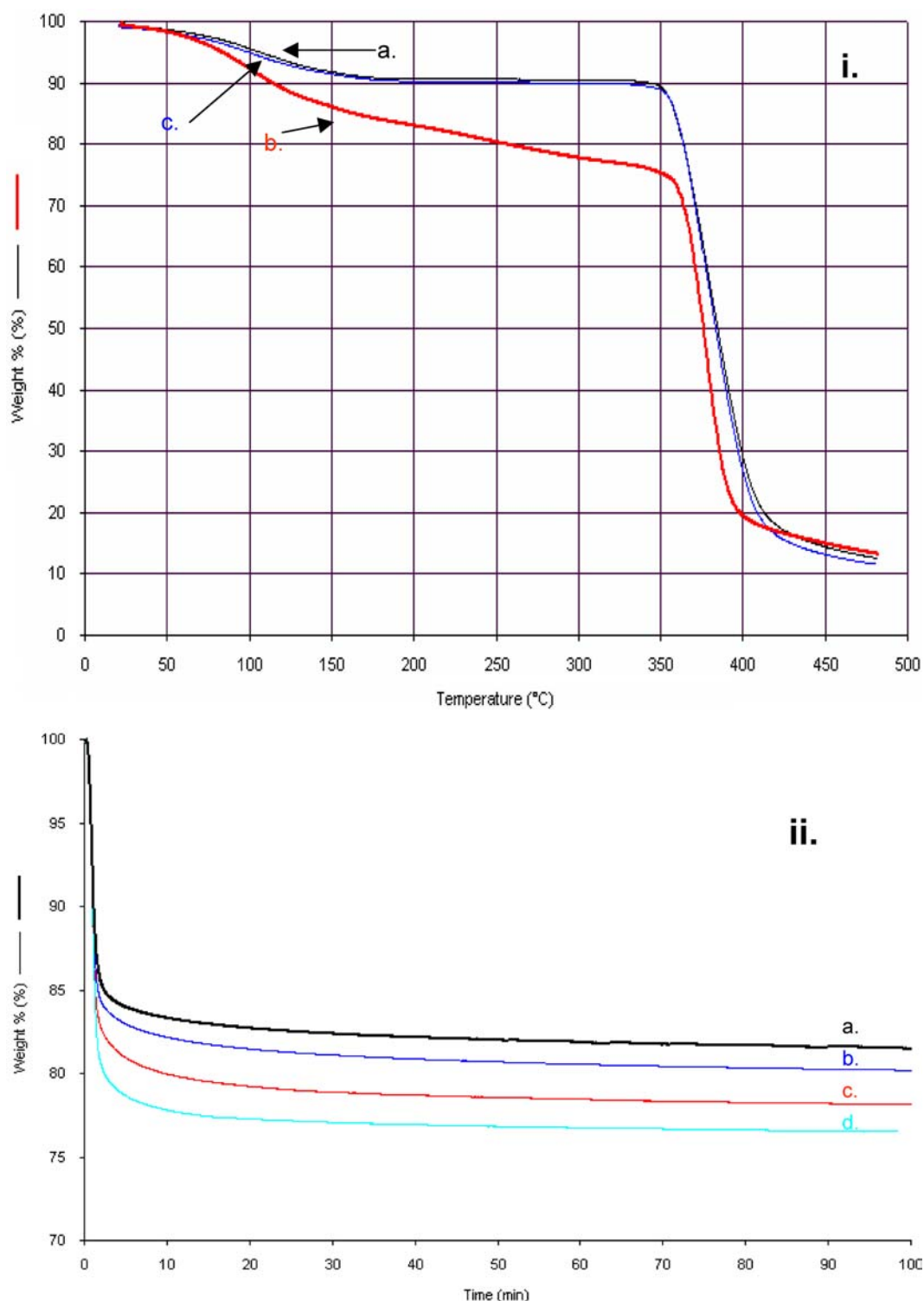
*Figure 5.* (i) TGA thermograms of (a) as-received γ-CD, (b), styrene/γ-CD-IC, and (c) physical mixture of styrene and γ-CD. (ii) Isothermal TGA thermograms of styrene/γ-CD-IC, (a) 180, (b) 200, (c) 220, and (d) 265 °C. All samples were rapidly heated (200 °C/min) to reach these constant target temperatures and held there for 100 min.

