Molecular Mixing of Incompatible Polymers Through Formation of and Coalescence from Their Common Crystalline Cyclodextrin Inclusion Compounds

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ABSTRACT: We describe the successful mixing of polymer pairs and triplets that are normally incompatible to form blends that possess molecular-level homogeneity. This is achieved by the simultaneous formation of crystalline inclusion compounds (ICs) between host cyclodextrins (CDs) and two or more guest polymers, followed by coalescing the included guest polymers from their common CD–ICs to form blends. Several such CD–IC fabricated blends, including both polymer1/polymer2 binary and polymer1/polymer2/polymer3 ternary blends, are described and examined by means of X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, Fourier transform infrared spectroscopy, and solid-state NMR to probe their levels of mixing. It is generally observed that homogeneous blends with a molecular-level mixing of blend components is achieved, even when the blend components are normally immiscible by the usual solution and melt blending techniques. In addition, when block copolymers composed of inherently immiscible blocks are coalesced from their CD–ICs, significant suppression of their normal phase-segregated morphologies generally occurs. Preliminary observations of the thermal and temporal stabilities of the CD–IC coalesced blends and block copolymers are reported, and CD–IC fabrication of polymer blends and reorganization of block copolymers are suggested as a potentially novel means to achieve a significant expansion of the range of useful polymer materials. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 4207–4224, 2004

Keywords: polymer blends; intimate mixing; cyclodextrin; inclusion complexes; block copolymers; compatibilization
INTRODUCTION

During the past several years we have been forming crystalline inclusion compounds (ICs) between host cyclodextrins (CDs) and a wide variety of high-molecular-weight guest polymers. More recently we have formed CD–ICs containing two and even three different polymers. When these are washed with hot water or treated with an amylase enzyme the CD–IC crystals are disrupted, the CD is removed, and the two or more commonly included guest polymers are forced to coalesce into a solid blend, as depicted schematically in Figure 1, provided neither guest is soluble in water. As illustrated in Figure 2, although the highly extended polymer chains occupying the narrow channels of their CD–IC crystals are segregated from each other by the host CD bracelets, they...
are nevertheless in close spatial proximity. Thus, it seems reasonable to expect that when a polymer1/polymer2- or a polymer1/polymer2/polymer3-CD–IC is washed with hot water, an intimate blend may result during the simultaneous coalescence of the common guest polymers.

In this article we summarize and review our attempts to form intimately mixed polymer blends of two or more polymers, normally thought to be inherently immiscible, by coalescing them from their common CD–IC crystals. The level of mixing achieved between polymers coalesced from their common CD–ICs is assessed both thermally [by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA)] and spectroscopically [by Fourier transform infrared spectroscopy (FTIR) and NMR]. In addition, the coalescence of block copolymers composed of inherently incompatible blocks from their CD–IC crystals are examined for potential effects on the phase segregation of their blocks.26,29 Preliminary observations of the thermal and temporal stabilities of mixing in these polymer blends and block copolymers are described, and we suggest that the CD–IC fabrication of polymer blends and block copolymers may provide a potentially novel means to significantly expand the range of useful polymer materials. At the very least, the CD–IC fabrication of polymer blends offers a means to achieve and study the behaviors of intimately blended polymers, which heretofore has not been possible.

**EXPERIMENTAL**

**Materials**

Formation of poly(ε-caprolactone) (PCL)/poly(L-lactic acid) (PLLA)-α-, PCL/atactic poly(β-hydroxy butyrate) (a-PHB)-α-, bisphenol-A polycarbonate (PC)/poly(methyl methacrylate) (PMMA)-γ-, PC/ polystyrene (PS)-γ-, poly(ethylene terephthalate) (PET)/poly(ethylene 2,6-naphthalate) (PEN)-γ-common-CD–ICs and the PCL-b-PLLA-α- and PCL-b-poly(propylene oxide) (PPO)-b-PCL-α-, and γ-CD–ICs have been previously described.10,21,23,24,26,29,30 The coalesced blends and block copolymers were prepared by washing their corresponding CD–ICs with hot water (50–70°C). More recently28 PCL-b-PLLA-α-CD–IC crystals were treated with an amylase enzyme in order to coalesce the PCL-b-PLLA block copolymer chains from their IC crystals at a lower temperature (35°C). The coalesced PCL-b-PLLA samples obtained by hot water washing and the room temperature enzymatic treatment of PCL-b-PLLA-α-CD–IC were quite comparable with regard to both their morphologies and thermal behaviors. Solution-cast PCL-b-PLLA, PCL/a-PHB, PC/PMMA, PC/PS, and PET/PEN blends were obtained from dioxane, chloroform, tetrahydrofuran, and chloroform/trifluoroacetic acid solutions. PCL-b-PLLA and PCL-b-PPO-b-PCL block copolymers were cast from acetone solutions to provide control samples for comparison, in addition to the as-received or as-synthesized samples.

