Nanostructuring polymers with cyclodextrins

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Bulk solid polymer samples formed by the coalescence of guest polymer chains from their inclusion compounds (ICs) formed with host cyclodextrins (CDs) can result in significant reorganization of their phase structures, morphologies, and even chain conformations from those more commonly produced from randomly-coiled, entangled polymer solutions and melts. When the cyclic host CDs are threaded by polymer chains to form crystalline polymer-CD-ICs, the guest polymers become highly extended due to the narrow host CD diameters (5, 7, and 9 Å for α-, β-, and γ-CDs) and are segregated from neighboring guest polymer chains by the CD-IC channel walls. As a consequence, when polymer-CD-IC crystals are treated with CD solvents that do not dissolve the guest polymers or are treated with amylase enzymes, the resulting coalesced bulk polymer samples often display properties distinct from those of normally produced bulk samples of the same polymers. In this article the CD-IC processing of polymers to generate novel polymer microstructures and morphologies are described, to control the phase separation of immiscible blocks in block copolymers, and to form well-mixed intimate blends of two or more polymers that are normally incompatible. The thermal and temporal stabilities of polymer samples coalesced from their ICs formed with CDs will also be mentioned, and it is suggested that the range of polymer properties can be greatly expanded by their CD-IC processing. Copyright © 2005 John Wiley & Sons, Ltd.

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INTRODUCTION

Enzymatic degradation of starch leads to the production of cyclic oligosaccharides named cyclodextrins (CDs),¹² with six (α-CD), seven (β-CD), and eight (γ-CD) α-(1,4)-linked D(+)-glucopyranose units as depicted in Fig. 1. The hydrophilic exteriors and hydrophobic interiors of the CD bracelets confer on them water solubility and the ability to complex in their interiors a variety of small-molecule guests to form soluble inclusion complexes (ICs), which in many cases can be crystallized.³⁴ More recently, CDs have demonstrated an ability to form crystalline ICs with a wide variety of polymer guests.¹⁰⁻¹⁵ The guest polymers are included in the continuous narrow channels (0.5–1.0 nm in diameter) formed by the host CD stacks, and so are highly extended and segregated from neighboring chains by the walls of the host CD bracelets, as depicted in Fig. 2. As a consequence, when polymer-CD-ICs are treated with solvents for CDs that are non-solvents for the included polymers or with amylase enzymes, the CD-IC coalesced and consequently reorganized polymer samples exhibit properties that are distinct from their normally processed bulk samples.

In this article the CD-IC processing of several homopolymers and their blends and block copolymers are described, with special emphasis placed on their improved and controllable properties. For example, the phase segregation and consequent crystallinities of normally incompatible biodegradable/bioabsorbable homopolymer blends and block copolymers, may be controlled in this manner, leading to improved properties such as biodegradability.

EXPERIMENTAL

Preparation and coalescence of polymer-CD-ICs

The general method for the preparation of polymer-CD-ICs¹¹⁻²⁵ is presented schematically in Fig. 4. In general, solutions of the host CDs and the guest polymers are combined to permit threading of the CDs by the guest polymers to form crystalline polymer-CD-ICs (see Fig. 2), which are isolated as precipitates. Most recently²² it has been possible to obtain CDs...
(α and γ) which crystallize in the columnar or channel form, CD_{αCS} illustrated in Fig. 2, but which do not contain any included guests aside from water of hydration. It was observed^{23,24} that suspending CD_{αCS} crystals in polymer solutions that do not dissolve the CD_{αCS} resulted in the formation of polymer-CD–ICs. This latter development expands the range of possible polymer-CD-ICs that may be formed, because most polymers are soluble in at least one solvent that, in turn, does not dissolve CD_{αCS}.

Coalescence of guest polymers from their CD-ICs is normally accomplished by washing the polymer-CD-IC crystals with water or dimethylsulfoxide to remove the host CDs.^{11–22,25} Depending on the chemical nature of the included polymer, polymer-CD-IC crystals may be treated with an aqueous solution containing an amylase enzyme,^{21} which selectively removes the host CD by enzymatic degradation.