## DIP-MS

In general, DIP-MS facilitates analyses of material chemical structures and their degradation mechanisms using structural information from the thermal characterization of their degradation products [27–29]. In pyrolysis MS analysis, not only the detection of a peak, but also the variation of its intensity as a function of temperature, i.e., its evolution profile, is important. The trends in evolution profiles can be used to determine the source of the product, or the mechanism of thermal degradation.

The direct pyrolysis mass spectrometry analysis of styrene/γ-CD-IC and a physical mixture of styrene and γ-CD have been performed to investigate their thermal stabilities and thermal degradation behaviors (Figure 6).
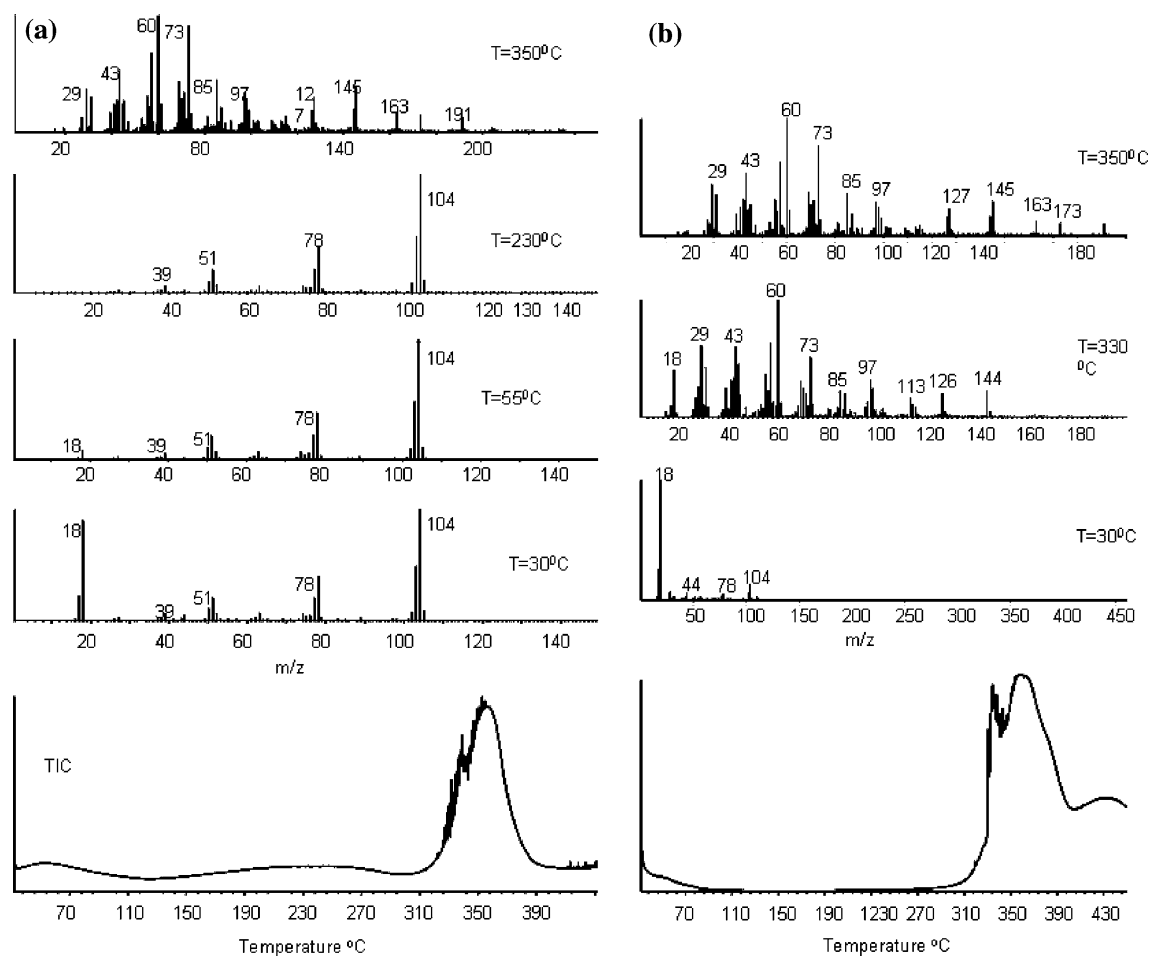
*Figure 6.* Total ion current (TIC) curves and pyrolysis mass spectra recorded at the maximum of the peaks and shoulders in the TIC curves of (a) styrene/$\gamma$-CD-IC and (b) the physical mixture of styrene and $\gamma$-CD.