**TGA**

TGA scans of 5–10 mg samples were obtained by using a PerkinElmer Pyris 1 thermogravimetric analyzer. The samples were placed in platinum pans that were hung in the heating furnace. The weight percentage of material remaining in the pan was recorded while heating from 25–800°C at a heating rate of 20°C/min. Nitrogen was used as the purge gas.
DSC

DSC was conducted on 3–10 mg samples in a PerkinElmer DSC-7 thermal analyzer. An indium standard was used for calibration, a heating rate of 10° C/min. was employed, and nitrogen was used as the purge gas. With its enhanced sensitivity to phase transitions over standard DSC, modulated DSC (MDSC) was performed using a TA Instruments DSC Q1000 on coalesced ternary blends to further elucidate their glass transition temperatures. The instrument used was a Thermal Analyst Q1000 MDSC under nitrogen purge. Indium was used for the temperature calibration and sapphire was used for the heat capacity calibration.

FTIR

Absorbance FTIR spectra were recorded on a Nicolet 510p spectrometer with Omnic software. Frequencies
from 400 to 4000 cm$^{-1}$ were covered, and 128 scans were recorded with a gain = 1 on samples mixed with KBr and pressed into pellets.

**X-Ray Diffraction**

A Siemens type-F X-ray diffractometer with a nickel-filtered Cu K$\alpha$ radiation source (wavelength = 1.54 Å) was used. Voltage and current were set to 30 kV and 20 mA, and a scan rate of $(2\theta = 1^\circ)/\text{min}$, between $2\theta = 5$ and $40^\circ$, were used to obtain the powder diffractograms. Powdered samples were mounted on a sample holder and X-ray scattering was monitored in the reflection mode.

**NMR**

Solid-state NMR measurements were performed on a Bruker DSX wide-bore spectrometer at 300.13 MHz for
\(^1\text{H}\) using a 7.0 mm magic-angle spinning probe at ambient temperature, and spinning speeds were regulated between 4–5 kHz. Proton \(T_{1p}\) relaxation times were measured using the cross polarization pulse sequence preceded by a variable proton spin-lock period.\(^3\) Two-dimensional \(^1\text{H}–^{13}\text{C}\) heteronuclear correlated (2D-\(^1\text{H}–^{13}\text{C}\) HETCOR) spectra were collected with a previously described pulse sequence.\(^33,34\) BLEW-12/BB-12 decoupling was applied during the evolution period to suppress homonuclear proton and \(^{13}\text{C}–^{1}\text{H}\) dipolar interactions, and the spectra were acquired with one WIM-24 windowless isotropic mixing cycle.\(^35\)

**RESULTS AND DISCUSSION**

**Homopolymer Blends**

**PCL/PLLA Blends**

Coalescence of PCL and PLLA from their common PCL/PLLA-\(\alpha\)-CD–IC resulted\(^10\) in a PCL/PLLA blend that appeared to be well-mixed even though the PCL/PLLA pair is generally regarded as incompatible.\(^36\) For example, a solution cast blend of PCL/PLLA revealed a phase separated morphology under a polarizing microscope. Small, large crystalline spherulites were observed for PCL and PLLA, which melted at 59 and 169 °C in the DSC, and correspond to \(~45\)% crystallinity for both blend component polymers. In contrast, under a polarizing microscope the coalesced PCL/PLLA blend appeared to be largely amorphous, with a few small PLLA spherulites homogeneously dispersed throughout. No melting was observed for PCL, while only \(~5\)% crystallinity was detected by DSC for PLLA in the coalesced blend. This behavior is strongly supported by the X-ray diffractograms for PCL, PLLA, and their solution-cast and coalesced blends presented in Figure 3. Their comparison confirms the phase-separated nature of the solution-cast blend, because distinct diffraction peaks are observed there for both PCL and PLLA components. On the other hand, the PCL/PLLA blend coalesced from its \(\alpha\)-CD–IC only barely reveals diffraction peaks for the PLLA component, because only \(~5\)% of the PLLA chains are crystalline, according to DSC observation.\(^10\)

