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Reorganization of the Structures, Morphologies, and Conformations of Polymers by Coalescence from Their Crystalline Inclusion Compounds Formed with Cyclodextrins

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Summary: We and several other research groups have recently reported the ability of cyclodextrins (CDs) to act as hosts in the formation of inclusion compounds (ICs) with guest polymers. Polymer-CD-ICs are crystalline materials formed by the close packing of host CD stacks, which results in a continuous channel of ~5-10Å in diameter running down the interior of the CD stacks. The guest polymers are confined to the narrow, continuous CD channels, and so are necessarily highly extended and segregated from neighboring polymer chains by the walls of the CD stacks. We have shown that coalescence of guest polymers from their CD-IC crystals can result in a significant reorganization of the structures, morphologies, and even conformations that are normally observed in their bulk samples. For example, when poly(ethylene terephthalate) (PET) is coalesced from its γ-CD-IC, we find that in the non-crystalline regions of the sample the PET chains are adopting highly extended kink conformations, which result in their facile recrystallization from the melt and prevent quenching of the coalesced PET to achieve an amorphous sample during rapid cooling from above T_m. We have also created well-mixed blends of normally incompatible polymers by coalescing them from CD-ICs containing both polymers, where they are necessarily spatially proximal. Finally we have found the unique morphologies created by the coalescence of homopolymers, block copolymers, and homopolymer pairs from their CD-ICs are generally stable to heat treatment for substantial periods above their T_m's and/or T_g's, and so may be thermoplastically processed without loss of the unique morphologies achieved through coalescence from their CD-IC crystals.

Keywords: compatibilization; cyclodextrins; morphology; polymer inclusion chemistry; solid-state structure

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Introduction

During the past decade it has been demonstrated that crystalline inclusion compounds (ICs) may be formed between host cyclodextrins (CDs) and a wide variety of guest polymers.[1-13] In Figure 1(a) the structures and dimensions of the host α-, β-, and γ-CDs are presented along with the channel crystal structure of CD-ICs (b) and a single α-CD stack of the α-CD-IC channel structure crystal containing a guest polymer (c). Two important features of polymer-CD-IC crystals are (i.) the segregation of polymer chains occupying different CD-IC channels, and (ii.) the highly extended conformations required of the included, guest polymers by the narrow cross-sections (5-10Å) of the CD-IC channels. As a consequence of the unique environment provided by CD-ICs for their guest polymers, it might be expected that consolidation of guest polymers from their CD-ICs could yield bulk polymer samples with structures and morphologies that are significantly altered from those normally achieved from their disordered solutions and melts. When guest polymers are coalesced from their 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 may retain some degree of their extended, unentangled natures. As is apparent from Figure 1 (b), polymer guests in neighboring CD-IC channels are necessarily proximal, because of their separation by the walls created by the CD bracelets in adjacent IC stacks. Consequently, if two or more polymers are dissolved in a common solvent and this mixed polymer solution is used to form a CD-IC containing both or more polymers, then the subsequent coalescence of polymer guests from the common CD-IC could possibly result in their intimate blending.

Here we present the results of our studies[5,7-10,12,14-19] of the coalescence of homopolymers and block copolymers from their CD-IC crystals. The effects produced by coalescing polymers from their CD-IC crystals may be generally summarized in the following ways: (i.) crystallizable homopolymers can evidence increased levels of crystallinity and higher melting and decomposition temperatures than samples consolidated from their disordered solutions and melts; (ii.) molecularily 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 greatly supressed when block copolymers are coalesced from their CD-IC crystals, and (iv.) the thermal and temporal stabilities of the well-mixed homopolymer blends and block copolymers obtained by coalescence from their CD-ICs appear to be substantial, thereby suggesting retention of their as-coalesced structures and morphologies under normal thermal processing conditions. In addition, through complexation with CD, we describe the ability to control the rheology of a **h**ydrophobically modified **a**lkali-**s**oluble **e**mulsion (HASE) copolymer system,[20] whose uncomplexed hydrophobic side chains normally associate in alkali solution to form physically cross-linked networks.

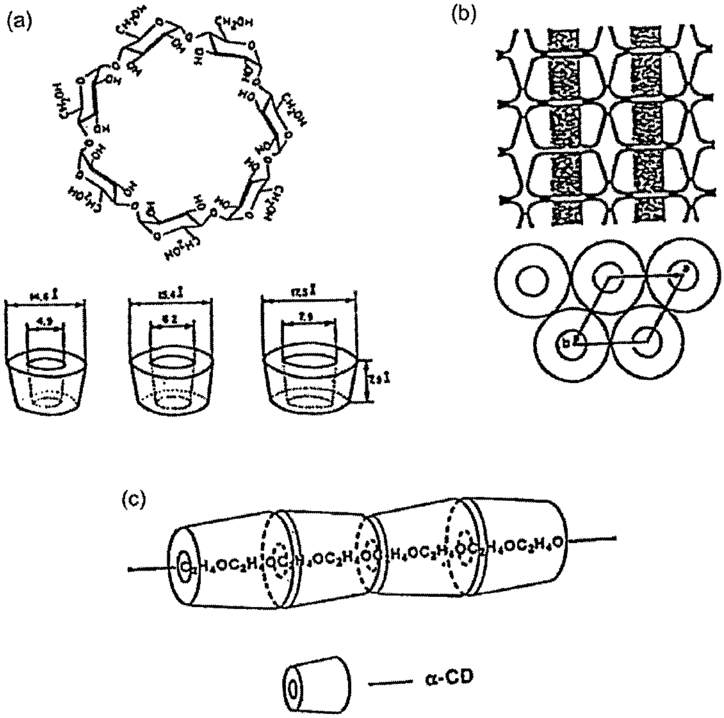

Fig. 1. β-CD structure and dimensions of α-, β-, and γ-CD bracelets (a); CD-IC channel crystal structure (b); and a single α-CD-IC channel with included poly(ethylene oxide) guest (c).