The presence of styrene in the sample was identified by detection of the classical mass spectrum of styrene with peaks due to $C_8H_8$, $C_6H_6$ molecular ions and $C_4H_3$, $C_3H_3$ fragments at $m/z = 104,78$ and $51,39$ Da, respectively. Pyrolysis analysis of the styrene and $\gamma$-CD physical mixture (Figure 6b) indicated that the release of water ($H_2O$, $m/z = 18$ Da) and styrene from the mixture is completed at very low temperatures (below 80 °C). This finding is consistent with TGA data where the low temperature weight loss was recorded and attributed to removal of water and styrene for this sample. The thermal degradation of $\gamma$-CD occurs over a broad temperature range starting around 300 °C. The variation of total ion current (TIC) as a function of temperature shows two peaks; a sharp peak and a broad peak with a shoulder in the high temperature range having maxima at 330 and 350 °C, respectively. Yet, the fragmentation patterns observed in the pyrolysis mass spectra recorded throughout the pyrolysis were nearly identical and the main degradation products are due to the cleavage of weak C–O bonds, yielding intense $C_2H_4O_2$ and $C_3H_5O_2$ fragments at $m/z = 60$ and 73 Da, respectively. The recorded TIC for the styrene and $\gamma$-CD physical mixture is very similar to that of pure $\gamma$-CD [30]. This indicates the absence of styrene in the physical mixture at high temperatures and points out that the degradation behavior of $\gamma$-CD in the mixture is the same as pure $\gamma$-CD.

