Controlling PVA Hydrogels with γ-Cyclodextrin

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ABSTRACT: We report on the preparation and characterization of poly(vinyl alcohol) (PVA) hydrogels formed during freeze−thaw (F−T) cycles of their aqueous solutions containing γ-cyclodextrin (γ-CD). Crystalline inclusion compound (IC) formation was observed between PVA and γ-CD in these gels at low concentrations of γ-CD (γ-CD:PVA molar ratios $<$ 1:25). Confirmation of the existence of the channel structure for γ-CD was achieved by characterizing the dried PVA/γ-CD hydrogels with solid-state DSC, TGA, WAXD, and ^{13}C NMR. Some aspects regarding the mechanism and structure of PVA gels obtained via F−T cycles in the presence/absence of γ-CD are presented based on UV−vis, swelling, solution ^{1}H NMR, and rheological observations. It was observed that the swelling and rheological responses of the aqueous PVA gels formed during F−T cycles in the presence of γ-CD can be controlled by adjustment of the PVA:γ-CD molar ratio employed during their gelation.

Introduction

Cyclodextrins (CDs) are cyclic starch oligomers consisting of 6, 7, and 8 units and named α-, β-, and γ-CD, respectively. The chemical structure of γ-CD and the approximate dimensions of α-, β-, and γ-CD are shown in Figure 1a,b.[1] The apolar nature of the cavities facilitates the ability of CDs to act as hosts for both nonpolar and polar guests, which include small molecules as well as polymers.[2,3]

The crystal structures of CD inclusion complexes are classified into three main types: "cage", "layer", and "channel" structures (Figure 1c−e). The cage-type structure is likely to be observed when the entire guest molecule is small enough to be included within a single CD cavity, whereas the channel-type crystalline structure is formed when long-chain molecules like polymers are included as guests in the cavities of CD molecules (Figure 1f). Additionally, we successfully obtained a solid-state channel-type packing of CDs (CD$_{\text{channel}}$), with just water molecules included in their narrow channel cavities, by appropriate recrystallization from their aqueous solutions.[4] We observed that both small molecules and polymers can be included inside these nanoscale channels simply by suspension of CD$_{\text{channel}}$ into the neat guest liquids or their solutions.[5,6] Mole ratios of host cyclodextrin to guest polymer depend on the length of the polymer's repeat unit and the number of chains that can occupy the CD channels.

The mechanism and kinetics of the inclusion process, especially in the case of hydrophilic guests, have not yet been completely elucidated. Normally polymer−CD ICs are formed in solution, often by mixing solutions of the guest polymer with aqueous solutions of the host CDs, followed by precipitation of the polymer−CD IC, wherein the host CDs are crystallized into stacked columns and the guest polymer chains are included in the narrow channels (~0.5−1.0 nm in diameter) of the CD stacks. Thus, the net process of forming polymer−CD ICs involves the removal of randomly coiling guest polymer chains from solution by threading them with CD, during which time they become isolated and are highly extended. At the same time the host CDs are also removed from solution as they thread the guest polymers and form stacks that pack together and crystallize into polymer−CD ICs.[7]

However, when the inclusion complex is water-soluble, it is necessary to seek new methodologies for the characterization of such compounds. Previous results in our group have shown that ^{1}H NMR allows the observation of the formation of an inclusion complex between poly(*N*-acylethylenimine), which is a water-soluble polymer, and solid suspended γ-CD.[8] In this paper, we try to characterize the inclusion complex formed between poly(vinyl alcohol) (PVA), a water-soluble polymer, and γ-CD. Solvents and nonsolvents for PVA and γ-CD are the same, so the isolation and characterization of pure, solid PVA−γ-CD inclusion complex are not possible by traditional methods.

Aqueous solutions of PVA can undergo gelation when submitted to a series of freeze−thaw (F−T) cycles. In the F−T process, crystallization of water results in the creation of interstitial domains with high polymer concentrations, where the PVA chains hydrogen bond and crystallize. The properties of the cryogels depend on the molecular weight of the polymer, the concentration of the aqueous PVA solution, the temperature and time of freezing and thawing, and the number of F−T cycles.[9−11]

In this work, we are interested in taking advantage of the F−T method to produce PVA hydrogels with γ-CD and to study the structure of the PVA−γ-CD IC that might be formed. Furthermore, we will determine the swelling and rheological properties of the PVA/γ-CD hydrogels and will establish the influence of the presence of γ-CD during the cyclic F−T process of PVA gelation.