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

In Figure 4 the 2D-\(^{1}\text{H}–^{13}\text{C}\) HETCOR spectra of the solution-cast and coalesced PCL/PLLA blends are presented for short \((\tau_m = 50 \mu s)\) and long \((\tau_m = 1.0 \text{ ms})\) mixing times. With the shorter mixing time, a normal \(^1\text{H}–^{13}\text{C}\) correlation spectrum is observed for both the coalesced and solution-cast blends, where the proton chemical shifts of the PLLA methyl and PCL methylene groups are clearly distinguished. However, with the longer mixing time, these two proton chemical shifts approach each other in the HETCOR spectrum observed for the coalesced PCL/PLLA blend indicating effective spin-diffusion between them and their necessary spatial proximity. On the other hand, the HETCOR spectra of the solution-cast blend do not show significant proton spin diffusion between the component PCL and PLLA chains even when a long mixing time is employed. The intimately mixed and phase separated natures of the coalesced and solution-cast PCL/PLLA blends, respectively, are clearly revealed by the observation of efficient proton spin-diffusion in the former blend and the absence of spin-diffusion in the latter blend.

**PCL/a-PHB Blends**

In an attempt to improve both the biodegradability and physical characteristics of biodegradable polyesters, such as PCL and atactic poly(\(\beta\)-hydroxy butyrate) (a-PHB), a common \(\alpha\)-CD–IC containing both PCL and a-PHB was formed, followed by the coalescence of both polyesters to form a blend.\(^24\) Table 1 presents a summary of the thermal properties observed by DSC for two coalesced PCL/a-PHB blends with different compositions, a solution-cast PCL/a-PHB blend, and pure PCL and a-PHB component polyesters. Two important observations can be made from the DSC observations: (1) the levels of PCL crystallinity in the coalesced blends are much reduced from those observed in both pure PCL and the physical PCL/a-PHB blend, which are virtually identical, and (2) single glass-transition temperatures \(T_{g, s}\) intermediate to those of PCL (\(\sim 60^\circ \text{C}\)) and a-PHB (\(5^\circ \text{C}\)) are observed in the coalesced blends. While the solution-cast PCL/a-PHB is clearly phase-separated into PCL and a-PHB rich domains, the coalesced PCL/a-PHB samples show greatly reduced amounts of crystalline PCL embedded in an apparently well-mixed amorphous PCL/a-PHB phase.

**PC/PMMA and PC/PS Blends**

Completely amorphous blends of bisphenol-A polycarbonate (PC) with poly(methylmethacrylate) (PMMA) and with polystyrene (PS) were fabricated\(^21\) by the formation of and coalescence from their PC/PMMA- and
PC/PS-γ-CD–ICs. Coalesced PC/PMMA and PC/PS blends with different compositions were made and all exhibited single $T_g$s in the DSC (See Fig. 5, for example), even though both PC/PMMA and PC/PS pairs are thought to be incompatible. In fact, for the blends rich in PMMA and PS the observed $T_g$s were lower than the $T_g$s for pure PMMA and PS (173°C for PMMA, 177°C for PS, and PC, respectively). This may be a consequence of plasticization of the PS and PMMA chains by the relatively shorter, lower molecular weight PC chains. The coalesced PMMA/PC blends maintained their apparently homogeneous morphologies even after heating for 2 h at 200°C, which is well above the $T_g$s of both components of the blends, while the coalesced PS/PC phase-separated after a few minutes.

The TGA scans recorded for solution-cast and coalesced PC/PS blends are presented in Figure 6 (a) and (b), respectively. Note that, unlike the solution-cast PC/PS blends, which show distinct decompositions for both blend components, the coalesced blends decompose uniformly. Thus, it appears that PC and PS chains co-degrade together at a molecular level in the coalesced blends as a consequence of their intimate mixing. Similar observations were previously noted for the coalesced PC/PMMA blends.