Experimental

Materials

Except for nylon-6, the homopolymers and block copolymers utilized, and the formation of and coalescence from their CD-ICs, have been described previously.[1-12,14-20] The nylon 6 was obtained from Aldrich. A mixed formic acid/acetic acid solution was used in the formation of nylon-6-γ-CD-IC. A heated DMSO solution of γ-CD was slowly added to the heated nylon solution with stirring. The combined solutions were subjected to continued heating and stirring for 2 hrs, after which they were allowed to slowly cool to room temperature with stirring over a period of 6 hours. The resulting precipitate was filtered, washed with water to remove any free γ-CD and dried under vacuum at room temperature.

The nylon 6-γ-CD-IC was added to a stirred aqueous HCL solution (pH=1.0) at 80 °C for 10 min. to remove the γ-CD host, and the coalesced nylon was removed by filtration. The coalesced nylon was washed several times with water and dried in a vacuum oven at room temperature.

Characterization

X-ray Diffraction

A Siemens type-F x-ray diffractometer (30 kV, 20 mA) using Ni-filtered Cu K_α radiation was employed to examine the polymers, before and after coalescence from their CD-ICs, as well as their CD-ICs. All specimens were mounted on aluminum frames and scanned from $2\theta = 5\text{-}40°$ at a speed of $2\theta = 1.2°/\text{min}$..

Thermal Analyses

Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) and Pyris 1 thermo-gravimetric analyzer (TGA) were employed to analyze the thermal characteristics of the polymers (before and after coalescence), as well as their CD-IC samples. Heating and cooling rates were generally 10-20 and –200 °C/min, unless otherwise specified.

FTIR and NMR Spectroscopic Analyses

Solution ^1H NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer, while solid-state ^{13}C NMR spectra were recorded either on a Bruker 300 MHz DSX wide-bore system or a

200 MHz Chemagnetics 200S spectrometer. FTIR spectral studies were conducted with a Nicolet 510P instrument operating in the range 4000 to 750 cm^{-1}, with a 2 cm^{-1} resolution. All powder samples were pressed into KBr pellets for FTIR.

Results and Discussion

Homopolymers

Both poly(ε-caprolactone) (PCl) and poly(L-lactic acid) (PLLA) homopolymers exhibited greater crystallinities (82%, 69% for coalesced PCl, PLLA *vs* 74%, 60% for as-synthesized samples) and higher melting temperatures (69 °C, 164 °C for coalesced PCL, PLLA *vs* 65 °C, 162 °C for the as-synthesized samples) when they were coalesced from their α–CD-IC crystals.[19] As-synthesized and coalesced homopolymers isothermally crystallize with comparable Avrami coefficients, while the half-time for crystallizing the coalesced PLLA was significantly reduced compared to the as-synthesized PLLA sample.

The polycarbonate from bisphenol-A (PC) coalesced from its γ-CD-IC[7] showed only a melting endotherm on its first heating DSC run, in contrast to as-received PC, which is totally amorphous as evidenced by the observation of only a T_g at ~150 °C in the DSC. PC cast from THF also showed a melting endotherm, but with a T_m 15 °C below that of coalesced PC. After the first heating run, the coalesced PC appeared totally amorphous as judged by the observation of only a T_g on subsequent DSC heating runs. We have attributed this behavior to predominant extended-chain crystallization in the coalesced PC sample, while the solution casting of PC led to chain-folded crystallization.

Poly(ethylene terephthalate) (PET) coalesced from its γ-CD-IC crystals,[8] although semicrystalline, displays a T_m only marginally elevated from that of typical bulk or solution crystallized samples. However, after melting the γ-CD-IC-coalesced PET crystals, it is difficult to quench the resultant PET melt into the usual amorphous PET glass, characterized by a T_g ~ 80 °C. Instead, the coalesced PET melt rapidly crystallizes (See Figure 2) during the attempted quench, and so upon reheating, it displays neither a T_g nor a crystallization exotherm, which are normally observed in melt-quenched PETs, but simply remelts at the as-coalesced T_m. This behavior is unaffected by holding the coalesced sample above T_m for 2 hr, indicating that the extended, unentangled nature of the PET chains in the non-crystalline regions of the coalesced sample are not easily converted into the usual completely disordered, randomly coiled, entangled PET melt.

