

Cyclodextrins as a means to nanostructure and functionalize polymers

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Abstract The cyclic starches α -, β -, and γ -cyclodextrins (CDs) readily form inclusion complexes (ICs) with a large variety of polymers. In polymer-CD-ICs, the CD hosts are threaded by the guest polymers, which must be highly extended, and stacks of polymer threaded host CDs pack closely together and crystallize. When guest polymers are coalesced from their CD-IC crystals, by washing with a solvent good, bad for CD, polymer, or treatment with an amylase enzyme, the guest polymers coalesce into bulk samples whose structures, morphologies, and even conformations are distinct from bulk samples made from their solutions and melts. We generally observe (i) crystallizable homopolymers coalesced from their CD-ICs to evidence increased levels of crystallinity, unusual polymorphs, and higher melting, crystallization, and decomposition temperatures, while coalesced amorphous homopolymers exhibit higher glass-transition temperatures, than samples consolidated from their disordered solutions and melts; (ii) molecularly mixed, intimate blends of two or more polymers that are normally believed to be immiscible can be achieved by coalescence from their common CD-IC crystals, (iii) the phase segregation of incompatible blocks can be controlled (suppressed or increased) when block copolymers are coalesced from their CD-IC crystals, and (iv) the thermal and temporal stabilities of the coalesced and well-mixed homopolymer blends and block copolymers appear to be substantial, thereby suggesting retention of as-coalesced structures and morphologies under normal thermal processing conditions. Furthermore, CDs may be covalently incorporated in polymers both during and after

their syntheses, thereby providing a broad range of new functionalities for delivery of additives or to act as sensors or filters. Alternatively, additive-CD-ICs or additives ro-taxanated with CDs may be effectively delivered to polymers. As an example, TiO_2 -filled polypropylene fibers may be readily dyed in aqueous solution using water soluble CD-rotxanated azo-dyes.

Keywords Cyclodextrins · Polymers

Reorganization of polymers with CDs

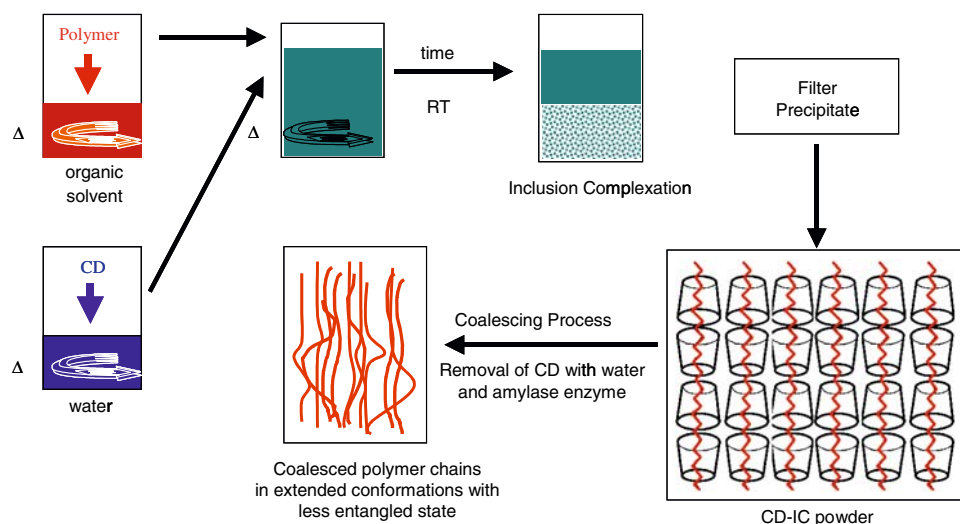
Homopolymers

When guest polymers are coalesced from their cyclodextrin-inclusion complexed (CD-IC) crystals by disruption of the IC and removal of CD with a solvent that is good for the CD host, but which is a non-solvent for the polymer, or by the selective degradation of the host CD with an amylase enzyme or an acid, the resultant consolidated guest polymer chains retain some degree of their extended, unentangled natures (see Fig. 1). Polymers coalesced from their CD-IC crystals generally evidence increased levels of crystallinity and higher glass transition, melting, crystallization, and decomposition temperatures than samples consolidated from their disordered solutions and melts, where polymer chains are randomly-coiled and entangled.