The thermal behavior styrene/$\gamma$-CD IC was found to be much different compared to that of styrene and $\gamma$-CD physical mixture (Figure 6a). The styrene/$\gamma$-CD IC pyrolysis mass spectra showed that the complete removal of water ($H_2O$, $m/z = 18$ Da) was again achieved at very low temperatures (below 50 °C). Yet, the continuous release of styrene was observed up to the main degradation region of the $\gamma$-CD (above 300 °C). This finding is consistent with TGA results, which elucidate the presence of styrene in the CD channels and its strong interaction with the CD cavities. Moreover, it was observed that the TIC recorded in the range of 300–450 °C (degradation region for $\gamma$-CD) for this sample was different than the physical mixture. Although, pyrolysis mass spectra recorded above 300 °C showed identical peaks, the low temperature peak with a shoulder around 300 °C in the single ion pyrograms of $\gamma$-CD based products became narrower while the second weak and broad peak around 390 °C diminished significantly. This indicated that the degradation behavior of $\gamma$-CD was affected by the presence of styrene, which may due to co-degradation of styrene and $\gamma$-CD.
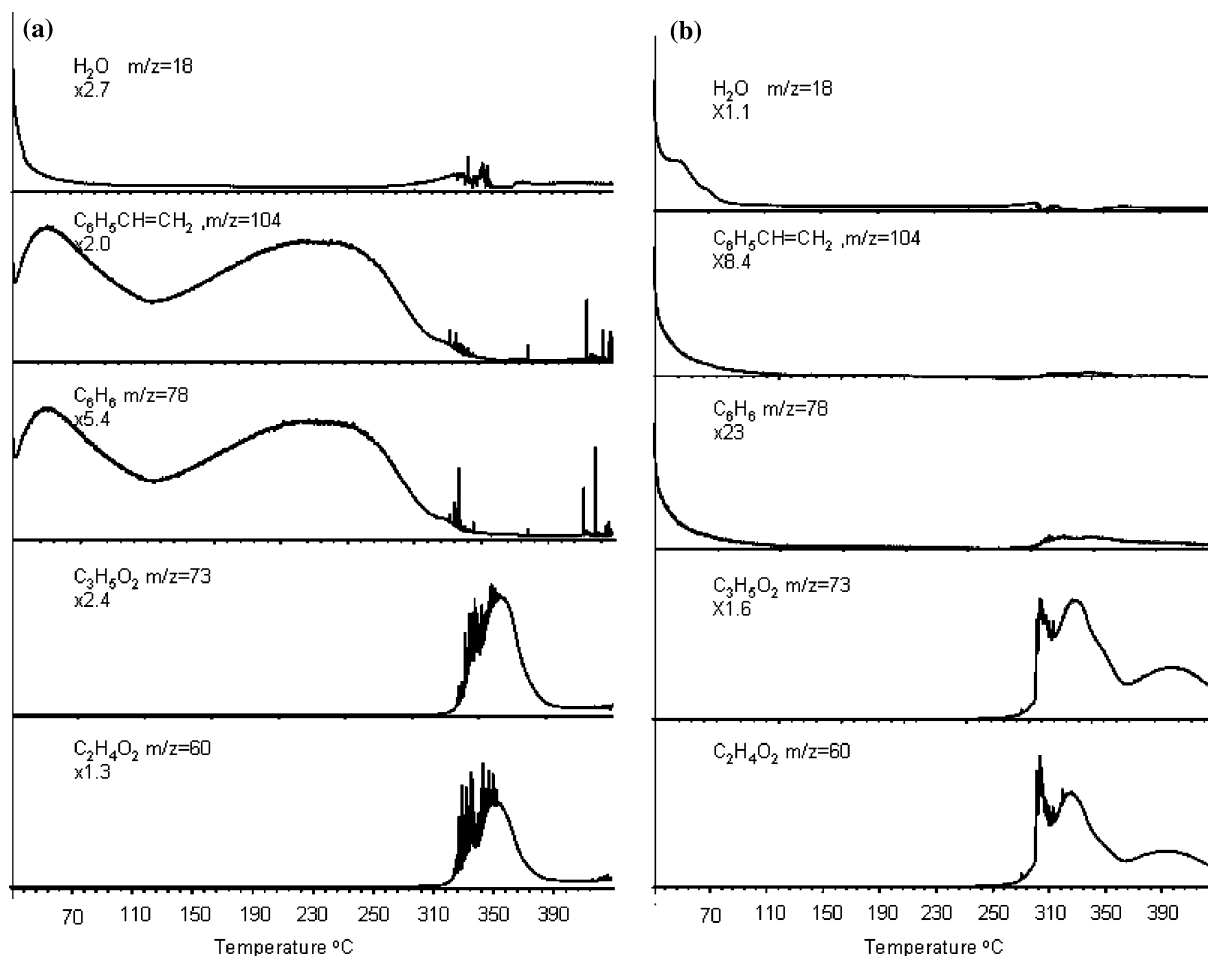
*Figure 7*. Evolution profiles of $C_2H_4O_2$ ($m/z = 60$ Da), $C_3H_5O_2$ ($m/z = 73$ Da), $C_6H_6$ ($m/z = 78$ Da), $C_8H_8$ ($m/z = 104$ Da), and $H_2O$ ($m/z = 18$ Da) in (a) styrene/$\gamma$-CD-IC and (b) the physical mixture of styrene and $\gamma$-CD.

In Figure 7, evolution profiles of some diagnostic thermal degradation products of styrene and $\gamma$-CD namely; $C_8H_8$ ($m/z = 104$ Da), $C_6H_6$ ($m/z = 78$ Da), $C_3H_5O_2$ ($m/z = 73$ Da), and $C_2H_4O_2$ ($m/z = 60$ Da) are shown. Evolution of styrene based products was observed at very low temperature and diminished below 100 °C in the physical mixture indicating the thermal instability of styrene due to lack of complexation with $\gamma$-CD. Styrene-based products from the thermal degradation of the styrene/$\gamma$-CD-IC sample showed two maxima at low (~50 °C) and at higher temperature (~230 °C). This behavior can be explained by supposing two different environments for styrene molecules in the complex. Styrene molecules having weaker interactions with $\gamma$-CDs in the host channels are released at lower temperatures than those with stronger interactions with $\gamma$-CD. It is also noted that the quantity of styrene released at low temperature is very low suggesting that most of the guest molecules have high stability in the $\gamma$-CD channels due to strong guest–host interactions. This was also confirmed by solution $^1$H-NMR, where the styrene/$\gamma$-CD-IC that was vacuum-dried for 24 h at 40 °C lost only 10 weight% of the total styrene in the complex. Moreover, significant changes were also observed for the evolution profiles of $C_3H_5O_2$ ($m/z = 73$ Da) and $C_2H_4O_2$ ($m/z = 60$ Da) from the styrene/$\gamma$-CD-IC sample, which

indicated that degradation of $\gamma$-CD was affected by styrene as mentioned earlier.