Analysis of the FTIR spectrum of the γ-CD-IC-coalesced PET sample has revealed[9] that extended kink conformations, with gauche ±, trans, gauche ∓ ethylene glycol bonds, necessary[22] for inclusion in the narrow channels of the γ-CD-IC crystals, are largely retained upon coalescence. It is not surprising that these kink conformations can be readily converted to the all trans crystalline conformation, *via* counter rotations about the $-O-CH_2-$ and $-CH_2-O-$ ethylene glycol bonds from their gauche ± and gauche ∓ conformations, leading to rapid crystallization of the coalesced PET chains. In contrast, the completely disordered amorphous PET chains normally found in PET melts and glasses possess a high concentration[23] (>80%) of ethylene glycol residues with energetically favorable gauche ± $-CH_2-CH_2-$ bonds, which retards their crystallization into the all trans conformation. However, what remains surprising is the observation that the kink conformers in the non-crystalline regions of the coalesced PET sample are not readily converted to the usual disordered, randomly coiling, entangled melt above T_m.

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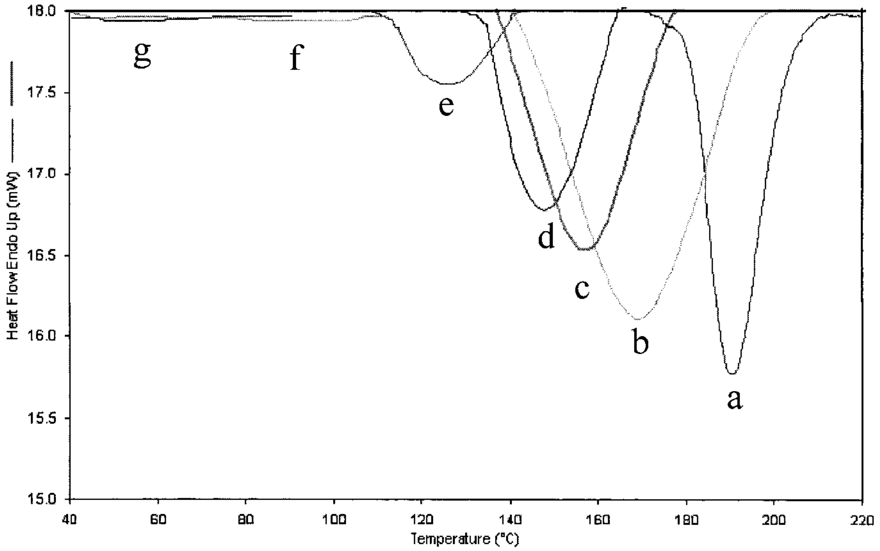

