

Feature Article

Nanostructuring and functionalizing polymers with cyclodextrins

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Abstract

We summarize our recent studies employing the cyclic starches called cyclodextrins (CDs) to both nanostructure and functionalize polymers. Two important structural characteristics of CDs are taken as advantages to achieve these goals. First the ability of CDs to form non-covalent inclusion complexes (ICs) with a variety of guest molecules, including many polymers, by threading and inclusion into their relatively hydrophobic interior cavities, which are roughly cylindrical with diameters of ~ 0.5 to 1.0 nm for α -, β -, and γ -CD containing 6, 7, and 8 α -1,4-linked glucose units, respectively. When guest polymers are coalesced from the CD-ICs by removing their host CDs, they are observed to solidify with structures, morphologies, and even conformations that are distinct from bulk samples made from their solutions and melts. Molecularly mixed, intimate blends of two or more polymers that are normally immiscible can be obtained from their common CD-ICs, and the phase segregation of incompatible blocks can be controlled (suppressed or increased) in CD-IC coalesced block copolymers. In addition, additives may be more effectively delivered to polymers in the form of their soluble or crystalline CD-ICs or rotaxanes. Secondly, many $-\text{OH}$ groups attached to the exterior rims of CDs, in addition to conferring water solubility, provide an opportunity to covalently bond them to polymers either during their syntheses or *via* post-polymerization reactions. Polymers containing CDs in their backbones or attached to their side chains are observed to more readily accept and retain additives, such as dyes, fragrances, etc. They may also be further reacted or treated through their CDs to cross-link and form networks or to form blends with other polymers having a propensity to thread through their attached CD cavities.

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1. Introduction

Though cyclodextrins (CDs) had long been known to form both soluble and crystalline inclusion compounds (ICs) with a variety of small-molecule guests, Harada and Kamachi first demonstrated in 1990 [1], using low molecular weight liquid poly(ethylene oxide) (PEO) oligomers, that non-covalent bonded crystalline ICs could be formed between guest polymers and host CDs as well. This is accomplished by threading of the guest polymers through the CD cavities to form polymer threaded crystalline stacks, as illustrated in Fig. 1. CDs are cyclic bracelets formed by 6 (α -CD), 7 (β -CD), and 8 (γ -CD) α -1,4-linked glucose units, with internal hydrophobic cavities of ~ 0.5 to 1.0 nm in diameter. Their 18–24 $-\text{OH}$ groups are located on the CD rims making them soluble in water.

Since the middle 1990s our research group have formed a large number of crystalline CD-ICs [2–69] containing either high molecular weight guest polymers or small-molecule guests that can serve as polymer additives. The motivation for our studies is threefold. First, polymer chains included in CD-ICs are necessarily both highly extended and isolated from neighboring chains, because they are threaded through and confined in the narrow CD channel cavities (see Fig. 1f). As suggested in Fig. 2, if the host CDs in polymer–CD-ICs are carefully removed and the guest polymer chains are permitted to coalesce into a bulk solid sample, then it can be reasonably expected that the arrangement of chains or their packing, might be significantly different from those normally produced from their randomly coiling and entangled solutions or melts. This expectation has been confirmed numerous times in our laboratory.

In fact, we generally observe upon coalescence from their CD-ICs that (i) crystallizable homopolymers evidence

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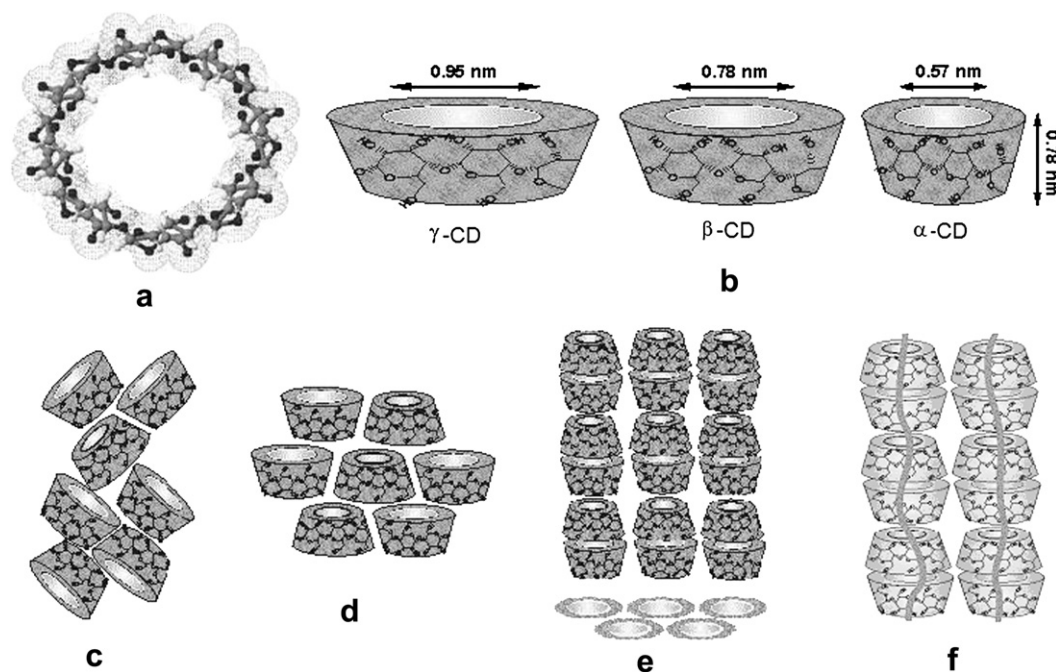


Fig. 1. (a) γ -CD chemical structure; (b) approximate dimensions of α -, β -, and γ -CDs; schematic representation of packing structures of (c) cage-type, (d) layer-type, and (e) head-to-tail channel-type CD crystals; and (f) CD-IC channels containing included polymer guests.

increased levels of crystallinity, unusual polymorphs, and higher melting, crystallization, and decomposition temperatures, while 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 obtained from their common CD-ICs, (iii) the phase segregation of incompatible blocks can be controlled (suppressed or increased) in coalesced block copolymers, 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 their as-coalesced structures and morphologies under normal thermal processing conditions.

In addition to altering their physical behaviors, coalescence of guest polymers from their CD-ICs permits us to obtain solid polymer samples whose structures, morphologies, and even chain conformations are distinct from bulk samples made from their solutions and melts. Clearly study of such reorganized coalesced polymer samples can contribute to our ability to understand and develop improved structure–property relationship for them.