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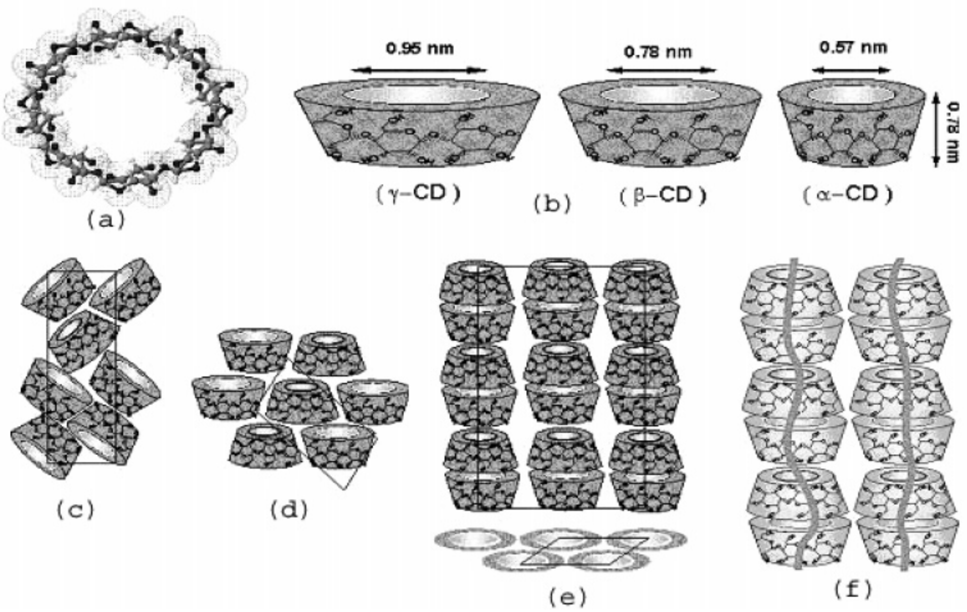

Figure 1. (a) γ-CD chemical structure; (b) approximate dimensions of α-CD, β-CD, and γ-CD; schematic representation of packing structures of (c) cage-type; (d) layer-type CD; and (e) head-to-tail channel-type CD crystals; (f) cyclodextrin inclusion compound (CD IC) channels with included polymer guests.

Table 1. Composition of Nascent PVA Gels

	PVA (mol)	γ-CD (mol)	PVA:γ-CD	%PVA (g/mL)
R1	0.09	0.0035	26:1	10
R2	0.09	0.0023	39.5:1	10
R3	0.09	0.0017	53.4:1	10

Experimental Section

Materials. Poly(vinyl alcohol), >99% hydrolyzed, with a weight-average molecular weight of 94 000 g/mol and a triad tacticity of syndio = 17.2, hetero = 54.1, and iso = 28.7%, was purchased from Aldrich and used without further purification. CDs were purchased from Cerestar Co.

PVA Gel Preparation. To a solution of polymer in water (polymer concentration 10% (g/mL)) vigorously stirred at 80 °C, different amounts of γ-CD were added. The mixtures were kept at 80 °C for 3 h and subsequently under moderate stirring at room temperature for 72 h. Turbid solutions were obtained after 72 h. The PVA solutions were poured into cylindrical molds (20 mm diameter, 2 mm thickness) and frozen by cooling to −20 °C for 30 min. After the freezing process, solutions were allowed to thaw at room temperature for 30 min. This process was repeated five times because fewer F−T cycles did not result in hard gels. We observed that the formation of PVA hydrogels in the presence of γ-CD through F−T cycles depended on the molar ratio between PVA and γ-CD. We could not obtain gels from aqueous solutions of PVA containing γ-CD with PVA:γ-CD molar ratios lower than 26:1. The composition of the obtained gels is shown in Table 1. The hydrogels obtained by this method are called nascent hydrogels. Films were obtained by simple drying of the nascent hydrogels at room temperature.

Characterization. *UV−Vis.* UV−vis spectra were recorded with a Cary-Varian Win UV spectrometer at room temperature. To a solution of PVA in water (polymer concentration 17.7 g/L) vigorously stirred at 50 °C, different amounts of γ-CD were added, but kept below the saturation degree of γ-CD in the PVA solutions (saturation degree of γ-CD in pure water is 23.2 g/100 mL at room temperature). The mixtures were kept at 50 °C for 3 h, and then they were transferred to the UV−vis cuvettes. The UV−vis absorbance measurement (at λ = 700 nm) of solution turbidity was started immediately after, and the reference sample was pure water.

