

The Nano-threading of Polymers

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Abstract

When guest polymers are threaded by host cyclodextrins (CDs) to form crystalline inclusion compounds (ICs), the included polymer chains are highly extended and separated from neighboring chains. This is a consequence of the stacking of the cyclic oligosaccharides, α -, β -, or γ -CD containing 6, 7, or 8 glucose units, respectively, which produces continuous narrow channels (~ 0.5 – 1.0 nm diameters), where the guest polymers are included and confined. Observations that illuminate several important aspects of the nano-threading of polymers to form polymer-CD-ICs are described. These include (i) the competitive CD threading of polymers with different chemical structures and molecular weights from their solutions containing suspended solid or dissolved CDs, (ii) the threading and insertion of undiluted liquid polymers into solid CDs, and (iii) suspension of polymer A or B-CD-IC crystals in a solution of polymer B or A and observation of the transfer of polymer B or A from solution to displace polymer A or B and form polymer B or A-CD-ICs, without dissolution of the CD-ICs. In addition, we report observations of polyolefins adsorbed on zeolites, where we believe the adsorbed polyolefin chains are actually threaded and absorbed into the interiors of the zeolite nano-pores, rather than adsorbed on the zeolite surfaces. All of the above observations were made to assist in answering the question “*Why do randomly-coiling polymer chains in solution or the melt become threaded or thread into the nano-pores of dissolved or solid CDs and solid zeolites, where they are highly extended and segregated from other polymer chains?*” Though still not fully able to answer this question, we are able to assess the importance of several factors that have been previously suggested to be important in the formation of CD-ICs with both polymer and small-molecule guests and to the nano-threading of polymers in general. In particular, the value in observations of the inclusion of guest polymers, as well as small-molecule guests, into solid CDs suspended in their solutions and in neat guest liquids were made apparent, because interactions between host CDs, between CDs and solvents, and between guests and solvents, which complicate and make understanding the formation of polymer-CD-ICs difficult, are either eliminated or can be independently varied in these experiments.

Introduction

For over a decade we and several other research groups have been forming crystalline inclusion compounds (ICs) between host cyclodextrins (CDs) and various guest polymers [1–72]. When guest polymers are threaded by host cyclodextrins (CDs) to form crystalline polymer-CD-ICs, the included polymer chains are highly extended and isolated from neighboring chains. This is a consequence of the stacking of the cyclic oligosaccharides, α -, β -, or γ -CD containing 6, 7, or 8 glucose units, respectively, which produces continuous narrow channels

(~ 0.5 – 1.0 nm diameters), where the guest polymers are included and confined (See Figure 1) [6].

Our laboratory alone has formed polymer-CD-ICs with more than three dozen high molecular weight polymer guests [1–51], covering a wide range of different chemical structures, including the fibroin protein from the *Bombyx mori* silk worm [46]. More recently it was observed that upon passing polyolefin solutions through columns packed with certain zeolites the polyolefins may be removed from solution and actually thread into and become absorbed in the interiors of the zeolite nano-pores, rather than being adsorbed only on the zeolite surfaces [73]. As a consequence of these related observations, we have been attempting to understand why randomly-coil-