Additionally, because crystalline CD-ICs are high-melting and thermally stable, even when containing small-molecule

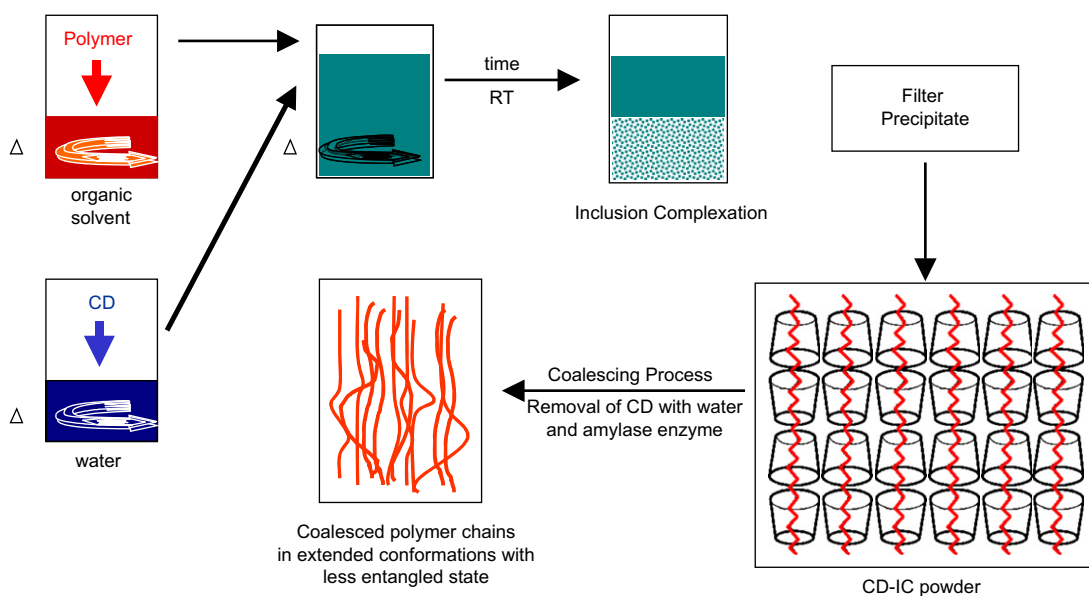


Fig. 2. Schematic representation of polymer–CD-IC formation, the coalescence process, and the coalesced polymer.

guests that are volatile liquids or even gases in the bulk, delivery of additives to polymer materials can be improved by using additive–CD-ICs, which may often be conveniently melt-processed into polymers. If we begin with appropriate soluble additive–CD-ICs and then react the unincluded ends of the guest additive with capping groups that prevent it from unthreading, we create CD–additive–rotaxanes. One advantage of CD–additive–rotaxanes is the protection (thermal, chemical, UV–vis, etc.) afforded by their CD coats. Another is the ability to utilize many –OH groups on the CD coat to target the delivery of the CD–additive–rotaxane to a particular polymer substrate.

Our second motivation for utilizing CDs with polymers is to alter their functionalities through incorporation of CDs into their backbones during polymerization or to attach them to polymer side chains *via* post-polymerization reactions. The presence of covalently bonded CDs in polymers serves to increase their acceptance and retention of additives, such as dyes, fragrances, anti-bacterials, etc. They may also be further reacted or treated through their covalently bonded CDs to cross-link and form networks or to form blends with other polymers having a propensity to thread through their attached CD cavities.

Thirdly, CDs are non-toxic, biodegradable, and bioabsorbable, and as such may be used in medical applications, as well as providing for the fabrication of “greener” polymer materials.

As indicated above, in this report we will summarize our recent studies employing the cyclic starches called cyclodextrins (CDs) to both nanostructure and functionalize polymer materials.

2. Experimental

2.1. Polymer–CD-ICs

CD-ICs formed with polymer guests are crystalline solids (see Fig. 1), which may be formed by mixing host CD solutions (usually aqueous) with guest polymer solutions (usually non-aqueous and organic) with the aid of heating, stirring, and sonication [6]. Solid CDs may also be suspended in polymer solutions [24,41] or neat bulk liquid polymers [45] to form polymer–CD-ICs. Because pure CDs with only water of hydration included in their cavities assume the crystal structures illustrated in Fig. 1(c) and (d), while polymer–CD-ICs assume the very different columnar, channel structure shown in Fig. 1(e) and (f), X-ray diffraction is utilized to test for successful polymer–CD-IC formation. This is supplemented by DSC, FTIR, and solid-state ^{13}C NMR observations to confirm that guest polymer is present and included in the CD-ICs formed.

Warm water washing of polymer–CD-ICs containing polymer guests insoluble in water or treatment with amylase enzymes serves to remove the host CDs and results in the coalescence of the guest polymers into solid samples. X-ray diffraction, DSC, TGA, and FTIR and NMR spectroscopies

are typically used to characterize the coalesced polymer samples.

2.2. Additive–CD-ICs and rotaxanes

Small-molecule additive–CD-ICs, both soluble and crystalline, may be prepared [7,9,13,17,52,53,65,68,69] by virtually the same means as polymer–CD-ICs. Soluble additive–CD–rotaxanes can be obtained by first forming a soluble additive–CD-IC, and then attaching bulky end-groups to portions of the guest additive nearest to the rims of or extending from the host CD cavity, thereby preventing the unthreading of the additive. An example of the synthetic route for obtaining an azo-dye– α -CD–rotaxane will be subsequently discussed.

3. Nanostructuring/functionalizing polymers *via* CD-IC formation and coalescence and additive delivery with additive–CD-ICs and –rotaxanes

3.1. Homopolymers coalesced from their CD-ICs

3.1.1. Poly(ethylene terephthalate) [21,33,59]

When PET chains are included in the ~ 1.0 nm channels of its γ -CD-IC [21] they adopt kink conformations, as drawn in Fig. 3, which are nearly as extended, but are narrower in cross-section than the crystalline all *trans* PET conformation also shown there. Upon coalescence from its γ -CD-IC, PET rapidly crystallizes, achieving $\sim 40\%$ crystallinity, while FTIR and solid-state NMR observations [21,33] indicate that the PET chains in the non-crystalline regions of coalesced PET largely retain the included kink conformations.

The reorganized morphology of the coalesced PET is manifested in its thermal behavior, as presented in the DSC scans shown in Fig. 4. Note that no glass-transition or crystallization is observed in either heating scan, with the former observation receiving support from temperature dependent solid-state NMR relaxation observations [21,33]. Instead, both heating scans simply evidence a large melting endotherm, indicating substantial crystallinity for the coalesced PET both after coalescence and subsequent to rapid cooling from the melt. In summary, including PET chains in and coalescing them from their γ -CD-IC crystals have reorganized them into a sample that is repeatedly and rapidly crystallizable from its melt, with non-crystalline regions that do not show a T_g , behavior that is normally very uncharacteristic of usually amorphous and slow to crystallize PET.