Characterization of polymers coalesced from their CD-ICs

Infrared studies were carried out with a Nicolet 510P FT-IR spectrometer in the range between 4000 and 600 cm\(^{-1}\), with a resolution of 2 cm\(^{-1}\). The sample powders were pressed into KBr pellets for observation in the FT-IR spectrometer. The wide-angle X-ray diffraction (WAXD) patterns of samples were obtained with a Siemens type-F X-ray diffractometer. The X-ray source was Ni-filtered Cu-K\(_{α}\) radiation (1.54 Å), with voltage and current set to 30 kV and 20 mA. The specimens were mounted on stainless steel frames and scanned from 5° to 40° at a rate of \((2\theta = 1.2°)/\text{min}\). Differential scanning calorimetry (DSC) thermal scans were performed with a Perkin–Elmer DSC-7. The measurements were run in the range 30–280°C at heating and cooling rates of 20 and –200°C/min, respectively.

Solid-state NMR data were collected using a Bruker DSX wide-bore system with a field strength corresponding to a \(^1\text{H}\) Larmor frequency of 300.13 MHz. Radiofrequency power levels were 71 kHz for spin-locking and decoupling, corresponding to \(π/2\) pulse widths of 3.5 μsec. Data were obtained using magic-angle spinning (MAS) speeds of 4–5 kHz on a commercial 7-mm probe. Cross polarization (CP) contact times were 1 msec. \(^1\text{H}\) spin-lattice relaxation times in the rotating frame \([T_{1\rho}(\text{H})]\) were measured by proton spin-locking relaxation experiments. A resonant spin-lock field, phase-shifted 90° relative to the initial exciting pulse, was applied to lock the \(^1\text{H}\) transverse magnetization. \(^1\text{H}\) relaxation was observed indirectly from the intensities of \(^13\text{C}\) resonances through CP after various spin-lock times. The \(^13\text{C}\)
spin-lattice relaxation times in the laboratory frame \( [T_1(13\text{C})] \) were detected by measuring the intensities of \( ^{13}\text{C} \) resonances in the inversion-recovery process, after the initial \( ^{13}\text{C} \) magnetizations were enhanced by CP.

Assessment of the biodegradation of polymers coalesced from their CD-ICs was described previously.\(^{21}\)

RESULTS AND DISCUSSION

Homopolymers

The results have shown that crystallizable polymers coalesced from their molecular complexes reveal semi-crystalline characters distinct from samples crystallized from their completely disordered solutions or melts.\(^{16,19,26}\) These observations suggest an extended-chain crystalline morphology for the IC-coalesced polymer samples.

When guest poly(ethylene terephthalate) (PET) was coalesced from its IC formed with host \( \gamma \)-CD, the coalesced PET was found\(^{16}\) to have a much higher crystallinity (~40%) than the as-received sample (~14%). Repeated heating and cooling DSC scans observed between 30 and 280 °C on the coalesced PET revealed an absence of both a glass transition and a crystallization exotherm upon heating, with only a melting endotherm that remained large. Even after holding the coalesced PET in the melt for 2 hr and following rapid cooling, the coalesced PET only showed a melting endotherm on subsequent reheating. Unlike as-received PET, the coalesced sample is apparently repeatedly and rapidly crystallizable from its melt, with non-crystalline portions of the sample that do not evidence a glass transition.

FT-IR observations\(^{16}\) of both as-received and coalesced samples were interpreted to indicate that the PET chains in their non-crystalline regions have very different conformations, with predominantly trans (t) and gauche (g) –CH\(_2–\)CH\(_2–\) and –O–CH\(_2–\)CH\(_2–\), –CH\(_2–\)O– bonds, respectively, in coalesced PET and g ± t –CH\(_2–\)O– and –O–CH\(_2–\) –CH\(_2–\)O– bonds, respectively, in the as-received sample. It was suggested that the kink conformers with g ± t (ethylene glycols (EGs)) are present in PET chains in the narrow host PET-\( \gamma \)-CD-IC channels are largely retained in the non-crystalline regions of the coalesced PET, apparently even after extended periods in the melt. The ability of coalesced PET to crystallize rapidly was attributed to facile interconversion of EGs with g ± t kink conformations to the ttt crystalline conformation (see Fig. 5) made possible by counter rotations about the –CH\(_2–\)O– and –O–CH\(_2–\) bonds, which do not require ‘swept-out’ volume.