*Quantum mechanics calculations*

Modeling the inclusion complexation of host CDs with various organic guests can be a powerful tool, because it can potentially provide valuable and deep insights into the non-covalent, weak intermolecular interactions governing their molecular recognition, as in enzyme substrate binding [31]. Owing to the relatively large molecular size of CDs, most of the modeling studies performed on CDs employed only molecular mechanics (MM) [32], molecular dynamics (MD) [33], and Monte Carlo simulations (MC) [34]. The first quantum mechanics study on CDs using a semi-empirical CNDO method was performed by Kitagawa *et al.* [35] in 1987. Thereafter, Yannakopoulou and co-workers [36] and the Huang group [37] carried out AM1 calculations on the ICs of $\beta$-CD. Recently, the PM3 method was used to study the inclusion of different guest molecules into CDs, which proved to be a powerful tool for the conformational analysis of supramolecular systems [38]. In the present study, efforts, utilizing the semi-empirical Quantum Mechanics PM3 method, were made to estimate the number of guest styrene molecules complexed

inside the host $\gamma$-CD cavity, and, if more than one is included, how they are oriented.

### Prediction of styrene UV-Vis behavior

For intermolecular $\pi$–$\pi$ interaction to take place between parallel and overlapping styrenes, their intermolecular distance should be 3.3 Å or less [39]. Such interactions result in bathochromic shifts of absorption bands to longer wavelengths. The bathochromic shift decreases significantly as the intermolecular distance goes beyond 3.3 Å. With this in mind, to account for such an effect and to simulate how intermolecular $\pi$–$\pi$ interactions might play a role in shifting the $\lambda_{max}$ (281 nm) of styrene, two parallel and overlapping styrene molecules were locked at an intermolecular distance of 2.55 Å. Then, the geometry was optimized using PM3 parameters. Following the geometry optimization, the UV-Vis spectrum was predicted using ZINDO/INDO1 parameters with a configuration interaction = 26.

Figure 8(i) shows the predicted absorption spectrum for two overlapping styrene molecules in the locked conformation (2.55 Å), showing the $\lambda_{max}$ at 353.9 nm, which is highlighted in red. Figure 8(ii) shows the two styrene molecules in this locked conformation with an intermolecular distance of 2.55 Å, and the molecular orbitals responsible for the electronic transition at 353.9 nm are superimposed on this molecular structure.

### UV-Vis absorption of styrene in solution and in the styrene/$\gamma$–CD-IC

The potential for intermolecular interactions between styrene molecules inside the $\gamma$-CD channel were assessed by comparing the solution UV-Vis spectrum (Figure 9(i)) of styrene to the solid-state UV-Vis spectrum of styrene/$\gamma$-CD-IC (Figure 9(ii)). Both spectra are nearly identical, indicating that there is no intermolecular $\pi$–$\pi$ interaction taking place inside the $\gamma$-CD cavity. This finding is also consistent with solid-state $^{13}$C-NMR data.

