Crystalline Cyclodextrin Inclusion Compounds Formed with Aromatic Guests: Guest-Dependent Stoichiometries and Hydration-Sensitive Crystal Structures

Tamer Uyar,†‡ Marcus A. Hunt,† Hanna S. Gracz,# and Alan E. Tonelli* †,‡

Fiber and Polymer Science Program, College of Textiles, Campus Box 8301, North Carolina State University, Raleigh, North Carolina 27695-8301, and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Received September 26, 2005; Revised Manuscript Received March 15, 2006

ABSTRACT: A series of solid inclusion complexes (ICs) containing the aromatic guests aniline, benzene, ethylbenzene, phenol, p-xylene, styrene, and toluene were formed with host γ-cyclodextrin (γ-CD). IC stoichiometry was observed to depend on the nature of the included aromatic guest. The molar ratio of styrene, aniline, and phenol guests to γ-CD host was ~2:1 in their individual IC crystals, whereas ethylbenzene, p-xylene, and toluene guests formed ~1:1 inclusion complexes with γ-CD. Thermogravimetric analysis showed that the thermal stabilities of these volatile aromatic guest molecules increased due to guest-host interactions once they were included in their γ-CD-ICs. X-ray diffraction (WAXD) observations performed on the aromatic guest-CD-IC crystals showed that all of them have channel-type crystalline structures. Moreover, it was observed that the presence of guest molecules inside the γ-CD cavities stabilized the channel structure of stacked γ-CDs. However, a solid-phase transition from tetragonal to hexagonal packing of γ-CD stacks was observed upon dehydration of the styrene−, toluene−, p-xylene−, benzene−, and ethylbenzene−γ-CD-IC crystals. We have also discovered that the solid-state transformation between tetragonal and hexagonal channel crystal structures is reversible upon the desorption or sorption of water. In the cases of aniline− and phenol−γ-CD-ICs, no solid-phase transition from tetragonal packing to hexagonal packing was observed upon dehydration. Instead, the tetragonal packing structure was stable even after vacuum-drying at elevated temperatures for an extended period. The stability of the tetragonal packing in aniline− and phenol−γ-CD-ICs was attributed to the presence of hydrogen bonding between the included guests and neighboring host γ-CD molecules.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven, and eight α-1,4-linked glucopyranose units and are named alpha (α), beta (β), and gamma (γ)-CDs, respectively (Figure 1). The depth of the cavities for the three CDs is the same (~7.8 Å), while the cavity diameters of α-, β-, and γ-CDs are ~6, 8, and 10 Å, respectively.1 Because of the unique chemical structure of the CD molecule, the cavity is hydrophobic relative to the outer surface. The hydrophobic nature of the CD cavities facilitates the ability of CDs to act as a host clathrate for both nonpolar and polar guests to form inclusion complexes (ICs).1 Several types of driving forces, such as van der Waals interactions, hydrogen bonding, release of high energy water, and decrease in the strain energy in the cyclodextrin cavity, have been proposed as contributing to the formation of CD-ICs.2 Though limited by the sizes of the host CD cavities and the cross sections of included guests, CDs can include small molecules, as well as polymers, to form guest−host CD-ICs.3−6 The stabilities of the guest molecules significantly increase once the inclusion compounds are formed, due to the binding forces between host CDs and the included guest molecules.

Soluble inclusion complexes of aromatic molecules, i.e., styrene, aniline, phenol, and their derivatives with CDs have been reported in the literature. These studies have found that the inclusion of substituted benzene derivatives in the CD cavities depends on a variety of factors, including their sizes, shapes, substitution positions (ortho, meta or para), ionic strengths, etc.9,10 In this study, we have formed and studied a series of solid γ-CD inclusion complexes containing the aromatic compounds aniline, benzene, ethylbenzene, phenol, p-xylene, styrene, and toluene as guests. These solid inclusion compounds (ICs) were obtained by mixing the guest molecules with an aqueous γ-CD solution, and the resulting crystalline precipitates of aromatic guest−γ-CD-IC crystals were recovered by filtration. Here, we summarize the characteristics of the ICs that we formed.