Swelling. Nascent hydrogel samples were immersed in an excess of water at room temperature. At definite intervals of time, the samples were removed from water, and the excessive surface water was dried with filter paper. They were weighed until the hydrated gels reached a constant weight. The swelling ratio (Q_r) of the samples was defined as the ratio of the weight gain of the swollen sample to that of the nascent sample.

$$Q_r = \frac{(W_s - W_r)}{W_r} \tag{1}$$

where the swollen sample and the nascent sample weights are W_s and W_r, respectively.

Viscoelastic Properties. Dynamic viscoelastic measurements were performed in a TA Instruments AR1000 rheometer, using the parallel-plate shear mode to measure the storage modulus, G', the loss modulus, G'', and the loss tangent, tan δ. The operating conditions were the following: temperature sweep between 10 and 100° C, plate diameter 20 mm, frequency 1 Hz, temperature scan 10° C/min, and a torque of 50 μNm. The linear viscoelastic region was located with the aid of a torque sweep. We did not sweep the temperature at a lower rate because of enhanced water evaporation, which lead to results not as reproducible as those observed at 10 °C/min, and thermal equilibrium is assumed.

Differential Scanning Calorimetry (DSC). DSC experiments were performed with a Perkin-Elmer DSC7 under nitrogen purge gas. Indium was used as a standard for calibration. All samples studied in this work were subjected to heating and cooling cycles (unless otherwise specified), consisting of 1.0 min hold at 5 °C, ramp to 250 °C at 20 °C/min, hold at 250 °C for 1 min, and ramping to 5 °C at 20 °C/min. Samples were subjected to a second cycle to investigate any changes in thermal behavior following the first heat.

Thermogravimetric Analysis (TGA). Thermal analyses of the samples were performed with a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA). Thermal decomposition of the samples was recorded between 25 and 600 °C. The heating rate was 20 °C/min, and nitrogen was used as a purge gas.

X-ray Diffraction. Wide-angle X-ray diffraction patterns of PVA/γ-CD films were obtained at ambient conditions on a Phillips diffractometer with a nickel-filtered Cu Kα radiation source. Data were collected at a rate of $2\theta = 1°$/min over the range $2\theta = 5°-40°$.

Solid-State ^{13}C NMR. High-resolution solid-state ^{13}C NMR experiments were carried out at 50.1 MHz on a Chemagnetics CMX200 spectrometer using cross-polarization and magic

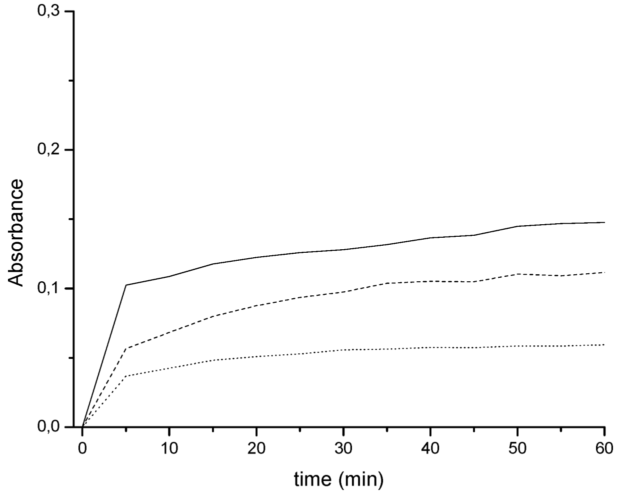

Figure 2. UV−vis experiments. Turbidity (absorbance at λ = 700 nm) vs time (minutes) as a function of PVA:γ-CD molar ratio. (—) 2.23:1.0, (- - -) 2.85:1.0, and (···) 4.0:1.0.

angle spinning (CP/MAS) with high-power proton dipolar decoupling (DD). The spinning speed ranged from 4 to 4.2 kHz. The spectra were obtained with 1000 transients, 1.0 ms contact time, and 3.0 s pulse delay. The spectral width was 15 kHz with 2K data points, which were zero-filled to 8K before Fourier transformation.