The contrasting thermal behaviors of the samples are further illustrated\(^{26}\) in Fig. 6, where for as-received PET, both the crystallization temperature \( (T_{cc}) \) and crystallization enthalpy \( (H_{cc}) \) observed on cooling decrease with increasing cooling rate. When \( T_{cc} \) is close to the glass transition temperature \( (T_g) \) of PET (~80 °C), \( H_{cc} \) is almost zero and crystallization for molten as-received PET ceases. However, the IC coalesced PET maintains a relatively constant \( H_{cc} \) with decreasing \( T_{cc} \) when \( T_{cc} > T_g \) and the crystallization of coalesced PET remains substantial even at \( T_{cc} < T_g \). These observations provide additional evidence that coalesced and as-received PETs are rapidly and slowly crystallizable, respectively. In fact, it can be estimated that the rate of crystallization of coalesced PET from its melt is ~1000 times greater than that for the as-received molten sample. Here it is clearly demonstrated that the highly extended, unentangled polymer chains in the CD inclusion complex are largely retained in the coalesced PET, and so locally are more readily able to rapidly crystallize.

The CP/MAS \( ^{13}\text{C} \)-NMR spectra of as-received, precipitated, and coalesced or included PETs are displayed in Fig. 7, where only the carbonyl and methylene carbon regions are presented. Note that in both spectral regions the least shielded, downfield resonance belongs to as-received PET and the most shielded, upfield resonance comes from coalesced or included PET-\( \gamma \)-CD-IC.\(^{16,26}\) The carbonyl carbons terminating EG fragments whose –CH\(_2–\)O– and –O–CH\(_2–\) bonds have g ± t conformations were expected\(^{27}\) to resonate upfield from those with t conformations. This is consistent with conclusions drawn previously from modeling the conformations of included PET chains\(^{28,29}\) and the FT-IR analysis\(^{16}\) of as-received and coalesced PET conformations.
methylene carbons in PETs are insensitive to the conformations, convincingly established that the resonance frequencies of the methylene carbon resonances belonging to t –CH2–O– and –O–CH2– bonds are predominantly those found in γ-CD (~8 Å), only the all trans (ttt) crystalline conformer was unable to interconvert to the other 8 xty channel conformers without leaving the 8 Å channel. Thus the PET g ± tg kink conformers, in addition to being nearly as extended (~95% of the ttt conformer fiber repeat) and narrower (~80% of the ttt conformer cross-section), are also entropically favored for inclusion in PET-γ-CD-IC compared with the all trans crystalline PET conformations.

One would normally expect the methylene carbon resonances of these PET samples to exhibit the same order of resonance frequencies, because they are γ to the carbonyl carbons and are either t or g ± g to them conformationally across the same –CH2–O– and –O–CH2– bonds.11 This is in fact what is observed in Fig. 7. However, a recent solid-state 13C-NMR study of PETs by Kaji and Schmidt-Rohr30 has convincingly established that the resonance frequencies of methylene carbons in PETs are insensitive to the conformations of the EG –CH2–O– and –O–CH2– bonds, and instead seem to only depend on the conformations of the –CH2–O– and –O–CH2– bond connecting them. On highly crystalline and predominantly amorphous PET samples with 13C-enriched methylene carbons they were able to separately observe methylene carbon resonances belonging to t and g ± –CH2–CH2– bonds. They found that in both PET samples the methylene carbons belonging to t –CH2–CH2– bonds resonated ~2 ppm upfield from those methylene carbons with g ± –CH2–CH2– bonds, even though the –CH2–O– and –O–CH2– bonds are predominantly t in the highly crystalline PET and significantly g ± in the nearly completely amorphous PET sample. As a consequence, it can be concluded that the coalesced and included PETs have predominantly t –CH2–CH2– bonds, while as-received PET predominantly g ± –CH2–CH2– bonds. Again this is consistent with molecular modeling28,29 and FT-IR16 results, so as-received PET has predominantly g ± –CH2–CH2– bonds and substantial amounts of t –CH2–O–, –O–CH2– bonds, while coalesced and included PETs have predominantly t and g ± –CH2–CH2– and –CH2–O–, –O–CH2– bonds, respectively.

The 13C-observed 1H spin-lattice relaxation times observed in the rotating frame [T1,1(1H)], which reflect motions in the kHz frequency regime, are presented as a function of temperature for the PET samples in Fig. 8. Generally the coalesced sample has the longest and the as-received sample the shortest T1,1(1H), indicating an increasing kHz mobility for PET chains in the as-received sample. Also note that the T1,1(1H) values of as-received PET show a marked sensitivity to temperature at T ~ Tg, which is largely unobserved in the coalesced sample. Initially, the molecular motion increases with temperature resulting in shorter T1,1(1H) values for both PET samples. However, the T1,1(1H) of the as-received PET reaches a minimum near Tg, and further heating results in molecular motions that are too rapid for efficient nuclear spin energy transfer, so T1,1(1H) increases for T > Tg. This is consistent with the presence and absence of a glass-transition observed5 in the DSC scans of as-received and coalesced PETs, respectively. Thus, both macroscopic (DSC) and microscopic (NMR) observations point to the absence of a glass-transition in the non-crystalline regions of coalesced PET.