For example, in Fig. 2 we compare the DSC thermograms [1, 2] of as-received, solution-cast, and coalesced poly(ethylene terephthalates) [PETs]. The last PET sample was coalesced from its γ -CD-IC, where it assumes a $g^+ t g^-$ (kink) ethylene glycol conformation in the narrow γ -CD-IC channels [3]. Upon coalescence, the extended, kinked PET chains rapidly crystallize ($t t t$) *via* facile counter-rotations,

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Fig. 1 Schematic representation of polymer-CD IC formation, the coalescence process, and the coalesced polymer



achieving high levels of crystallinity (see Scheme 1). Rapid crystallization is also observed upon rapid cooling ($-200\text{ }^{\circ}\text{C}/\text{min}$) from the melt, as evidenced by the absence of a glass transition and crystallization exotherm during the second heating of the coalesced PET, which are evident for the other two PET samples. This suggests retention of extended kinked conformations for PET in the melt, resulting in a repeatedly, rapidly crystallizing material, which is generally very uncharacteristic of PET (see Fig. 2).

Block copolymers

An example of controlling the microphase structure of block copolymers through processing with their CD-ICs

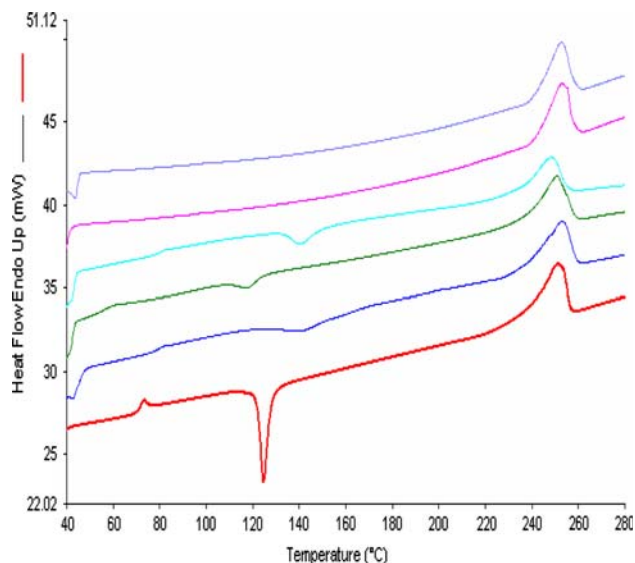


Fig. 2 From bottom to top, DSC scans of as-received PET runs I and II, solution-cast PET runs I and II, and IC-coalesced PET runs I and II

is afforded by examination of the triblock copolymer poly(ϵ -caprolactone)-*b*-poly(propylene glycol)-*b*-poly(ϵ -caprolactone) [PCL-*b*-PPG-*b*-PCL] before and after coalescence from its ICs formed with α - and γ -CDs [4]. Since only PCL blocks are included in the α -CD-block copolymer IC, the neighboring IC channels should be filled only with extended PCL blocks. Therefore, PCL blocks should aggregate readily when the α -CD molecules are washed away. Although PPG may affect the crystallization of PCL blocks in the as-synthesized copolymer, the aggregation of neighboring PCL blocks should not be affected by the uncomplexed PPG blocks in the process of copolymer coalescence. Therefore, an increased level of phase segregation and crystallinity of the PCL blocks in this coalesced sample may be anticipated. In contrast, both PCL and PPG blocks should have the opportunity to be included in the larger neighboring channels of the γ -CD-block copolymer-IC. This means that the aggregation of some PCL blocks might be hindered by PPG blocks in the process of copolymer coalescence from their γ -CD-IC, as did occur with PCL-*b*-poly(L-lactic acid) [PCL-*b*-PLLA] when coalesced from its α -CD-IC, where both blocks were also included. Therefore, a decrease in PCL crystallinity, as a consequence of reduced block segregation, might be reasonably expected for the sample coalesced from its γ -CD-IC crystals.