Solution ¹H NMR. ^{1}H NMR experiments were performed on D_2O solutions of PVA/γ-CD films that were obtained by drying nascent and swollen gels. A 300 MHz Inova spectrometer was used at room temperature, and the PVA: γ-CD molar ratios were obtained by comparing intensities of the PVA CH_2 protons at 1.5 ppm to that of the γ-CD H-1 proton at 4.9 ppm.

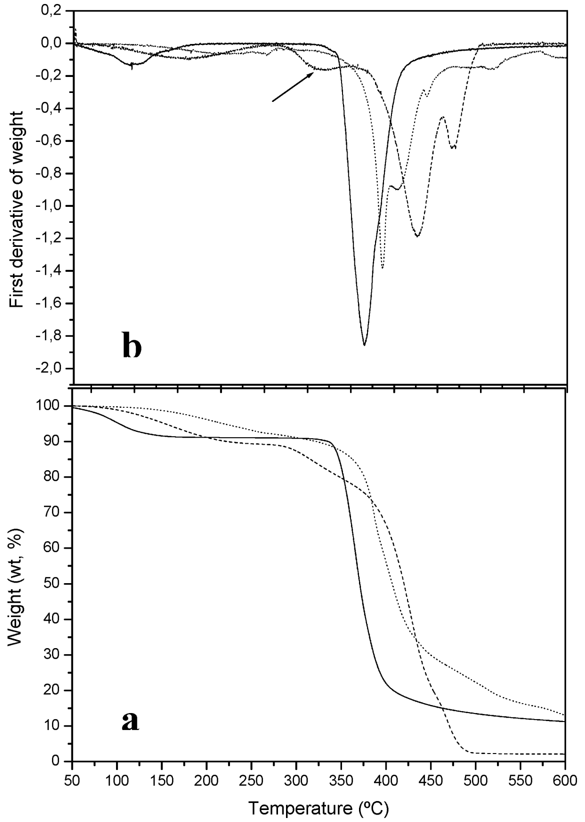

Figure 3. (a) TGA scans of samples. (b) First derivative of TGA weight loss. (—) γ-CD; (···) PVA/γ-CD (26:1); and (- - -) PVA 10% (g/mL).

Results and Discussion

When a defined amount of γ-CD was added to a PVA solution, it initially dissolved completely, but after a certain time the solution became progressively more turbid. This observation has already been reported in the literature[12] for aqueous solutions of α-CD and poly(ethylene glycol) (PEG), and it is presumably the end of a complex phenomenon that starts with the threading and sliding of α-CDs onto linear PEG chains and ends with the precipitation of large crystalline PEG−α-CD IC aggregates. In our case, the PVA/γ-CD solution also became more and more turbid with time, but we could not isolate any precipitate. [We also attempted to form an IC between PVA and α-CD, but without success, probably because the cavity dimensions (see Figure 1) of α-CD are too small to accommodate PVA chains.] However, the process of PVA complexation with γ-CD can be monitored by UV−vis experiments, whose results are shown in Figure 2. As can be seen there, all the solutions nearly reach a turbidity plateau in approximately 5 min for the three PVA/γ-CD molar ratios studied. Nevertheless, as the amount of γ-CD in the solution is increased, the absorbance achieved is higher. This could be an indication of the formation of a PVA−γ-CD IC. As the IC could not be isolated, we instead tried to characterize its structure through the analysis of dried films of the PVA hydrogels made in the presence of γ-CD.

The preparation of the PVA/γ-CD hydrogels is described in the Experimental Section, and Figure 3a shows the TGA scans for γ-CD, PVA/γ-CD film (26:1), and PVA film. We can see that the main decomposition of the PVA/γ-CD film (26:1) starts at 374 °C, which is intermediate between the decomposition temperatures of PVA (393 °C) and γ-CD (346 °C). This phenomenon of higher decomposition temperatures in polymer−CD ICs may imply that the polymer chains are included inside the polymer−CD IC channels and can improve the thermal stability of the host cyclodextrin. Furthermore, in Figure 3b we can observe that the transition located at $T \sim 300$ °C, which corresponds to the first stages of degradation and elimination of volatile products (mainly water)[13] in PVA films, is not present in PVA/γ-CD films. This also implies a change in the mechanism of degradation.

