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Polymerization of styrene in γ-cyclodextrin channels: Lightly rotaxanated polystyrenes with altered stereosequences

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Abstract

Modeling of polystyrene (PS) with various stereosequences in γ-cyclodextrin (γ-CD) channels has been conducted and it was found that only isotactic PS stereoisomers can fit into the γ-CD cavity. Thus, based on the modeling of stereoisomeric polystyrenes in narrow γ-CD channels, it was suggested that PSs with unusual microstructures might be produced *via* constrained polymerization of styrene monomer in its γ-CD-IC crystals. The *in situ* polymerization of styrene inside the narrow channels of its γ-CD-IC crystals suspended in aqueous media was performed. Alternatively, the solid-state polymerization of styrene/γ-CD-IC has also been conducted by exposure to γ-radiation. It was found that most host γ-CD molecules slip off during polymerization and the channel structure was not preserved. Consequently, much of the guest styrene monomer polymerizes outside of the host γ-CD channels, where the constrained environment is absent. Yet, a lightly rotaxanated structure has been obtained, where some threaded γ-CD molecules ~15 wt% (~1 γ-CD per 70 PS repeat units) are permanently entrapped along the PS chains after polymerization. ^{13}C NMR spectra of PSs synthesized from styrene/γ-CD-IC and homogeneously in toluene show some differences, which are presumably due to variations in the stereosequences of PSs obtained from the partially constrained polymerization of styrene/γ-CD-IC.

Keywords: Cyclodextrin; Inclusion compound; Polystyrene

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6, 7, and 8 units of α-1,4-linked glucopyranose, and are named alpha (α), beta (β), and gamma (γ)-CDs, respectively (Fig. 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]. Due to the unique chemical structure of CDs, their cavities are hydrophobic relative to their outer surfaces. The hydrophobic nature of the CD cavities facilitates their ability to act as host clathrates for both nonpolar and polar guests and to form inclusion complexes (ICs) [1]. 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 [2,3].

Solution or solid inclusion complexes of guest monomers, i.e., styrene [4,5], methyl methacrylate [4], pyrrole [6], bithiophene [7], aniline, [8] etc., with host CDs or modified CDs and their polymerization have been studied. In solution complexes, host CDs show the unique characteristic of complexing with water-insoluble hydrophobic guest monomers, which become water-soluble. Therefore, CDs were used to obtain complexes with various monomers in aqueous environments, and these complexed monomers were polymerized *via* free-radical initiation in aqueous media. It was reported that the resulting polymers were free of CD, precipitated rapidly in high yields, and the CDs slipped off step-by-step from the growing chain and thus remained in the water phase where they entrapped new monomers [5,6].

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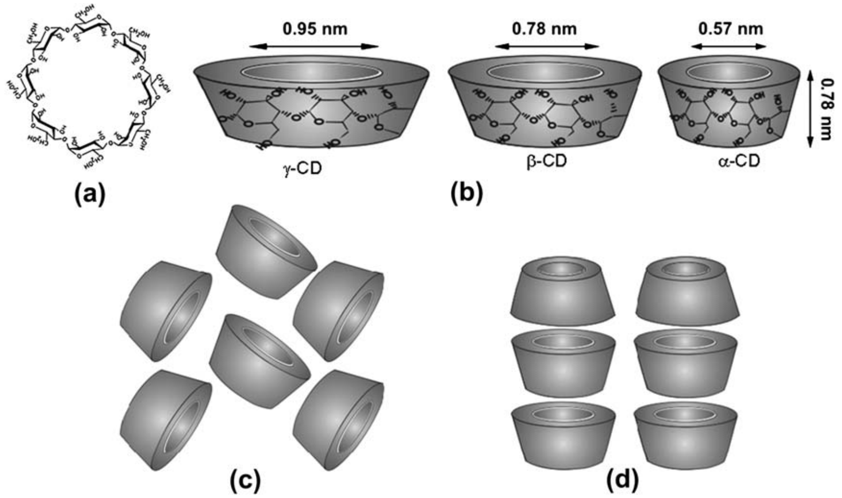

Fig. 1. (a) γ-CD chemical structure, (b) approximate dimensions of α-, β-, and γ-CDs, schematic representation of packing structures of (c) cage-type, and (d) head-to-head:tail-to-head:tail-to-tail channel-type γ-CD crystals.

In the case of solid monomer/CD complexes, the monomer resides in the CD cavities and can be polymerized either by solid-state polymerization or by suspending the crystals of monomer/CD inclusion compound in a solution where the inclusion compound is not soluble [4]. In order to obtain polymer, the CDs have to adopt continuous channel-type packing (Fig. 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 (Fig. 1c), since the monomers are entrapped in the CD cavities and are segregated from each other by the neighboring host CD molecules.

Recently, we have conducted molecular modeling of polystyrenes (PSs) with various stereosequences in narrow cylindrical channels corresponding to those found in γ-cyclodextrin inclusion compounds (γ-CD-ICs) [9]. Isotactic PS (i-PS) was found to fit in channels with narrower diameters than syndiotactic PS (s-PS), while atactic PS (a-PS) could be included in channels with diameters intermediate to those of i-PS and s-PS.