Coalesced PET has longer T1,1(13C) values than as-received PET. Thus motions in the MHz frequency regime are also more restricted in coalesced PET, compared with as-received PET, possibly because of both the higher crystallinity16 and the tighter packing of kink conformers in the non-crystalline regions. Temperature dependencies similar to those observed in the rotating frame for 1H, T1,1(1H) values, are also observed for the 13C spin-lattice relaxation times, T1,1(13C). This behavior implies that the non-crystalline regions of coalesced PET are distinct from the amorphous regions in as-received PET, because only in as-received PET are the kHz, MHz motions important to T1,1(1H), T1,1(13C) relaxations sensitive to whether or not the sample is below or above its Tg value. Again this is consistent with the failure to observe a glass-transition by DSC for coalesced16 PET.

When the conformations of the polystyrene (PS) tetramer stereosequence fragments (mmmm shown) were searched31 to determine whether or not they could be threaded into γ-CD (~9 Å diameter), the results presented in Table 1 were obtained. The most striking observation to be made is the disparity in the channel sizes (D = diameter) required to accommodate the different PS stereoisomers. While the i-PS stereoisomer (mmm) requires an ~8.5 Å channel, the s-PS
As a consequence of the modeling the tetrad stereoisomers of PS in narrow cylindrical channels, the following suggestions can be made: (i) while the formation of a γ-CD-IC with i-PS should be possible, it appears that s-PS may not be included in the ~8.5 Å channels of the γ-CD-IC crystalline lattice, and so the process of IC formation with γ-CD may be used to separate stereoregular i-PS from s-PS; (ii) the free-radical initiated polymerization of styrene monomer in the narrow channels of the styrene-γ-CD-IC, if it is possible, is likely to produce an unusual PS with alternating m and r diads and therefore repeating mr and rm, triads, which has never been reported. The authors are currently attempting the formation of γ-CD-ICs with i-, s-, and a-PSs, and have formed a styrene monomer (S)-γ-CD-IC. Various initiation schemes are being attempted to transform the (S)-γ-CD-IC to PS-γ-CD-IC via in situ polymerization in order to possibly realize a PS with the unique ...mrmrrm... stereosequence.37

**Homopolymer blends**

Because of the spatial proximity of included guest chains in CD-ICs, the coalescence of two included homopolymers from their common CD-IC might be expected to result in an intimately mixed blend (see Fig. 9). Attempts to improve the properties of biodegradable/bioabsorbable polymers like poly(e-caprolactone) (PCL) and atactic poly(β-hydroxybutyrate) (a-PHB) often lead to their blending. However, PCL and a-PHB are immiscible and phase separate into an inhomogeneous structure. However, as can be seen in Table 2, when PCL and a-PHB are coalesced from their common IC formed with γ-CD, their blends show a marked improvement in the intimacy of their mixing.22 While their physical blend obtained by solution casting shows individual Tg values for the phase segregated PCL and a-PHB components and a high level of crystallinity for the PCL phase, the IC-coalesced blends exhibit single Tg values and greatly reduced PCL crystallinities. Clearly the coalesced PCL/a-PHB blends exhibit substantial degrees of intimate mixing, and it can be

### Table 1. PS stereoisomer channel conformations

<table>
<thead>
<tr>
<th>Stereosomer</th>
<th>Channel diameter (Å)</th>
<th>Conformer</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmm</td>
<td>8.5</td>
<td>ttgtgtt</td>
<td>0.0000003</td>
</tr>
<tr>
<td>mrm</td>
<td>9.0</td>
<td>ttgtgtt</td>
<td>0.0012</td>
</tr>
<tr>
<td>rmm</td>
<td>9.2</td>
<td>ttgtgtt</td>
<td>0.0000002</td>
</tr>
<tr>
<td>mmr</td>
<td>9.3</td>
<td>ttgtgtt</td>
<td>0.000007</td>
</tr>
<tr>
<td>rmr</td>
<td>10.4</td>
<td>ttgtgtt</td>
<td>0.00005</td>
</tr>
<tr>
<td>rrr</td>
<td>10.5</td>
<td>ttgtgtt and ttgtgt</td>
<td>0.000005</td>
</tr>
</tbody>
</table>