Experimental Section

Materials. Cyclodextrins (α and γ) were purchased from Cerestar (Hammond, IN). Styrene (99.9%, Aldrich) and acrylonitrile (99.9%, Aldrich) were vacuum distilled prior to use. All the other chemicals, benzene (Aldrich, 99.8%), toluene (Aldrich, 99.8%), ethylbenzene (Aldrich, 99.8%), aniline (Aldrich, 99.5%), p-xylene (Aldrich, 99.0%), phenol (Fluka, ~90% w/w liquid), pyrrole (Aldrich, 98%), and methyl methacrylate (Aldrich, 99%) were used without further purification. The water used in this study was deionized (DI−H2O).

Formation of Channel-type Crystalline γ-Cyclodextrin (γ-CD-channel). γ-CD can exist in two classes of crystal structures called “cage” and “channel”.11 In the cage structure (Figure 1c), the γ-CD molecules have a “herringbone” arrangement, where each γ-CD cavity is blocked by neighboring γ-CDs. In the channel packing crystal structure (Figure 1d), the γ-CD molecules are stacked on top of each other to form long cylindrical channels in which guest molecules can reside. For γ-CD, a cage-type complex has only been obtained with water as the guest,12 i.e., pure γ-CD, whereas for other guest molecules, i.e., both small molecules12,13 and macromolecules,14 the channel-type structure is formed. It was reported that the orientation of γ-CD channels is head-to-head/tail-to-tail/tail-to-tail,13 resulting in a three-molecule repeating unit in each γ-CD stack (Figure 1d). The as-received γ-CD has a cage-type crystalline structure. We successfully obtained a channel-type packing of crystalline γ-CD (γ-CD-channel), with only water molecules...
included in their narrow channel cavities, by appropriate recrystallization from its aqueous solutions. The details of the preparation of \( \gamma \)-CD channel were described in our previous study.\(^{15}\)

**Formation of Solid Aromatic Guest–\( \gamma \)-Cyclodextrin Inclusion Compounds.** The solid inclusion compounds (ICs) were prepared by mixing the guest molecules with an unsaturated \( \gamma \)-CD aqueous solution. Precipitation occurred as the guest molecules were included in the host \( \gamma \)-CD molecules and then aggregated and crystallized. The as-received \( \gamma \)-CD has a cage-type crystalline structure, and the resulting solid inclusion compounds were found to have a channel-type crystalline structure, indicating that the inclusion complexation of the guest molecules with the \( \gamma \)-CD molecules was successful.

A total of 6.5 g (0.005 mol) of as-received \( \gamma \)-CD cage was dissolved in 100 mL of deionized water at room temperature (RT). 0.0125 mol of guest molecules (aniline, benzene, ethylbenzene, phenol, \( p \)-xylene, styrene, or toluene) was added dropwise to the aqueous solution of \( \gamma \)-CD, while the solution was stirred and kept at RT. The initially clear \( \gamma \)-CD solution became turbid, and a white precipitate formed immediately after addition of the guest molecules, which indicated the IC formation. The resulting white suspension was stirred for an additional 24 h at RT and filtered, and the collected precipitate was dried in the laboratory hood for 24 h. The channel packing structure of the IC crystals was confirmed by X-ray study, as shown later (Figure 4a).

**Characterization.**

**Wide-Angle X-ray Diffraction.** Wide-angle X-ray diffraction (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 0.2°/min. The supplied voltage and current were 30 kV and 20 mA, respectively.