Here, we have performed further molecular modeling of stereoisomeric polystyrenes in γ-CD channels, utilizing quantum mechanical methods. The calculations were performed in MOPAC using PM3 parameters, with the MOZYME algorithm implemented in the CAChe WorkSystem 6.1.12.33, on i-, s-, and a-PS tetrads (*mmm*, *m* = *meso diad*; *rrr*, *r* = *racemic diad*; and *mrm*, *mmr*, *rmr*, *rrm*). Unlike the previous modeling [9], where the PS stereoisomeric tetrads were allowed to adopt all energetically allowable conformations, here all the distances between the carbon atoms attached to the phenyl ring and the backbone carbons were locked. This was done to prevent the i-PS segment from relaxing into conformations other than the fully extended all *trans* conformation, which the previous modeling [9] indicated to have the narrowest cross-section. It was found that i-PS segments (tetrad) can fit inside the γ-CD cavity, and Fig. 2a and b shows the equilibrium molecular geometry of the i-PS tetrad before and after inclusion in the γ-CD channel. On the other hand, identical molecular modeling of s-PS (Fig. 2c) and a-PS showed that they do not spatially fit inside the γ-CD cavity. The molecular cross-sections of fully extended a-PS and s-PS tetrad fragments were found to be wider than the interior diameter of γ-CD, making it impossible for them to thread into the γ-CD cavity. Fig. 2d shows the representation of the collision between the hydrogen atoms of the fully extended all *trans* s-PS tetrad fragment and the hydrogens of the γ-CD channel structure. The molecular modeling data of PS in γ-CD cavities were consistent with our experimental observations. All our attempts to form inclusion compounds of a-PS and s-PS with γ-CD failed, and we were unable to obtain PS/γ-CD-ICs. According to our modeling, it was expected that γ-CD could form an IC with i-PS. Therefore, we also attempted to form the γ-CD-IC with i-PS (90% isotactic, Aldrich), but again we were not able to obtain i-PS/γ-CD-IC. This may be due to the presence of 10% irregular stereosequences (*racemic diads*) in these polymer chains, which could prevent IC formation, since the γ-CD molecules appear only to be able to thread onto the all *meso* i-PS.

Thus, based on the modeling of stereoisomeric polystyrenes (PSs) in narrow γ-CD channels, it was suggested [9], and confirmed here, that polystyrene with unusual microstructures might be produced *via* constrained polymerization of styrene monomer in its γ-CD-IC crystals, as was described in a preliminary report [4]. Consequently, here we present the details of the polymerizations of styrene monomer in its channel structure inclusion compound formed with γ-CD, as well as the characterization of the resulting PSs.

2. Experimental

2.1. Formation of styrene/cyclodextrin inclusion compounds

Two different approaches can be followed to form styrene/γ-CD inclusion compounds (styrene/γ-$\mathrm{CD}_{\mathrm{channel}}$-ICs), where the resulting γ-CD-IC has a channel packing structure (see

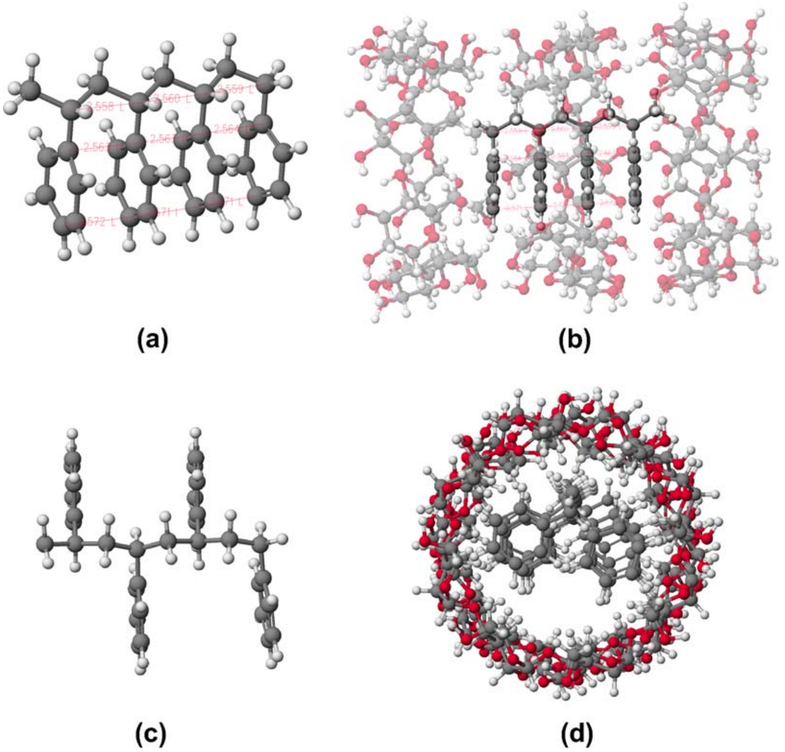

Fig. 2. (a) Molecular geometry of the isotactic PS tetrad, (b) i-PS/γ-CD-IC, (c) molecular geometry of the s-PS tetrad, and (d) representation of the collision between the hydrogen atoms of s-PS and γ-CD. (Note that in (d) a s-PS decad stereosequence is shown.).

Fig. 1d). The first approach is a "suspension" method in which preformed [10] γ-$CD_{channel}$ crystals containing only water of hydration are suspended into neat styrene to form the inclusion compound [4]. In the case of the suspension method, we have found that only the preformed γ-$CD_{channel}$ crystals, and not as-received cage structure γ-CD crystals, form styrene/γ-$CD_{channel}$-ICs when suspended in neat styrene. The second approach is a "precipitation" method, which is comparatively more convenient. In this method, styrene is added directly to an unsaturated γ-CD aqueous solution and precipitation occurs as the guest styrene molecules form the IC with host γ-CD molecules, resulting in styrene/γ-CD-IC having a channel structure [2].