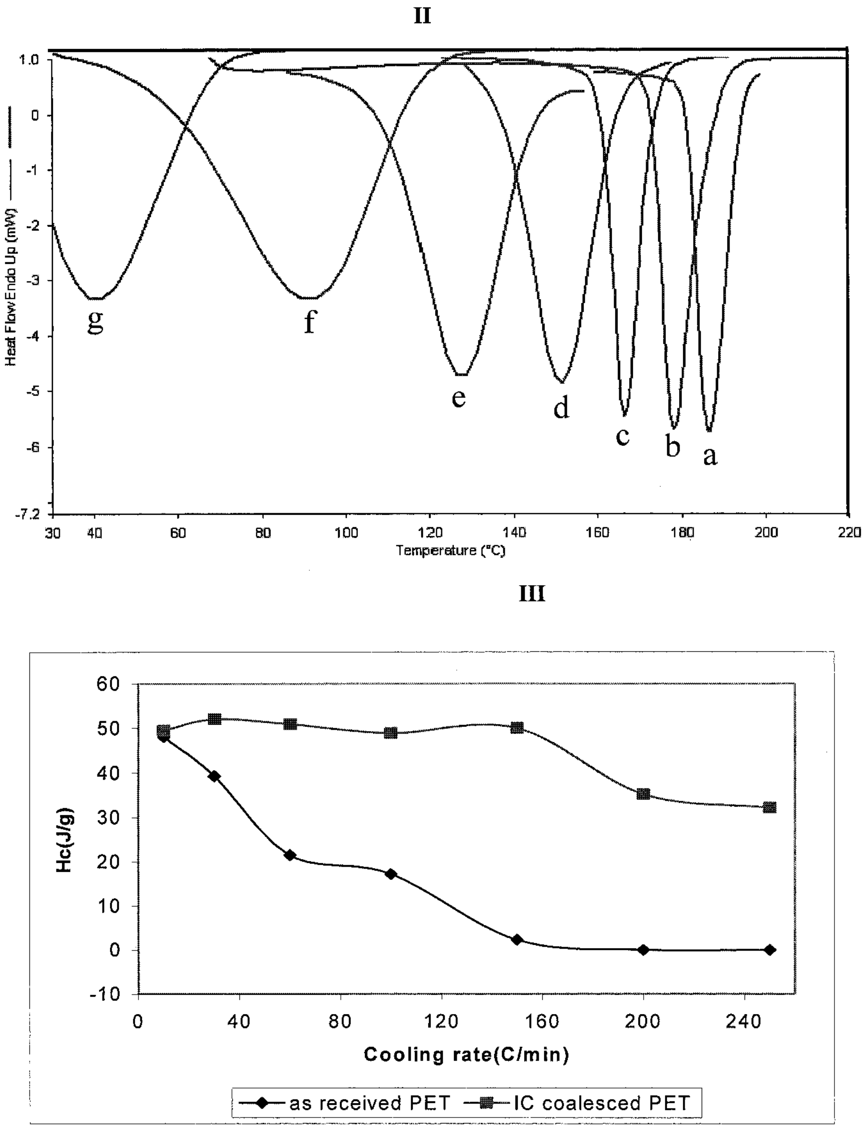

Fig. 2. The DSC crystallization curves observed[21] for as-received (I) and γ-CD-IC-coalesced PET (II) at cooling rates of –10 °C/min (a), -30 °C/min (b), -60 °C/min (c), -100 °C/min (d), -150 °C/min (e), -200 °C/min (f), and -250 °C/min (g). Crystallization enthalpies, H_c, observed at different cooling rates for as-received (lower) and γ-CD-IC-coalesced (upper) PETs (III).

Nylon-6 has been included as a guest in the narrow channels of the IC formed with host α-CD. The nylon-6 sample coalesced from its α-CD-IC crystals showed a nearly two-fold increase in the level of crystallinity (See Figure 3). In addition, only the α-form crystalline polymorph was produced by the coalescence process, while the as-received nylon-6 contained both α- and γ-form crystals, as confirmed by solid-state ^{13}C NMR[24] and FTIR[25] observations. This result seems consistent with the narrower, nearly all-trans α-form crystalline conformation being included preferentially in the α-CD-IC channels compared with the broader, non-planar γ-form crystalline conformation. Also the anti-parallel packing of nylon-6 chains in the α-form crystals would lead to an anticipated maximum level of crystallinity of ~50% for the coalesced sample, if nylon-6 chains were included randomly in up and down directions in the α-CD-IC crystalline channels. This is in fact close to the level of crystallinity (~53%) actually observed for the nylon 6 sample coalesced from its α-CD-IC.

HASE emulsion copolymers of methylacrylic acid, ethylacrylate, and a macromonomer with hydrophobic side chains – $(\text{-O-CH}_2\text{-})_{40}\text{-}(\text{-CH}_2\text{-})_{21}\text{-CH}_3$ associate in alkali solutions, through the micellar interactions between their surfactant-like side chains, to form physically cross-linked networks, which enhance the viscosity and viscoelastic properties of their solutions. Though this enhancement leads to many technological applications, the ability to control the viscosities of HASE solutions is often desirable and may be achieved through complexation of the hydrophobic HASE side chains with CDs.[20] Following their complexation with β-CD, the hydrophobic side chains are no longer able to associate to form a physically cross-linked network, and so the viscosity of the β-CD complexed HASE solution is dramatically reduced, as seen in Figure 4. Addition of surfactant to the β-CD complexed HASE solution results in the recovery of the high viscosity of the uncomplexed HASE solution as the complexes between β-CD and the HASE side chains are replaced by those with the surfactant.

Block Copolymers

When the biodegradable/bioabsorbable diblock copolymer PCL-b-PLLA is coalesced from its α-CD-IC[16] the phase segregation of immiscible PCl and PLLA is greatly surpressed, 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.[19]