### Modeling styrene molecules inside the $\gamma$-CD cavity

Quantum mechanical semi-empirical PM3 parameters were used to determine the stability of $\gamma$-CD complexes with different numbers of styrene molecules included in the host by calculating the energy difference between host and guest and their IC. Our main focus was to study the likelihood of more than one styrene molecule entering the host $\gamma$-CD, and, if so, how they are oriented and what is the intermolecular distance between them in the $\gamma$-CD cavity. To determine the stability of different complexes, the binding energy was calculated from the energy difference between the IC and the energy sum of the isolated host and guest, which are shown in Table 2. The results obtained from semi-empirical PM3 parameters for $\gamma$-CD containing one and two styrene molecules
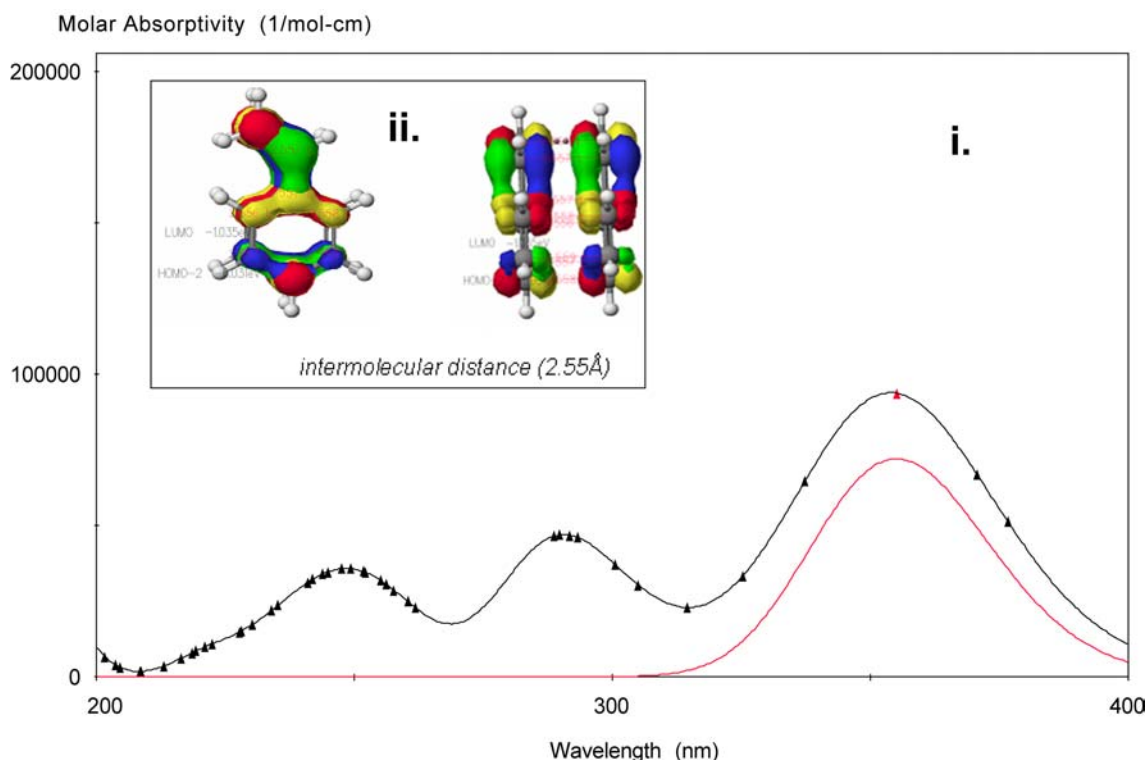


*Figure 8.* (i) Predicted absorption spectrum ($\lambda_{max}$ = 353.9 nm) of two parallel and overlapping styrene molecules at an intermolecular distance (2.55 Å). (ii) Two views of the MO orbitals responsible for the electronic transition at 353.9 nm, superimposed on two locked styrene molecules: (left) two overlapped styrene molecules parallel to the plane of the paper, (right) two styrene molecules perpendicular to the plane of the paper.
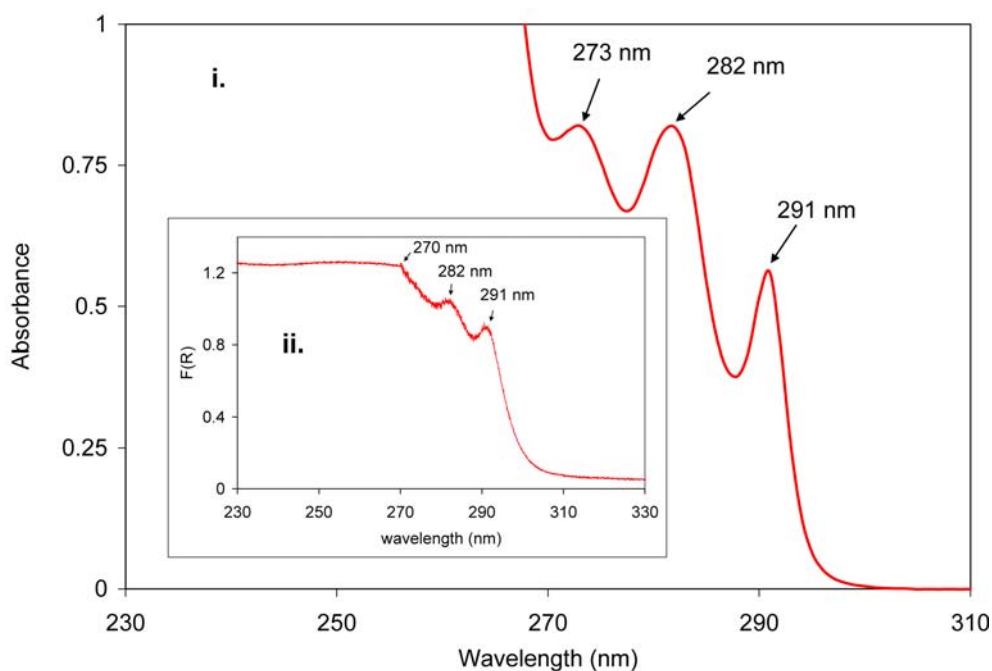
*Figure 9.* (i) UV-Vis absorbance spectrum of styrene in methanol. (ii) Solid-state UV-Vis spectrum of styrene/γ-CD-IC.