Since cyclodextrins and their ICs will decompose while melting, we only tested them below their melting temperatures in the DSC (below 250 °C). Figure 4c,d shows the DSC scans for a PVA film. It has a melting temperature of 205.7 °C during the first heating, and after cooling the sample at 20 °C/min, it shows a melting temperature of 226.5 °C during the second heating. Under the same testing conditions, we recorded the DSC curves for PVA/γ-CD films (Figure 4a,b). By comparing them, the decrease in the melting enthalpy and the melting temperature (217.9° C) can be explained because, though not all the PVA chains are included inside the channels of γ-CD, the included PVA chains are prevented from associating and crystallizing. A peak observed at 200.5 °C in the PVA-γ-CD films in the first heating scan, but which disappears in the second heating scan, may be due to a small amount of γ-CD that forms channel structure and contains only moisture.[4] After heating to 250 °C the moisture is evaporated, and this peak disappears in the second heating.

Figure 5 presents the wide angle X-ray diffractograms of (a) PVA film, (b) PVA/γ-CD (26:1) film, and (c) pure γ-CD. We may compare the known diffraction pattern

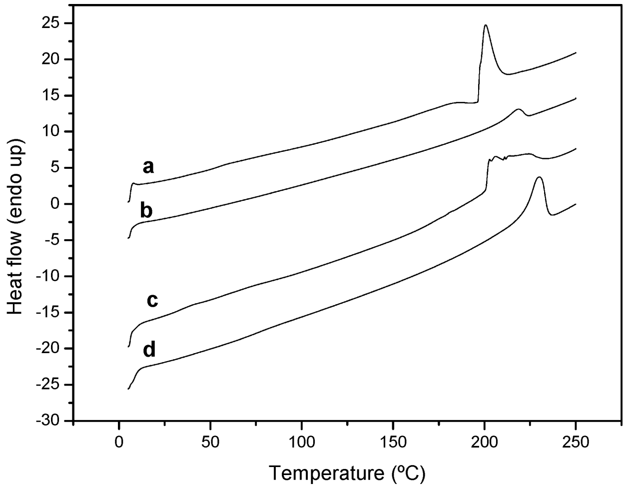

Figure 4. DSC thermograms for films of PVA/γ-CD (26:1), first (a) and second heating (b), and PVA 10% (g/mL), first (c) and second heating (d).

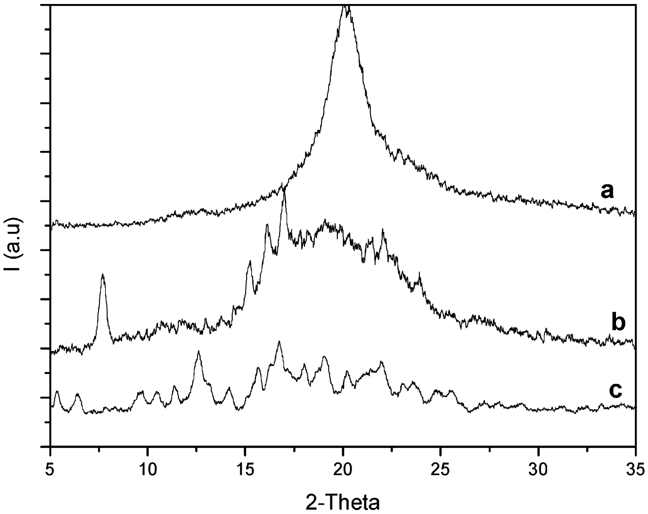

Figure 5. X-ray diffraction patterns for PVA 10% (g/mL) (a) and PVA/γ-CD (26:1) (b) films and pure γ-CD (c).

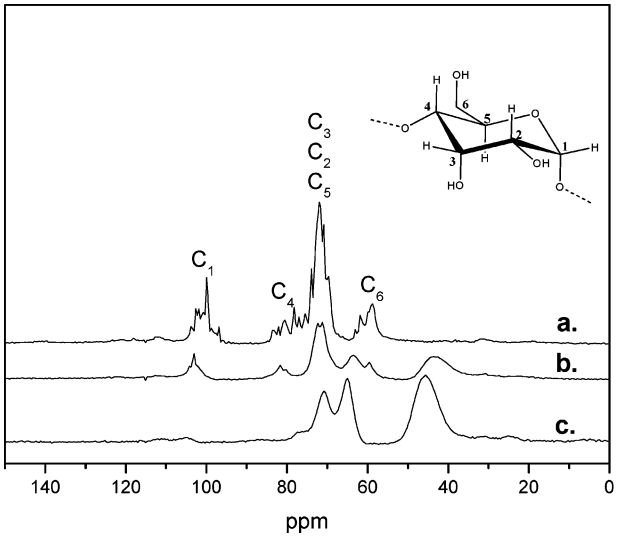

Figure 6. ^{13}C CP/MAS NMR spectra of γ-CD (a) and the PVA-γ-CD (26:1) (b) and PVA films 10% (g/mL) (c).