2.2. Polymerization of styrene/γ-$CD_{channel}$-IC

The polymerization of styrene/γ-$CD_{channel}$-IC was performed in two ways; solid-state polymerization by exposure to γ-radiation and by suspension/solution polymerization in aqueous medium. In the former instance, styrene/γ-$CD_{channel}$-IC crystals were placed under a γ-radiation source (^{60}Co) for 240 h with a total dose of 2.1 Mrad. ^{1}H NMR confirmed the polymerization of styrene and the conversion of monomer to polymer was about 50%.

In the suspension/solution polymerization, styrene/γ-$CD_{channel}$-IC crystals were suspended in deionized water and polymerized by adding free-radical initiator under argon atmosphere for 24 h. Water-soluble free-radical, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (5% molar) at 60 °C, or redox $K_2S_2O_8/NaHSO_3$ (5% molar) at room temperature, initiators were used. The polymerization was terminated either with 10% w/w quencher (4-methoxy phenol) or by placing the reaction flask in an ice bath.

The usual homogeneous free-radical polymerizations of styrene were also performed in toluene solution in the presence or absence of as-received γ-CD_{cage} and were initiated with 2,2′-azoisobutyronitrile (AIBN) to produce control samples for comparison. Additionally, styrene/γ-$CD_{channel}$-IC was suspended in toluene instead of water, and the polymerization was carried out under the same conditions to provide another control sample. It was found that styrene monomer migrates from the γ-CD channels and polymerizes outside of the channels when toluene (organic solvent) was used, and the resulting polystyrene did not contain any γ-CD. It was found that the molecular weight (MW) of the PS synthesized in the γ-CD channels (aqueous medium) is higher ($M_n = 10{,}900$ g/mol, $M_w = 59{,}000$ g/mol, PDI = 5.43) than the PSs synthesized in toluene, either in the presence ($M_n = 2600$ g/mol, $M_w = 5000$ g/mol, PDI = 1.92) or absence ($M_n = 2300$ g/mol, $M_w = 3600$ g/mol, PDI = 1.57) of γ-CD, along with a higher polydispersity index (PDI) [4].

2.3. Characterization of styrene/γ-$CD_{channel}$-IC and polystyrenes

2.3.1. Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) measurements were performed with a Siemens type-F X-ray diffractometer using a Ni-filtered Cu Kα radiation source ($\lambda = 1.54$ Å). The supplied voltage and current were 30 kV and 20 mA, respectively. The white powder of styrene/γ-$CD_{channel}$-IC and rotaxanated PS/CD-IC samples were placed in the diffractometer to obtain diffractograms and the diffraction intensities were measured every 0.1° from $2\theta = 5-30°$ at a rate of $2\theta = 3°$/min.

2.3.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments were performed with a Perkin–Elmer DSC-7 instrument 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 and ramping to the target temperature at a rate of 20 °C/min, and quenching at a cooling rate of 200 °C/min, followed by a second heating cycle.

2.3.3. Thermogravimetric analyses (TGA)

Thermogravimetric analyses (TGA) of the samples were performed with a Perkin–Elmer Pyris 1 thermogravimetric analyzer. Thermal decompositions were recorded between 25 and 550 °C. The heating rate was 20 °C/min and nitrogen was used as a purge gas.

2.3.4. Fourier transform infrared spectroscopy (FT-IR)

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

2.3.5. Gel permeation chromatography (GPC)

Molecular weights and molecular weight distributions of polystyrene samples were measured via gel permeation chromatography (GPC) using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector under a flow rate of 1 mL/min at room temperature on two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are reported to be relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.).

2.3.6. Nuclear magnetic resonance (NMR)

One and two-dimensional (1D and 2D) ^1H and ^{13}C NMR experiments were performed on Bruker Avance 500 MHz and Varian Mercury 400 MHz spectrometers, respectively. One dimensional ^1H data sets contained 16K data points and sufficient scans were collected to obtain good *S/N*. γ-CDs were either suspended in acetone solutions of styrene or styrene was added to solutions of γ-CD in D_2O. PSs were dissolved in *o*-dichlorobenzene-d_4, DMSO-d_6, or DMSO-d_6/*o*-dichlorobenzene-d_4, and tetramethylsilane (TMS) was used as the internal standard.

2D-^1H NOESY spectra were acquired using the phase-sensitive TPPI (time proportional phase incrementation) pulse sequence, with three mixing times of 50, 350, and 500 ms and a recycle delay of 3 s. Data sets with 2048 complex points in t_2 and 512 complex points in t_1 were acquired with a 6000 Hz sweep width in both dimensions and 128 scans per slice. All spectra were processed with a combination of exponential weighting and sine-skewed functions and were zero-filled to yield 2k × 2k data points, using Bruker XWINNMR software. Two samples were observed: a physical mixture of PS/γ-CD and a coalesced PS/γ-CD-IC both dissolved in a mixture of DMSO-d_6 and *o*-dichlorobenzene-d_4. Though 2D-^1H ROESY spectra were also recorded for both PS/CD samples, the ROESY spectrum of coalesced PS/γ-CD-IC was of low resolution with a smeared appearance, making its interpretation difficult. Apparently during the spin-locking period, transverse cross-relaxation of proton spins is not the only significant interaction taking place.