Also note that, with the exception of the mrm and rmr PS tetrads, the probabilities of channel conformers found for the PS tetrad stereoisomers are very small. In this connection, it should be remembered that if each of the $2^4 = 16.384$ conformations permitted for a PS tetrad were equally likely, then each would have a probability of $1/16.384 = 0.00006$. In contrast, the probability for the rmr PS stereoisomer channel conformer is nearly two-orders of magnitude higher. In addition to the mrm isomer, only the rmr tetrad channel conformer has a substantial probability (0.00005). This would imply that the free-radical polymerization of styrene in the narrow channels of its IC formed with γ-CD, for example, might produce a PS with alternating m and r diads rather than a-, i-, or s-PSs. This suggestion is made by analogy to a previous model32 of poly(propylene) (PP) stereoisomers in narrow channels of its IC formed with perhydrotriphenylene (PHTP), and urea hosts. There it was observed that all PP tetrad stereoisomers could be included in a 5.5 Å channel, but the probability of the channel conformers for the rrr isomer, or s-PP, were again at least two-orders of magnitude greater than those of the other stereoisomeric channel conmers. When propylene monomer was formed into an IC with PHTP and then free-radically polymerized in situ, the resulting PP was found to be predominantly syndiotactic, as suggested by the modeling of PP stereoisomers in channels appropriate to PHTP-ICs.

### Table 2. Thermal properties of as-synthesized a-PHB and PCL and their physical and coalesced blends

<table>
<thead>
<tr>
<th>Identity</th>
<th>Composition a-PHB:PCL</th>
<th>Tm (°C)</th>
<th>Tg (°C)</th>
<th>AHm (kJ/g)</th>
<th>Zc-PCL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>—</td>
<td>62</td>
<td>−60</td>
<td>95.6</td>
<td>68.8</td>
</tr>
<tr>
<td>Physical blend</td>
<td>1:1.76</td>
<td>62</td>
<td>−60.5</td>
<td>65.5</td>
<td>67.3</td>
</tr>
<tr>
<td>Coalesced blend A</td>
<td>1:1.76</td>
<td>56</td>
<td>−26</td>
<td>36.5</td>
<td>37.3</td>
</tr>
<tr>
<td>Coalesced blend B</td>
<td>1:4.91</td>
<td>56</td>
<td>−7</td>
<td>14.9</td>
<td>22.7</td>
</tr>
<tr>
<td>a-PHB</td>
<td>—</td>
<td>—</td>
<td>5</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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reasonably expected that they will evidence properties that are superior to their phase segregated physical blends.

When the incompatible biodegradeable/bioabsorbable polymers PCL and poly(l-lactic acid) (PLLA) were similarly coalesced from their common \( \alpha \)-CD-IC\(^{15} \) a predominantly intimate mixture of amorphous PCL and PLLA chains was obtained without evidence (DSC and X-ray) of PCL crystallinity and only \( \sim 5\% \) of the PLLA exhibited crystallinity. Furthermore, no evidence of phase separation was observed even following over night annealing at 200 \(^\circ\)C, which exceeds the \( T_g \) and \( T_m \) values of both PCL and PLLA.

Figure 10 shows the modulated differential scanning calorimetry (MDSC) thermograms of the 1.6/1.0/1.4 ternary blend of polycarbonate (PC)/poly(methyl methacrylate) (PMMA)/poly(vinyl acetate) (PVAc) (PC/PMMA/PVAc) coalesced from its common \( \gamma \)-CD-IC.\(^{35} \) The total signal of heat flow may be separated in reversing and non-reversing heat flow as a result of the temperature modulation employed. Thermal transitions in the reversing signal arise from thermodynamic phenomena such as \( T_g \) and melting. The non-reversing signal exhibits kinetic phenomena and includes evaporation and recrystallization. By plotting the reversing heat flow versus temperature, the effect of the solvent release as well as enthalpic recovery—an endothermic peak that occurs just above \( T_g \)—are eliminated, revealing a clear, single glass transition. In both the first and second MDSC heating scans, only a single glass transition can be observed at 57 \(^\circ\)C. This result indicates the presence of a single homogeneous amorphous phase in the ternary blend of PC/PMMA/PVAc, where the three component polymer chains are intimately mixed with each other. The appearance of one glass transition in the second scan as well confirms the stability and molecular degree of mixing of the PC, PMMA, and PVAc chains in the PC/PMMA/PVAc ternary blend.