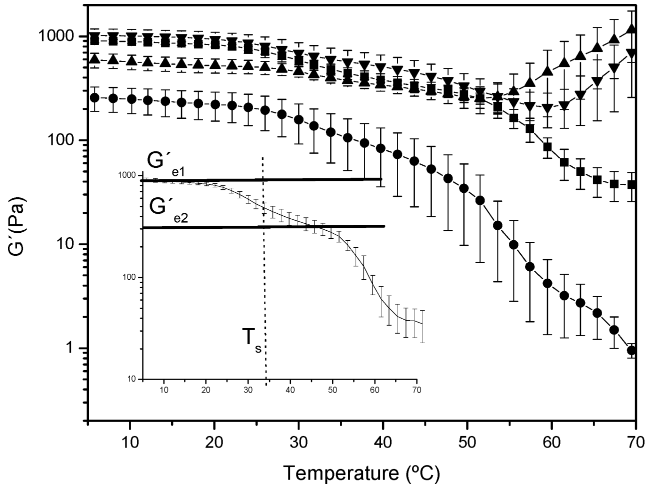

Figure 7. Storage modulus, G', vs temperature as a function of PVA:γ-CD molar ratio. (●) PVA 10% (g/mL); (●) PVA:γ-CD (26:1); (▲) PVA:γ-CD (39.5:1); (▼) PVA:γ-CD (53.4:1). Inset: typical spectrum of aged gels: PVA 10% (g/mL) hydrogel subjected to five freeze–thaw cycles.

of 1-propanol–γ-CD IC,[14] which has been identified from the structure of its single crystal to be of the channel form, with those of pure γ-CD and PVA and PVA/γ-CD films. The key feature that serves as a fingerprint for the channel-type structure of γ-CD ICs is the peak at about $2\theta = 8°$. As can be observed, this feature is not present in the pure γ-CD, which adopts a cage structure, but is observed in the PVA/γ-CD film. This strongly supports the inclusion of PVA chains within the cylindrical cavities of γ-CD and crystallization of the stacked host γ-CDs. Nevertheless, the γ-CD does not cover all the polymer chain as can be inferred from the presence of a broad diffraction peak at $2\theta = 20°$ that is characteristic for PVA films.[15]

The solid-state CP/MAS ^{13}C NMR spectra of free γ-CD (Figure 6a) shows splitting in several of the carbon resonances. This indicates that in the pure cage structure γ-CD crystals the bracelet of glucose rings is adopting rigid, nonsymmetric conformations.[1] As can be seen in the PVA/γ-CD (26:1) spectrum (Figure 6b), the carbon resonances that correspond to γ-CD show reduced splitting and are broadened. This is a good indicator[16] for the crystal–crystal (cage–channel) transition from pure γ-CD to PVA–CD IC. The γ-CD resonance peaks are broader in the inclusion complex, reflecting a more mobile, symmetric structure.[1] In the ^{13}C CP/MAS NMR spectrum of PVA in the solid state, the ^{13}C signal for the CH carbon shows three peaks (65–80 ppm), as is evident in Figure 6c. Terao et al.[17] explained such splitting by the number of intramolecular hydrogen bonds formed between neighboring hydroxyl groups. The most downfield peak (peak I), the central peak (peak II), and the most upfield peak (peak III) come from the CH carbons forming two hydrogen bonds, one hydrogen bond, and no hydrogen bonds with their hydroxyl groups, respectively.