The observation frequency of ^{13}C NMR was 100.625 MHz, with broadband proton decoupling at 400.137 MHz, and the $\pi/4$ pulse width was 4.95 μs. A variable temperature probe was employed for observations in *o*-dichlorobenzene-d_4 at 120 °C. The number of transients recorded was 12,000, and the total run time was about 8.5 h.

3. Results and discussion

3.1. Formation of styrene/γ-$CD_{channel}$-IC

A kinetic study was performed by suspending as-received CDs (cage structure α-, β-, and γ-CDs) and the channel crystalline structure of γ-CD (γ-$CD_{channel}$) [10] in solutions of styrene in deuterated acetone, where the insoluble γ-CD crystals settled on the bottom of the NMR tube. γ-$CD_{channel}$ crystals and their included guests, H_2O or styrene, are transparent to solution ^1H NMR. Subsequently, the decrease in intensity of styrene peaks and the increase in intensity of the H_2O peak were recorded as a function of time as the styrene displaced H_2O from the γ-CD cavities during the inclusion and complexation processes. It was observed that the styrene/acetone peak ratio decreases as a function of time when γ-$CD_{channel}$ crystals were suspended in the styrene/acetone solution. From its solution, the styrene monomer enters the channels of the γ-$CD_{channel}$ crystals, where it is not visible by ^1H NMR, confirming the inclusion process of styrene monomer into γ-$CD_{channel}$ to form styrene/γ-$CD_{channel}$-IC. No change in the styrene/acetone peak ratio was observed in the cases of α-CD_{cage}, β-CD_{cage} or γ-CD_{cage} (Fig. 3), the latter somewhat to our surprise [11]. Thus, styrene did not form inclusion compounds with as-received α-, β-, or γ-CD "cage type" crystals, when suspended in styrene solution, or even when suspended in pure styrene monomer.

The inclusion complexation of styrene with various CDs (α-, β-, methylated β- or γ-CD) has been reported when styrene was added to these CD solutions to form soluble inclusion complexes [5,12]. However, in the case of solid CD crystals, we observed styrene molecules not to be included in CD cavities except for γ-$CD_{channel}$. This result is likely a consequence [1] of the fact that γ-CD, unlike α- and β-CDs, crystallizes only in the γ-$CD_{channel}$ structure when forming an IC with any guest except water.

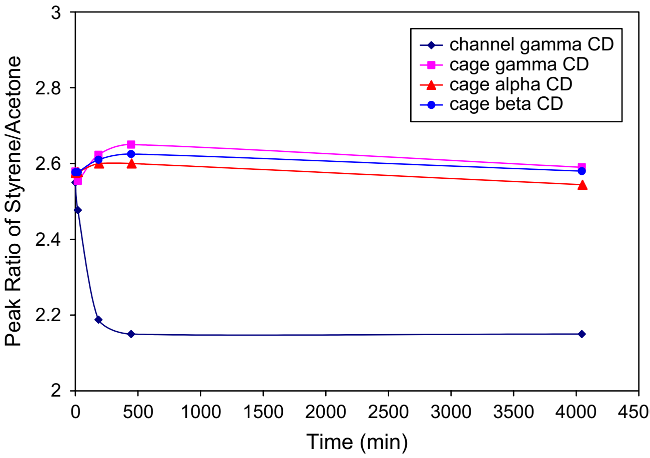

Fig. 3. The variation of ^1H NMR peak intensity of styrene relative to the solvent peak (acetone) in the suspensions of α-CD_{cage}, β-CD_{cage}, γ-CD_{cage}, and γ-$CD_{channel}$.

We have also studied the kinetics of the "precipitation" method [2], where the inclusion complexation of styrene with γ-CD was monitored by ^1H NMR. An unsaturated γ-CD solution was prepared in an NMR tube using deuterated water (D_2O). Then, styrene was added to the γ-CD solution. The clear γ-CD solution became turbid and a white precipitate formed immediately after the addition of styrene, which indicated the formation of the styrene/γ-CD-IC crystals. It was observed that the γ-CD molecules disappeared from the solution as they form insoluble styrene/γ-CD-IC crystals. The decrease in intensity of γ-CD peaks and the increase in intensity of the H_2O peak were recorded as a function of time as the styrene displaces H_2O from the γ-CD cavities during the inclusion process. It is clear from the overlay NMR spectra in Fig. 4 that γ-CD peaks have disappeared ~1 h after mixing, suggesting that almost all the γ-CD molecules were complexed with styrene and form insoluble IC crystals.

3.2. Stability of styrene/γ-$CD_{channel}$-IC crystals in aqueous medium

The stability of styrene/γ-$CD_{channel}$-IC crystals under the polymerization conditions used here was studied. γ-CD is soluble in water [1] (23 g/100 mL), however, once CDs form inclusion complexes with guest molecules, their solubility decreases significantly. Here, we studied the stability of the γ-CD channels containing included styrene suspended in aqueous medium at different temperatures. One gram of styrene/γ-$CD_{channel}$-IC crystals was suspended in 10 mL of water and stirred for 24 h at room temperature. At the end of this time, about 80% (0.8 g) of styrene/γ-CD-IC crystals were collected showing that only 20% became soluble and passed through the filter during filtration. X-ray study showed that the channel structure for styrene/γ-CD-IC was preserved, confirming its stability in aqueous medium.