FTIR observations suggest stronger interactions between the well-mixed chains in coalesced PC/PMMA blends compared with those in the coalesced PC/PS blends. Though not shown, the FTIR spectra for pure PC and PS, and their physical and coalesced blends are very similar. By this we mean that all vibrational frequencies unique to PC and PS are nearly identical in all four samples. However, in the FTIR spectrum of the coalesced PC/PMMA blend [Figure 7 (d)], the C=O bands of PMMA and PC shift from 1732 (pure) to 1741 cm$^{-1}$ (coalesced blend) and from 1775 (pure) to 1770 cm$^{-1}$ (coalesced blend), respectively. In addition, the PMMA methyl group vibration shifts from 2950 (pure) to 2921 cm$^{-1}$ (coalesced blend). These vibrational shifts in the well-mixed blends of PC/PMMA coalesced from their common γ-CD–ICs may imply specific interactions between the carbonyl and methyl groups of PMMA with the carbonate and phenyl groups of PC. These may be stronger than the interactions in the coalesced PC/PS blends, and this may account for their superior thermal stability.

Table 2 presents the $^{13}$C observed $^1$H relaxation times, $T_{1p}(^1H)$, measured for pure PC, PMMA, and PS and for PC/PMMA and PC/PS physical (solution-cast) and coalesced blends. For both coalesced blends, single $T_{1p}(^1H)$s are observed for each blend component, while in their physical blends distinct $T_{1p}(^1H)$s are detected for each blend component, with values nearly identical to the $T_{1p}(^1H)$s observed for the pure polymers. So while the solution-cast PC/PMMA and PC/PS blends are clearly phase-segregated, the constituent polymer chains in both coalesced blends are intimately mixed on a size-scale smaller than 50Å. This assessment is also confirmed by

**Table 1.** Thermal Properties of As-Synthesized PCL and α-PHB and Their Physical and Coalesced Blends, as Revealed in Their First Heating DSC Scans

<table>
<thead>
<tr>
<th>Identity</th>
<th>Composition$^a$ (r_{a-PHB/PCL})</th>
<th>$T_m$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_\text{s}$ (J/g)</th>
<th>$\chi_{\text{c-PCL}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>—</td>
<td>62.2</td>
<td>−60</td>
<td>95.6</td>
<td>68.8</td>
</tr>
<tr>
<td>Physical blend</td>
<td>1:1.76</td>
<td>62.3</td>
<td>−60, 5.0</td>
<td>65.5</td>
<td>67.3</td>
</tr>
<tr>
<td>Coalesced blend A</td>
<td>1:1.76</td>
<td>56.3</td>
<td>−26.1</td>
<td>36.3</td>
<td>37.3</td>
</tr>
<tr>
<td>Coalesced blend B</td>
<td>1.48:1</td>
<td>56.3</td>
<td>−7.2</td>
<td>14.9</td>
<td>22.7</td>
</tr>
<tr>
<td>α-PHB</td>
<td>—</td>
<td>—</td>
<td>5.0</td>
<td>—</td>
<td>—</td>
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</tbody>
</table>

$^a$ The molar ratio of repeat units of α-PHB and PCL.
comparison of the 2D $^1$H–$^{13}$C HETCOR spectra of PC/PMMA physical and coalesced blends recorded with different mixing times and that are presented in Figure 8. Note that at the longer mixing time (1.0 ms) in the coalesced blend the resonance frequencies of the PC and PMMA protons approach each other, indicating increased correlations between the $^1$H–$^{13}$C nuclei on each polymer. Both observations are the result of rapid spin
diffusion between the protons on intimately mixed PC and PMMA chains, which is not observed in the 2D-HETCOR spectra observed for the phase-segregated PC/PMMA blend cast from solution.

**PET/PEN Blends**

PEN has recently received significant attention in the packaging industry because of thermal and barrier properties that are superior to PET. Due to the higher cost of PEN, blending and copolymerization of PEN and PET have been attempted to produce an affordable barrier plastic, but without much success due to their incompatibility and propensity to undergo transesterification. Coalescence of PET/PEN blends from their common γ-CD–IC seems to achieve some level of miscibility between PET and PEN chains, as indicated in the DSC scans presented in Figures 9 and 10.