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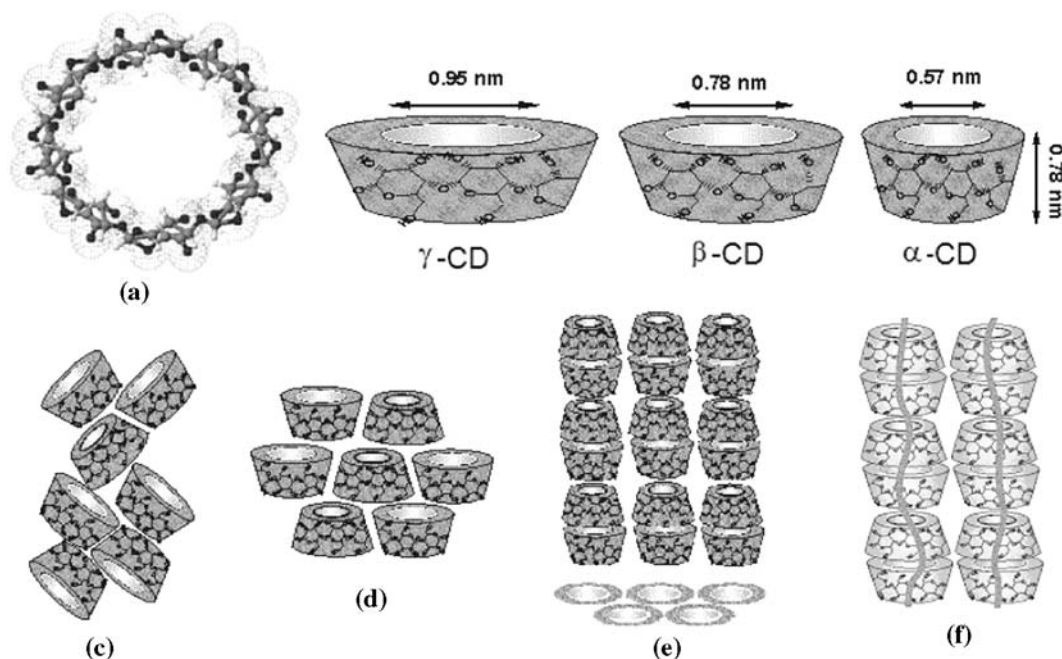


Figure 1. (a) γ -CD chemical structure; (b) approximate dimensions of α -, β -, and γ -CDs; schematic representation of packing structures of (c) cage-type, (d) layer-type, and (e) head-to-tail channel-type CD crystals; and (f) CD-IC channels containing included polymer guests.

ing polymer chains in solution or the melt become threaded or thread into the nano-pores of dissolved or solid CDs and solid zeolites, where they are highly extended and segregated from other polymer chains. The nano-threading of guest polymers into CDs to form ICs and into nanoporous zeolites has added importance, because they can serve as model systems to probe various aspects of molecular recognition and supramolecular chemistry, which are so critical to life processes.

In the present contribution we bring together and summarize observations previously made in our laboratory that illuminate several important aspects of the nano-threading of polymers to form polymer-CD-ICs. These include (i) competitive CD threading of polymers with different chemical structures and molecular weights from their solutions containing suspended solid or dissolved CDs, (ii) the threading and insertion of undiluted liquid polymers into solid CDs, and (iii) suspension of polymer A or B-CD-IC crystals in a solution of polymer B or A and observation of the transfer of polymer B or A from solution to displace polymer A or B and form polymer B or A-CD-ICs, without dissolution of the CD-ICs. Comparison of these observations has enabled an assessment of the relative importance of several factors that have been previously suggested to be crucial in the formation of CD-ICs with both polymer and small-molecule guests and to the nano-threading of polymers in general.

Observations of the nano-threading of polymers into CDs and zeolites

Here we summarize our previous observations concerning the nano-threading of polymers. Only pertinent

experimental results are mentioned, because more detailed descriptions may be found in the original references.

Formation of polymer-CD-ICs from solution

Two studies were conducted to probe the potential for using the complexation of polymers with CDs as a means to separate them according to their molecular weight (MW) or chain lengths [9, 15]. In the first investigation two poly (ethylene glycol) (PEG) samples, with number-average MW = 600 (PEG₆₀₀) and 20,000 (PEG₂₀₀₀₀) and narrow MW distributions of 1.1 and 1.34, respectively, were dissolved in water and added to an aqueous solution of α -CD to form PEG- α -CD-ICs. α -CD-ICs were formed with PEG₆₀₀, PEG₂₀₀₀₀, and various mixtures of the two PEG samples. By comparing the viscosities of their solutions after filtering off the PEG- α -CD-ICs formed, it was found that the PEG- α -CD-IC formed from an equimolar PEG₆₀₀/PEG₂₀₀₀₀ solution, using enough α -CD to complex either all of one or half of each PEG, contained 80% of the higher molecular weight PEG₂₀₀₀₀.