The same procedure was applied to styrene/γ-$CD_{channel}$-IC crystals at a higher temperature (60 °C). This time, a 40% weight loss was observed, indicating that more γ-CD molecules became soluble at higher temperature, but again, the channel structure of styrene/γ-CD-IC was preserved. This stability experiment showed that the polymerization of styrene can be potentially performed inside the γ-CD channels (confined environment) in aqueous medium at room temperature or even at higher temperatures. Therefore, we repeated the same procedure by suspending styrene/γ-$CD_{channel}$-IC crystals in aqueous medium and added a water-soluble initiator for polymerization. To our surprise, we obtained about 0.1 g of powder (90% weight loss) at the end of 24 h of polymerization, which indicates that most γ-CD molecules are freed during polymerization and therefore become soluble in water.

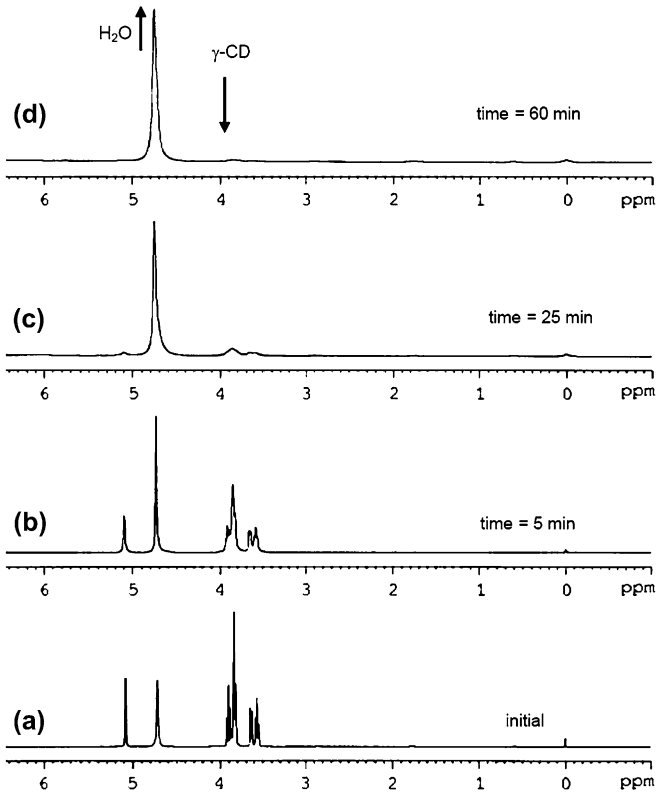

Fig. 4. Overlay of ^1H NMR spectra of (a) γ-CD solution in D_2O, (b) 5, (c) 25, and (d) 60 min after the addition of styrene to γ-CD in aqueous solution.

In the end, we obtained a lightly rotaxanated polystyrene/γ-CD structure, where some γ-CD molecules (~1 γ-CD/70 PS repeat units) were threaded and entrapped along the PS chains after the polymerization. Though not presented here, X-ray diffraction showed that the resulting polyrotaxane (PS lightly rotaxanated by γ-CD) has an amorphous structure.

3.3. Characterization of PSs obtained by polymerization of styrene/γ-CD-IC

The polymerization of styrene/γ-$CD_{channel}$-IC was performed by both solid-state polymerization and suspension/solution polymerization in aqueous medium. The resulting polystyrene/γ-cyclodextrin inclusion compounds (PS/γ-CD-IC) were washed with an excess of hot water at 80 °C for

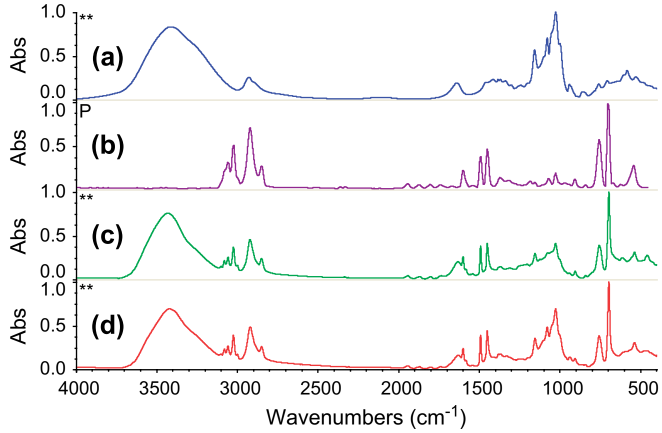

Fig. 5. FT-IR overlay of (a) γ-CD, (b) polystyrene, (c) PS/γ-CD-IC obtained by suspension/solution polymerization, and (d) PS/γ-CD-IC obtained by solid-state polymerization.