In the first heating scan of a 1:1 PET/PEN coalesced blend [Fig. 9(a)] only a complex melting endotherm is observed, which we believe is due to crystalline, phase-separated PEN (sharp, high temperature component) and a more well-mixed PET/PEN phase (broad, lower temperature component). In the second heat, however, $T_g$ at 68 and 86°C are observed [Fig. 9(b)], indicating pure amorphous PET and amorphous PET/PEN blend phases. The crystallization exotherm observed in the second heat occurs at a higher temperature than that of pure PET, which is also consistent with some PET/PEN mixing, and receives confirmation from the cooling scans observed between the first and second heats that are presented in Figure 10. The PET-rich and PEN-rich precipitated blends behave as though phase separated PET and PEN phases, respectively, are crystallizing. On the other hand, the coalesced 1:1 PET/PEN blend shows a shallow, broad crystallization exotherm, which is apparently

![Figure 7. 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).](image)

### Table 2. $T_1(1H)$s for PC, PMMA, PS, and PC/PMMA and PC/PS Blends

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>150</th>
<th>130</th>
<th>120</th>
<th>40</th>
<th>30</th>
<th>PMMA</th>
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<tr>
<td>PMMA</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>178</td>
</tr>
<tr>
<td>PC</td>
<td>5.1</td>
<td>5.5</td>
<td>5.5</td>
<td>5.2</td>
<td>5.6</td>
<td>14.8</td>
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<td>Cast</td>
<td>5.2</td>
<td>5.4</td>
<td>5.4</td>
<td>5.1</td>
<td>5.2</td>
<td>—</td>
</tr>
<tr>
<td>Coalesced</td>
<td>6.8</td>
<td>7.0</td>
<td>7.6</td>
<td>6.9</td>
<td>6.7</td>
<td>—</td>
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</tbody>
</table>

<table>
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<th>Peak (ppm)</th>
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<th>130</th>
<th>120</th>
<th>40</th>
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<tr>
<td>PS</td>
<td>6.6</td>
<td>6.8</td>
<td>—</td>
<td>6.9</td>
<td>—</td>
</tr>
<tr>
<td>PC</td>
<td>5.1</td>
<td>5.5</td>
<td>5.5</td>
<td>5.2</td>
<td>5.6</td>
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<tr>
<td>Cast</td>
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<td>6.4</td>
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<tr>
<td>Coalesced</td>
<td>6.7</td>
<td>6.6</td>
<td>6.8</td>
<td>6.7</td>
<td>6.4</td>
</tr>
</tbody>
</table>
caused by the crystallization of a wide range of PET/PEN mixtures that hamper crystal formation.

It should be mentioned that the formation of and coalescence from the common PET/PEN-γ-CD–IC did not result in transesterification, as determined from the 1H NMR spectra of the coalesced PET/PEN measured in a trifluoroacetic acid/deuterated chloroform solution. On the other hand, an indication of the degree of intimacy of the coalesced PET/PEN blend is provided by our observation that after only several heating/cooling scans in the DSC, melting endotherms disappear and only a single $T_g$ is observed, indicating a facile, thermally induced transesterification between the well-mixed PET and PEN chains. The precipitated PET/PEN blends, on the other hand, did not evidence transesterification in our DSC measurements because the transesterification between PET and PEN chains is retarded by their phase segregated natures.

Figure 8. 2D $^1$H–$^{13}$C HETCOR NMR spectrum of solution-cast and coalesced PC/PMMA blends.
**Coalesced PC/PMMA/PVAc Ternary Blends**