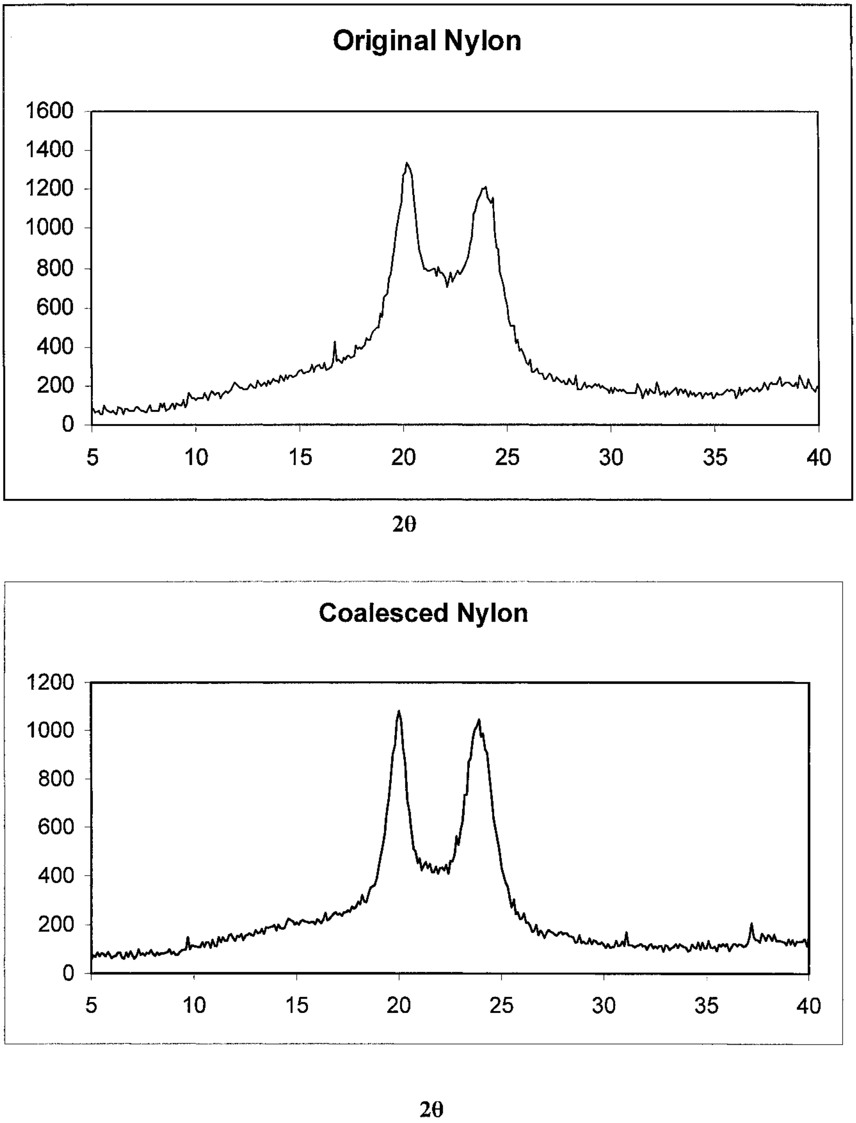

Fig. 3. X-ray diffractograms of original and coalesced nylon-6.

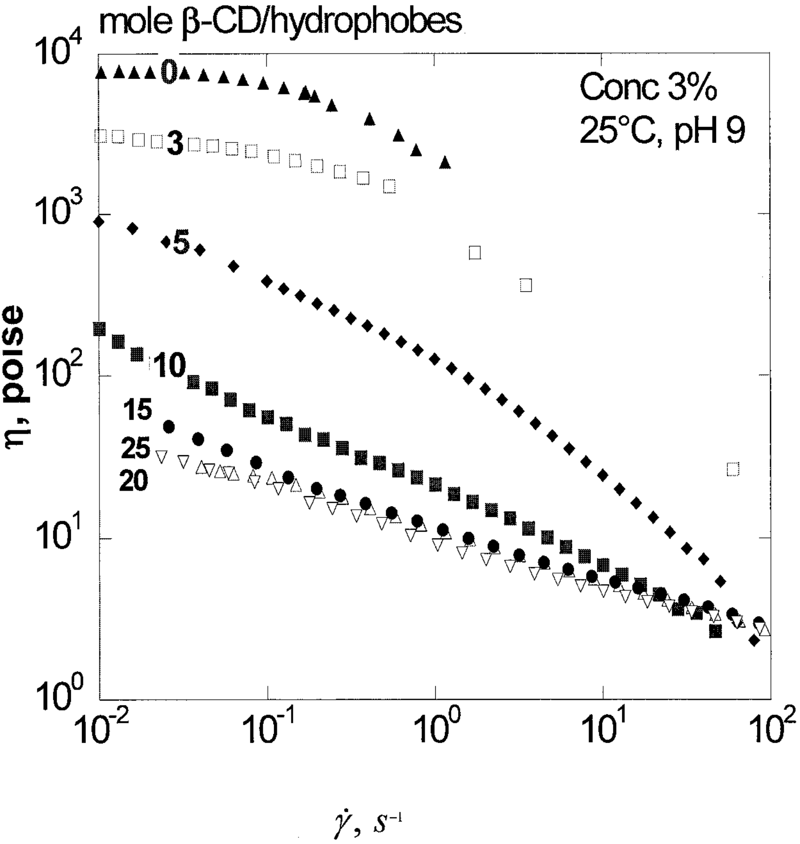

Fig. 4. Effect of β-CD on the steady shear viscosity of a 3% HASE polymer solution.

The biodegradation of as-received and coalesced PCL-b-PLLA samples using the lipase from *Rhizopus arrhizus* were compared.[18] The coalesced diblock copolymer was observed to undergo much more rapid biodegradation as demonstrated in Figure 5. 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 6 presents the wide angle X-ray diffraction 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 enzymatic degradation of the coalesced PCL-b-PLLA, and this is a consequence of the preference of the lipase enzyme for the amorphous sample regions, which are initially more plentiful compared with the as-synthesized sample. It is apparent that the biodegradation of the PCL-b-PLLA block copolymer can be controlled by coalescence from its α-CD-IC, and this can have important implications for its use in drug delivery and controlled release applications.

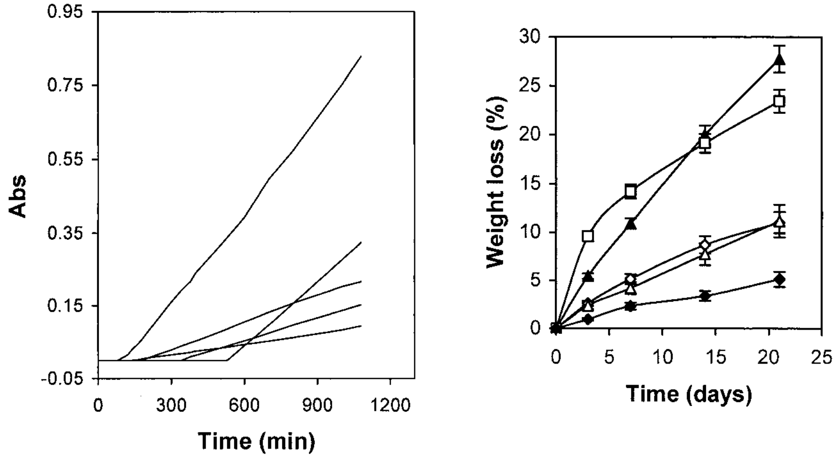

Fig. 5. UV absorbance monitored continuously at 205 nm during the initial (left) and weight loss measured during the 3-week (right) enzymatic degradation of coalesced PCL-b-PLLA, PCL, as-synthesized PCL-b-PLLA, PCL/PLLA physical blend, and PLLA, respectively, as given in the curves from top to bottom at degradation times between 900 min. and 10 days.[18]