Time-dependent WAXD experiments were designed to track the phase transformation of \( \gamma \)-CD\(_{\text{channel}}\) from tetragonal to hexagonal packing that was observed upon dehydration of the ICs. Previously vacuum-dried, dehydrated samples were placed in a 100% humidity chamber for different times during the experiment and placed in the diffractometer to collect diffractograms as a function of hydration time. Characteristic peaks for the hydrated tetragonal and dehydrated hexagonal 200 planes are observed at 2\( \theta = 7.5 \) and 6.0°, respectively.\(^{13}\) To minimize the time spent outside of the humidity chamber, diffractograms for the sample were only collected from 2\( \theta = 5 \)–30°, which includes the aforementioned characteristic reflections. The time spent outside of the humidity chamber was approximately 10 min for each X-ray scan.

**Fourier Transform Infrared Spectroscopy (FT-IR).** A Nicolet 510P FT IR spectrometer was utilized to obtain the infrared spectra of samples mixed with potassium bromide (KBr) and pressed into pellets. The spectra were collected over a range of 4000 to 400 cm\(^{-1}\), with a resolution of 2 cm\(^{-1}\) obtained after 64 scans.

**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 a 1.0 min hold at the starting temperature, ramping to the target temperature at a rate of 20 °C/min, and quenching at a cooling rate of 200 °C/min.

Differential scanning calorimetry (DSC) is a useful tool for determining whether guest molecules are included inside the CD cavities. Thermal transitions, i.e., melting points (\( T_m \)) for guests, would be observed if there are any uncomplexed guest molecules present in the CD-ICs. No guest melting peaks were observed in the DSC scans.

---

**Figure 1.** (a) \( \gamma \)-CD chemical structure; (b) approximate dimensions of \( \alpha \)-, \( \beta \)-, and \( \gamma \)-CDS; schematic representation of packing structures of (c) cage-type and (d) head-to-head/tail-to-head/tail-to-tail channel-type CD crystals.

**Figure 2.** TGA thermograms of (a) as-received \( \gamma \)-CD and (b) toluene–, (c) benzene–, (d) styrene–, (e) aniline–, (f) phenol–, (g) ethylbenzene–, and (h) \( p \)-xylene–\( \gamma \)-CD-ICs.

**Figure 3.** X-ray diffraction patterns of (a) \( \gamma \)-CD\(_{\text{cage}}\), (b) \( \gamma \)-CD\(_{\text{channel}}\), and (c) \( \gamma \)-CD\(_{\text{channel}}\) vacuum dried for 24 h at 40 °C.
Crystalline Cyclodextrin Inclusion Compounds

**Results and Discussion**

**³H-Nuclear Magnetic Resonance (³H NMR).** It is widely known that cyclodextrins can be used for the separation of molecules, since they are very selective for the size of the guest molecules to be included in their cavities. Additionally, the type of cyclodextrin used (α-, β-, or γ-CD) is also very important, since the diameter of the cavity gets wider as the number of glucose units is increased from six, to seven, or to eight. For instance, α-CD was found to be more selective in the inclusion of small guests, due to tight binding of the guest molecules within the cavity, compared to β- or γ-CD. Larger guest molecules that do not fit into the α-CD cavity can form inclusion complexes with β- or γ-CD. Larger guest molecules that do not fit into the α-CD cavity can form inclusion complexes with β- or γ-CD, due to their larger cavities, but those guestforming α-CD-ICs may not necessarily be included in the larger CDs. In this study, we have also found that the formation of CD inclusion compounds and their guest to host stoichiometries are highly dependent on the molecular structures and the geometrical sizes of the guest molecules.

**Thermogravimetric Analysis.** Thermogravimetric analyses (TGA) of the samples were performed with a Perkin-Elmer Pyris 1 thermalgravimetric analyzer. Thermal decompositions were recorded between 25 and 500 °C, and the molar ratios of guest to cyclodextrin molecules were calculated by integrating the respective characteristic ³H resonance peaks observed for each.