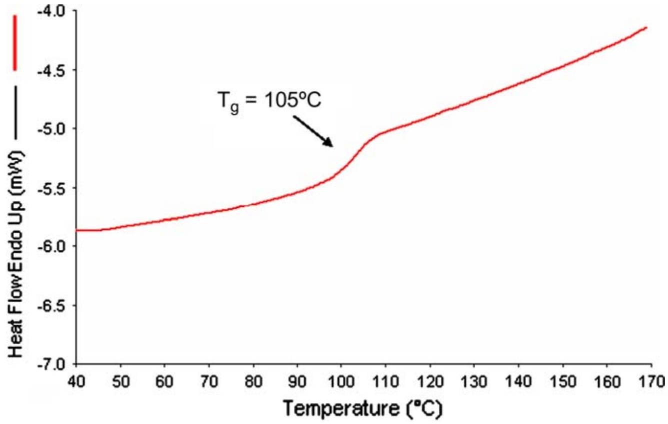

Fig. 7. DSC 2nd heating scan of PS obtained by solid-state polymerization of styrene/γ-CD-IC.

24 h to remove the γ-CD from the PS. The removal of CDs from polymer/CD-ICs with hot water (coalescence process) is a technique that we have applied to obtain coalesced polymers essentially free of CD [13]. However, in the present case we repeatedly applied the hot water coalescence process to the PS/γ-CD-IC, but we were unable to completely remove the γ-CD from the PS. Fig. 5 shows the FT-IR spectra of PSs obtained by solid-state and solution polymerizations of styrene/γ-CD-IC, and the FT-IR spectra of pure polystyrene and pure γ-CD are also given for comparison. Both samples were repeatedly washed with hot water to remove γ-CD, but it was found that both samples still contain γ-CD molecules. Thermogravimetric analyses showed that the samples contained ~15 wt% γ-CD, or ~1 γ-CD/70 PS repeat units (see Fig. 6).

A glass transition temperature (T_g) of 105 °C was observed for this PS (see Fig. 7). We know that polymer/CD-ICs usually do not show T_gs in their DSC scans if the polymer chains are fully covered by the host CD molecules [13]. Here, the observation of a T_g for PS containing a small amount of threaded γ-CD indicated that PS chains were only partially covered by γ-CD molecules. We also ran an X-ray diffraction scan for this PS (data not shown), which was found to be amorphous, suggesting that the entrapped γ-CDs are widely separated and therefore do not crystallize.

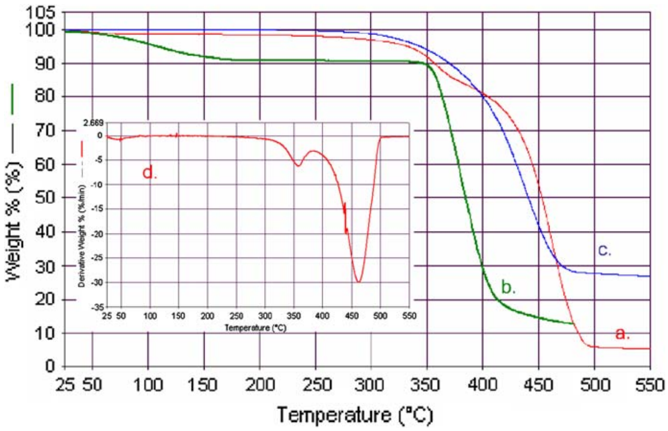

Fig. 6. TGA overlay of (a) PS/γ-CD-IC obtained by solid-state polymerization, (b) γ-CD, (c) polystyrene, and (d) derivative weight percent loss of PS/γ-CD-IC.

The results of two-dimensional ^{1}H NMR NOESY observations performed on the solutions of the lightly rotaxanated PS obtained by polymerization of styrene/γ-CD$_{\text{channel}}$-IC and PS and γ-CD dissolved in the same concentrations (~1γ-CD/70 PS repeat units) are presented in Fig. 8. In the PS/γ-CD-IC spectrum (Fig. 8a), cross-peaks between both the aromatic (~6.8–7.6 ppm) and aliphatic (~1.2–2.6 ppm) PS protons and the γ-CD (~3.4–4.1 ppm) protons are clearly evident and indicate that they are closer than ~3.5 Å. However, for the physical mixture of PS and γ-CD, no cross-peaks between PS and γ-CD protons can be seen in the spectrum (Fig. 8b). This comparison provides strong confirmation for partially threaded and trapped γ-CDs on the backbone of PS obtained by polymerization of styrene/γ-CD-IC, resulting in a permanently and lightly rotaxanated structure for the PS.

Solid-state ^{13}C NMR observations not presented here also indicate [10,13] rotaxanation of PS by γ-CD, because the splitting observed for γ-CD resonances in the physical mixture with PS, where unthreaded γ-CD is crystallized in its cage structure (see Fig. 1c), is absent in the PS obtained by polymerization of styrene/γ-CD-IC, where γ-CD is threaded by PS.

Based on our modeling, we expected to obtain polystyrene that is predominantly isotactic when styrene was polymerized inside the γ-CD channels, since only isotactic stereosequences can fit in the narrow cavity of γ-CD. We have preliminarily examined the microstructures of the PS samples by ^{13}C NMR. The ^{13}C NMR spectra of PS synthesized from styrene in the channels of γ-CD were compared with that of the PS sample homogeneously polymerized in toluene (Fig. 9). For the PS samples synthesized in the γ-CD channels (Fig. 9b and c), the most up-field aromatic C-1 peaks, which are due to syndiotactic stereosequences (*..rr..*, where *r* = *racemic diad*) [14,15], are reduced somewhat in intensity compared