As is apparent from the results presented in Table 1, both expectations were realized, because the level of PCL crystallinity is observed to be higher and lower compared with the as-synthesized triblock copolymer when PCL-*b*-PPG-*b*-PCL is coalesced from its α - and γ -CD-ICs, respectively. The smaller than might have been expected decrease in PCL crystallinity observed in the triblock copolymer coalesced from its γ -CD-IC may be a result of the ability of two side-by-side parallel PCL block chains to occupy each γ -CD-IC channel [5]. If this is the case, then at

Table 1 Thermal properties and crystallinities of various PCL-PPG-PCL triblock copolymer samples as revealed by DSC [4]

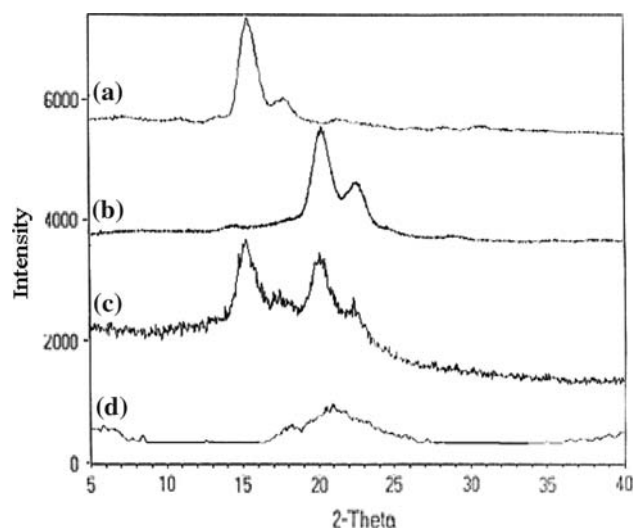
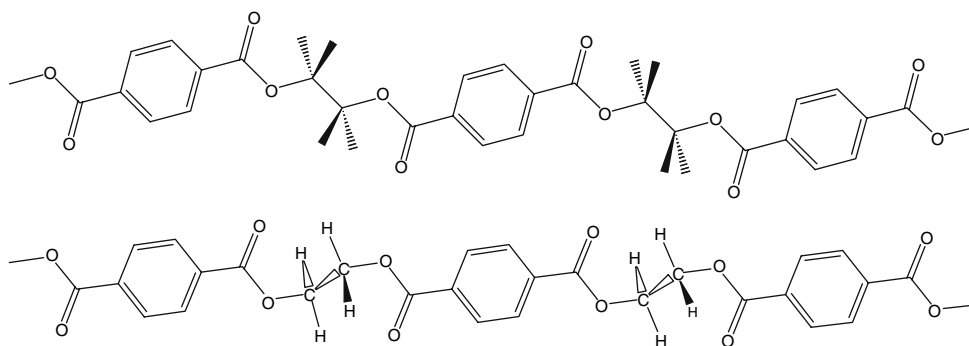
Identity	T_{m-PCL} (°C)	ΔH_{PCL} (J/g)	χ_{c-PCL} (%)
As-synthesized copolymer	57.3	58.6	56.5
Sample coalesced from α -CD-copolymer IC	63.8	76.8	74.1
Sample coalesced from γ -CD-copolymer IC	63.0	51.3	49.5

least some pairs of PCL blocks would aggregate within some γ -CD-IC channels.

Polymer blends

Recently we have formed CD-ICs containing two and even three different polymers [6]. When these are washed with hot water or treated with an amylase enzyme [7], the CD-IC crystals are disrupted, the CD is removed, and the two or more commonly included guest polymers are forced to coalesce into a solid blend, provided neither guest is soluble in water. As illustrated in Fig. 1, though the highly extended polymer chains occupying the narrow channels of their CD-IC crystals are segregated from each other by the host CD bracelets, they are nevertheless in close spatial proximity. Thus, it seems reasonable to expect that when polymer 1/polymer 2- or polymer 1/polymer 2/polymer 3-CD-ICs are washed with hot water or treated with an amylase enzyme, intimate blends may result during the simultaneous coalescence of the common guest polymers.

Coalescence of PCL and PLLA from their common PCL/PLLA- α -CD-IC resulted [8] in a blend that appeared to be well-mixed even though the PCL/PLLA pair is generally regarded as incompatible [9]. For example, a solution cast blend of PCL/PLLA revealed a phase separated morphology under a polarizing microscope. Small, large crystalline spherulites were observed for PCL, PLLA, which melted at 59, 169 °C in the DSC, and corresponded to $\sim 45\%$ crystallinity for both component polymers in the solution-cast blend. In contrast, under a polarizing