**Water Vapor Sorption Isotherms.** A custom-built gravimetric balance[16,17] was used to measure the sorption of water vapor in styrene-γ-CD-IC. Samples weighing approximately 0.3 g were first dried in a vacuum oven at 40 °C and then vacuum-dried in the balance chamber at 40 °C to remove any water adsorbed after removal from the vacuum oven. The samples were then tested at 40 °C with water activities ranging from 0.1 to 1.0. By the use of flow meters for regulation, dry nitrogen gas was mixed with nitrogen gas bubbled through a water-containing reservoir to achieve the desired water activity, a = (partial pressure of water vapor)/(saturation pressure of water vapor)]. The humid gas was then passed through the sample chamber at a constant flow rate. Samples were allowed to sorb water until the equilibrium weight gain was achieved at each water activity. After reaching a constant weight, the water activity was increased by approximately 0.15, and equilibration was reestablished. This was repeated up to the saturation concentration of water vapor in the nitrogen gas. A desorption isotherm was also collected by decreasing the water activity in increments of ~0.15, down to a water activity of approximately 0.1. The results of these experiments are plotted as sorption–desorption isotherms at 40 °C.

A sorption kinetics experiment was also conducted to determine the time dependence of the channel γ-CD phase transformation from the dehydrated hexagonal to the hydrated tetragonal structure. Approximately 0.15 g of styrene–γ-CD-IC was placed in the gravimetric balance chamber at 25 °C and a = 1.0, after vacuum-drying at 40 °C, and water uptake was subsequently measured as a function of time.

**Fourier Transform Infrared Spectroscopy.** The presence of guest molecules in IC samples was confirmed by Fourier Transform Infrared spectroscopy (FT-IR) though the FT-IR spectra of guest–γ-CD-ICs are not presented here. The absorption bands at 1080, 1158, and 2927 cm⁻¹ correspond to the coupled C=C/C=O stretching vibrations, the antisymmetric stretching vibration of the C=O–C glycosidic bridge, and C=H vibration of γ-CD, respectively. Since the absorption bands of γ-CD cover the entire fingerprint region, it is not easy to identify all the absorption peaks belonging to the guest molecules in the infrared spectra of their γ-CD-ICs. However, a close examination of the 1600–1500 cm⁻¹ spectral region, where the aromatic C=C ring stretching vibrations are expected to be observed, enable us to confirm the presence of guest molecules in the γ-CD-ICs. The absorption peaks are observed at 1604...
and 1500 cm\(^{-1}\) for the aniline and phenol ICs, as well as the absorption peak near 1495 cm\(^{-1}\) for ethylbenzene, p-xylene, styrene, and toluene \(\gamma\)-CD-ICs. No distinct absorption peak was observed for the benzene \(-\gamma\)-CD-IC sample in the 1600–1500 cm\(^{-1}\) region, which indicates that the amount of benzene is very small in the inclusion compound. This is consistent with NMR results, where the molar ratio of benzene \(-\gamma\)-CD was 0.25:1.

It is known that guest molecules having \(-\text{NH}_2\) or \(-\text{OH}\) groups can form intermolecular hydrogen bonds with the \(-\text{OH}\) groups of cyclodextrins. For example, circular dichroism studies have shown that aniline, phenol, and their derivatives form hydrogen bonds with cyclodextrin in their common solutions once they are included in the CD cavities. In the present case, it is possible that intermolecular hydrogen bonding between guest and \(\gamma\)-CD molecules in aniline- and phenol-\(\gamma\)-CD-IC crystals occurs. However, we were unable to isolate and identify vibrational peaks that could be attributed to hydrogen bonding in any of the spectra, since the 3000–3600 cm\(^{-1}\) region is dominated by the intense \(-\text{OH}\) absorptions of the predominant host \(\gamma\)-CDs.