The triblock copolymer PCL- atactic-poly(propylene glycol) (a-PPG)-PCL has been included in ICs formed with both α- and γ-CDs.[10] In the IC formed with α-CD only the PCL blocks were included, while the entire triblock copolymer was included in the γ-CD-IC. Upon coalescence of the triblock from its α- and γ-CD-ICs, the crystallinity of PCL blocks was found to increase and decrease, respectively, from that observed in the as-synthesized triblock copolymer. Since only PCL blocks are included in the α-CD-IC, neighboring IC channels are filled only with extended PCL blocks, which should aggregate easily when the α-CD are washed away during coalescence. Though the a-PPG blocks may affect crystallization of PCL in the as-synthesized copolymer, the aggregation of neighboring PCL blocks should not be affected by the uncomplexed a-PPG blocks during coalescence from the α-CD-IC, leading to a higher level of PCL crystallinity. The neighboring γ-CD-IC channels may contain either copolymer block, and so the aggregation of some PCL blocks during coalescence may be hindered by PPG blocks that occupy proximal channels in the γ-CD-IC. Therefore, the observed decrease in the crystallinity of PCL blocks for this coalesced sample also seems reasonable.

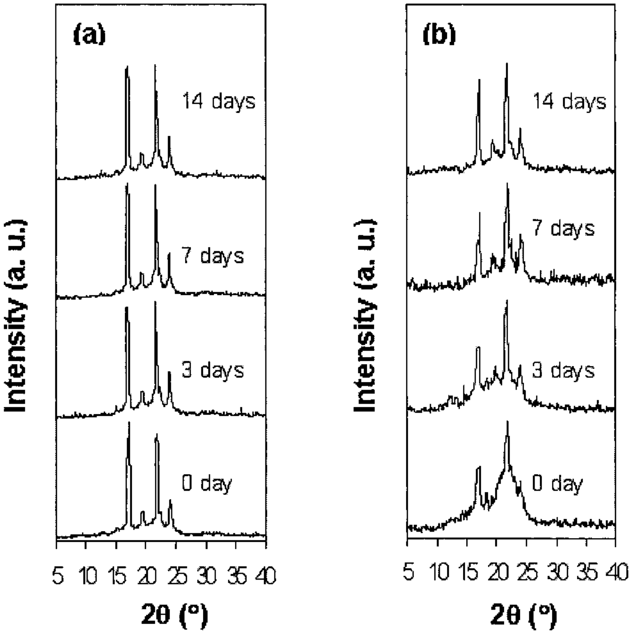

Fig. 6. X-ray diffraction patterns of as-synthesized (a) and coalesced (b) PCL- b-PLLA films observed following various enzymatic degradation times.

Homopolymer Blends

When PCl and PLLA chains are dissolved in dioxane at 50 °C and added to a saturated aqueous solution of α-CD also maintained at 50 °C with stirring, common α-CD-IC crystals containing both polymers (PCL/PLLA-α-CD-IC) result.[5] Coalescence of PCL and PLLA chains from their common α-CD-IC crystals appears to yield a well-mixed predominantly amorphous blend, as is evidenced by the comparison of x-ray diffractograms presented in Figure 7, where the degrees of crystallinity of both PCL and PLLA are dramatically reduced following the coalescence from their common α-CD-IC. DSC observations in fact do not detect a melting endotherm for PCL and only a very small endotherm for PLLA, which indicate that 0 and 5% of their chains, respectively have crystallized, which may be compared to ~50% PCL and PLLA crystallinities in the pure homopolymers and their solution-cast blend.