This contrasting thermal behavior for coalesced and normal PETs is further emphasized in the density results presented in Table 1. There the densities measured for as-received PET before and after high temperature annealing (110 °C for 30 min) are compared with the density of the coalesced sample. Not surprisingly the densities of both the annealed and the coalesced samples are higher than that of the as-received PET, because the former samples are more crystalline than the latter one. What is initially surprising, however, is, even though the annealed and coalesced PET samples have closely similar levels of crystallinity (DSC, X-ray), the density of the

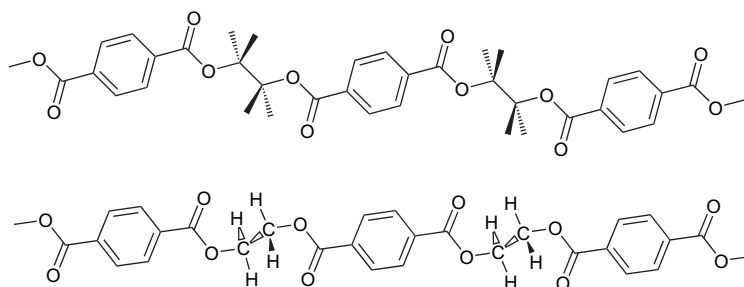


Fig. 3. All *trans* (top) and $g\pm tg\mp$ kink (bottom) conformations of crystalline and amorphous or IC-included, respectively, PET chains.

coalesced sample is much higher. Thus it appears that the PET chains in the non-crystalline regions of the coalesced PET film are more densely packed (by $\sim 1.4\%$) than in the amorphous regions of the annealed PET film, even though each film is $\sim 65\%$ non-crystalline. The coalesced PET film has a higher density non-crystalline phase, because there the chains are more extended and tightly packed, and possibly more oriented, with a higher *trans* conformer content for the $-\text{CH}_2-\text{CH}_2-$ bonds (FTIR results not presented [21]). In fact, the density estimated for the non-crystalline regions in coalesced PET ($\rho_{\text{nc}} = 1.354 \text{ g/cm}^3$) exceeds slightly the overall density of the annealed PET film (1.3497 g/cm^3).

In Fig. 3 the all *trans* crystalline conformation of PET and non-crystalline, though also highly extended, kink conformation of PET are drawn. PET chains in the narrow channels of their γ -CD-IC crystals adopt the kink conformations, which after coalescence were also demonstrated to persist in the non-crystalline regions [21,33,59]. PET kink conformers have been suggested to occupy only $\sim 2/3$ of the volume occupied by the all *trans* crystalline PET conformation [70]. If the kink conformers also dominate the non-crystalline regions of coalesced PET, then the observation that $\rho_{\text{nc}} = 1.354 \text{ g/cm}^3$ exceeds

the overall density of annealed PET, $\rho_{\text{anneal}} = 1.3497 \text{ g/cm}^3$, may be understood.

In addition, the kink conformations adopted by PET included in its γ -CD-IC may upon coalescence be easily and rapidly converted into the crystalline all *trans* conformation solely by facile counter rotations about the $-\text{O}-\text{CH}_2-$ and $-\text{CH}_2-\text{O}-$ bonds, a conformational transformation producing little swept out volume and resulting in a highly crystalline sample. Largely amorphous as-received PET, on the other hand, is slow to crystallize, because its largely *gauche* $-\text{CH}_2-\text{CH}_2-$ bonds must be rotated to the *trans* conformation during crystallization, a conformational transformation that must sweep out a large volume [21]. What remains to be fully understood is “why coalesced PET retains or readopts its reorganized coalesced structure upon rapid cooling after extended periods in the melt”.

3.1.2. Polyolefins

3.1.2.1. *Coalesced i-PP* [42]. Wide-angle X-ray diffractograms of as-received, precipitated, and coalesced isotactic polypropylene (i-PP), though not presented here, clearly indicated that only the α -form polymorph is present in the as-received and coalesced samples and a very poor α -form or almost a smectic form is obtained in the precipitated one. Careful analysis of all diffractograms revealed that the γ -CD inclusion/coalescence process does not modify the crystalline form of the coalesced i-PP, but does yield a higher crystallinity for the coalesced i-PP, with an increase of about 27% in comparison with that of as-received i-PP. A significant increase in the crystallization rate from the melt was also observed for coalesced i-PP, which crystallized at 130°C compared with a melt-crystallization temperatures of 117°C for as-received i-PP or 121°C for precipitated i-PP. Holding the coalesced i-PP sample in the melt at 200°C for an extended period did not alter its recrystallization behavior. Similar behavior has been observed in other semicrystalline coalesced polymers,

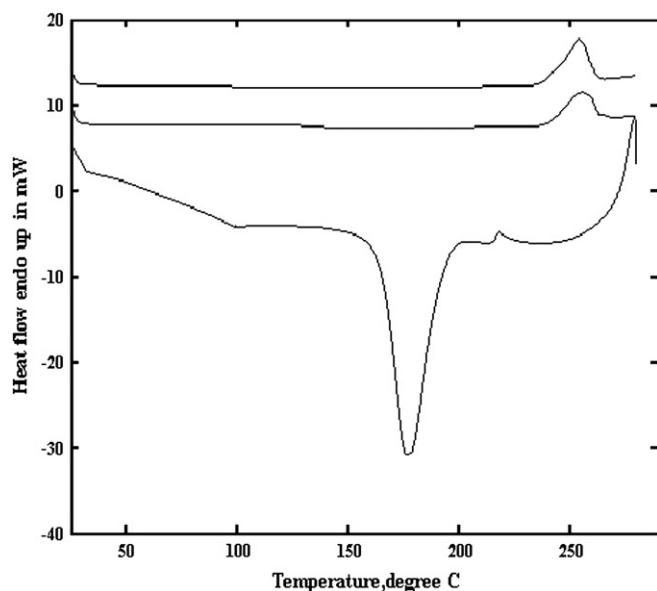


Fig. 4. DSC thermogram of coalesced PET. First (upper), second (middle) heating (20°C/min) and (lower) interim cooling scans. Note recrystallization exotherm observed on rapid cooling from the melt (-200°C/min), which is not observed for PETs normally processed from their solutions or melts.

Table 1
PET film densities [59]

Sample	Density, ρ (g/cm^3)	Crystallinity from DSC	Crystallinity from X-ray
Coalesced PET	1.3670	0.39	0.32
Annealed	1.3497	0.39	0.31
as-received PET			
As-received PET	1.3442	0.10	0.06

such as PET, and can be explained by considering that the included polymer chains retain a certain degree of their extended and untangled natures even after coalescence, which facilitates their rapid crystallization.

3.1.2.2. Coalesced i-PB [42]. X-ray diffractograms of as-received, precipitated, and coalesced isotactic poly(1-butene) (i-PB) are presented in Fig. 5. The diffractograms of both as-received and precipitated i-PB show clearly the form I polymorph with the (110) reflection at 9.9° , the (300) at 17.3° , and the (220) at 20.2° (2θ). In contrast, the coalesced i-PB predominantly adopts the form II polymorph, along with some form III, which are normally obtained from the melt or from solution casting, respectively. The characteristic diffraction peaks of form II appear at $2\theta = 11.8^\circ$ (200), 16.8° (220), and 18.1° (213). Form III has a strong reflection (110) at $2\theta = 11.8^\circ$ and three weak (200), (111), and (120) reflections at $2\theta = 13.8^\circ$, 16.8° , and 20.7° , respectively. Although very noisy, the peak at 13.8° indicates the presence of form III. The diffraction peak of form III at $2\theta = 20.7^\circ$ overlaps with a diffraction peak belonging to form I'. However, the weak peak at $2\theta = 10.0^\circ$ reveals a (110) reflection from form I or form I'. Form I and form I' cannot be distinguished by X-rays, but exhibit different T_m s in the DSC.