**Thermogravimetric Analyses.** TGA thermograms of pure \(\gamma\)-CD and the aromatic guest-\(\gamma\)-CD-ICs are presented in Figure 2. Pure \(\gamma\)-CD evidenced two weight loss stages (Figure 2a): the one below 100 °C was attributed to removal of water and the second, with a maximum above 300 °C corresponding to the major weight loss, was associated with the main degradation of \(\gamma\)-CD.\(^{21}\) In the case of complexation, the stability of normally volatile guest molecules would be expected to increase upon inclusion due to guest–host interactions, which was the case for our guest-\(\gamma\)-CD-ICs. In the TGA thermograms of guest-\(\gamma\)-CD-ICs (Figure 2b–h), there was a continuous weight loss up to the main degradation of \(\gamma\)-CD, suggesting the presence of guest molecules at temperatures much higher than their boiling points. The presence and increased thermal stability of guest molecules at elevated temperatures is strong evidence of complexation with \(\gamma\)-CD. It is also noted that the percent weight loss for styrene-\(\gamma\), aniline-\(\gamma\), and phenol-\(\gamma\)-CD-ICs was higher than the other ICs, indicating the presence of a higher molar ratio of guest molecules in these ICs. This finding is consistent with the \(^1\)H NMR determined stoichiometries presented above.

**X-ray Studies of Inclusion Compounds.** WAXD is a useful characterization technique for investigating the crystalline phase transition between the cage structure of as-received \(\gamma\)-CD and the channel structure of guest-\(\gamma\)-CD-ICs. Once the guest molecules are included in the \(\gamma\)-CD cavities, it is expected that the resulting IC crystals adopt a channel-type structure. Figure 3 shows WAXD patterns for as-received \(\gamma\)-CD\(_{\text{age}}\) and \(\gamma\)-CD-\(\text{channel}\) with only water included in the channels formed by our recrystallization method.\(^{15}\) As subsequently evident in Figure 4a, the styrene-\(\gamma\)-CD-IC exhibits a diffraction pattern characteristic of \(\gamma\)-CD channel-type crystals reported in the literature.\(^{13}\) The ICs of \(\gamma\)-CD formed with aniline, ethylbenzene, phenol, p-xylene, and toluene showed diffraction patterns similar to styrene-\(\gamma\)-CD-IC, suggesting that all the ICs have channel-type packing regardless of the guest types. Therefore, the WAXD data represents strong evidence that \(\gamma\)-CD molecules form a channel structure with the inclusion of guest molecules residing in the \(\gamma\)-CD cavities.

In the case of benzene-\(\gamma\)-CD-IC, the X-ray diffraction pattern (data not shown) exhibits peaks for both cage and channel packing indicating that the resulting IC crystals are a mixture of both cage and channel structures. The NMR data showed that there are four \(\gamma\)-CD molecules per benzene molecule, suggesting that three-fourths of the \(\gamma\)-CD molecules are empty.

Thus, it is not a surprise to have a mixture of cage and channel structures for this sample, since the \(\gamma\)-CD molecules hosting benzene would result in channel-type packing, whereas the empty \(\gamma\)-CD molecules would pack in cage-type crystals.

We have also formed a solid inclusion complex of styrene with \(\alpha\)-CD (1:1 molar ratio). It is known that, unlike \(\gamma\)-CD, \(\alpha\)-CD can crystallize with cage-type packing upon inclusion of small molecule guests.\(^{12}\) For instance, the acrylonitrile/\(\alpha\)-CD-IC (1:1 molar ratio) that we have formed in this study has cage-type packing; conversely, styrene-\(\alpha\)-CD-IC crystals exhibit channel-type packing by WAXD. The characteristics of the diffraction patterns observed here, but not shown, for cage and channel structure are consistent with our earlier reports.\(^{13–17}\)

The as-received \(\alpha\)-CD has three salient characteristic peaks associated with its cage-type crystal structure occurring at 2\(\theta\) = 12.0, 14.4, and 21.7°. The styrene-\(\alpha\)-CD-IC has two salient peaks centered at 2\(\theta\) = 12.9 (110 plane) and 19.3° (120 plane) associated with the channel-type packing structure. To conclude, styrene forms solid inclusion complexes with \(\alpha\)-CD and \(\gamma\)-CD, and both have a channel-type structure, containing one and two styrene guests, respectively, in each host CD cavity.