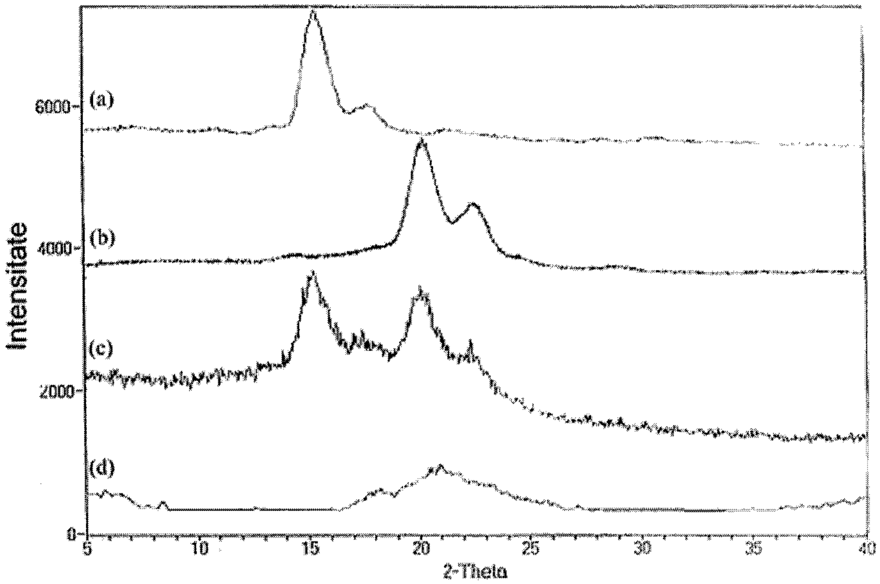

Fig. 7. X-ray diffractograms of pure PCL (a) and PLLA (b) and PCL/PLLA blends obtained by casting from dioxane solution (c) and hot water coalescence from PCL/PLLA-α-CD-IC (d)^5.

Surprisingly, when the coalesced PCL/PLLA blend is heated at 200 °C for up to 12 hrs, which exceeds the T_ms for both components, the DSC thermogram recorded after annealing did not change from that of the original coalesced sample. Apparently the initially well-mixed, almost entirely amorphous PCL/PLLA blend achieved by coalescence is thermally stable and has not phase-segregated following high temperature annealing.

Figure 8 presents the first heating DSC scans of solution-cast and γ-CD-IC-coalesced blends of PCL and atactic-poly (β-hydroxybutyrate) (a-PHB), of pure a-PHB and the common γ-CD-IC of PCL/a-PHB.[9] Note that the coalesced PCL/a-PHB blends exhibit single T_gs between those of pure PCL (-60 °C) and a-PHB(5 °C), while the T_g observed for the solution-cast blend is the same as that of a-PHB, reflecting the intimate mixing of PCL and a-PHB chains in the coalesced blends and phase separated PCL and a-PHB chains in the solution-cast blend, respectively. Additionally, for the two coalesced PCL/a-PHB blends shown in Figure 8, the % crystallinity observed for the PCL chains are ~37 and ~23%, which is much reduced from the ~68% PCL crystallinity observed in both pure PCl and the physical PCL/a-PHB blend. Thus we have achieved significant molecular-level mixing of the inherently immiscible PCL and a-PHB chains by coalescing them from their common γ–CD-IC crystals.

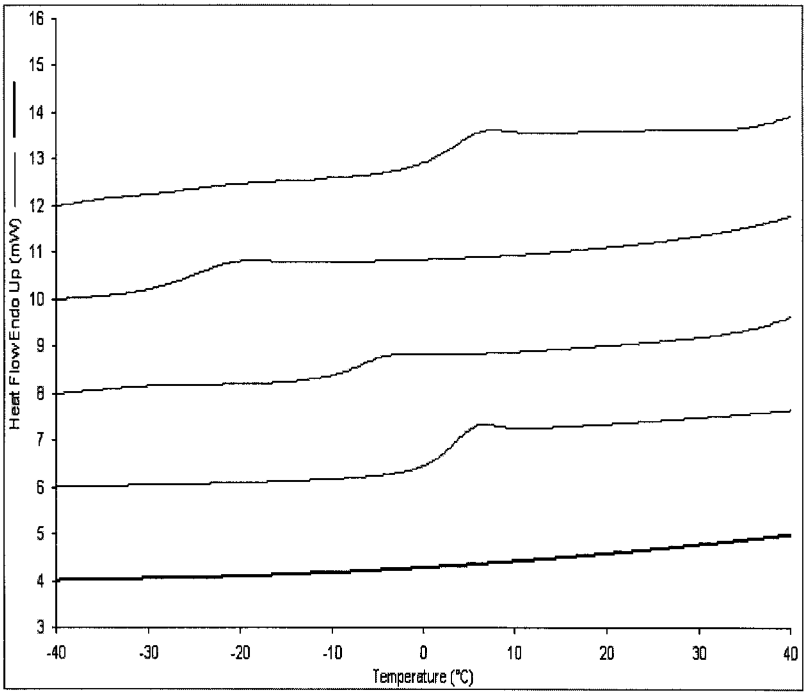

Fig. 8. First heating run DSC thermograms from top to bottom, respectively, of physical PCL/a-PHB blend (1.76:1), coalesced PCL/a-PHB blend (1.76:1), coalesced PCL/a-PHB blend (1:1.48), a-PHB, and PCl/a-PHB- γ-CD common IC.[9]

Amorphous, well-mixed intimate blends of atactic polystyrene (PS) and poly(methyl methacrylate) (PMMA) with PC may be achieved[7,17] by coalescence of the common γ-CD-ICs containing PS/PC and PMMA/PC chains as guests, respectively. Initially both types of intimately mixed blends exhibit single T_gs, which lie between those of the parent homopolymers (PS ~100, PMMA ~ 120, and PC ~ 150 °C). However, upon annealing at $T > T_g$ (PC), the PS/PC and PMMA/PC coalesced blends respond distinctly. While the PMMA/PC blend apparently remains well-mixed after 2 hrs of annealing, as evidenced by the retention of a single intermediate T_g,

the initially well-mixed coalesced PS/PC blend appears to segregate into separate PS and PC phases, with distinct T_gs observed by DSC, after only several minutes of annealing. Clearly the initially intimate coalesced PMMA/PC blend is more stable to high temperature annealing than the PS/PC blend.