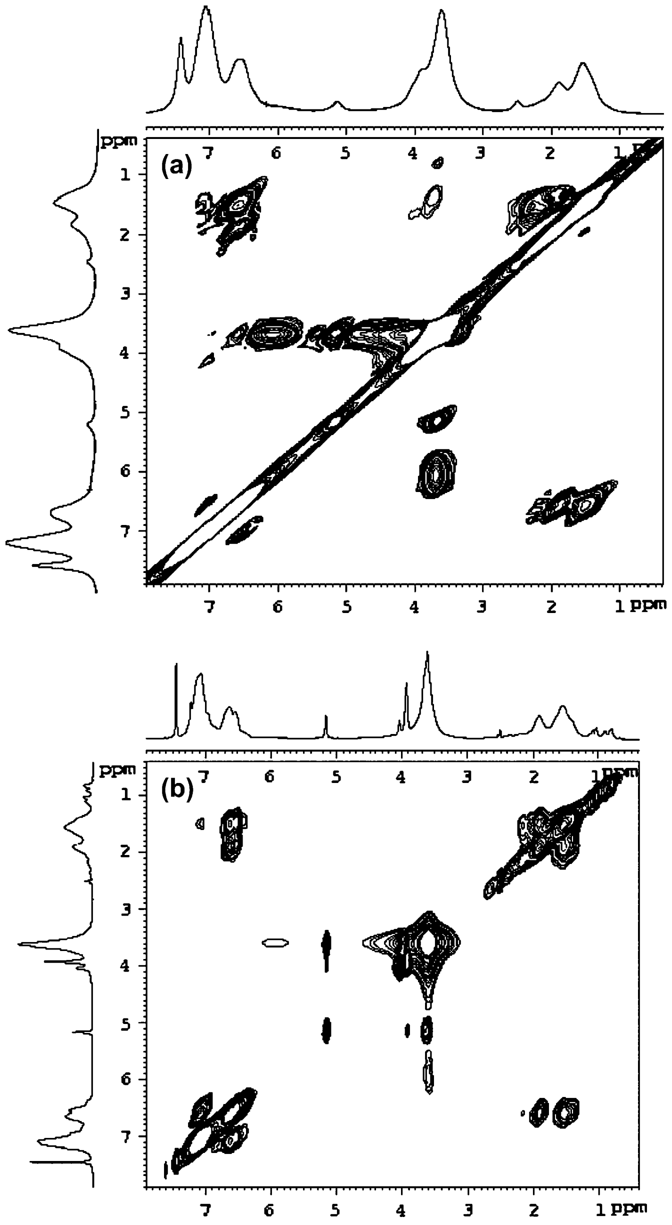

Fig. 8. 2D NOESY ^{1}H NMR solution spectra in DMSO-d_6/*o*-dichlorobenzene-d_4 at 25 °C of (a) PS polymerized in styrene/γ-CD-IC, with a mixing time of 50 ms and (b) a mixture of PS and γ-CD, with a mixing time of 350 ms.

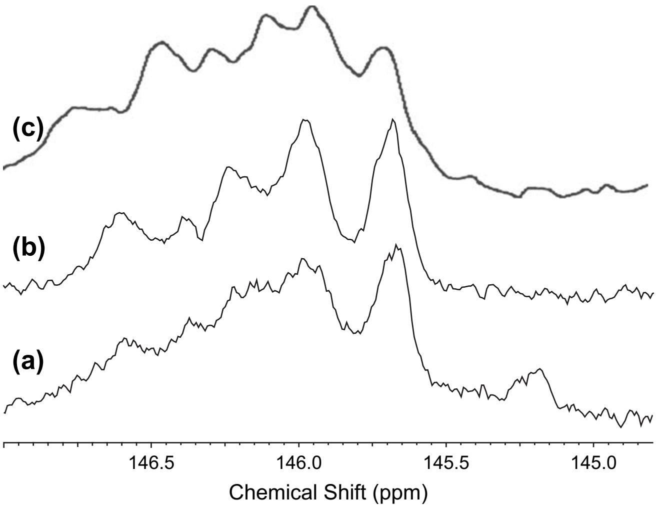

Fig. 9. ^{13}C NMR of aromatic C-1 region of PSs at 120 °C. *d-o*-dichlorobenzene and a mixture of *o*-dichlorobenzene-d_4/DMSO-d_6 were used as solvents for polystyrene and PS/γ-CD-IC, respectively: (a) PS synthesized in toluene, AIBN, 24 h, 60 °C, (b) PS/γ-CD-IC obtained by suspension/solution polymerization, and (c) PS/γ-CD-IC obtained by solid-state polymerization.

with the most downfield peaks, which are due to isotactic stereosequences (*..mm..*) [14,15], when compared to the PS homogeneously polymerized in toluene (Fig. 9a). In this comparison [16] we have ignored the small group of resonances observed in Fig. 9a between ~145.0 and 145.3 ppm, which are likely to be contributed by terminal styrene repeat units in this low molecular weight solution polymerized PS sample [4].

Other anticipated differences [4,9] for the stereosequences of PSs polymerized in the narrow (~1 nm) γ-CD channels are not prominently noticeable. This may be due to the lack of or failure to fully retain the confined environment when γ-CD molecules begin to slip off during polymerization, thereby producing a largely atactic PS, but with an enhanced content of short isotactic stereosequences (*..mm..*) rotaxanated with γ-CDs and reduced quantities of syndiotactic stereosequences (*..rr..*). Two styrene monomers are initially included in each γ-CD in the styrene/γ-CD$_{\text{channel}}$-IC [2b], while three PS repeat units are expected to reside in each γ-CD in the resulting PS/γ-CD$_{\text{channel}}$-IC following polymerization. Thus, it may not be surprising that some γ-CDs in the styrene/γ-CD$_{\text{channel}}$-IC dissolve when one or both of their included styrene guests migrate to and are polymerized on included and growing PS chains. Additionally, both the solid-state and suspension/solution polymerizations of styrene/γ-CD$_{\text{channel}}$-IC produced PSs with similar stereosequences, indicating that the polymerization method employed with styrene/γ-CD$_{\text{channel}}$-IC was not a major factor.