The crystallographic characteristics of channel \(\gamma\)-CD containing no guest except water of hydration (\(\gamma\)-CD\(_{\text{channel}}\)) and styrene-\(\gamma\)-CD-IC crystals are summarized in Table 1. The calculated d spacings from the two-dimensional tetragonal unit cell with lattice parameters\(^{13}\) \(a = b = 23.7\text{ Å}\) are in good agreement with observed values as shown in Table 1. Although it was potentially possible that guest molecules can also be entrapped in the interstitial sites between the columns of \(\gamma\)-CD stacks, given the size of the aromatic guest molecules under study here, an expansion of the channel \(\gamma\)-CD crystal would be expected if they reside within these interstitial sites. Since observed d spacings for \(\gamma\)-CD channel crystals containing only water of hydration and styrene-\(\gamma\)-CD-IC are nearly identical, we conclude that these aromatic guest molecules do not occupy interstitial sites; rather, they are only included in the \(\gamma\)-CD channels.

We have shown that\(^{15,17}\) \(\gamma\)-CD\(_{\text{channel}}\), with no guest molecules included in the channels other than water of hydration, is destabilized by the removal of water under a vacuum at 40 °C, resulting in an amorphous structure, as can be seen in Figure 3c. The relatively large interstitial sites between the \(\gamma\)-CD channel stacks is where a portion of the adsorbed water resides in the fully hydrated structure. When this interstitial, loosely bound water is removed, the channel structure is destabilized. This would suggest that water residing in interstitial sites between \(\gamma\)-CD stacks stabilizes the structure through primary \(\gamma\)-CD···water and possibly secondary \(\gamma\)-CD···water···water···\(\gamma\)-CD hydrogen bonds. On the other hand, the \(\gamma\)-CD channel

<table>
<thead>
<tr>
<th>(\gamma)-CD(_{\text{channel}}) channel</th>
<th>styrene-(\gamma)-CD(_{\text{channel}}) IC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(\theta)(obs)</td>
<td>d(obs) (Å)</td>
</tr>
<tr>
<td>110</td>
<td>5.8</td>
</tr>
<tr>
<td>200</td>
<td>7.8</td>
</tr>
<tr>
<td>220</td>
<td>10.9</td>
</tr>
<tr>
<td>310</td>
<td>12.4</td>
</tr>
<tr>
<td>132</td>
<td>14.5</td>
</tr>
<tr>
<td>400</td>
<td>15.2</td>
</tr>
<tr>
<td>330</td>
<td>16.1</td>
</tr>
<tr>
<td>420</td>
<td>17.0</td>
</tr>
<tr>
<td>620</td>
<td>24.0</td>
</tr>
</tbody>
</table>

* Calculated assuming a tetragonal unit cell with \(a = b = 23.7\text{ Å}\).\(^{15}\)
transformation from tetragonal to hexagonal packing reported by Takeo and Kuge. The crystal structure of the IC crystals is the same as the pattern for the channel structure with hexagonal packing. The diffraction pattern of styrene-γ-CD-IC vacuum-dried for 24 h at 40 °C are summarized in Table 2. The crystallographic characteristics of hexagonally packed styrene-γ-CD-IC crystals are presented in Figure 5. The (200) plane at 2θ = 6.0° (observed) and at high (2θ = 230°) temperatures. This behavior was explained by supposing two different environments for styrene molecules in the host channels. Styrene molecules having weaker interactions with γ-CDs in the host channels are released at higher temperatures.

The tetragonal channel packing transforms to hexagonal packing upon removal of water residing in the interstitial sites between γ-CD stacks, which results in a more closely packed structure. It is also worth mentioning that the presence of guest molecules inside the γ-CD stacks facilitates the stabilization of the channel structure, which undergoes a solid-solid phase transition from tetragonal to hexagonal packing upon dehydration and not to an amorphous structure, which is the case for γ-CD-channel with no guest molecules included other than water.