The second study compared the α -CD-ICs formed in solution with poly (ϵ -capro-lactone) (PCL) and hexanoic acid (HA), which closely mimics the PCL repeat unit [15]. FT-IR observations of the α -CD-ICs formed with PCL, HA, and PCL/HA mixtures were used to determine the presence of PCL and HA guests (PCL and HA C=O stretching bands at 1734 and 1714 cm^{-1} , respectively). Both guests were observed to be equally present in the α -CD-ICs when equal amounts of PCL and HA were mixed with enough α -CD to complex both guests. However, when half the amount of α -CD was used, i.e., enough to complex all of the PCL, or all of the HA, or

half of each, PCL was observed to be predominantly included.

Thus, both studies showed a preference for the inclusion of the longer, higher MW guest polymer, irrespective of their very different chemical natures: PEGs are hydrophilic and soluble in water, while PCL and HA are not. This suggests that the formation of α -CD-ICs in solution with both PEG and PCL guests may be dominated by the kinetics of the process, which favor higher MW, longer guests. It was suggested that longer polymer chains partially threaded with CDs would nucleate the growth of polymer-CD-IC crystals more readily than partially threaded shorter chains, because the unthreading of CDs from the longer chains would be slower or retarded compared with the unthreading of CDs from the shorter chains.

The dependence of CD-IC formation from solution for polymers with different stereosequences was investigated for isotactic (i) and atactic (a) poly (3-hydroxybutyrate) (i-PHB and a-PHB) [26]. I-PHB was found to form an IC with α -CD, but not with β - or γ -CDs, while only γ -CD formed an IC with a-PHB. From these observations it was concluded that extended conformations available to i-PHB were too narrow, thin for a tight-packing fit with β - or γ -CDs, while the much broader, thicker extended conformations available to a-PHB chains precluded their inclusion in the narrower α - and β -CDs, but fit tightly in the channels of its IC formed with γ -CD.

The solution complexation of PCL and the related aliphatic polyester poly (L-lactic acid) (PLLA) with CDs was studied [29]. PCL was observed to be able to form ICs with both α - and γ -CDs, with the latter containing two PCL chains in each γ -CD channel, while only α -CD formed an IC with PLLA. When a solution containing equivalent amounts of PCL and PLLA was added to an aqueous solution containing enough α -CD to complex with all of the PCL, or all of the PLLA, or half of each, only PCL- α -CD-IC was formed. Furthermore, when a PCL solution was added to an aqueous solution containing the same molar quantities of α - and γ -CDs, each sufficient to fully complex with the added PCL, only PCL- α -CD-IC was formed. These observations led to the following tentative conclusions: (i) interactions between extended and included PCL chains and α -CD may be more favorable than the average of the interactions between the two parallel side-by-side PCL chains included in PCL- γ -CD-IC and the two included PCL chains with γ -CD, or the double-threading of PCL chains required to form the PCL- γ -CD-IC might retard the kinetics of its formation, (ii) interactions between included PCL chains and α -CD channels are more favorable than those involving PLLA, (iii) differences in PCL/solvent and PLLA/solvent interactions are not important, and (iv) the preference of PCL over PLLA inclusion by α -CD is not a consequence of a difference in the cross-sections of their extended conformations nor a difference in the kinetics of their threading by α -CD, because the PLLA sample consisted of longer chains than the PCL sample.