Interestingly, after quiescent storage for 6 months at room temperature, the coalesced i-PB, with a high molecular weight of 380,000, shows exactly the same diffraction pattern. It is very well-known in the literature that form II (tetragonal) is metastable and transforms to form I (hexagonal) at atmospheric pressure and room temperature with a half-life in the range 250–1600 min. We did not observe the same crystalline stability of the form II crystals when low molecular weight i-PB was coalesced from its γ -CD-IC.

As previously mentioned, CD-IC formation forces the included polymer chains to adopt a more extended conformation in the host narrow channels, which in the case of i-PB favors the formation of form I, with a more extended conformation, from among its polymorphs. However, an investigation of the phase transformations in i-PB upon drawing has demonstrated the formation of form II upon tensile drawing and

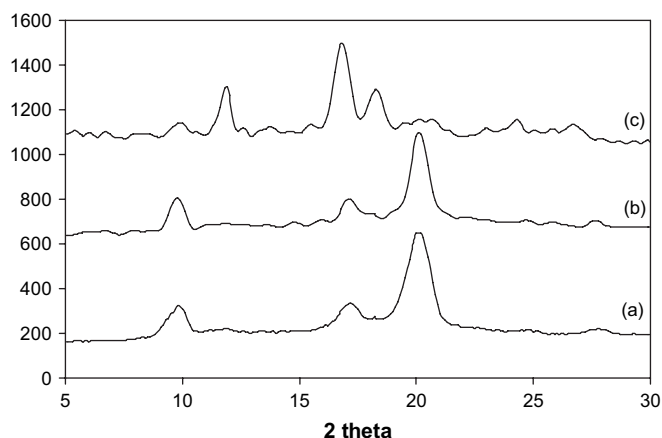


Fig. 5. WAXD patterns (scattered intensity vs. scattering angle) of (a) as-received, (b) precipitated, and (c) coalesced high molecular weight i-PB.

a strong dependence of the deformation process on the crystal form of the initial starting sample. These observations suggest further study of the polymorphic transformations of coalesced i-PB samples, which are in progress. It is also noteworthy to mention the observation of a similar, yet even more significant, increase in the recrystallization kinetics from the melt of coalesced i-PBs (crystallizes at 71°C upon cooling), compared with as-received or precipitated i-PBs (both crystallize at 42°C upon cooling).

3.2. Homopolymer blends coalesced from their common CD-ICs

By combination of a solution containing two distinct dissolved polymers with a CD solution, it is possible to form a common CD-IC containing both polymers. Assuming that each of the guest polymers is randomly included or “mixed” in the CD channels of their common CD-IC (see Figs. 1f and 2), we may anticipate that upon coalescence an intimate blend would result. The intimate blending of polymers, both binary and ternary blends, by coalescence from their common CD-ICs has in fact been demonstrated [40].

3.2.1. PCL/PLLA blends [12,27,46]

In Fig. 6 the X-ray diffractograms of the biodegradable/bioabsorbable polyesters poly(ϵ -caprolactone) (PCL), poly(L-lactic acid) (PLLA), and their blends, either cast from dioxane solution or coalesced from a common α -CD-IC containing both PCL and PLLA as guests, are presented. Their solution-cast blend shows extensive crystallinities for both phase-segregated components, while the PCL/PLLA blend coalesced from their common α -CD-IC crystals shows virtually none and very little PCL and PLLA crystallinities, respectively. Unlike the solution-cast blend, the largely amorphous

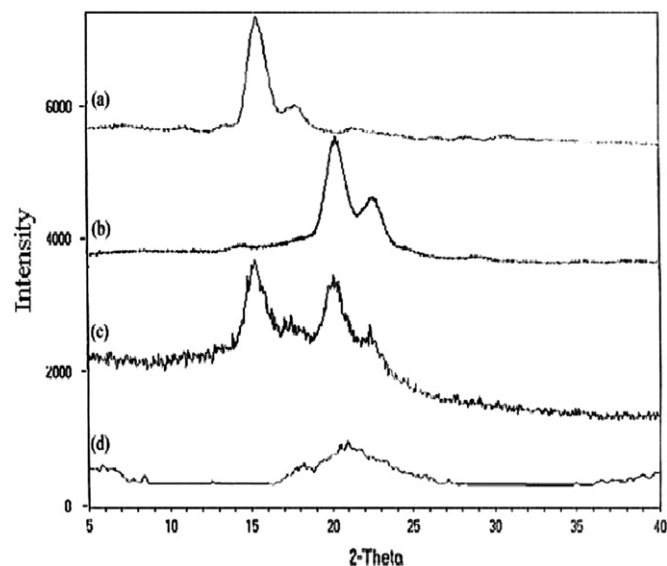


Fig. 6. X-ray diffractograms of pure (a) PCL and (b) PLLA and (c) PCL/PLLA blends obtained by casting from dioxane solution and (d) hot water coalescence from PCL/PLLA- α -CD-IC [12].

coalesced blend strongly suggests intimate mixing of PCL and PLLA chains, which prevents their separate crystallization. In fact detailed analyses of two-dimensional Hetcor NMR spin-diffusion experiments [46] revealed that the length scale of mixing in the coalesced PCL/PLLA blend is smaller than the radii of gyration of both components and the mobility of PLLA chains in this blend is greater than in the amorphous regions of pure PLLA. Both observations confirm that PCL and PLLA chains are indeed intimately mixed in the blend coalesced from their common α -CD-IC crystals.

3.2.2. PVAc/PMMA blends [40,47,49,51]

Direct insertion probe mass spectrometric (DIP-MAS) analyses of poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc), and their coalesced and precipitated blends were performed [51]. The thermal degradation behaviors of both PVAc and PMMA were changed in the blend coalesced from their common γ -CD-IC.