Binary blends of PC/PMMA and PMMA/poly(vinyl acetate) (PVAc) have been intensively studied, while the PC/PVAc pair has not,\(^{47-53}\) and to the best of our knowledge the ternary PC/PMMA/PVAc has not been reported. Depending on the temperature and solvent from which they are cast, the PC/PMMA and PMMA/PVAc binary blends were found to be immiscible or somewhat compatible. The 1.6:1.0:1.4 molar PC/PMMA/PVAc blend obtained by coalescence from their common \(\gamma\)-CD–IC appears\(^{31}\) to be well-mixed. Note in the DSC scans presented in Figure 11 that in the first and second heats a single \(T_g\) at 57° C is observed, indicating formation of an intimate PC/PMMA/PVAc ternary blend. By plotting the reversing heat flow versus temperature, the effect of trace solvent release, as well as the enthalpic recovery of an endothermic peak that occurs just above the \(T_g\) are eliminated, revealing clearly a single glass transition. Though not shown, a PC/PMMA/PVAc blend made by coprecipitation from a common tetrahydrofuran (THF) solution showed four distinct \(T_g\)s at 38, 56, 82, and 133° C, which correspond to separate PVAc, PMMA/PVAc, PMMA, and PC phases. Also note the appearance of only one glass transition in the second

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**Figure 8.** (Continued)
heating of the coalesced ternary blend that confirms the stability of the intimate molecular mixing of PC, PMMA, and PVAc chains in their coalesced ternary blend.

The TGA scans of coprecipitated and coalesced PC/PMMA/PVAc blends are presented in Figure 12. Three distinct degradation events, one for each component, are observed in the phase segregated coprecipitated blend, whereas the coalesced PC/PMMA/PVAc blend shows a single broad thermal decomposition that is consistent with its well-mixed character. This significant difference in thermal decomposition behaviors likely comes from specific interactions between component polymer chains in the molecularly mixed coalesced ternary blend that are absent in the phase segregated coprecipitated blend.

The molecular-level miscibility of all three component polymers in the coalesced PC/PMMA/PVAc blend receives support from the \( T_1 \) results presented in Table 3. Separate, distinct \( T_1 \)s are observed for each component in the solution-cast blend with values closely similar to the pure homopolymers. On the other hand, only a single \( T_\varphi \) is observed for the protons in the IC-coalesced ternary blend.

**Stability of Coalesced Homopolymer Blends**

With the exception of the coalesced PS/PC and PET/PEN blends, the other CD-processed homopolymer blends seem to remain intimately mixed even after annealing above their \( T_g \)s and \( T_m \)s for substantial periods (\( \geq 30 \) min.). While the coalesced PET/PEN blend rapidly transesterified into a PET–PEN copolymer, the PS/PC coalesced blend did in fact segregate into two phases with distinct \( T_g \)s close to those of pure PS and pure PC. For all the other CD-processed homopolymer blends the intimacy of their mixing was not affected by rather prolonged heating at high temperatures, even though both component homopolymers should have possessed mobility sufficient to phase separate.

![Figure 9](image_url)
under the thermodynamic driving force provided by their inherent incompatibility, that is, 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, 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 of $M_w = 360,000$ in the melt is $D \sim 10^{-15} - 10^{-14}$ cm$^2$/s. 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) would then be $\sim 1.6$ h. The intimately mixed PC and PMMA chains in the blend coalesced from their common $\gamma$-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 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.

**Block Copolymers**

**PCL-b-PLLA**

The biodegradable/bioabsorbable block copolymer PCL-b-PLLA has been synthesized, included in and coalesced from its $\alpha$-CD–IC, and its phase structure and biodegradation behavior have been studied. As can be seen from the DSC data presented in Table 4, the as-synthesized diblock copolymer is phase separated, with high levels of crystallinity in both the PCL and PLLA phases. After coalescence from its $\alpha$-CD–IC, the phase segregation is greatly reduced, as evidenced by $\sim 50$ and $\sim 80\%$ reductions, respectively, in the levels of PCL and PLLA crystallinity. This implies substantial mixing of PCL and PLLA blocks in the amorphous portions of the coalesced diblock copolymer sample, which is corroborated by the

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**Figure 10.** Cooling DSC scans of (a) PEN-rich precipitated, (b) PET-rich precipitated, and (c) coalesced 1:1 PET/PEN blends.
Figure 11. MDSC scans \(^{31}\) of the (a) first and (b) second heating scans recorded for the 1.6:1.0:1.4 molar PC/PMMA/PVAc blend. The sample was held for 3 min at 170° C after the first heating scan.

Figure 12. TGA thermograms \(^{31}\) of (a) coprecipitated, and (b) coalesced 1.6:1.0:1.4 molar PC/PMMA/PVAc blends.
X-ray diffractograms presented in Figure 13. It is clear that the coalesced diblock is much more amorphous than the as-synthesized sample.