Scheme 1 Schematic of the crystalline all trans (top) and γ -CD-included g^{\pm} t g^{\mp} Kink (bottom) conformations of PET**Fig. 3** X-ray diffractograms of pure PCL (a) and PLLA (b) and PCL/PLLA blends obtained by casting from dioxane solution (c) and hot water coalescence from PCL/PLLA- α -CD-IC (d) [8]

microscope the coalesced PCL/PLLA blend appeared to be largely amorphous, with a few small PLLA spherulites homogeneously dispersed throughout. No melting was observed for PCL, while only $\sim 5\%$ crystallinity was detected by DSC for PLLA in the coalesced blend. This behavior is strongly supported by the X-ray diffractograms of PCL, PLLA, and their solution-cast and coalesced blends presented in Fig. 3. Their comparison confirms the phase-segregated nature of the solution-cast blend, because distinct diffraction peaks are observed there for both PCL and PLLA components. On the other hand, the PCL/PLLA blend coalesced from its α -CD-IC only barely reveals diffraction peaks for the PLLA component, because only $\sim 5\%$ of the PLLA chains are crystalline according to DSC observation [8].

Annealing the coalesced PCL/PLLA blend for up to 24 h at 200 °C, which is well above the T_{ms} for both component polyesters, did not alter its morphology, as evidenced by polarized microscopy and DSC observations. In addition, we were unable to dissolve the coalesced PCL/PLLA blend in dioxane or other solvents common for both PCL and PLLA.

2D Hetero NMR methods were applied to the coalesced PCL/PLLA blend [10]. ^1H spin-diffusion coefficients and the length scale of mixing were determined, and both confirmed and quantified the intimate nature of mixing in this blend. For example, the ^1H spin-diffusion coefficient observed for PLLA in the coalesced blend was only half that observed on pure PLLA. These values translate into ^1H spin-diffusion coefficients for the pure and well-mixed PLLA reflective of the expected increased chain mobility (and decreased value of the ^1H spin-diffusion coefficient) of PLLA when it forms an intimate amorphous mixture with PCL, which has a much lower glass transition temperature.

In a related study [11], a PCL-*b*-PLLA block copolymer was coalesced from its α -CD-IC. There it was observed that the degree of crystallinity of both blocks in the coalesced sample were dramatically reduced from the levels observed in the as-synthesized di-block copolymer, which were very similar to those observed in the separate PCL and PLLA homopolymers. Coalescence from its α -CD-IC served to reduce phase segregation and improve mixing of PCL and PLLA blocks. This improved mixing produced a marked increase in the biodegradation rate of coalesced PCL-*b*-PLLA in comparison to the highly phase-segregated as-synthesized di-block copolymer.

Functionalization of polymers with CDs

Polymers containing CDs and/or additive-CD-ICs

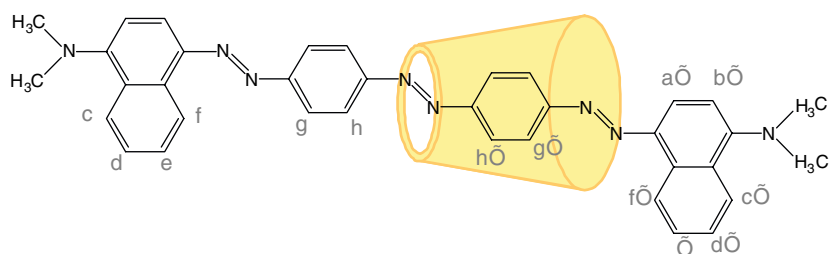
Because crystalline CD-ICs are thermally stable to $\sim 300\text{ }^\circ\text{C}$, they may be readily melt-processed in tact into

polymer matrices that melt below this temperature. Antibacterial and flame retardant polymer fibers and films have been prepared [12–14] in this manner by addition of antibacterial- and flame retardant-CD-ICs during their melt-processing. Incorporating functionalities in polymers through additive-CD-ICs can also be achieved during electrospinning to produce a nanoweb. We have demonstrated [15] that soluble CDs and CD-ICs can be added to the polymer solution to be electrospun, and are carried over into the high surface area nanoweb produced, where they can be used to remove impurities or deliver additives, respectively.