For the coalesced PVAc/PMMA blend two decompositions were observed at 360 and 424 °C, very close to those observed in their physical mixture at 360 and 422 °C and to corresponding values observed for pure PVAc and PMMA. For both blends, the mass spectra recorded at around 360 °C are mainly dominated by peaks diagnostic for PVAc and those recorded at around 430 °C are dominated by peaks diagnostic for PMMA. Though the total ion current (TIC) curves of the physical and coalesced blends are quite similar, the fragmentation patterns recorded in the related pyrolysis mass spectra were significantly different. At high temperatures the relative intensities of high molecular weight fragments were decreased for the coalesced blend. In particular, the decrease in PMMA monomer yield was quite drastic for the coalesced blend. In Table 2

Table 2

The relative intensities and assignments of characteristic and intense peaks in the pyrolysis mass spectra of physical and coalesced PVAc/PMMA blends at temperatures corresponding to maxima in their TIC curves [51]

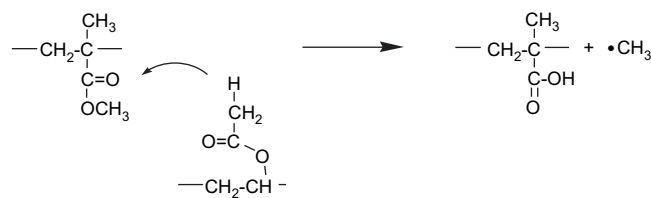
<i>m/z</i> (Da)	Physical blend (°C)		Coalesced blend (°C)			Assignments
	360	430	310	360	430	
15	75	46	80	152	151	CH ₃
41	585	1000	1000	276	1000	CH ₂ CCH ₂
43	1000	207	979	1000	725	CH ₂ CHO, CH ₃ CO
45	769	115	505	509	352	COOH, CHOO
60	690	85	566	300	195	CH ₃ COOH
69	546	924	649	141	544	CH ₂ CCH ₃
73	13	17	241	16	20	C ₃ H ₅ O ₂
78	103	14	22	63	49	C ₆ H ₆
86	6	8	37	3	77	C ₄ H ₅ O ₂ , VAc
91	46	51	73	26	164	C ₇ H ₇
100	215	351	140	39	116	MMA
128	51	42	36	24	83	C ₁₀ H ₈
141	25	37	26	8	58	C ₁₂ H ₉
179	15	38	25	7	31	C ₁₄ H ₁₁
180	13	13	5	6	21	C ₁₄ H ₁₂
215	6	16	21	3	24	C ₁₄ H ₁₂
232	3	5	4	2	8	C ₁₈ H ₁₆
284	1	2		1	4	C ₂₂ H ₂₀
315	1	3		1	7	C ₂₄ H ₂₇

relative ion yields of intense and/or characteristic peaks in the pyrolysis mass spectra recorded at the maxima of the TIC (the variation of *total ion current* as a function of temperature) curves of both blends were collected. It was noteworthy that the relative intensities of high molecular weight products diminished noticeably for the coalesced PVAc/PMMA blend, as was the case for coalesced PVAc. In an attempt to better understand these observations, single ion pyrograms of thermal degradation products for the physical and coalesced blends were studied.

Significant differences in the evolution profiles were detected. Drastic changes in the relative yields of the PVAc and PMMA based products were noticed. The evolution profiles of PVAc based fragments recorded during the thermal degradation of the coalesced blend showed nearly similar trends up to 380 °C with those recorded for coalesced PVAc. Unlike the as-received and coalesced PVAc and the physical blend, shoulders at around 400 °C appeared. Furthermore, significant decrease in the relative intensity of the MMA monomer peak, compared to those recorded for as-received and coalesced PMMA and the physical blend, was observed. On the other hand, for the coalesced blend the relative intensities of the 15 (CH₃•) and 86 (VAc) Da peaks increased noticeably, especially in the temperature region where PMMA based products evolved.

It was clear that the thermal degradation behaviors of both PVAc and PMMA were changed in the coalesced blend. The decrease in MMA monomer yield may be associated with inhibition of PMMA depolymerization. Depolymerization of PMMA can be inhibited if the loss of side chains is favored, which implies that proton-transfer to the C=O groups of PMMA occurs. So, for the coalesced PVAc/PMMA blend, PMMA depolymerization was likely inhibited as a result of proton-transfer to the C=O groups of the MMA units, as depicted in Scheme 1.

Because both coalesced and as-received PMMA degrade mainly by depolymerization reactions, the source for the depolymerization inhibiting proton-transfer in the coalesced blend could only be PVAc. However, it is clear that the simple presence of PVAc was not sufficient for proton-transfer, as depolymerization of PMMA was also recorded for the PVAc/PMMA physical blend. Instead, it may be suggested that such a proton-transfer can only be possible if the separation between PMMA and PVAc chains is comparable to the distance between γ -H and C=O groups within a single PMMA chain.



Scheme 1. McLafferty type rearrangement *via* intermolecular proton-transfer to PMMA chains from PVAc chains in the well-mixed coalesced PVAc/PMMA blend [51].

Clearly in the blend coalesced from their common γ -CD-IC the PVAc and PMMA chains are very intimately mixed.

It should be mentioned that usually, but not always, intimate blends of polymers produced by coalescence from their common CD-ICs evidence considerable thermal stabilities. They generally remain well-mixed even after heating for considerable periods of time above their T_g s and/or T_m s [40], even though their component homopolymers should have possessed mobility sufficient to phase separate under the thermodynamic driving force provided by their inherent incompatibility, i.e., their $\Delta H_{\text{mix}} > 0$. Of course opposing their unfavorable heat of mixing is the entropy of their intimately mixed blend, which though presumably small for pairs of high molecular weight polymers [71], should still hinder their phase segregation. Apparently the net (enthalpic–entropic) driving force for segregation of these CD-processed, intimately mixed, yet normally incompatible, homopolymer pairs into separate phases is sufficiently small to require substantial times to achieve, and thus may be kinetically controlled.

For example, the diffusion coefficient for PMMA [16] of $M_w = 360,000$ in the melt is $D \sim 10^{-15}–10^{-14}$ cm²/s [72]. The distance x moved by a PMMA chain during a time t can be estimated from $x = (6tD)^{1/2}$. The time required for a PMMA chain to move a distance equal to its radius of gyration (~ 170 Å) [71] would then be ~ 1.6 h. The intimately mixed PC and PMMA chains in the blend coalesced from their common γ -CD-IC must be able to diffuse apart if they are to phase separate, and PC and PMMA chain separations of at least a radius of gyration of their polymer coils must be achieved. Thus, the significant temporal stability of intimately mixed polymer blends obtained by their CD-IC processing may not be totally surprising, given the slow diffusion expected for their molten polymer chains.

Whatever detailed factors influence the substantial thermal and temporal stabilities of CD-processed polymer/polymer blends, the net results are intimately mixed blends that are likely able to be thermally processed into useful articles (films, fibers, and molded articles) with a homogeneous composition of polymer blend components. In turn, these intimately blended polymer materials may lead to properties that are unique and hopefully improved over those of their pure homopolymer components.

3.3. Coalescence of block copolymers from their CD-ICs

Inherently incompatible blocks in block copolymers normally segregate into separate phases in the bulk. However, if block copolymers are included in and then subsequently coalesced from their CD-ICs, the phase segregation of their blocks may be controlled. For example, if all blocks of a block copolymer are included in its CD-IC, then, similar to the case for common CD-ICs containing two or more homopolymers, upon coalescence we would expect a reduction in block phase segregation. On the other hand, if some blocks are included in their CD-ICs, while others are not, then we might anticipate an increased phase segregation of their constituent blocks upon coalescence.