Formation of polymer-CD-ICs by suspension of solid CDs in polymer solutions or in neat polymer liquids

We have discovered a simple precipitation method for forming solid CDs in a channel structure, CD_{CS}, (See Figure 1e) containing no complexed guest aside from water of hydration [24]. When propionic acid (PA), which in solution forms a cage structure α -CD-IC (See Figure 1c) with dissolved α -CD, is dissolved in a non-solvent for α -CD and α -CD_{CS} is suspended therein, PA entered α -CD_{CS} and transformed it to a cage structure PA- α -CD-IC. However, when α -CD_{CS} is vacuum-dried before suspension in the same PA solution, a columnar structure PA- α -CD-IC was formed. Clearly the role of water, some of which is displaced from the air-dried α -CD_{CS} channels upon inclusion of PA, is important in the formation of CD-ICs, as well as the packing interactions between host α -CDs. Apparently the vacuum drying of α -CD_{CS} stabilizes the packing of α -CDs in the columnar structure, because as PA is included, the solid-state transformation to a cage structure PA- α -CD-IC is prevented.

α - and γ -CD-ICs formed with PCL were suspended in acetone and aqueous solutions of γ - and α -CDs, respectively [29]. In the first case nothing happened, but in the second case the PCL chains in suspended PCL- γ -CD-IC were removed and complexed with the originally dissolved α -CD to form PCL- α -CD-IC. In another set of experiments [29], PCL- and PLLA- α -CD-ICs were suspended in dioxane solutions initially containing dissolved PLLA and PCL, respectively. After several days the suspended α -CD-ICs crystals were filtered out and observed by FT-IR (distinct C=O absorption bands of PCL and PLLA) to determine whether PCL, PLLA, or both were included. The α -CD-IC resulting from the suspension of PLLA- α -CD-IC in the PCL solution was found to contain only PCL guest chains, while the α -CD-IC resulting from the suspension of PCL- α -CD-IC in the PLLA solution contained only a very small amount of PLLA guest chains. The above results were interpreted to signify the importance of both guest polymer hydrophobicity and guest/host steric compatibility in the formation of polymer-CD-ICs.

The ability of poly (N-acylthylenimine) (PNAI) to be complexed from its solutions containing suspended cage and columnar structure γ -CDs was investigated [40]. PNAIs with two different MWs were synthesized and two different PNAI solvents (acetone and chloroform) were employed. Complexation of the PNAIs from solutions containing suspended γ -CDs was directly monitored by ¹H NMR. The time-dependent intensities of PNAI and water ¹H resonances were observed and permitted an evaluation of the kinetics of the PNAI inclusion. In the acetone solutions the inclusion of PNAIs by columnar γ -CD was both greater in quantity and faster than for cage γ -CD. In both cases PNAI inclusion was accomplished without any dissolution of the suspended γ -CDs, because ¹H resonances were never observed for dissolved γ -CDs. In comparison to the

lower MW sample, more of the higher MW PNAI was included in γ -CD_{CS}, but the rate of PNAI inclusion was the same for both samples. Of the six water molecules residing in the channels of each γ -CD_{CS} [24, 29], only two were observed to be removed upon inclusion of the PNAI guest chains. Furthermore, when the γ -CDs were suspended in chloroform solutions of the PNAIs, no ejection of hydration water nor inclusion of PNAI chains was observed.

Thus, the inclusion of PNAIs in suspended γ -CDs was both thermodynamically and kinetically preferred in the case of γ -CD_{CS}, while the inclusion of high MW PNAI is apparently thermodynamically favored. Most of the water initially residing in the γ -CD_{CS} channels remained after PNAI complexation, and using chloroform as a solvent for PNAI and as a suspension medium for the γ -CDs prevented PNAI inclusion, presumably because of the unfavorable environment provided by chloroform for the potentially displaced and ejected water. By comparison to the estimated increase in conformational free energy experienced by randomly-coiling polymers as they are extended and confined in γ -CD channels [74], which is mainly entropic in origin, it could be estimated that each water molecule ejected during PNAI inclusion in γ -CD_{CS} must lower its free energy by ~ 1 kcal/mol.