When both PCL-b-PLLA samples are subject to enzymatic degradation [5000 units of lipase from R. arrhizus in phosphate buffer (pH 7) at 37 °C], the coalesced diblock copolymer degrades much more rapidly, as is evident from the X-ray diffractograms in Figure 13. Clearly the amorphous portions of the coalesced diblock copolymer are preferentially attacked by the enzyme, because as the degradation time increases its diffraction patterns increasingly reflect a higher degree of crystallinity. As a consequence of this example, it appears that the biodegradation behavior of biodegradable block copolymers can be regulated by formation of and coalescence from their CD–ICs, and this has importance in their drug delivery and controlled release applications.

**PCL-b-PPG-b-PCL**

An additional example of controlling the microphase structure of block copolymers through processing with their CD–ICs is afforded by examination of the triblock copolymer PCL-b-poly(propylene glycol) (PPG)-b-PCL before and after coalescence from its ICs formed with α- and γ-CDs. The thermal degradation behavior of α-CD, as-synthesized PCL-b-PPG-b-PCL, and PCL-b-PPG-b-PCL-α-CD–IC are presented as TGA scans in Figure 14. Note that the as-synthesized triblock copolymer exhibits separate decompositions for the phase separated PCL and PPG domains at low and high temperatures, respectively. PPG decomposition can also be observed in the TGA scan of PCL-b-PPG-b-PCL-α-CD–IC, and this indicates that the PPG blocks are excluded from the α-CD–IC channels, where only the PCL blocks are included. In the TGA scan of PCL-b-PPG-b-PCL-γ-CD–IC (not shown) only a single broad decomposition is seen, with no evidence for distinct PPG decomposition. Thus, it appears that only the PCL blocks and the entire triblock copolymer are included in the PCL-b-PPG-b-PCL-α- and -γ-CD–ICs, respectively.

Since only PCL blocks are included in the α-CD-copolymer IC, the neighboring IC channels should be filled only with extended PCL blocks. Therefore, PCL blocks will aggregate readily when the CD molecules are washed way. Although PPG may affect the crystallization of PCL blocks in the as-synthesized copolymer, the aggregation of neighboring PCL blocks should not be affected by the uncomplexed PPG blocks in the process of copolymer coalescence. Therefore, an increased level of phase separation and crystallinity of the PCL blocks in this coalesced sample may be anticipated. In contrast, PCL and PPG blocks should have the opportunity to be included in neighboring channels of the γ-CD-block copolymer-IC, since both PCL and PPG blocks have been included. This means that the aggregation of some PCL blocks might be hindered by PPG blocks in the process of copolymer coalescence, as occurred with PCL-b-PLLA when coalesced from its α-CD–IC, where both blocks were included. Therefore, a decrease in PCL

Table 3. T弛(1H)s of Solution-Cast and Coalesced PC/PMMA/PVAc Blends

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>PC 150</th>
<th>PC 128</th>
<th>PC 120</th>
<th>PC 43</th>
<th>PC 30</th>
<th>PMMA 171</th>
<th>PMMA 68</th>
<th>PMMA 21</th>
<th>PVAc 178</th>
<th>PVAc 52</th>
<th>PVAc 45</th>
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<tbody>
<tr>
<td>PC</td>
<td>5.1</td>
<td>5.5</td>
<td>5.5</td>
<td>5.2</td>
<td>5.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PMMA</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<td>—</td>
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<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PPG</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>10.6</td>
<td>12.2</td>
<td>11.2</td>
<td>14.8</td>
<td>14.9</td>
<td>15.5</td>
</tr>
<tr>
<td>Cast</td>
<td>5.7</td>
<td>6.2</td>
<td>6.3</td>
<td>6.4</td>
<td>6.0</td>
<td>—</td>
<td>—</td>
<td>7.6</td>
<td>—</td>
<td>14.0</td>
<td>—</td>
</tr>
<tr>
<td>Coalesced</td>
<td>6.5</td>
<td>7.0</td>
<td>6.9</td>
<td>7.4</td>
<td>7.1</td>
<td>—</td>
<td>21.7</td>
<td>—</td>
<td>20.2</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 4. Thermal Properties of As-Synthesized and Coalesced PCL-b-PLLA Diblock Copolymer