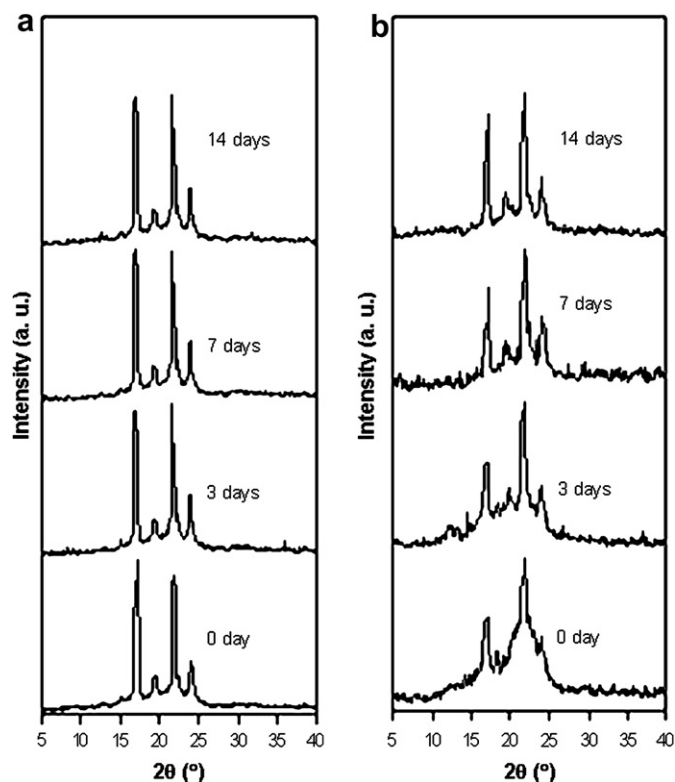


Fig. 7. X-ray diffraction patterns of (a) as-synthesized and (b) coalesced PCL-*b*-PLLA melt-pressed films observed following various enzymatic degradation times [20].

3.3.1. PCL-*b*-PLLA [18,20,27]

When melt-pressed films of as-synthesized PCL-*b*-PLLA and PCL-*b*-PLLA that had been included in and then coalesced from its α -CD-IC are observed by X-ray diffraction (see Fig. 7) [20], it is clear that the coalesced film is predominantly amorphous, as a consequence of the mixing of PCL and PLLA blocks, while the as-synthesized PCL-*b*-PLLA film shows substantial crystallinity for both the PCL and PLLA blocks (compare with Fig. 6), indicating a phase segregation of blocks. These PCL-*b*-PLLA films were then subjected to enzymatic degradation and their structures were monitored with X-ray diffraction. From Fig. 7 we can see that the phase-segregated as-synthesized block copolymer film underwent only limited degradation even after 2 weeks of enzymatic digestion. The coalesced PCL-*b*-PLLA film, on the other hand, experienced much more extensive degradation, as evidenced by the transition of its X-ray diffraction pattern from that of a largely amorphous material initially to the one that is highly crystalline after 14 days of degradation. Clearly the enzyme exclusively attacked the abundant amorphous sample regions of the coalesced film, where the PCL and PLLA blocks are well mixed. Thus, the biodegradation of block copolymers, and by extension, homopolymer blends can be controlled by processing them with CDs.

3.3.2. PCL-PPG-PCL [25]

When ICs are formed between guest PCL-poly(propylene oxide) (PPG)-PCL triblock copolymer and α - and γ -CD hosts

Table 3
Thermal properties and crystallinities of various PCL–PPG–PCL triblock copolymer samples as revealed by DSC [25]

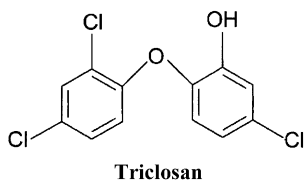
Sample	T_m (°C)	ΔH_m (J/g)	χ_c (%)
As-synthesized copolymer	57.3	58.6	56.5
Coalesced from α -CD-IC	63.8	76.8	74.1
Coalesced from γ -CD-IC	63.0	51.3	49.5

[25], in the first case only the PCL blocks are included, while in the PCL–PPG–PCL– γ -CD-IC entire triblock copolymer chains are included. As a result, in comparison to the as-synthesized triblock copolymer, we would expect that upon coalescence from the PCL–PPG–PCL– α - and γ -CD-ICs an increase and a decrease in the phase segregation of PCL and PPG blocks would occur, respectively. As can be seen in Table 3, these expectations are in fact realized as indicated by the increased, decreased level of PCL block crystallinity in PCL–PPG–PCL coalesced from its α -, γ -CD-ICs. Because two side-by-side PCL blocks may be included in the channels of the γ -CD-IC [73,74], while only single PPG blocks may be included, the less than expected minor reduction in the phase segregation achieved upon coalescence from the PCL–PPG–PCL– γ -CD-IC can be understood.

3.4. Additive–CD-ICs and –rotaxanes

3.4.1. Additive–CD-ICs [7,9,13,17,52,53,65,69]

Because crystalline CD-ICs are high-melting and thermally stable, even when containing small-molecule guests that are volatile liquids [52,53] or even gases [75] in the bulk, delivery of additives to polymer materials can be improved by using additive–CD-ICs, which may often be conveniently melt-processed into polymers. An example of CD-IC delivery of a polymer additive is provided by the commercial antibacterial triclosan [17].



Triclosan– β -CD-IC was formed and small amounts were mixed with PCL powder, which was sprinkled onto cotton fabric and then covered with another piece of cotton fabric. The cotton–PCL/triclosan– β -CD-IC–cotton was ironed into a laminate, placed on an agar plate, and then tested against the growth of *Escherichia coli* bacteria. As can be observed from the test results shown in Table 4, *E. coli* bacteria were unable to grow upon the laminated cotton fabric containing triclosan– β -CD-IC. In fact the laminated fabric was just as effective as films of PCL containing triclosan– β -CD-IC or pure triclosan.