PEG oligomers (MWs = 200 and 400), which are liquids at room temperature, were mixed with solid, as-received cage structure α -CD and observed by x-ray diffraction to convert to columnar structure PEG- α -CD-ICs [44]. Both the time and temperature dependences of the solid-state conversion of cage to columnar structure α -CD through inclusion of bulk liquid PEG oligomers were investigated. An activation energy of 8.3 kcal/mol of α -CD was determined from the temperature dependent kinetic observations. Increasing the PEG/ α -CD ratio increased the rate of PEG inclusion, while increasing the MW of PEG slowed the inclusion. Drying the as-received cage structure α -CD before mixing with the PEG oligomers had little effect on the rate of PEG inclusion. (More recent observations indicate that the rate and extent of PEG inclusion may be effected by the degree of α -CD hydration.)

In addition, as-received cage α -CD was suspended in acetone solutions of the PEGs, and its solid-state conversion to channel structure as PEG chains were included and formed PEG- α -CD-IC crystals was observed by solution ^1H NMR. The rate of PEG inclusion from solution was ~ 10 times faster than the rate observed for the neat PEGs, even though the PEG concentration in solution was only $\sim 1\%$ that of neat PEG.

These observations may be generally summarized as follows: as the mobility of PEG increases, i.e., moving from neat to dissolved PEG and/or from higher to lower MW, so does the rate of inclusion of PEG into suspended cage α -CD *via* the solid–solid cage-to-columnar crystal structure transition. Since drying the as-received cage structure α -CD did not effect the rate of its transition to columnar α -CD, α -CD_{CS}, by the inclusion of

neat PEG, apparently this process is not sensitive to the hydration level of the suspended cage structure α -CD.

The inclusion of neat and dissolved PEG oligomers into suspended columnar structure α -CD, α -CD_{CS}, was preliminarily observed by DSC and solution ^1H NMR [44] to proceed at much faster rates than inclusion by suspended cage structure α -CD, because of the absence of the need to transform the solid-state packing of α -CDs upon inclusion of PEG. As a consequence, analysis of the temperature-dependent kinetics of PEG oligomer inclusion in α -CD_{CS} should enable an experimental assessment of the free energy change experienced by randomly-coiling PEG oligomers as they are extended and thread into the narrow α -CD_{CS} channels.

Penetration of zeolite nano-pores by polyolefins

Very recently Macko et al. [75–77] observed that both polyethylene (PE) and isotactic polypropylene (PP) may be adsorbed from solutions formed with specific solvents onto certain zeolites. Once adsorbed, it was found, in both cases, to be very difficult to desorb the polyolefins from the zeolites. This prompted the authors to suggest that the adsorbed PE and PP chains actually enter and are retained in the narrowest ($D < 2$ nm) zeolite nano-channels (See Figure 2).

We have performed solid-state DSC and ^{13}C NMR observations on the zeolites containing adsorbed PE and PP to investigate whether or not these polymers adsorb on zeolite by penetrating and occupying the narrowest internal pores [73]. DSC scans show an absence of melting endotherms for both PE and PP when adsorbed by zeolites, which supports the view that the adsorbed polymers have been separated by penetration and

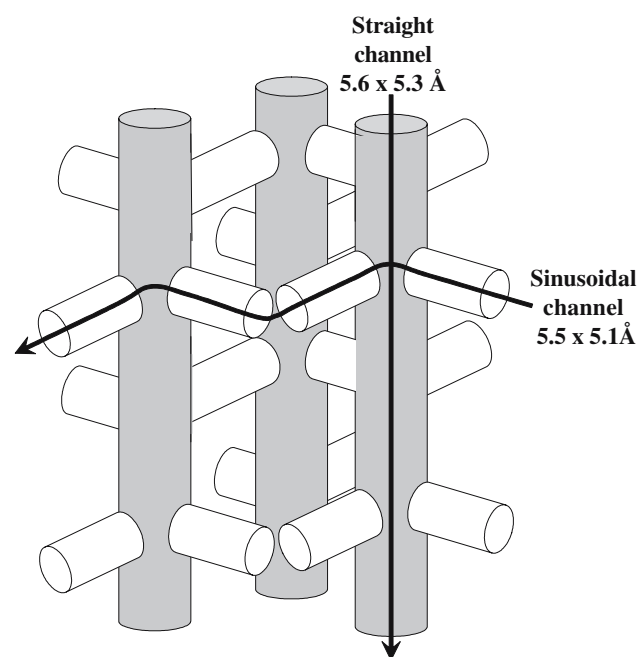


Figure 2. Schematic of the nano-pore structure in zeolite SH-300, which irreversibly absorbs PE from its decalin, 1,3,5-trimethyl-benzene, and 1,1,2,2-tetrachloroethane solutions [75–77].