<table>
<thead>
<tr>
<th>Identity</th>
<th>T弛-PCL (°C)</th>
<th>T弛-PCL (°C)</th>
<th>ΔH弛-PCL (J/g)</th>
<th>χ弛-PCL (%)</th>
<th>T弛-PLLA (°C)</th>
<th>T弛-PLLA (°C)</th>
<th>ΔH弛-PLLA (J/g)</th>
<th>χ弛-PLLA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized block copolymer</td>
<td>56.1</td>
<td>17.6</td>
<td>66.9</td>
<td>48</td>
<td>160</td>
<td>77.9</td>
<td>61.4</td>
<td>66</td>
</tr>
<tr>
<td>Coalesced sample</td>
<td>63.7</td>
<td>29.3</td>
<td>35.0</td>
<td>25</td>
<td>164</td>
<td>93.9</td>
<td>12.5</td>
<td>13</td>
</tr>
</tbody>
</table>
crystallinity, as a consequence of reduced block segregation, might be reasonably expected for this coalesced sample.

As is apparent from the results presented in Table 5, both expectations were realized, because the level of PCL crystallinity is observed to be higher and lower compared with the as-synthesized triblock copolymer when PCL-b-PPG-b-PCL is coalesced from its α- and γ-CD–ICs, respectively. The smaller than might have been expected decrease in PCL crystallinity observed in the triblock copolymer coalesced from its γ-CD–IC may be a result of the ability of two side-by-side parallel PCL block chains to occupy each γ-CD–IC channel.15 If this is the case, then at least some pairs of PCL blocks would be segregated within some γ-CD–IC channels.

### CONCLUSIONS

We have clearly demonstrated that intimately mixed polymer1/polymer2 binary and polymer1/polymer2/polymer3 ternary blends of normally immiscible polymers can be fabricated by the formation of CD–ICs containing all blend component polymers, followed by coalescence from their common CD–IC crystals. Preliminary thermal treatments of these intimate blends for extended periods (as much as hours) at temperatures above the $T_{g}$s and/or $T_{m}$s of both blend components did not, in most cases, lead to macroscopic phase separation, even though the blend components are generally thought to be immiscible. As a consequence, normal melt processing of these well mixed polymer blends may produce fibers, films, and molded articles with homogeneous rather than the usual phase-segregated, heterogeneous morphologies. Assuming that the unique homogeneous morphologies of these blends will affect, and hopefully improve their physical properties, then a significant expansion of the range of potentially useful polymer materials may be possible beginning from CD–IC fabricated, well-mixed polymer blends.

In addition, the phase-segregated morphologies of block copolymers appear controllable by forming block copolymer–CD–ICs and subsequently coalescing the block copolymer chains from their CD–IC crystals. Aside from their potential practical applications, polymers processed with their CD–ICs can at the very least

<table>
<thead>
<tr>
<th>Identity</th>
<th>$T_{m}$-PCL (°C)</th>
<th>$\Delta H_{PCL}$ (J/g)</th>
<th>$\chi_{o}$-PCL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized copolymer</td>
<td>57.3</td>
<td>58.6</td>
<td>56.5</td>
</tr>
<tr>
<td>Sample coalesced from α-CD-copolymer IC</td>
<td>63.8</td>
<td>76.8</td>
<td>74.1</td>
</tr>
<tr>
<td>Sample coalesced from γ-CD-copolymer IC</td>
<td>63.0</td>
<td>51.3</td>
<td>49.5</td>
</tr>
</tbody>
</table>

### Table 5. Thermal Properties and Crystallinity of Various PCL-PPG-PCL Triblock Copolymer Samples as Revealed by DSC

![Figure 13. X-ray diffraction patterns of (a) as-synthesized and (b) coalesced PCL-b-PLLA films observed following various enzymatic degradation times.](image)

![Figure 14. TGA scans of (a) α-CD, (b) as-synthesized PCL-PPG-PCL, and (c) PCL-PPG-PCL-α-CD–IC.](image)
produce samples with unique morphologies whose investigation should serve to further our understanding of the processing-dependent physical properties of polymer materials.

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REFERENCES AND NOTES

54. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953; Chap. XII.