The use of triclosan– β -CD-IC to deliver the antibacterial properties of triclosan has an important advantage over the pure anti-bacterial. Triclosan is crystalline, but melts in the range of 55–60 °C. Though it is possible to blend pure

Table 4
Escherichia coli test results for cotton fabric laminated with PCL films embedded with triclosan or triclosan– β -CD-IC [17]

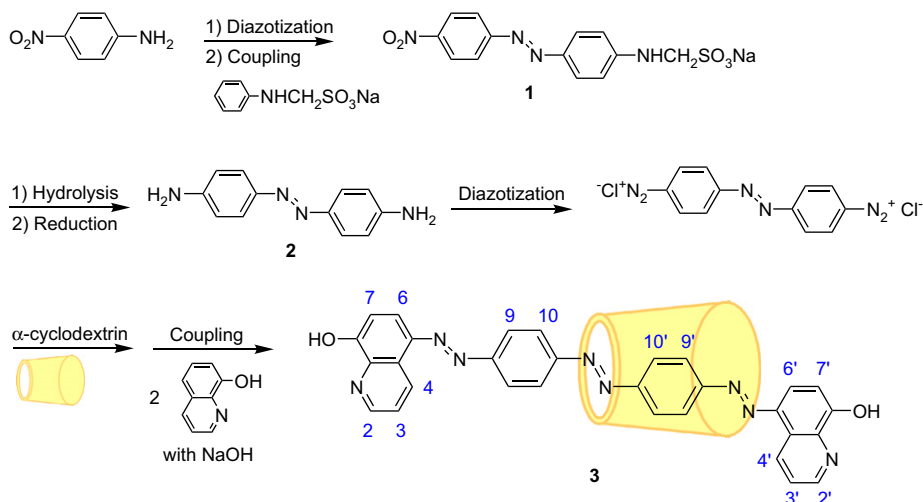
Sample	Zone of inhibition (diameter in mm)
PCL (between pieces of fabric) (1 g of PCL)	0
PCL (1 g of PCL)	0
PCL + triclosan (between pieces of fabric) (1 g of PCL and 0.1 g of triclosan)	15
PCL + triclosan (1 g of PCL and 0.1 g of triclosan)	15
PCL + triclosan– β -CD-IC (between pieces of fabric) (1 g of PCL and 0.1 g of triclosan– β -CD-IC)	12–15
PCL + triclosan– β -CD-IC (1 g of PCL and 0.1 g of triclosan– β -CD-IC)	14–17

triclosan with low melting polymers like PCL ($T_m \sim 60$ °C), this would not be the case for polymers with higher melting or softening temperatures. On the other hand, triclosan– β -CD-IC is thermally stable and solid well above 200 °C, and so may be melt-processed into many polymeric materials. The thermal stabilities [53,69] of small-molecule–CD-IC crystals has permitted us to more conveniently and effectively deliver [7,9,13,17,52,53,65,69] several additives to polymer materials, including, anti-bacterials, flame retardants, spermicides, insect repellants, etc.

3.4.2. Additive–CD–rotaxanes

Soluble additive–CD–rotaxanes can be obtained by first forming a soluble additive–CD-IC and then attaching bulky end-groups to portions of the guest additive nearest to or extending from the host CD rims, thereby preventing the unthreading of the additive. Scheme 2 illustrates an example of the synthetic route for obtaining an azo-dye– α -CD–rotaxane [64,76]. While the original azo-dye is not water soluble, the azo-dye– α -CD–rotaxane is soluble. Because it has been demonstrated that CDs have a strong affinity to bind with TiO₂ films [76], when i-PP fibers, containing small amounts of particulate TiO₂ as a delusterant, are heated in aqueous solution of the azo-dye– α -CD–rotaxane, they are quickly dyed, as is apparent from the top of Fig. 8. As far as we are aware, this is the first demonstration of the solution dyeing of a polyolefin yarn, which are normally pigmented due to their unreactive and hydrophobic surfaces, without chemical or plasma pretreatments or introduction of a comonomer. The characteristics of dyeing i-PP with the azo-dye– α -CD–rotaxane are also presented in Fig. 8. Not shown there, however, is that the dyed i-PP yarns are both light and wash fast.

The general procedure of delivering additives in the form of their CD–rotaxanes appears to offer improved solutions to a wide-range of polymer–additive and textile-finishing problems, because of two factors. First, CD–rotaxanation of an additive permits control of its solubility and offers protection (UV and chemical) to the threaded additive. Second, chemical modification of the –OH groups on the CD coat permits specific substrate targeting of the additive–CD–rotaxane, without the need to modify the chemistry of the additive



Scheme 2. Synthesis of an azo-dye rotaxane 3 (RD) with 8-hydroxyquinoline as coupling components [75].

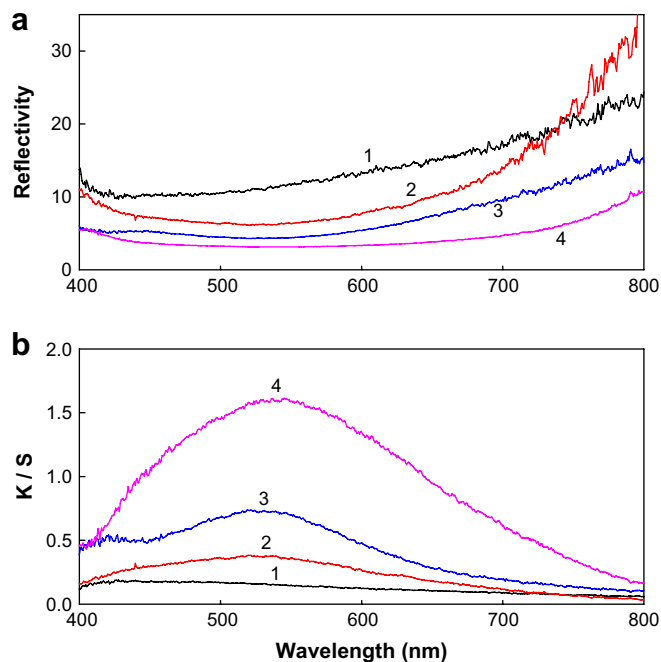
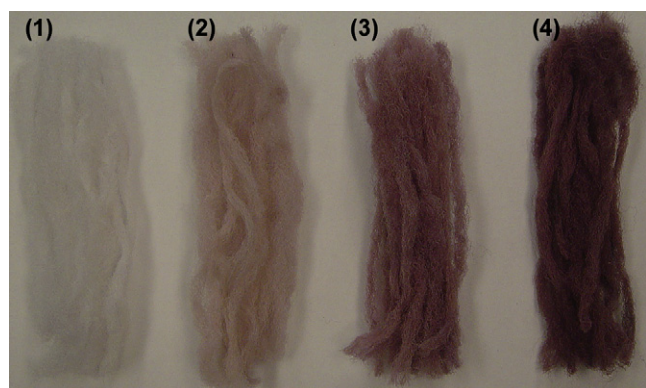


Fig. 8. (a) Reflectivity and (b) K/S curves of PP fibers: (1) PP before dyeing, (2) after dyed with AzoxFD (free dye), (3) after dyeing with AzoxRD (rotaxanated dye), and (4) after dyeing with AzoxRD complexed with Cu^{2+} . (Note also photos of the corresponding PP yarns in the top panel.)

itself. Together these advantages should soon lead to a new class of polymer and textile additives in the form of their CD-rotaxanes.

4. Polymers functionalized *via* covalent attachment of CDs

Many $-\text{OH}$ groups attached to CDs enable them to be covalently bonded to polymers, either directly to their backbones during or attached to their side chains subsequent to polymerization. In a modified interfacial polymerization, nylon-6,10 containing various amounts of covalently bonded mBCDs have been obtained. (In mBCDs, 2 of the 3 $-\text{OH}$ s on each glucose ring are converted to $-\text{OCH}_3$, and then reacted with sebacoyl chloride [77].) These mBCD-nylon-6,10 polymers show thermal degradation characteristics very similar to pure nylon-6,10, and are more rapidly dyed to higher dye levels than pure nylon-6,10, as indicated in Fig. 9.