Additive-CD rotaxanes

Recently, we have demonstrated the feasibility of delivering functionalites to polymers by using additives that are rotaxanated with CDs [16]. A CD-rotaxane (see Fig. 4) is formed by reacting a soluble small-molecule guest-CD host-IC to produce bulky end-groups or stoppers on unincorporated exposed portions of the guest, which prevent it from unthreading the host CD. Rotaxation of additives with CDs has several advantages for their delivery to polymers. First, the CD-rotaxanated additive is protected from the environment by its permanent CD jacket. Encapsulation with CDs make the guests chemically stable, as well as making them exceedingly resistant to photobleaching, thus making encapsulated dyes a good candidate for biological imaging. Second, the additive-CD-rotaxane is rendered water-soluble by its $-\text{OH}$ coated CD jacket, irrespective of the solubility of the pure guest. Third, the many $-\text{OH}$ groups on the CD exterior, either inherently or following

Fig. 4 Top: Chemical structure of a rotaxanated azo dye. Bottom: Left to right: Undyed PP, PP dyed with the rotaxanated azo dye and with the Cu^{+2} -complexed polyrotaxanated azo dye in water at $90\text{ }^\circ\text{C}$ for 60 min



derivitization, can serve or be tailored to interact and bind to a particular polymer substrate.

The structure of a recently synthesized [17] rotaxanated azo-dye is presented in Fig. 4. While the pure azo-dye is not soluble in water, the azo-dye rotaxanated with α -CD is. There it was also demonstrated that the α -CD rotaxanated azo-dye has a strong affinity for thin TiO₂ films. As a consequence, when delustered polypropylene (PP) fibers containing TiO₂ are added to an aqueous solution of the α -CD rotaxanated azo-dye they are readily dyed [16]. *We believe this to be the first demonstration of the solution dyeing of a polyolefin that has not been chemically modified.*

It is readily apparent that this approach can be tailored and expanded to improve the delivery of many additives, not just dyes, to polymeric materials.

Covalent CD attachment during or post-polymerization

It is also possible to covalently bond CDs to polymers during or after their syntheses. Proof that CD-modified polymers can improve the properties of textile materials has appeared in a recent U.S. patent application (#20050043482) [18] which describes attachment of CDs to polyolefins that have grafted reactive sites. An example would be polyethylene with a small amount of grafted maleic anhydride to which CDs are attached. The CD-grafted polyolefin is blended into pure polyolefin to produce a well-dispersed distribution of CDs for the purpose of trapping small molecules or delivering additives complexed with the grafted CDs. In a second example, cotton fabric treated with monochloro-triazinyl- β -CD (CDMCT) results in grafting of the CDMCT to the cellulose chains [19]. When soaked in an insecticide solution, the β -CDs complex with the insecticide, rendering the cotton fabric insecticidal. These examples illustrate the increasing interest and activity in utilizing CD-modified polymers to improve textiles and other polymer material.

Because of the high functionality (–OH groups) of CDs, CD-containing polymers synthesized with a modified interfacial polymerization process are usually cross-linked and cannot be spun into fibers using conventional fiber-forming processes. To overcome this limitation, we are synthesizing linear polymers containing controlled amounts of CDs.

The hydroxyl groups on CDs have been successfully functionalized with vinyl groups by reacting with acryloyl chloride to produce an ester. Homo- and co-polymerization of this CD-modified monomer is being explored using free radical initiators. Co-monomers such as t-butyl acrylate, methyl methacrylate and styrene are being used, since their side groups confer solubility in common solvents. The CD

content of the copolymer can be controlled by varying the co-monomer content.

Thionyl chloride converts the carboxyl side groups of poly (acrylic acid) to acid chlorides, which will then react with the hydroxyl groups on CDs. The degree of CD modification can be varied by controlling the stoichiometry of the CD reaction. Alternatively, the starting material can be a copolymer of acrylic acid or acryloyl chloride with a non-CD-containing co-monomer. Incorporation of CD is again achieved by converting the side groups of the acrylic monomer to CD esters. The CD content of this copolymer can be controlled by varying the initial composition of the copolymer. Copolymers of acryloyl chloride with methyl methacrylate and styrene have already been synthesized, compositional control has been achieved, and the acid chloride side groups have been successfully esterified with CD.

The CD molecule, with its many reactive hydroxyl groups can be functionalized with a vinyl monomer such as t-butyl acrylate, methyl methacrylate, styrene or acrylonitrile, followed by polymerization with additional monomer to form a star polymer with CD at the center. The length of the star arms can be controlled by using atom-transfer radical polymerization, which is known to produce highly controlled and uniform polymer molecular weights [20]. The CD content of these star polymers can be adjusted by changing the length of the arms. This synthetic scheme is applicable to a wide variety of vinyl monomers, and it could become a general method for preparing CD-containing star polymers of differing chemical composition. The CD-containing star polymers will be explored primarily as a component of a blend with a homopolymer having the same chemical composition as the star arms.

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