inclusion in the narrowest zeolite pores (See Figure 2), and therefore are unable to aggregate and crystallize. Control DSC experiments were performed on the same zeolites, but with PE and PP at the same concentrations simply adsorbed on the surface through evaporation of solvent from their solutions containing the suspended zeolites. For these samples, melting endotherms were observed for both PE and PP. Solid-state ^{13}C NMR observations of both unadsorbed bulk and zeolite-adsorbed PE and PP samples reveal dramatically (PE) and significantly (PP) reduced spin-lattice relaxation times for the adsorbed polyolefins and even some differences in the chemical shifts observed between bulk and adsorbed PPs. The control samples mentioned above, with PE and PP simply adsorbed on the zeolite surfaces, evidenced ^{13}C NMR responses very similar to the bulk PE and PP samples. We interpreted these NMR observations as providing strong support for the inclusion of both polyolefins in the internal nano-pores/channels of zeolites when they are adsorbed. The penetration of and inclusion in the narrow internal zeolite channels produces strong binding of PE and PP chains that is manifested by the observed difficulty in desorbing both polyolefins.

Not only do polyolefins form ICs with CDs [42], but they apparently penetrate into the comparably narrow nano-pores in certain zeolites. Because PP was observed [75–77] not to penetrate the narrow pores in the zeolite that were penetrated by PE [78, 79], and PE was not observed to penetrate the larger nano-pores penetrated by PP, apparently the steric compatibility between low energy guest polymer chain conformations and the host zeolite nano-pores is important. Because the nano-pores in the zeolites have cross-sections closely similar to the channels in CDs, particularly γ -CD (See Figures 1 and 2), we believe the nano-threading of polymer chains into both CD and zeolite hosts are appropriately considered together.

Discussion and conclusions

Recently Liu and Guo [80] have summarized the interactions/driving forces that are often cited as playing significant roles in the formation of soluble small-molecule guest/host CD-ICs, and attempted to prioritize them in order of importance. Even though here we are discussing the formation of solid columnar structure CD-ICs containing polymer guests, where either both components are initially in solution or with solid CDs suspended in solutions of or in neat polymer guests, we believe it is also useful to discuss and evaluate these same potential interactions/driving forces in connection with their formation. At the same time, because soluble and crystalline solid CD-ICs are most significantly distinguished by the regular packing of host CDs in the IC crystals, this distinction must also be considered in the present discussion.

Electrostatic interactions

The dipolar interactions between polar host CDs and included guests with permanent dipole moments are considered to at least affect the conformations and structures of soluble small-molecule guest/host CD-ICs [80]. Our observations [29] of the preference for inclusion of PCL over PLLA chains in both dissolved and crystalline suspended α -CD (α -CD_{CS}), as well as the displacement of PLLA chains by PCL from PLLA- α -CD-ICs when suspended in PCL solution, indicate that dipole–dipole electrostatic interactions may not be critical to the formation of polymer-CD-ICs. If they were, then we might expect PLLA to be preferentially included in α -CD compared to PCL, because two PLLA repeat units and two ester group dipoles occupy each α -CD, while only single PCL repeat units with a single identical ester group dipole are included in each α -CD.