Figure 7 presents the storage modulus (G') as a function of temperature for the nascent PVA hydrogels (10% g/mL) with different concentrations of γ-CD. As can be observed in the inset to this figure, all the samples present the response typical of aged gels.[18,19] It is possible to define the following parameters: G'_{e1} is the storage modulus at the first plateau (low temperatures), G'_{e2} is the storage modulus at the second plateau (medium temperatures), and T_s is the temperature at which transition from the first plateau to the second plateau takes place, with its value obtained from

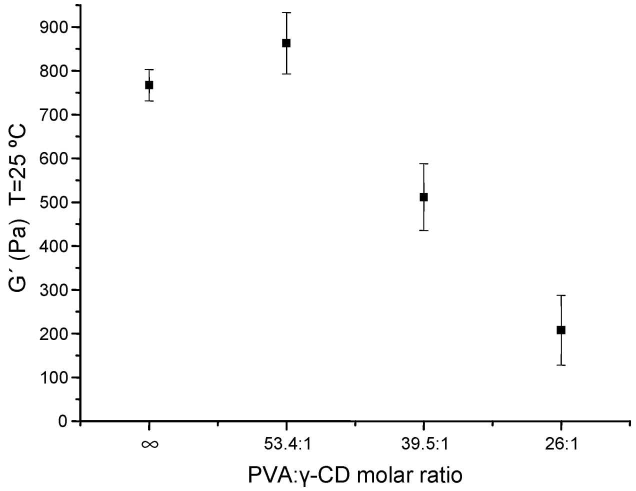

Figure 8. G' at $T = 25$ °C as a function of PVA:γ-CD molar ratio.

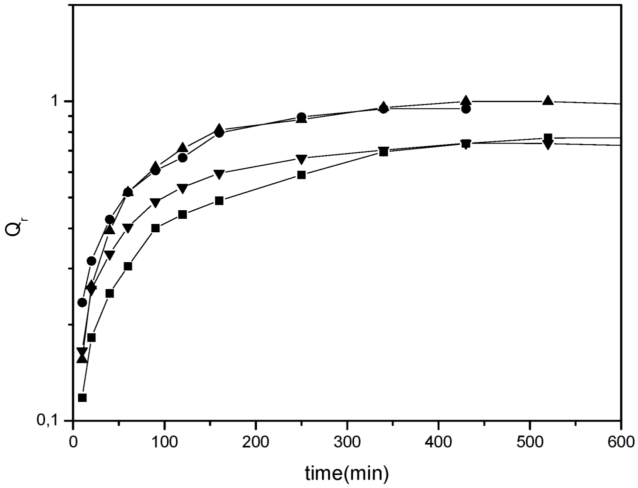

Figure 9. Swelling measurements of PVA−γ-CD hydrogels subjected to five freezing−thawing cycles as a function of time for different PVA:γ-CD molar ratios: (■) PVA 10% (g/mL); (●) PVA/γ-CD (26:1); (▲) PVA/γ-CD (39.5:1); and (▼) PVA/γ-CD (53.4:1).

the minimum of the first derivative. The evaporation of water starting from around 45 °C, which is indicated by a sudden observed increase in the modulus, prevents the observation of the evolution of the storage modulus beyond this temperature.

The representation of G' at $T = 25$ °C as a function of PVA:γ-CD molar ratio is shown in Figure 8. As can be seen there, PVA hydrogels with γ-CD formed during five F−T cycles present a lower G' than pure PVA hydrogels subjected to the same treatment. The value of G' is a function of the quantity of γ-CD present in the hydrogels. When the concentration of γ-CD increases, G' decreases.

Similarly, the swelling equilibrium achieved for PVA/γ-CD hydrogels is higher than that corresponding to the PVA gel without γ-CD, as can be observed in Figure 9. According to viscoelastic theories, the decrease in the modulus and the corresponding increase in swelling can be explained by a smaller number of cross-links. Thus, the presence of γ-CD in PVA hydrogels prevents their complete gelation during freeze−thaw cycles. This can be explained because of the threading of PVA chains by γ-CD, thereby isolating them and preventing their cooperative hydrogen bonds and crystallization, which limits the primary source of the physical cross-links in these gels.[20]