In addition intimate blends of PC/PMMA and PC/PS were also obtained\(^{19} \) by coalescence from their common \( \gamma \)-CD-ICs. While the PC/PS blend showed signs of phase segregation (two \( T_g \) values) after several heating to 200 \(^\circ\)C/cooling to 25 \(^\circ\)C cycles in the DSC, the intimately mixed PC/PMMA blend continued to evidence a single \( T_g \) even after heating for several hours at 200 \(^\circ\)C. The superior thermal stability of the PC/PMMA coalesced blend was consistent with FT-IR observations,\(^{19} \) which indicated specific interactions between PC and PMMA chains in the coalesced blend. However, the FT-IR spectra of phase segregated solution cast and intimately mixed coalesced PC/PS blends were nearly identical, which imply an absence of specific interactions between PC and PS chains in the coalesced blend, and are consistent with its poor thermal stability.

**Block copolymers**

As indicated in Fig. 11, it may be anticipated that the formation of and coalescence from block copolymer-CD-ICs may be utilized to control the phase segregation of immiscible constituent blocks When the biodegradable/bioabsorbable diblock copolymer PCL-b-PLLA is coalesced from its \( \alpha \)-CD-IC\(^{21} \) the phase-segregation of immiscible PCL and PLLA blocks is greatly suppressed, as observed by 50–60% and 54–79% reductions in the crystallinities of PCL and PLLA blocks, respectively, from those observed in the as-synthesized sample. In addition, the rates of crystallization of PCL and PLLA blocks are much faster in the coalesced PCL-b-PLLA.\(^{26} \)

The biodegradation of as-received and coalesced PCL-b-PLLA samples using the lipase from *Rhizopus arrhizus* were
Table 3. Thermal properties and crystallinity of various PCL-PPO-PCL triblock copolymer samples as revealed by DSC

<table>
<thead>
<tr>
<th>PCL-PPO-PCL sample</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)$^a$</th>
<th>$\chi_{c-PCL}$ (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td>57.3</td>
<td>58.6</td>
<td>56.5</td>
</tr>
<tr>
<td>Coalesced from tri-block-z-CD-IC</td>
<td>63.8</td>
<td>76.8</td>
<td>74.1</td>
</tr>
<tr>
<td>Coalesced from tri-block-γ-CD-IC</td>
<td>63.0</td>
<td>51.3</td>
<td>49.5</td>
</tr>
</tbody>
</table>

$^a$ Percentage of PCL repeat units that are crystalline.

Coalesced diblock copolymer was observed to undergo much more rapid biodegradation. The increased rate of biodegradation of the coalesced PCL-b-PLLA is apparently attributable to the suppressed phase-segregation of PCL and PLLA blocks in the coalesced sample, which led to reduced PCL and PLLA crystallinities. Figure 12 presents the WAXD patterns of as-synthesized (a) and coalesced (b) PCL-b-PLLA films observed after various enzymatic degradation times. The level of crystallinity clearly increases with the rate of biodegradation of the coalesced PCL-b-PLLA is apparently attributable to the suppressed phase-segregation of PLLA. The coalesced diblock copolymer was included in ICs formed with a-CDs, which should be compared.21 The coalesced diblock copolymer was observed to undergo much more rapid biodegradation. The increased rate of biodegradation of the coalesced PCL-b-PLLA is apparently attributable to the suppressed phase-segregation of PCL and PLLA blocks in the coalesced sample, which led to reduced PCL and PLLA crystallinities. Figure 12 presents the WAXD patterns of as-synthesized (a) and coalesced (b) PCL-b-PLLA films observed after various enzymatic degradation times. The level of crystallinity clearly increases with the rate of biodegradation of the coalesced PCL-b-PLLA is apparently attributable to the suppressed phase-segregation of PLLA. The coalesced diblock copolymer was included in ICs formed with a-CDs, which should be compared.21

As-synthesized, 57.3 58.6 56.5
Coalesced from tri-block-z-CD-IC, 63.8 76.8 74.1
Coalesced from tri-block-γ-CD-IC, 63.0 51.3 49.5

a Percentage of PCL repeat units that are crystalline.

Comparison of as-synthesized and coalesced samples with morphologies that are significantly altered from those normally obtained from their disordered solutions and melts, where the polymer chains are randomly-coiling and entangled. When CD processing is applied to homopolymers, their blends, and block copolymers it has been demonstrated that it is possible to control their morphologies, conformations and possibly even their microstructures, as well as the phase segregation in their blends and block copolymers. Thus, it is believed that the potential for modifying the properties of polymers, including their biodegradation, by processing them into and coalescing them from their CD-ICs has been demonstrated.

REFERENCES