Because both aliphatic polyesters likely adopt nearly fully extended all-trans conformations when included in their α -CD-ICs, the dipole moments in neighboring repeat units point in approximately opposite directions. This might cause partial cancellation of the net PLLA dipole moment in each α -CD, because two PLLA repeat units occupy each host α -CD, while only a single PCL ester group is included. Aside from this potential caveat, and because purely non-polar hydrocarbon polymers may be included in CDs [42], *it is likely that dipolar electrostatic interactions do not play a major role in the nano-threading and subsequent formation of polymer-CD-ICs.*

van der Waals interactions

Liu and Guo [80] concluded that van der Waals interactions are a major driving force for the formation of soluble small-molecule guest/host CD-ICs. Because van der Waals interactions depend on molecular polarizabilities, and the two PLLA repeat units included in each α -CD are more polarizable than a single included PCL repeat unit, we tentatively suggest that *van der Waals interactions may not be important in the formation of polymer-CD-ICs*, because inclusion of PCL was observed to be preferred over that of PLLA [29].

Hydrophobic interactions

Because PCL is less polar than PLLA, with an increased potential for hydrophobic interactions, we conclude that *hydrophobic interactions may be important in the formation of polymer-CD-ICs*, because, compared to PLLA, PCL is preferentially included by α -CD [29]. In addition, the observed [33, 45] competitive preference for solution inclusion of bisphenol-A polycarbonate (PC) by γ -CD in the presence of poly(methyl methacrylate) and/or poly(vinyl acetate) further strengthens this conclusion, because PC is more hydrophobic than the other two polymers.

Hydrogen bonding

Once again the preference of PCL over PLLA inclusion [29] and the fact that all hydrocarbon polyolefins can form CD-ICs [42] imply that *hydrogen-bonding between included guest polymers and host CDs is not likely crucial in the formation of polymer-CD-ICs.*

Relief of conformational strain in CDs

Relief of conformational strain found in pure cage structure CDs, which adopt asymmetric conformations [80], cannot occur during polymer-CD-IC formation from solutions, where CDs are dissolved, *may play a minor role in the case of the formation of polymer-CD-ICs through suspension of solid cage structure CDs in polymer solutions [40] or in neat polymers [44].*

Exclusion of cavity-bound, high-energy water

This is not likely to be an important factor for polymer-CD-ICs formed in solution. When forming polymer-CD-ICs by suspension of CDs in neat liquid polymers [44] or in their solutions [40], however, some of the water bound in CD cavities must be displaced by polymer chains as they thread and are included in the suspended host CDs. We saw, in the case of PNAI, inclusion from acetone solutions into both suspended cage and columnar structure γ -CDs, which was prevented when using chloroform solutions. This strongly implies that the cavity water in CDs must have a suitable place to go when displaced by the inclusion of polymer guests, and *likely is important in the formation of polymer-CD-ICs by suspension of CDs in their solutions and possibly also in neat polymer liquids.* Drying cage structure α -CD before suspending into neat PEG did not affect PEG inclusion, but this may have been the result of the compatibility between water and PEG.

To further assess whether or not exclusion of cavity-bound, high-energy water is an important factor when forming polymer-CD-ICs by suspension of CDs in neat liquid polymers or in their solutions, α -CD_{CS} should be utilized. Vacuum drying of α -CD_{CS} removes water of hydration residing in the α -CD channels, but does not result in changes in the columnar crystalline packing of α -CDs [24]. As a consequence, if air-dried and vacuum-dried α -CD_{CS} are suspended in neat polymers or their solutions, we would expect the inclusion of polymers to be faster in the vacuum-dried α -CD_{CS} if exclusion of cavity-bound, high-energy water is an important factor. Such experiments are currently in progress.

We have recently observed [81] that when vacuum-dried α -CD (cage structure) is added to neat PEG or the hydrocarbon hexatriacontane (HTC) both guests are included yielding PEG- and HTC- α -CD-ICs with columnar structures. However, their inclusion depends on the environmental relative humidity: PEG is included 6–10 times faster at a water activity of $a=0.5$, than under dry ($a=0.0$) and saturated ($a=1.0$) conditions,

while HTC is only included when water is present ($a > 0.0$). These observations add further support to the importance of providing an environment external to CDs, where cavity-bound water may migrate to as it is displaced by the penetrating guest polymer.