In summary, these results suggest that when styrene/γ-CD$_{\text{channel}}$-IC was polymerized a lightly rotaxanated structure was obtained with a few γ-CD molecules permanently entrapped along each PS chain. It is likely that γ-CD molecules are threaded by and entrapped upon short isotactic stereosequences, since only isotactic stereosequences can fit into the γ-CD cavity. The lightly rotaxanated structure is a consequence of their likely termination by *racemic diads*, which prevent the γ-CDs from slipping off the polystyrene chain. The trapping of γ-CDs on the PS chains may at least partially result from the disparity between the stoichiometries of styrene/and PS/γ-CD-ICs, where 2 guest styrenes [2] and three guest-PS repeat units (see Fig. 2b) are included in each γ-CD, respectively.

We are beginning to study the behavior of PS lightly rotaxanated with γ-CDs obtained here by polymerization of styrene/γ-CD$_{\text{channel}}$-IC. In particular the comparison of the dynamics of free atactic PS chains, both in solution and the bulk, with those exhibited by PS chains lightly rotaxanated and threaded by bulky γ-CDs should prove to be interesting and informative. Also it should be possible to readily cross-link the lightly rotaxanated PS through the reactivities of the −OH groups on the threaded γ-CDs, using, for example, a diacidchloride. A recent example of cross-linking rotaxanated polymers has appeared [17] and demonstrated several advantages of this approach.

References

[1] Szejtli J, Osa T, editors. Comprehensive supramolecular chemistry. Cyclodextrins, vol. 3. Oxford: Pergamon; 1996.

[2] (a) Uyar T, Hunt MA, Gracz HS, Tonelli AE. Cryst Growth Des 2006; 6(5):1113–9;
(b) Uyar T, El-Shafei A, Hacaloglu J, Tonelli AE. J Inclusion Phenom Macrocyclic Chem 2006;55:109–21.

[3] (a) Uyar T, Rusa CC, Hunt MA, Aslan E, Hacaloglu J, Tonelli AE. Polymer 2005;46:4762;
(b) Rusa M, Wang XW, Tonelli AE. Macromolecules 2004;37(18): 6898–903;
(c) Rusa CC, Fox J, Tonelli AE. Macromolecules 2003;36(8):2742–7.

[4] Uyar T, Rusa M, Tonelli AE. Macromol Rapid Commun 2004;25:1382.

[5] (a) Storsberg J, van Aert H, van Roost C, Ritter H. Macromolecules 2003;36(1):50–3;
(b) Storsberg J, Ritter H. Macromol Rapid Commun 2000;21(5):236–41.

[6] Storsberg J, Ritter H, Pielartzik H, Groenendaal L. Adv Mater 2000; 12(8):567–9.

[7] Takashima Y, Oizumi Y, Sakamoto K, Miyauchi M, Kamitori S, Harada A. Macromolecules 2004;37:3962–4.

[8] Wang B, He J, Sun DH, Zhang R, Han BX, Huang Y, et al. Eur Polym J 2005;41(10):2483–7.

[9] Hunt MA, Jung D-W, Shamsheer M, Uyar T, Tonelli AE. Polymer 2004; 45(4):1345.

[10] Rusa CC, Bullions TA, Fox J, Porbeni FE, Wang X, Tonelli AE. Langmuir 2002;18:10016–23.

[11] Peet JH, Rusa CC, Hunt MA, Tonelli AE, Balik CM. Macromolecules 2005;38:537.

[12] (a) Cao YJ, Xiao XH, Lu RH, Guo QX. J Mol Struct 2003;660(1–3):73;
(b) Cao YJ, Xiao XH, Ji SF, Lu RH, Guo QX. Spectrochim Acta Part A 2004;60(4):815–20.

[13] (a) Uyar T, Rusa CC, Rusa M, Wang X, Hacaloglu J, Tonelli AE. J Polym Sci Part B Polym Phys 2005;43(18):2578;
(b) Rusa CC, Rusa M, Gomez M, Shin ID, Fox JD, Tonelli AE. Macromolecules 2004;37(21):7992–9;
(c) Bullions TA, Wei M, Porbeni FE, Gerber MJ, Peet J, Balik M, et al. J Polym Sci Part B Polym Phys 2002;40(10):992–1012.

[14] Kawamura, Toshima N, Matsuzaki K. Macromol Rapid Commun 1994; 14:479.

[15] Sato H, Tanaka Y. J Polym Sci Part B Polym Phys Ed 1983;21:1667.

[16] We only examine and discuss the aromatic C-1 carbon region of the PS spectra, because, unlike the methine and methylene carbon resonances, C-1 resonances in mm, rr, mr(rm) stereosequences do not overlap [14].

[17] Wang X-S, Kim H-K, Fujita Y, Sudo A, Nishida H, Endu T. Macromolecules 2006;39:1046.