The FTIR spectra of PMMA and PC homopolymers and their blends cast from THF solution and coalesced from their common γ-CD-IC are presented in Figure 9.[7] The FTIR spectrum of PC is characterized by an intense C=O band at ~1775, a phenyl ring structure band at ~1505, and a strong C-O band at 1194 cm^{-1}. In pure PMMA the C=O band occurs at ~1731 cm^{-1}, and the absorptions at 2950 and 2998 cm^{-1} are contributed by the methyl groups. Note that only minor differences exist between the PC and PMMA vibrational frequencies observed in the pure polymers and their solution-cast physical blend [See Figure 9 (a)-(c)]. However, in Figure 9 (d) we note that in the coalesced PMMA/PC blend sample the PMMA and PC C=O absorptions have shifted to 1741 and 1770 cm^{-1} and partially overlap. In addition, the absorption peak characteristic for the PMMA methyl groups has shifted from 2950 to 2921 cm^{-1} in the coalesced blend. These shifts in vibrational frequencies may result from interactions occurring between the carbonyl and methyl groups of PMMA with the carbonate groups and phenyl rings of PC, which may be facilitated when the chains of the two polymers are close enough, as in the intimately mixed, γ-CD-IC coalesced PMMA/PC blends. Various solid-state NMR techniques are currently being applied to the coalesced PMMA/PC blends in an effort to more accurately define the length scale of molecular mixing of their constituent chains.

The suggested specific interactions between the intimately mixed PMMA and PC chains in their coalesced blends may explain their thermal stabilities, as mentioned above. Furthermore, though not presented here, the FTIR spectra of PS, PC, and their physical and coalesced blends do not suggest comparable specific interchain interactions between PS and PC chains in their coalesced blends, which we also noted are not as thermally stable as the coalesced PMMA/PC blends.

Blends of PET and poly(ethylene 2,6-naphthalate) (PEN) have been coalesced from their common γ-CD-IC crystals.[12] Based on DSC and solution NMR observations we conclude that intimate PET/PEN blends are obtained by coalescence and without trans-esterification between PET and PEN chains. In fact it has been observed that coalesced PET/PEN blends are much more readily transesterified when heated than their solution-cast counterparts, likely due to the intimate mixing of PET and PEN chains in the coalesced blends.

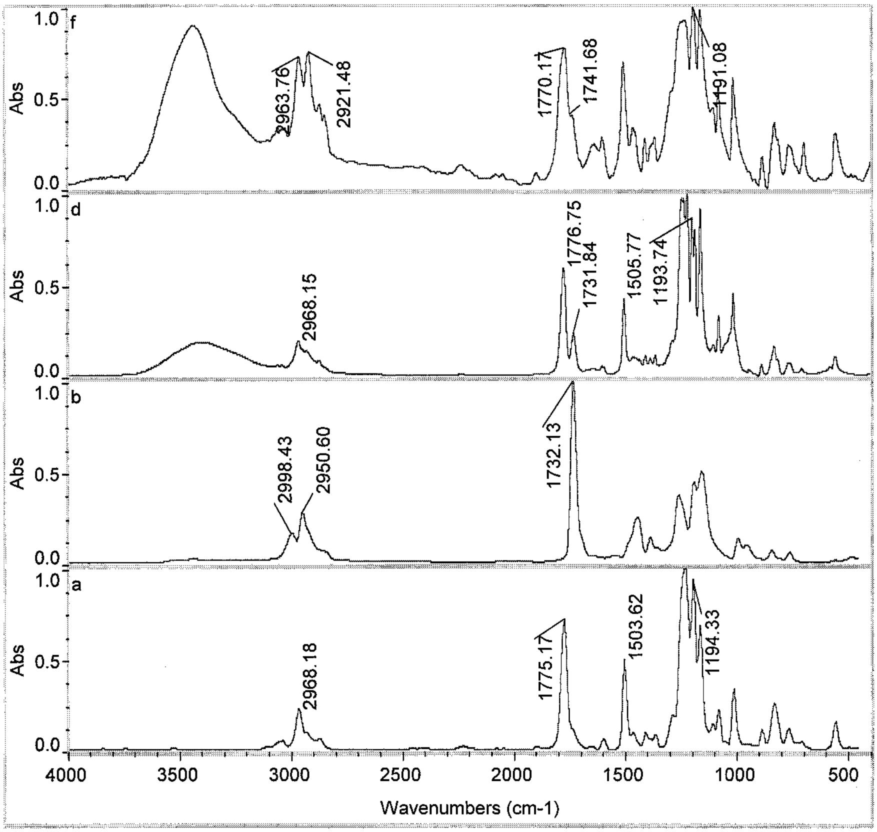

Fig. 9. FTIR spectra of (a) PC, (b) PMMA, (c) PC/PMMA physical blend (PC: PMMA = 1:1 molar ratio) and (d) PC/PMMA-γ-CD IC coalesced (washed with hot water, PC: PMMA = 1:1 molar ratio).[7]

Conclusions

By way of the many examples presented above, it is possible to conclude that formation of and coalescence from their CD-ICs can lead to consolidated bulk solid polymer samples with significantly altered structures, morphologies, and even chain conformations.

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