*Table 2.* Energy of host, guest and complex, and energy of stabilization upon complexation, computed using PM3 parameters

| Species (starting geometry) | | $E$ | $\Delta E$ (optimized geometry)* | | Method |
|---|---|---|---|---|---|
| | | (kcal/mol) | kcal/mol | kJ/mol | |
| One styrene molecule | Figure 10(i)b | 39 | – | | Quantum Mechanical PM3 parameters |
| 2 Styrene molecules, no IMI | Figure 10(v)a | 74 | – | | |
| 2 Styrene molecules, at 2.55 Å | Figure 10(ii)a | 78 | – | | |
| 2 Styrene molecules, at 3.3 Å | Figure 10(ii)b | 78 | – | | |
| γ-CD | Figure 10(i)a | −1663 | – | | |
| IC/one styrene | Figure 10(i)c | −1626 | −2.4 | −10.0 | |
| IC/two styrene, no IMI | Figure 10(v)b, c | −1594 | −5.7 | −23.8 | |
| IC/two styrene, at 2.55 Å | Figure 10(iii) | −1593 | −8.6 | −36.0 | |
| IC/two styrene, at 3.3 Å | Figure 10(iv) | −1593 | −8.9 | −37.2 | |

*IMI = intermolecular interaction, $E$ = total heat of formation, $\Delta E$ = stabilization energy upon complexation = $E_{complex} - E_{host} - E_{guest}$.

with and without potential intermolecular π–π interactions (Figure 10(i)–(iv)) indicated that the IC formed with γ-CD containing two styrene molecules (Figure 10(iv)b) is the most energetically favorable, as inferred from the larger negative energy changes (Table 2). This is consistent with the experimental observation, where the molar ratio of styrene: γ-CD was found to be 2:1 in the IC by solution ^{1}H-NMR.

The binding energy of the complex with parallel and overlapped styrenes shown in Figure 10(iv) is 13.4 kJ/mol lower than that of the complex with non-overlapped styrenes shown in Figure 10(v). Although it seems that all the complexes with two overlapped and parallel styrenes (Figure 10(ii)–(iv)) are energetically favored, the intermolecular distances following geometry optimization, in the cases of 2.55 and 3.3 Å initial separations, shifted to 4.146 and 4.173 Å, (Figure 10(iii), (iv)), respectively, the distance at which no intermolecular π–π

interactions can be expected [39] or is experimentally observed for the styrene/γ-CD complex in its UV-Vis spectrum (Figure 9(ii)). However, their binding energies were the strongest. This indicates that complexes with overlapped and parallel styrenes are more likely to exist in the γ-CD cavity at a distance ∼4.1 Å, where there is no intermolecular π–π interaction. This is also confirmed by the UV-Vis solution spectra of styrene (Figure 9(i)), which is nearly identical to the UV-Vis spectrum of the styrene-γ-CD complex (Figure 9(ii)), both of which show no indication of π–π interactions.