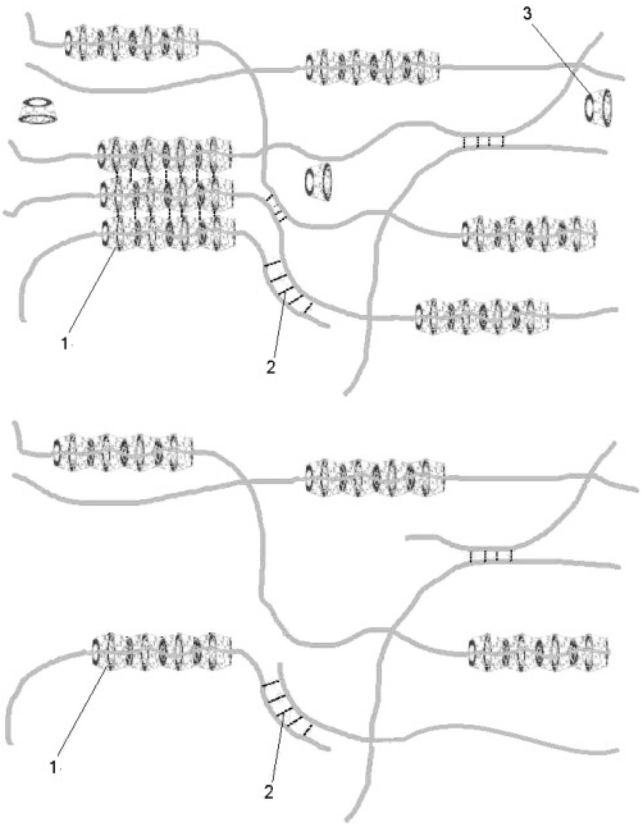

Figure 10. Schematic illustrations of the proposed structures of PVA/γ-CD dried films (upper) and swollen gels (lower) produced by F−T cycling: (1) channel structure of PVA−γ-CD IC, (2) hydrogen-bonded interactions/crystals/cross-links between PVA chains, and (3) free γ-CD molecules.

^{1}H NMR observations performed on the PVA/γ-CD hydrogels before and after swelling in D_2O revealed that ~30% of the γ-CD present in the nascent gels is removed after swelling reaches equilibrium (600 min, see Figure 9). Consequently, the swelling ratios, Q_r, obtained from eq 1 by simple weighing of the nascent and swollen gels do not seriously underestimate the net gain of water upon swelling. As an example, the 26:1 PVA/γ-CD nascent gel has a PVA:γ-CD weight ratio of 0.89:1.0, with PVA and γ-CD concentrations both ~0.1(g/mL) or roughly 10 wt %. A 30 mol % loss of γ-CD during the equilibrium swelling of this gel translates to an ~3 wt % (g/mL) loss in gel weight, which is small in comparison to the ~100% increase in the weight (W_s) of the PVA/γ-CD (26:1) hydrogel swollen to equilibrium (see Figure 9).

According to the experimental results presented in this paper, we have proposed structures for PVA gels formed in the presence of γ-CD, which are shown in Figure 10. As can be seen there, some small portions of the PVA polymer chains may be covered by γ-CD. Unlike the nascent (Figure 5) and swollen gels (not shown) observed as films after drying, WAXD observation of the PVA/γ-CD hydrogels show no evidence of crystallinity, so the γ-CD remaining after swelling the nascent PVA/γ-CD gels is only threaded on the PVA chains, as illustrated, or it is dissolved in the water and is removed from the gel upon swelling. In fact, ^{1}H NMR observations of the PVA/γ-CD hydrogels performed upon dissolution in D_2O indicated that most (~70%) of the γ-CD present in the nascent gels remains after swelling. The portions of the PVA chains that are not covered by γ-CD can presumably interact through PVA hydrogen bonds, leading to the formation of the PVA/γ-CD hydrogels via freeze−thaw cycling and subsequent swelling.

Whether relaxed or swollen, all of our PVA and PVA/γ-CD hydrogels were found to be soluble in D_2O, indicating an absence of the formation of chemical cross-links produced by the scission of PVA chains during their F−T preparation, which have been reported previously.[11] It is clear that the elasticities of the PVA and PVA/γ-CD hydrogels studied here are a result of the physical cross-linking of PVA chains.

Conclusions

We report for the first time high molecular weight polymer ICs formed between γ-CD and PVA by a heating technique and subsequent freeze−thaw cycling of PVA gels. DSC, TGA, WAXD, and ^{13}C NMR were used to observe the guest PVA chains included in the channels formed by stacks of host γ-CDs that crystallize upon drying of the gels. PVA−γ-CD IC could not be isolated from solution/gel, so UV−vis, swelling, and rheological measurements were employed to learn about its formation and the structures of the PVA gels formed in the presence of γ-CD. The PVA/γ-CD gels are weaker (lower G') and swell more (higher Q_r) than those formed without γ-CD. As a consequence, we have demonstrated that the structures and properties of PVA/γ-CD hydrogels may be controlled by adjusting the amount of γ-CD employed during their formation by the F−T cycling of their aqueous solutions.

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