It is also of interest to note that the solid-state transition of tetragonal to hexagonal packing is reversible. Figure 4c shows the diffraction pattern of vacuum-dried styrene-γ-CD-IC, which was stored at 100% humidity and room temperature for 51 h. The diffraction pattern is the same as before the vacuum drying, indicating that the transformation of hexagonal packing to tetragonal packing occurs upon hydration of the previously vacuum-dried styrene-γ-CD-IC crystals.

Time-dependent WAXD experiments were performed to track the phase transformation of hexagonal to tetragonal structure by hydration of previously vacuum-dried styrene-γ-CD-IC. The WAXD patterns collected for anhydrous styrene-γ-CD-IC (vacuum-dried) as a function of time subsequently stored at 100% humidity and room temperature are presented in Figure 5. It is clear that the (200) plane at 2θ = 7.5°, which is characteristic for tetragonal packing, gradually increases as the 2θ = 6.0° peak, which is characteristic for hexagonal packing, exhibits a gradual reduction in intensity over time. The peak at 2θ = 6.0° disappeared after 12 h, suggesting that the transformation from hexagonal to tetragonal packing is essentially complete after 12 h of hydration.

A sample of styrene-γ-CD-IC crystals underwent multiple cycles of dehydration/hydration by repeatedly vacuum drying at 40 °C and then storing at 100% humidity and room temperature. The solid-state transformation from tetragonal to hexagonal structure and from hexagonal to tetragonal structure is clearly reversible upon water desorption and sorption, respectively. Figure 6 shows the peak intensity changes for 2θ = 7.5° and 6.0°. The increase in peak intensity at 2θ = 7.5° and the decrease at 2θ = 6.0° are used to follow the kinetics of the transition. The peak at 2θ = 6.0° disappeared after 12 h of hydration for cycle 1 and after 6 h of hydration for cycles 2 and 3. Similarly, the maximum peak area at 2θ = 7.5° was reached in the shortest time in cycle 3, and sooner in cycle 2 than cycle 1, indicating that the transformation from hexagonal to tetragonal packing takes place much faster after repeated desorption-sorption cycles.

Water Vapor Sorption–Desorption Studies. To further understand the water vapor-induced phase transformation from hexagonal to tetragonal structure, complementary water vapor sorption kinetics experiments were carried out under the same conditions as the aforementioned X-ray studies. Figure 7 shows the equilibrium sample weight upon desorption via vacuum drying at 40 °C and resorption at 25 °C and at constant (2θ = 60°) peaks. The difference in the hydrated and dehydrated weights as a function of cycle number also show a continual reduction, with a rate that is reduced between cycles 2 and 3. This suggests that a constant difference in anhydrous and hydrate weight would occur after a sufficient number of cycles.

The weight losses, shown in Figure 7 as a function of cycle number, are potentially a result of some loosely bound styrene in the γ-CD cavities. In our previous study, we observed that the styrene-based products from the thermal degradation of the styrene-γ-CD-IC sample showed two maxima at low (40 °C) and at high (95 °C) temperatures. This behavior was explained by supposing two different environments for styrene molecules in the complex. Styrene molecules having weaker interactions with γ-CDs in the host channels are released at higher temperatures.
lower temperatures than those with stronger interactions with the host γ-CDs. It was also noted that the quantity of styrene released at low temperature was found to be very small, suggesting that most of the guest molecules have high stability in the γ-CD channels due to strong guest–host interactions. This was also confirmed by solution 1H NMR, where the styrene–γ-CD-IC that was vacuum dried for 24 h at 40 °C lost only 10 wt % of the total styrene in the as-formed, undried, fully hydrated complex.

Interval water sorption by styrene–γ-CD-IC was also performed. A vacuum-dried sample was allowed to sorb water vapor at 40 °C and at varying water activities. The shape of the sorption curve is similar to that of pure γ-CD in the cage structure.17 However, the sorption levels are slightly lower. Upon desorption, the equilibrium weight at approximately a = 0.1 is less than the initial weight. γ-CD typically exhibits similar equilibrium weight at low activities upon sorption and desorption.17 This means that styrene was lost during either the sorption or the desorption stages of the experiment or possibly during both. This correlates with the weight loss seen in the sorption–desorption data of Figure 7.