Crystalline packing of host CDs in solid CD-ICs

When the α -CD-IC with guest propionic acid (PA) is formed either from solution or by suspending as-precipitated, air-dried α -CD_{CS} in neat PA, a cage structure PA- α -CD-IC results. Vacuum-drying α -CD_{CS}, which removes nearly 2/3 of the water contained by air-dried α -CD_{CS}, apparently stabilizes the columnar packing structure sufficiently to force PA to be included without structural reversion to the generally preferred cage structure PA- α -CD-IC [24]. Thus, interactions (presumably hydrogen-bonding) between neighboring α -CDs are increased by removal of interstitial hydration water upon vacuum-drying.

Columnar structure CD-ICs are always formed with polymer guests, because of their long-chain nature, which requires their threading and inclusion by many CDs. This is consistent with the observation [44] that neat PEG oligomers are included in both as-received and vacuum-dried cage structure α -CDs at the same rate and to the same quantity even though vacuum-dried cage structure α -CDs have lost $\sim 1/3$ of their hydration water [82], presumably from their cavities, where they do not affect or stabilize the cage packing of α -CDs. However, when comparing the inclusion of both PEG oligomers [44], neat and in solution, and PNAI chains [40] in solution, into suspended cage and columnar structure α -CDs, the inclusion into α -CD_{CS} is observed to be more facile. In the former, latter case the packing structure of α -CDs is altered, unaltered, thereby illustrating *the importance of the crystalline packing of hosts CDs in the formation of polymer-CD-ICs with solid CDs.*

Nano-threading of polymers into solid CDs and zeolites

Some all-hydrocarbon polyolefins in certain solutions have been observed to thread into γ -CDs and form polyolefin- γ -CD-ICs [42] and to penetrate and become absorbed in the nano-pores of certain zeolites [73, 75–77], despite the very different chemical characters of the comparably sized CD and zeolite nano-channels (See Figures 1 and 2). This comparison, in concert with the large number of CD-ICs that have been formed with guest polymers having a wide variety of chemical structures, strongly suggests that *the nano-threading of polymers is a general phenomenon characteristic of their long-chain natures, or polymer physics, and not their detailed chemical structures, or polymer chemistry.*

By observation of (i) the competitive CD threading of polymers with different chemical structures and molecular weights from their solutions containing suspended solid or dissolved CDs, (ii) the threading and insertion of undiluted liquid polymers into solid CDs,

(iii) suspension of polymer A or B-CD-IC crystals in a solution of polymer B or A and observation of the transfer of polymer B or A from solution to displace polymer A or B and form polymer B or A-CD-ICs, without dissolution of the CD-ICs, and (iv) the threading and absorption of polyolefins from solution into the nano-pores of certain zeolites, we have been able to illuminate several important aspects of the nano-threading of polymers. In particular, the value in observations of the inclusion of guest polymers, as well as small-molecule guests, into solid CDs suspended in their solutions and in neat guest liquids were made apparent, because interactions between host CDs, between CDs and solvents, and between guests and solvents, which complicate and make understanding the formation of polymer-CD-ICs difficult, are either eliminated or can be independently controlled in these experiments.

Extension of the investigations summarized here should eventually permit a more complete answer to the question “*Why do randomly-coiling polymer chains in solution or the neat melt become threaded or thread into the nano-pores of dissolved or solid CDs and zeolites, where they are highly extended and segregated from other polymer chains?*” However, we can currently conclude that electrostatic, van der Waals, and hydrogen-bonding interactions and relief of conformational strain in CDs are not important, while hydrophobic interactions, exclusion of high energy, cavity-bound water, and crystalline packing of host CDs are important in the formation of polymer-CD-ICs. Also the nano-threading of polymers appears to be a general phenomenon characteristic of their long-chain natures, or polymer physics, and not their detailed chemical structures, or polymer chemistry.

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