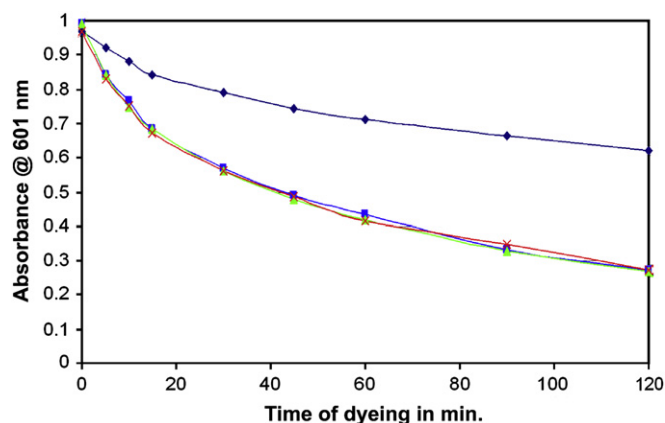


Fig. 9. Disappearance of blue-29 dye from dye bath upon introduction of nylon-6,10 fibers without (upper curve) and with (lower curves) various contents of covalently bonded mBCDs in their backbones.

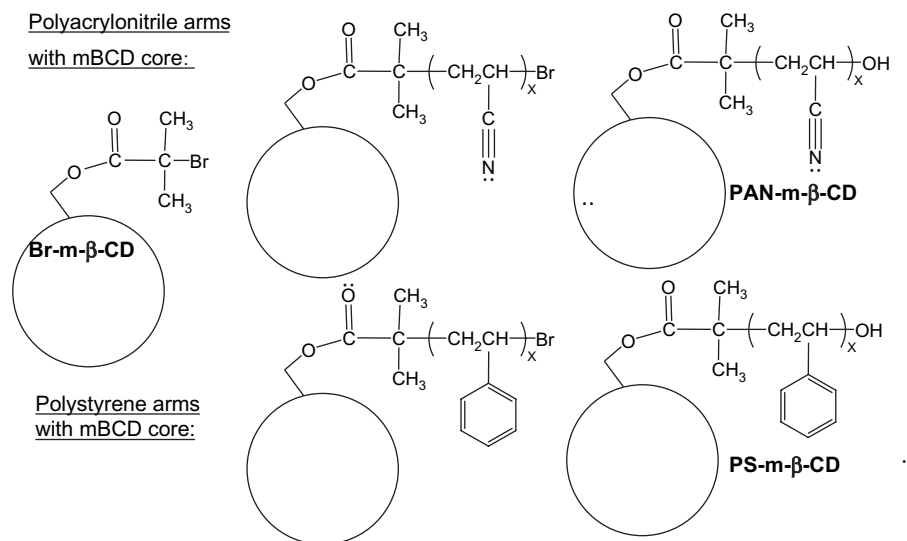


Fig. 10. ATRP syntheses of PAN and PS stars with mBCD cores.

Likewise, mBCD–nylon-6,6 fibers have been synthesized in a similar fashion. DSC data collected for all mBCD–nylon-6,6 compositions show a characteristic T_m for nylon-6,6 at 255 °C, and all are fully soluble in *m*-cresol. Thus, it is reasonable to assume that the inherent chain mobility of nylon-6,6 is retained in the mBCD–nylon-6,6s, suggesting that they can be traditionally processed. This approach to functionalizing polymers/textiles is readily extendable to other step-growth polymers.

CDs have several reactive hydroxyl groups which can be chemically modified and then functionalized with vinyl monomers, such as *t*-butyl acrylate, methyl methacrylate, styrene or acrylonitrile, producing star polymers with CD at their centers (see Fig. 10). One way to control the length of the star arms is through use of atom-transfer radical polymerization (ATRP) [78], which is known to produce highly controlled and uniform polymer molecular weights. 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.

These star polymers with mBCD cores have the ability to complex with a variety of additives *via* formation of CD-ICs. In addition, they may be able to be blended with a second normally incompatible polymer, such as PPG, with a strong propensity to thread through and complex with their mBCD cores.

5. Summary and conclusions

We have demonstrated that the structures, morphologies, and even chain conformations of solid polymer samples may be altered by including them in and then coalescing them from their CD-ICs. In addition to altering their physical behaviors, coalescence of guest polymers from their CD-ICs permits us to obtain solid polymer samples that are distinct from bulk

samples made from their solutions and melts. Clearly study of such reorganized coalesced polymer samples can contribute to our ability to understand and develop improved structure–property relationship for them.

Additionally, because crystalline CD-ICs are high-melting and thermally stable, even when containing small-molecule guests that are volatile liquids or even gases in the bulk, delivery of additives to polymer materials can be improved by using additive–CD-ICs, which may often be conveniently melt-processed into polymers. If we begin with appropriate soluble additive–CD-ICs and then react the unincorporated ends of the guest additive with capping groups that prevent it from unthreading, we create CD–additive–rotaxanes. One advantage of CD–additive–rotaxanes is the protection (thermal, chemical, UV–vis, etc.) afforded by the CD coat. Another is the ability to utilize many –OH groups on the CD coat to target the delivery of the CD–additive–rotaxane to a particular polymer substrate.

CDs may also be covalently bonded to polymers to alter their functionalities through incorporation of CDs into their backbones during polymerization or attachment to their side chains *via* post-polymerization reactions. The presence of covalently bonded CDs in polymers serves to increase their acceptance and retention of additives, such as dyes, fragrances, anti-bacterials, etc. They may also be further reacted or treated through their covalently bonded CDs to cross-link and form networks or to form blends with other polymers having a propensity to thread through their attached CD cavities.

Because CDs are non-toxic, biodegradable, and bioabsorbable, they may be used in medical applications as well as providing for the fabrication of “greener” polymer materials.

In this report we have summarized only our recent studies employing the cyclic starches called cyclodextrins (CDs) to both nanostructure and functionalize polymer materials. Lest the reader gets the erroneous impression that our studies have been carried out in isolation, we refer them to a recent

review and a summary of related research [79,80] that also attempt to utilize CDs and polymers to create polymer materials with improved and new properties for advanced applications.

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His research interests include the conformations, configurations, and structures of synthetic and biological polymers, their determination, principally by NMR, and establishing their effects on the physical properties of polymer materials. Most recently, the formation of and coalescence from inclusion compounds (ICs) formed between cyclodextrin (CD) hosts and polymer guests have been utilized to nanostructure bulk polymers, including homopolymers and their blends and block copolymers. In addition, small-molecule guest–CD–host-ICs and –rotaxanes, and the covalent incorporation of CDs into polymers both during and subsequent to their syntheses, have been used to improve the delivery of additives to polymer materials.