## Conclusions

The formation and characterization of the channel structure solid inclusion compound formed between guest styrene and host γ-CD have been described. Two
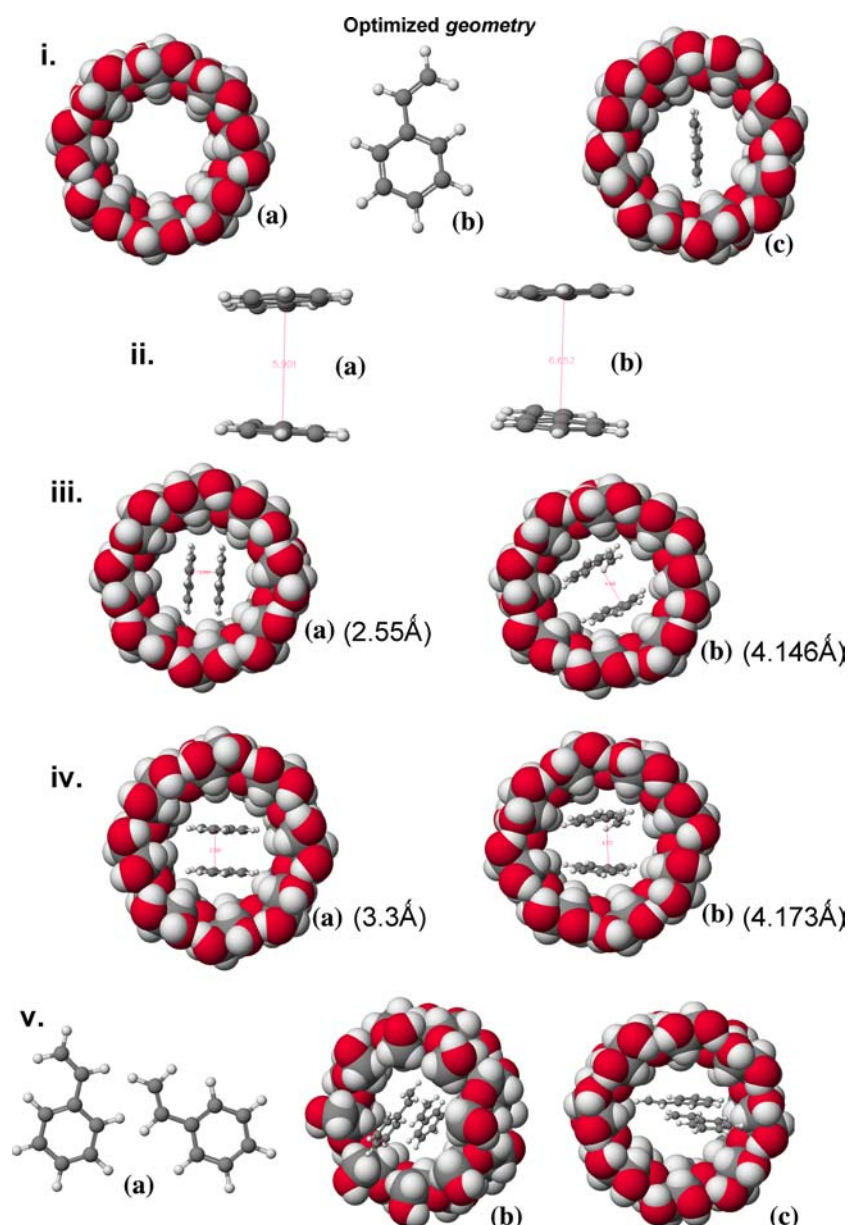
Figure 10. (i) Optimized geometry of host (a), guest (b), and IC (c) containing one styrene molecule using semi-empirical PM3 parameters and the MOZYME algorithm. (ii) Optimized geometry of two styrene molecules initially set at (a) 2.55 and (b) 3.3 Å. (iii) Starting (a) and optimized geometry (b) of γ-CD-IC containing two overlapped, parallel styrene molecules. (iv) Starting (a) and optimized geometry (b) of IC containing two styrene molecules. (v) Optimized geometry of non-overlapped styrenes (a) and two views (b and c) of the optimized IC containing two styrene molecules with no overlap and no π–π interactions.

styrene guests reside in each host γ-CD. TGA and DIP-MS observations demonstrate a remarkable affinity of guest styrenes to remain in the host γ-CD channels at high temperatures, even at ∼300 °C where the γ-CD host lattice begins to decompose. In addition, the γ-CD decomposition products observed in the degradation of the styrene/γ-CD-IC are different from those seen when pure γ-CD is thermally degraded. This observation also affirms the strong affinity/interaction between guest styrene and host γ-CDs in the channel structure inclusion complex. Molecular modeling has confirmed the observed 2:1 styrene:γ-CD stoichiometry and has further suggested that the guest styrenes are arranged in a parallel and overlapped configuration at a separation distance of ∼4.1 Å, the distance at which no π–π

interactions can be observed. This was confirmed by observation of the UV-Vis spectra of styrene in methanol and in the styrene/γ-CD-IC. With this information at hand, we will be better able to interpret the results of the constrained solid-state polymerization of styrene confined to the narrow channels of its IC formed with γ-CD.[14]

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