Hexagonal packing was also observed for toluene–, p-xylene–, benzene–, ethylbenzene–γ-CD-IC crystals upon dehydration, but not for aniline– and phenol–γ-CD-ICs. In the cases of the aniline– (Figure 8) and phenol–γ-CD-ICs (data not shown), the tetragonal packing structure was stable after vacuum drying at 40 °C for 24 h, and even after vacuum drying at 90 °C for 24 h. Phenol and aniline differ from the other aromatic guest molecules studied here, because of their ability to form intermolecular hydrogen bonds with γ-CD molecules. It has been shown in solution9,10 that the γ-CD cavity has a strong affinity for complexing with the phenyl ring due to strong hydrophobic interactions, while the hydroxyl in phenol or the amine group in aniline protrude from the γ-CD cavity. Therefore, hydrogen bonding between the amine group in aniline (or the hydroxyl group in phenol) and a hydroxyl group in a neighboring γ-CD molecule is possible. Hydrogen bonding of the included guest molecule with the neighboring γ-CD would connect γ-CD molecules along each γ-CD channel stack, thereby strengthening them and making the transformation from tetragonal to hexagonal packing unfavorable. We have also observed similar behavior for polymer–CD-IC crystals.14,22 Guest polymer chains included in the γ-CD channels make the γ-CD stacks rigid and prevent their rearrangement to hexagonal packing upon dehydration of the polymer–CD-IC samples.

Conclusions

The formation and characterization of channel structure solid inclusion compounds formed between the aromatic guests aniline, benzene, ethylbenzene, phenol, p-xylene, styrene, and toluene with host γ-CD have been described.1H NMR showed that both their inclusion complex formation and resulting complex stoichiometric ratios depend on the type of aromatic guest molecule included. It was found that the molar ratio of styrene, aniline, and phenol to γ-CD was ~2:1 in their individual IC crystals, whereas ethylbenzene, p-xylene, and toluene formed ~1:1 solid inclusion complexes with γ-CD. Thermal analysis showed that the thermal stability of these volatile guest molecules increased remarkably (much above their boiling points) once they were included in the host γ-CD cavities, likely the result of guest–host interactions.

X-ray diffraction (WAXD) experiments confirmed that all the aromatic guest–γ-CD-IC crystals have a channel-type crystalline structure. We observed that the presence of guest molecules inside the γ-CD cavity stabilized the channel packing of γ-CD stacks. However, a solid-phase transition from tetragonal to hexagonal packing of the host γ-CD stacks occurred upon dehydration of the γ-CD-IC crystals formed with styrene, toluene, p-xylene, benzene, and ethylbenzene guests. To our surprise, we found that the solid-state transformation from tetragonal to hexagonal packing and from hexagonal to tetragonal packing was reversible, when the samples were subjected to cycles of water desorption and sorption, respectively.

For aniline– and phenol–γ-CD-ICs, the tetragonal packing structure is apparently more stable, and no solid-phase transition from tetragonal to hexagonal packing was observed even after vacuum drying these samples at 90 °C for 24 h. Aniline and phenol differ from the other guest molecules in their ability to form intermolecular hydrogen bonds with γ-CD molecules. The stability of their tetragonal packing might be due to the presence of hydrogen bonding between the included guest molecules with neighboring γ-CD molecules in the same host γ-CD stack. That is, in the case of hydrogen bonding of the included guest molecule with neighboring γ-CDs, γ-CD molecules would be connected along each channel, resulting in rigid γ-CD stacks, thereby preventing their transformation from tetragonal to hexagonal packing.

Acknowledgment. The authors would like to thank the National Textile Center (U.S. Department of Commerce) and North Carolina State University for funding and support.
References